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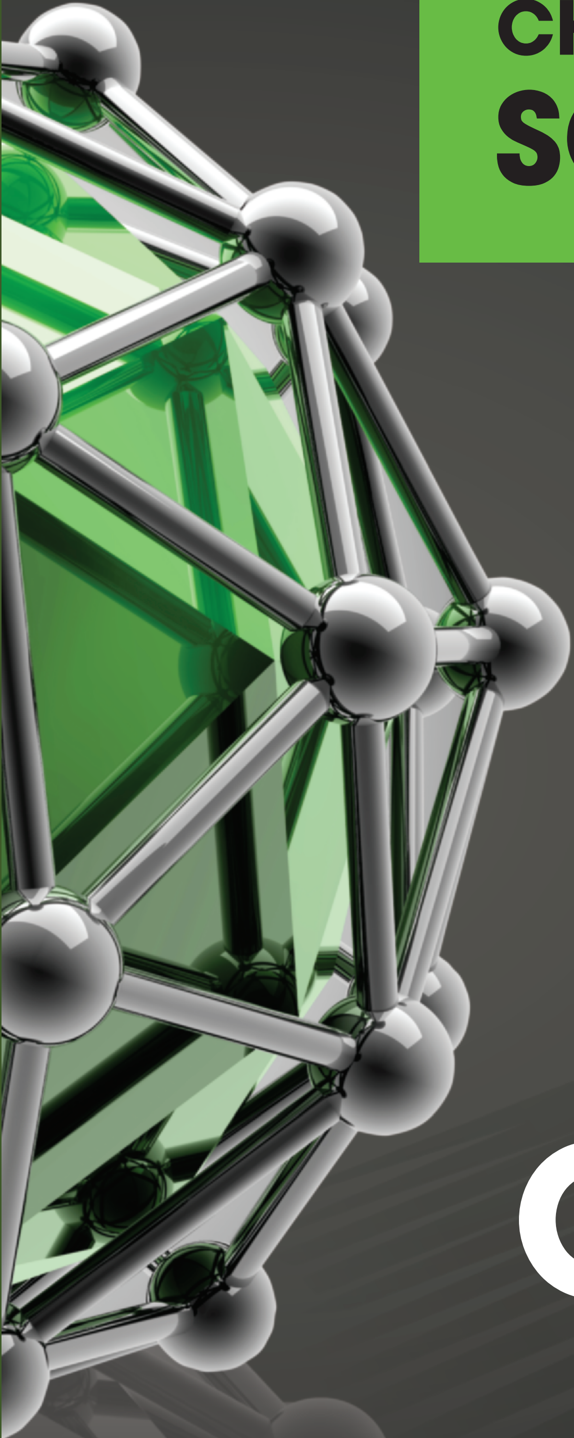

Chemistry

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Arihant Prakashan (Series), Meerut

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CONTENTS

SYLLABUS

JEE MAIN

Section A : PHYSICAL CHEMISTRY

UNIT I Some Basic Concepts in Chemistry

Matter and its nature, Dalton's atomic theory; Concept of atom, molecule, element and compound; Physical quantities and their measurements in Chemistry, precision and accuracy, significant figures, S.I. Units, dimensional analysis; Laws of chemical combination; Atomic and molecular masses, mole concept, molar mass, percentage composition, empirical and molecular formulae; Chemical equations and stoichiometry.

UNIT II States of Matter

Classification of matter into solid, liquid and gaseous states.

Gaseous State Measurable properties of gases; Gas laws - Boyle's law, Charle's law, Graham's law of diffusion, Avogadro's law, Dalton's law of partial pressure; Concept of Absolute scale of temperature; Ideal gas equation, Kinetic theory of gases (only postulates); Concept of average, root mean square and most probable velocities; Real gases, deviation from Ideal behaviour, compressibility factor, van der Waals' equation, liquefaction of gases, critical constants.

Liquid State Properties of liquids - vapour pressure, viscosity and surface tension and effect of temperature on them (qualitative treatment only).

Solid State Classification of solids: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea); Bragg's Law and its applications, Unit cell and lattices, packing in solids (fcc, bcc and hcp lattices), voids, calculations involving unit cell parameters, imperfection in solids; electrical, magnetic and dielectric properties.

UNIT III Atomic Structure

Discovery of sub-atomic particles (electron, proton and neutron); Thomson and Rutherford atomic models and their limitations; Nature of electromagnetic radiation, photoelectric effect; spectrum of hydrogen atom, Bohr model of hydrogen atom - its postulates, derivation of the relations for energy of the electron and radii of the different orbits, limitations of Bohr's model; dual nature of matter, de-Broglie's relationship, Heisenberg uncertainty principle.

Elementary ideas of quantum mechanics, quantum mechanical model of atom, its important features, ψ and ψ_2, concept of atomic orbitals as one electron wave functions; Variation of ψ and ψ_2 with *r* for *1s* and *2s* orbitals; various quantum numbers (principal, angular momentum and magnetic quantum numbers) and their significance; shapes of *s*, *p* and *d* - orbitals, electron spin and spin quantum number; rules for filling electrons in orbitals – aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of elements, extra stability of half-filled and completely filled orbitals.

UNIT IV Chemical Bonding and Molecular Structure

Kossel Lewis approach to chemical bond formation, concept of ionic and covalent bonds.

Ionic Bonding Formation of ionic bonds, factors affecting the formation of ionic bonds; calculation of lattice enthalpy.

Covalent Bonding Concept of electronegativity, Fajan's rule, dipole moment; Valence Shell Electron Pair Repulsion (VSEPR) theory and shapes of simple molecules.

Quantum mechanical approach to covalent bonding Valence bond theory - Its important features, concept of hybridization involving *s*, *p* and *d* orbitals; Resonance.

Molecular Orbital Theory Its important features, LCAOs, types of molecular orbitals (bonding, antibonding), sigma and pi-bonds, molecular orbital electronic configurations of homonuclear diatomic molecules, concept of bond order, bond length and bond energy.

Elementary idea of metallic bonding. Hydrogen bonding and its applications.

UNIT V Chemical Thermodynamics

Fundamentals of thermodynamics System and surroundings, extensive and intensive properties, state functions, types of processes.

First law of thermodynamics Concept of work, heat internal energy and enthalpy, heat capacity, molar heat capacity, Hess's law of constant heat summation; Enthalpies of bond dissociation, combustion, formation, atomization, sublimation, phase transition, hydration, ionization and solution.

Second law of thermodynamics Spontaneity of processes; ΔS of the universe and ΔG of the system as criteria for spontaneity, ΔG° (Standard Gibb's energy change) and equilibrium constant.

UNIT VI Solutions

Different methods for expressing concentration of solution - molality, molarity, mole fraction, percentage (by volume and mass both), vapour pressure of solutions and Raoult's Law - Ideal and non-ideal solutions, vapour pressure - composition plots for ideal and non-ideal solutions.

Colligative properties of dilute solutions - relative lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure; Determination of molecular mass using colligative properties; Abnormal value of molar mass, van't Hoff factor and its significance.

UNIT VII Equilibrium

Meaning of equilibrium, concept of dynamic equilibrium.

Equilibria involving physical processes Solid -liquid, liquid - gas and solid - gas equilibria, Henry's law, general characteristics of equilibrium involving physical processes.

Equilibria involving chemical processes Law of chemical equilibrium, equilibrium constants (K and K) and their significance, significance of ΔG and ΔG° in chemical equilibria, factors affecting equilibrium concentration, pressure, temperature, effect of catalyst; Le -Chatelier's principle.

Ionic equilibrium Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted - Lowry and Lewis) and their ionization, acid-base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.

UNIT VIII Redox Reactions and Electrochemistry

Electronic concepts of oxidation and reduction, redox reactions, oxidation number, rules for assigning oxidation number, balancing of redox reactions.

Eectrolytic and metallic conduction, conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration: Kohlrausch's law and its applications.

Electrochemical cells - Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half - cell and cell reactions, emf of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

UNIT IX Chemical Kinetics

Rate of a chemical reaction, factors affecting the rate of reactions concentration, temperature, pressure and catalyst; elementary and complex reactions, order and molecularity of reactions, rate law, rate constant and its units, differential and integral forms of zero and first order reactions, their characteristics and half - lives, effect of temperature on rate of reactions - Arrhenius theory, activation energy and its calculation, collision theory of bimolecular gaseous reactions (no derivation).

UNIT X Surface Chemistry

Adsorption - Physisorption and chemisorption and their characteristics, factors affecting adsorption of gases on solids- Freundlich and Langmuir adsorption isotherms, adsorption from solutions.

Catalysis Homogeneous and heterogeneous, activity and selectivity of solid catalysts, enzyme catalysis and its mechanism.

Colloidal state distinction among true solutions, colloids and suspensions, classification of colloids - lyophilic, lyophobic; multi molecular, macromolecular and associated colloids (micelles), preparation and properties of colloids Tyndall effect, Brownian movement, electrophoresis, dialysis, coagulation and flocculation; Emulsions and their characteristics.

Section B INORGANIC CHEMISTRY

UNIT XI Classification of Elements and Periodicity in Properties

Periodic Law and Present Form of the Periodic Table, *s, p, d* and f Block Elements, Periodic Trends in Properties of Elementsatomic and Ionic Radii, Ionization Enthalpy, Electron Gain Enthalpy, Valence, Oxidation States and Chemical Reactivity.

UNIT XII General Principles and Processes of Isolation of Metals

Modes of occurrence of elements in nature, minerals, ores; steps involved in the extraction of metals - concentration, reduction (chemical and electrolytic methods) and refining with special reference to the extraction of Al, Cu, Zn and Fe; Thermodynamic and electrochemical principles involved in the extraction of metals.

UNIT XIII Hydrogen

Position of hydrogen in periodic table, isotopes, preparation, properties and uses of hydrogen; physical and chemical properties of water and heavy water; Structure, preparation, reactions and uses of hydrogen peroxide; Classification of hydrides ionic, covalent and interstitial; Hydrogen as a fuel.

UNIT XIV *s* - Block Elements

(Alkali and Alkaline Earth Metals)

Group 1 and 2 Elements

General introduction, electronic configuration and general trends in physical and chemical properties of elements, anomalous properties of the first element of each group, diagonal relationships.

Preparation and properties of some important compounds - sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate; Industrial uses of lime, limestone, Plaster of Paris and cement; Biological significance of Na, K, Mg and Ca.

UNIT XV *p* - Block Elements

Group 13 to Group 18 Elements

General Introduction Electronic configuration and general trends in physical and chemical properties of elements across the periods and down the groups; unique behaviour of the first element in each group.Group wise study of the *p* – block elements

Group 13 Preparation, properties and uses of boron and aluminium; structure, properties and uses of borax, boric acid, diborane, boron trifluoride, aluminium chloride and alums.

Group 14 Tendency for catenation; Structure, properties and uses of allotropes and oxides of carbon, silicon tetrachloride, silicates, zeolites and silicones.

Group 15 Properties and uses of nitrogen and phosphorus; Allotrophic forms of phosphorus; Preparation, properties, structure and uses of ammonia nitric acid, phosphine and phosphorus halides,(PCl_3, PCl_5); Structures of oxides and oxoacids of nitrogen and phosphorus.

Group 16 Preparation, properties, structures and uses of dioxygen and ozone; Allotropic forms of sulphur; Preparation, properties, structures and uses of sulphur dioxide, sulphuric acid (including its industrial preparation); Structures of oxoacids of sulphur.

Group 17 Preparation, properties and uses of chlorine and hydrochloric acid; Trends in the acidic nature of hydrogen halides; Structures of Interhalogen compounds and oxides and oxoacids of halogens.

Group 18 Occurrence and uses of noble gases; Structures of fluorides and oxides of xenon.

UNIT XVI *d*–and *f*–Block Elements

Transition Elements General introduction, electronic configuration, occurrence and characteristics, general trends in properties of the first row transition elements - physical properties, ionization enthalpy, oxidation states, atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation; Preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$.

Inner Transition Elements

Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction. Actinoids - Electronic configuration and oxidation states.

UNIT XVII Coordination Compounds

Introduction to coordination compounds, Werner's theory; ligands, coordination number, denticity, chelation; IUPAC nomenclature of mononuclear coordination compounds, isomerism; Bonding Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; importance of coordination compounds (in qualitative analysis, extraction of metals and in biological systems).

UNIT XVIII Environmental Chemistry

Environmental pollution Atmospheric, water and soil.

Atmospheric pollution - Tropospheric and stratospheric.

Tropospheric pollutants Gaseous pollutants Oxides of carbon, nitrogen and sulphur, hydrocarbons; their sources, harmful effects and prevention; Green house effect and Global warming; Acid rain;

Particulate pollutants Smoke, dust, smog, fumes, mist; their sources, harmful effects and prevention.

Stratospheric pollution Formation and breakdown of ozone, depletion of ozone layer - its mechanism and effects.

Water pollution Major pollutants such as, pathogens, organic wastes and chemical pollutants their harmful effects and prevention.

Soil pollution Major pollutants such as: Pesticides (insecticides, herbicides and fungicides), their harmful effects and prevention.

Strategies to control environmental pollution.

Section C ORGANIC CHEMISTRY

UNIT XIX Purification & Characterisation of Organic Compounds

Purification Crystallisation, sublimation, distillation, differential extraction and chromatography principles and their applications.

Qualitative analysis Detection of nitrogen, sulphur, phosphorus and halogens.

Quantitative analysis (basic principles only) Estimation of carbon, hydrogen, nitrogen, halogens, sulphur, phosphorus.

Calculations of empirical formulae and molecular formulae; Numerical problems in organic quantitative analysis.

UNIT XX Some Basic Principles of Organic Chemistry

Tetravalency of carbon; Shapes of simple molecules hybridization (*s* and *p*); Classification of organic compounds based on functional groups: —C=C—,—C=C— and those containing halogens, oxygen, nitrogen and sulphur, Homologous series; Isomerism - structural and stereoisomerism.

Nomenclature (Trivial and IUPAC)

Covalent bond fission Homolytic and heterolytic free radicals, carbocations and carbanions; stability of carbocations and free radicals, electrophiles and nucleophiles.

Electronic displacement in a covalent bond Inductive effect, electromeric effect, resonance and hyperconjugation.

Common types of organic reactions Substitution, addition, elimination and rearrangement.

UNIT XXI Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions.

Alkanes Conformations: Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes.

Alkenes Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization.

Alkenes acidic character; addition of hydrogen, halogens, water and hydrogen halides; polymerization.

Aromatic hydrocarbons Nomenclature, benzene structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

UNIT XXII Organic Compounds Containing Halogens

General methods of preparation, properties and reactions; Nature of C—*X* bond; Mechanisms of substitution reactions.

Uses/environmental effects of chloroform, iodoform, freons and DDT.

UNIT XXIII Organic Compounds Containing Oxygen

General methods of preparation, properties, reactions and uses. Alcohols, Phenols and Ethers

Alcohols Identification of primary, secondary and tertiary alcohols; mechanism of dehydration.

Phenols Acidic nature, electrophilic substitution reactions: halogenation, nitration and sulphonation, Reimer - Tiemann reaction.

Ethers: Structure

Aldehyde and Ketones Nature of carbonyl group; Nucleophilic addition to >C=O group, relative reactivities of aldehydes and ketones; Important reactions such as - Nucleophilic addition reactions (addition of HCN, NH_3 and its derivatives), Grignard reagent; oxidation; reduction (Wolff Kishner and Clemmensen); acidity of α - hydrogen, aldol condensation, Cannizzaro reaction, Haloform reaction; Chemical tests to distinguish between aldehydes and Ketones.

Carboxylic Acids Acidic strength & factors affecting it.

UNIT XXIV Organic Compounds Containing Nitrogen

General methods of preparation, properties, reactions and uses.

Amines Nomenclature, classification, structure basic character and identification of primary, secondary and tertiary amines and their basic character.

Diazonium Salts Importance in synthetic organic chemistry.

UNIT XXV Polymers

General introduction and classification of polymers, general methods of polymerization-addition and condensation, copolymerization; Natural and synthetic rubber and vulcanization; some important polymers with emphasis on their monomers and uses - polythene, nylon, polyester and bakelite.

UNIT XXVI Biomolecules

General introduction and importance of biomolecules.

Carbohydrates Classification aldoses and ketoses; monosaccharides (glucose and fructose), constituent monosaccharides of oligosacchorides (sucrose, lactose, maltose) and polysaccharides (starch, cellulose, glycogen).

Proteins Elementary Idea of α-amino acids, peptide bond, . polypeptides; proteins: primary, secondary, tertiary and quaternary structure (qualitative idea only), denaturation of proteins, enzymes. Vitamins Classification and functions.

Nucleic Acids Chemical constitution of DNA and RNA. Biological functions of Nucleic acids.

UNIT XXVII Chemistry in Everyday Life

Chemicals in medicines Analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamins - their meaning and common examples.

Chemicals in food Preservatives, artificial sweetening agents - common examples.

Cleansing agents Soaps and detergents, cleansing action.

Unit XXVIII Principles Related to

Practical Chemistry

- Detection of extra elements (N, S, halogens) in organic compounds; Detection of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl and amino groups in organic compounds.

  Chemistry involved in the preparation of the following
- Inorganic compounds Mohr's salt, potash alum.
- Organic compounds Acetanilide, *p*-nitroacetan ilide, aniline yellow, iodoform.
- Chemistry involved in the titrimetric excercises - Acids bases and the use of indicators, oxali acid vs $KMnO_4$, Mohr's salt vs $KMnO_4$.
- Chemical principles involved in the qualitative salt analysis
- Cations — Pb^{2+} , Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+} , Mg^{2+} NH^{4+}. Anions – CO_3^{2-}, S^{2-}, SO_4^{2-}, NO_2, NO_3, Cl^-, Br^-, I^- (Insoluble salts excluded).
- Chemical principles involved in the following experiments
  1. Enthalpy of solution of $CuSO_4$
  2. Enthalpy of neutralization of strong acid and strong base.
  3. Preparation of lyophilic and lyophobic sols.
  4. Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature.

JEE ADVANCED

PHYSICAL CHEMISTRY

General Topics Concept of atoms and molecules, Dalton's atomic theory, Mole concept, Chemical formulae, Balanced chemical equations, Calculations (based on mole concept) involving common oxidation-reduction, neutralisation, and displacement reactions, Concentration in terms of mole fraction, molarity, molality and normality.

Gaseous and Liquid States Absolute scale of temperature, ideal gas equation, Deviation from ideality, van der Waals' equation, Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature, Law of partial pressures, Vapour pressure, Diffusion of gases.

Atomic Structure and Chemical Bonding Bohr model, spectrum of hydrogen atom, quantum numbers, Wave-particle duality, de-Broglie hypothesis, Uncertainty principle, Qualitative quantum mechanical picture of hydrogen atom, shapes of s, p and d orbitals, Electronic configurations of elements (up to atomic number 36), Aufbau principle, Pauli's exclusion principle and Hund's rule, Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only, Orbital energy diagrams for homonuclear diatomic species, Hydrogen bond, Polarity in molecules, dipole moment (qualitative aspects only), VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

Energetics First law of thermodynamics, Internal energy, work and heat, pressure-volume work, Enthalpy, Hess's law, Heat of reaction, fusion and vaporization, Second law of thermodynamics, Entropy, Free energy, Criterion of spontaneity.

Chemical Equilibrium Law of mass action, Equilibrium constant, Le-Chatelier's principle (effect of concentration, temperature and pressure), Significance of DG and DGo in chemical equilibrium, Solubility product, common ion effect, pH and buffer solutions, Acids and bases (Bronsted and Lewis concepts), Hydrolysis of salts.

Electrochemistry Electrochemical cells and cell reactions, Standard electrode potentials, Nernst equation and its relation to DG, Electrochemical series, emf of galvanic cells, Faraday's laws of electrolysis, Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's law, Concentration cells.

Chemical Kinetics Rates of chemical reactions, Order of reactions, Rate constant, First order reactions, Temperature dependence of rate constant (Arrhenius equation).

Solid State Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices, Nearest neighbours, ionic radii, simple ionic compounds, point defects.

Solutions Raoult's law, Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point.

Surface Chemistry Elementary concepts of adsorption (excluding adsorption isotherms), Colloids, types, methods of preparation and general properties, Elementary ideas of emulsions, surfactants and micelles (only definitions and examples).

Nuclear Chemistry Radioactivity, isotopes and isobars, Properties of rays, Kinetics of radioactive decay (decay series excluded), carbon dating, Stability of nuclei with respect to proton-neutron ratio, Brief discussion on fission and fusion reactions.

INORGANIC CHEMISTRY

Isolation/Preparation and Properties of the following Non-metals Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens, Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur.

Preparation and Properties of the following Compounds Oxides, peroxides, hydroxides, carbonates, bicarbonates, chlorides and sulphates of sodium, potassium, magnesium and calcium, Boron, diborane, boric acid and borax, Aluminium, alumina, aluminium chloride and alums, Carbon, oxides and oxyacid (carbonic acid), Silicon, silicones, silicates and silicon carbide, Nitrogen, oxides, oxyacids and ammonia, Phosphorus, oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine, Oxygen, ozone and hydrogen peroxide, Sulphur, hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate, Halogens, hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder, Xenon fluorides.

Transition Elements (3d series) Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Coordination compounds: nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

Preparation and Properties of the following Compounds.

Oxides and chlorides of tin and lead, Oxides, chlorides and sulphates of Fe^{2+}, Cu^{2+} and Zn^{2+}, Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate.

Ores and Minerals Commonly occurring ores and minerals of iron, copper, tin, lead, magnesium, aluminium, zinc and silver.

Extractive Metallurgy Chemical principles and reactions only (industrial details excluded), Carbon reduction method (iron and tin), Self reduction method (copper and lead), Electrolytic reduction method (magnesium and aluminium), Cyanide process (silver and gold).

Principles of Qualitative Analysis Groups I to V (only Ag^{+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+}), Nitrate, halides (excluding fluoride), sulphate and sulphide.

ORGANIC CHEMISTRY

Concepts Hybridisation of carbon, Sigma and pi-bonds, Shapes of simple organic molecules, Structural and geometrical isomerism, Optical isomerism of compounds containing up to two asymmetric centres, (R,S and E,Z nomenclature excluded), IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi-functional compounds), Conformations of ethane and butane (Newman projections), Resonance and hyperconjugation, Keto-enol tautomerism, Determination of empirical and molecular formulae of simple compounds (only combustion method), Hydrogen bonds, definition and their effects on physical properties of alcohols and carboxylic acids, Inductive and resonance effects on acidity and basicity of organic acids and bases, Polarity and inductive effects in alkyl halides, Reactive intermediates produced during homolytic and heterolytic bond cleavage, Formation, structure and stability of carbocations, carbanions and free radicals.

Preparation, Properties and Reactions of Alkanes Homologous series, physical properties of alkanes (melting points, boiling points and density), Combustion and halogenation of alkanes, Preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Preparation, Properties and Reactions of Alkenes and Alkynes Physical properties of alkenes and alkynes (boiling points, density and dipole moments), Acidity of alkynes, Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination), Reactions of alkenes with $KMnO_4$ and ozone, Reduction of alkenes and alkynes, Preparation of alkenes and alkynes by elimination reactions, Electrophilic addition reactions of alkenes with X_2, HX, HOX and H_2O (X=halogen), Addition reactions of alkynes, Metal acetylides.

Reactions of Benzene Structure and aromaticity, Electrophilic substitution reactions, halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation Effect of o-, m- and p-directing groups in monosubstituted benzenes.

Phenols Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation), Reimer-Tiemann reaction, Kolbe reaction.

Characteristic Reactions of the following (including those mentioned above) Alkyl halides, rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions, Alcohols, esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, $ZnCl_2$/concentrated HCl, conversion of alcohols into aldehydes and ketones, Ethers, Preparation by Williamson's Synthesis, Aldehydes and Ketones, oxidation, reduction, oxime and hydrazone formation, aldol condensation, Perkin reaction, Cannizzaro reaction, haloform reaction and nucleophilic addition reactions (Grignard addition), Carboxylic acids, formation of esters, acid chlorides and amides, ester hydrolysis. Amines, basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines, Sandmeyer and related reactions of diazonium salts, carbylamine reaction, Haloarenes, nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and Cine substitution).

Carbohydrates Classification, mono and disaccharides (glucose and sucrose), Oxidation, reduction, glycoside formation and hydrolysis of sucrose.

Amino Acids and Peptides General structure (only primary structure for peptides) and physical properties.

Properties and Uses of Some Important Polymers Natural rubber, cellulose, nylon, teflon and PVC.

Practical Organic Chemistry Detection of elements (N, S, halogens), Detection and identification of the following functional groups, hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro, Chemical methods of separation of mono-functional organic compounds from binary mixtures.

1

Some Basic Concepts of Chemistry

Topic 1 Mole Concept

Objective Questions I (Only one correct option)

1. 5 moles of AB_2 weight $125 \quad 10^{\ 3}$ kg and 10 moles of A_2B_2 weight $300 \quad 10^{\ 3}$ kg. The molar mass of $A\,(M_A)$ and molar mass of $B\,(M_B)$ in kg mol $^{\ 1}$ are **(2019 Main, 12 April I)**

(a) $M_A \quad 10 \quad 10^{\ 3}$ and $M_B \quad 5 \quad 10^{\ 3}$

(b) $M_A \quad 50 \quad 10^{\ 3}$ and $M_B \quad 25 \quad 10^{\ 3}$

(c) $M_A \quad 25 \quad 10^{\ 3}$ and $M_B \quad 50 \quad 10^{\ 3}$

(d) $M_A \quad 5 \quad 10^{\ 3}$ and $M_B \quad 10 \quad 10^{\ 3}$

2. The minimum amount of $O_2(g)$ consumed per gram of reactant is for the reaction (Given atomic mass : Fe 56, O 16, Mg 24, P 31, C 12, H 1) **(2019 Main, 10 April II)**

(a) $C_3H_8(g) \quad 5O_2(g) \qquad 3CO_2(g) \quad 4H_2O(l)$

(b) $P_4(s) \quad 5O_2(g) \qquad P_4O_{10}(s)$

(c) $4Fe(s) \quad 3O_2(g) \qquad 2Fe_2O_3(s)$

(d) $2Mg(s) \quad O_2(g) \qquad 2MgO(s)$

3. At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is **(2019 Main, 10 April I)**

(a) C_4H_7Cl (b) C_4H_6 (c) C_4H_{10} (d) C_4H_8

4. 10 mL of 1 mM surfactant solution forms a monolayer covering 0.24 cm^2 on a polar substrate. If the polar head is approximated as a cube, what is its edge length? **(2019 Main, 9 April II)**

(a) 2.0 pm (b) 0.1 nm (c) 1.0 pm (d) 2.0 nm

5. For a reaction,

$N_2(g) \quad 3H_2(g) \qquad 2NH_3(g)$, identify dihydrogen ($H_2$) as a limiting reagent in the following reaction mixtures. **(2019 Main, 9 April I)**

(a) 56 g of N_2 10 g of H_2 (b) 35 g of N_2 8 g of H_2

(c) 14 g of N_2 4 g of H_2 (d) 28 g of N_2 6 g of H_2

6. The percentage composition of carbon by mole in methane is **(2019 Main, 8 April II)**

(a) 75% (b) 20% (c) 25% (d) 80%

7. 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg $^{\ 1}$) of the solution respectively are **(2019 Main, 12 Jan II)**

(a) 0.2, 11.11 (b) 0.167, 22.20

(c) 0.2, 22.20 (d) 0.167, 11.11

8. The volume strength of 1 M H_2O_2 is

(Molar mass of $H_2O_2 \quad 34$ g mol $^{\ 1}$) **(2019 Main, 12 Jan II)**

(a) 16.8 (b) 22.4 (c) 11.35 (d) 5.6

9. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is **(2019 Main, 10 Jan II)**

(a) 17.1 g (b) 68.4 g (c) 136.8 g (d) 34.2 g

10. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is :

$$2C_{57}H_{110}O_6(s) \quad 163O_2(g) \quad 114CO_2(g) \quad 110\ H_2O(l)$$

(2019 Main, 9 Jan II)

(a) 490 g (b) 495 g (c) 445 g (d) 890 g

11. A solution of sodium sulphate contains 92 g of Na ions per kilogram of water. The molality of Na ions in that solution in mol kg $^{\ 1}$ is **(2019 Main, 9 Jan I)**

(a) 16 (b) 4 (c) 132 (d) 8

12. The most abundant elements by mass in the body of a healthy human adult are oxygen (61.4%), carbon (22.9%), hydrogen (10.0 %), and nitrogen (2.6%). The weight which a 75 kg person would gain if all ^{1}H atoms are replaced by ^{2}H atoms is **(2017 JEE Main)**

(a) 15 kg (b) 37.5 kg

(c) 7.5 kg (d) 10 kg

13. 1 g of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 in g mol $^{\ 1}$ is **(2017 JEE Main)**

(a) 1186 (b) 84.3 (c) 118.6 (d) 11.86

14. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion, the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is **(2016 JEE Main)**

(a) C_3H_8 (b) C_4H_8 (c) C_4H_{10} (d) C_3H_6

15. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (molecular weight 206). What would be the maximum uptake of Ca^{2} ions by the resin when expressed in mole per gram resin? **(2015 JEE Main)**

(a) $\frac{1}{103}$ (b) $\frac{1}{206}$ (c) $\frac{2}{309}$ (d) $\frac{1}{412}$

16. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is **(2015 JEE Main)**

(a) 18 mg (b) 36 mg (c) 42 mg (d) 54 mg

17. The ratio mass of oxygen and nitrogen of a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is **(2014 Main)**

(a) 1 : 4 (b) 7 : 32 (c) 1 : 8 (d) 3 : 16

18. The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be **(2013 Main)**

(a) 0.875 M (b) 1.00 M (c) 1.75 M (d) 0.0975M

19. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is **(2011)**

(a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M

20. Given that the abundances of isotopes $_{54}Fe$, $_{56}Fe$ and $_{57}Fe$ are 5%, 90% and 5%, respectively, the atomic mass of Fe is **(2009)**

(a) 55.85 (b) 55.95
(c) 55.75 (d) 56.05

21. Mixture X 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L solution.

1 L of mixture X + excess of $AgNO_3$ solution Y

1 L of mixture X + excess of $BaCl_2$ solution Z

Number of moles of Y and Z are **(2003, 1M)**

(a) 0.01, 0.01 (b) 0.02, 0.01
(c) 0.01, 0.02 (d) 0.02, 0.02

22. Which has maximum number of atoms? **(2003, 1M)**

(a) 24 g of C (12) (b) 56 g of Fe (56)
(c) 27 g of Al (27) (d) 108 g of Ag (108)

23. How many moles of electron weighs 1 kg? **(2002, 3M)**

(a) $6.023 \quad 10^{23}$ (b) $\frac{1}{9.108} \quad 10^{31}$

(c) $\frac{6.023}{9.108} \quad 10^{54}$ (d) $\frac{1}{9.108 \quad 6.023} \quad 10^{8}$

24. The normality of 0.3 M phosphorus acid (H_3PO_3) is **(1999, 2M)**

(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6

25. In which mode of expression, the concentration of a solution remains independent of temperature? **(1988, 1M)**

(a) Molarity (b) Normality (c) Formality (d) Molality

26. A molal solution is one that contains one mole of solute in **(1986, 1M)**

(a) 1000 g of solvent (b) 1.0 L of solvent
(c) 1.0 L of solution (d) 22.4 L of solution

27. If 0.50 mole of $BaCl_2$ is mixed with 0.20 mole of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is **(1981, 1M)**

(a) 0.70 (b) 0.50 (c) 0.20 (d) 0.10

28. 2.76 g of silver carbonate on being strongly heated yields a residue weighing **(1979, 1M)**

(a) 2.16 g (b) 2.48 g (c) 2.32 g (d) 2.64 g

29. When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is **(1979, 1M)**

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4

30. The largest number of molecules is in **(1979, 1M)**

(a) 36 g of water
(b) 28 g of CO
(c) 46 g of ethyl alcohol
(d) 54 g of nitrogen pentaoxide (N_2O_5)

31. The total number of electrons in one molecule of carbon dioxide is **(1979, 1M)**

(a) 22 (b) 44 (c) 66 (d) 88

32. A gaseous mixture contains oxygen and nitrogen in the ratio of 1:4 by weight. Therefore, the ratio of their number of molecules is **(1979, 1M)**

(a) 1 : 4 (b) 1 : 8 (c) 7 : 32 (d) 3 : 16

Numerical Value Based Questions

33. Galena (an ore) is partially oxidised by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the content undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is ....

(Atomic weights in g mol ^{1} : O = 16, S 32, Pb 207) **(2018 Adv.)**

34. To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction,

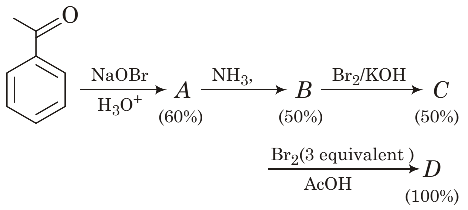
$MnCl_2 + K_2S_2O_8 + H_2O \quad KMnO_4 + H_2SO_4 + HCl$

(equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is ....

(Atomic weights in g mol ^{1}: Mn 55, Cl 35.5) **(2018 Adv.)**

35. In the following reaction sequence, the amount of ***D*** (in gram) formed from 10 moles of acetophenone is …….
(Atomic weights in g mol^{1} : H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)



(2018 Adv.)

Fill in the Blanks

36. The weight of $1 \quad 10^{22}$ molecules of $CuSO_4 \quad 5H_2O$ is …………. . **(1991, 1M)**

37. 3.0 g of a salt of molecular weight 30 is dissolved in 250 g water. The molarity of the solution is ……… **(1983, 1M)**

38. The total number of electrons present in 18 mL of water is …………. . **(1980, 1M)**

39. The modern atomic mass unit is based on the mass of …………. . **(1980, 1M)**

Integer Answer Type Questions

40. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{3}. The ratio of the molecular weights of the solute and solvent, $\frac{m_{\text{solute}}}{m_{\text{solvent}}}$ is ... . **(2016 Adv.)**

41. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is **(2014 Adv.)**

42. 29.2% (w/W) HCl stock solution has density of 1.25g mL^{1}. The molecular weight of HCl is 36.5 g mol^{1}. The volume (mL) of stock solution required to prepare a 200 mL solution 0.4 M HCl is **(2012)**

Subjective Questions

43. 20% surface sites have adsorbed N_2. On heating N_2 gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is 2.46 cm^3. Density of surface sites is $6.023 \quad 10^{14}/\text{cm}^2$ and surface area is 1000 cm^2, find out the number of surface sites occupied per molecule of N_2. **(2005, 3M)**

44. In a solution of 100 mL 0.5 M acetic acid, one gram of active charcoal is added, which adsorbs acetic acid. It is found that the concentration of acetic acid becomes 0.49 M. If surface area of charcoal is $3.01 \quad 10^2\, m^2$, calculate the area occupied by single acetic acid molecule on surface of charcoal. **(2003)**

45. Find the molarity of water. Given: = 1000 kg/m^3 **(2003)**

46. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molar mass. **(1999, 3M)**

47. $8.0575 \quad 10^{2}$ kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of solution of density 1077.2 kg m^{3}. Calculate the molality, molarity and mole fraction of Na_2SO_4 in solution. **(1994, 3M)**

48. *A* is a binary compound of a univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid *B*, that forms a hydrated double salt, *C* with $Al_2(SO_4)_3$. Identify *A, B* and *C*. **(1994, 2M)**

49. Upon mixing 45.0 mL 0.25 M lead nitrate solution with 25.0 mL of a 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of species left behind in the final solution. Assume that lead sulphate is completely insoluble. **(1993, 3M)**

50. Calculate the molality of 1.0 L solution of 93% H_2SO_4, (weight/volume). The density of the solution is 1.84 g/mL. **(1990, 1M)**

51. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture. **(1990, 4M)**

52. *n*-butane is produced by monobromination of ethane followed by Wurtz's reaction.Calculate volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90% yield and the Wurtz's reaction with 85% yield. **(1989, 3M)**

53. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate (i) molal concentration and (ii) mole fraction of sugar in syrup. **(1988, 2M)**

54. An unknown compound of carbon, hydrogen and oxygen contains 69.77% C and 11.63% H and has a molecular weight of 86. It does not reduces Fehling's solution but forms a bisulphate addition compound and gives a positive iodoform test. What is the possible structure(s) of unknown compound? **(1987, 3M)**

55. The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g per mL. Calculate (i) the percentage by weight of sodium thiosulphate (ii) the mole fraction of sodium thiosulphate and (iii) the molalities of Na and $S_2O_3^{2}$ ions. **(1983, 5M)**

56. (a) 1.0 L of a mixture of CO and CO_2 is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 L. The volumes are measured under the same conditions. Find the composition of mixture by volume.

(b) A compound contains 28 per cent of nitrogen and 72 per cent of a metal by weight. 3 atoms of metal combine with 2 atoms of nitrogen. Find the atomic weight of metal. **(1980, 5M)**

57. 5.00 mL of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 mL) and the mixture exploded by means of electric spark. After explosion, the volume of the mixed gases remaining was 25 mL.

On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. **(1979, 3M)**

58. In the analysis of 0.5 g sample of feldspar, a mixture of chlorides of sodium and potassium is obtained, which weighs 0.1180 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in the sample? **(1979, 5M)**

59. The vapour density (hydrogen = 1) of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture. **(1979, 5M)**

60. Accounts for the following. Limit your answer to two sentences, "Atomic weights of most of the elements are fractional". **(1979, 1M)**

61. Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. **(1978, 2M)**

Topic 2 Equivalent Concept, Neutralisation and Redox Titration

Objective Questions I (Only one correct option)

1. An example of a disproportionation reaction is **(2019 Main, 12 April I)**

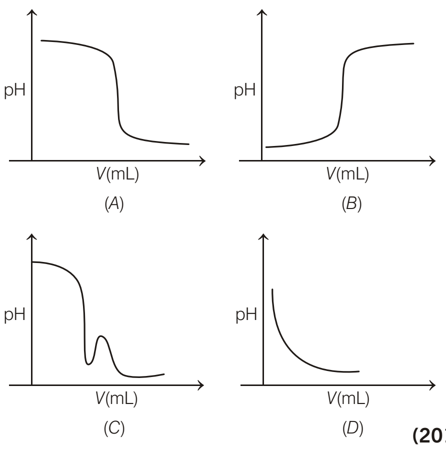
(a) $2MnO_4$ 10I 16H $2Mn^2$ $5I_2$ $8H_2O$

(b) 2NaBr Cl_2 2NaCl Br_2

(c) $2KMnO_4$ K_2MnO_4 MnO_2 O_2

(d) 2CuBr $CuBr_2$ Cu

2. In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? **(2019 Main, 9 April II)**



(2019 Main, 9 April II)

(a) (*D*) (b) (*A*)
(c) (*B*) (d) (*C*)

3. 0.27 g of a long chain fatty acid was dissolved in 100 cm^3 of hexane. 10 mL of this solution was added dropwise to the surface of water in a round watch glass. Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer? [Density of fatty acid 0.9 g cm ^{3}; 3] **(2019 Main, 8 April II)**

(a) 10 ^{6} m (b) 10 ^{4} m
(c) 10 ^{8} m (d) 10 ^{2} m

4. In order to oxidise a mixture of one mole of each of FeC_2O_4, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium, the number of moles of $KMnO_4$ required is **(2019 Main, 8 April I)**

(a) 2 (b) 1 (c) 3 (d) 1.5

5. 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 g of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is (molar mass of calcium bicarbonate is 162 g mol ^{1} and magnesium bicarbonate is 146 g mol ^{1}) **(2019 Main, 8 April I)**

(a) 5,000 ppm (b) 1,000 ppm
(c) 100 ppm (d) 10,000 ppm

6. 50 mL of 0.5 M oxalic acid is needed to neutralise 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is **(2019 Main, 12 Jan I)**

(a) 40 g (b) 80 g (c) 20 g (d) 10 g

7. 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? **(2019 Main, 11 Jan II)**

(a) 75 mL (b) 25 mL (c) 12.5 mL (d) 50 mL

8. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is **(2019 Main, 10 Jan II)**

(a) 2 (b) 5 (c) 1 (d) 10

9. The ratio of mass per cent of C and H of an organic compound ($C_xH_yO_z$) is 6 : 1. If one molecule of the above compound ($C_xH_yO_z$) contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. The empirical formula of compound $C_xH_yO_z$ is **(2018 Main)**
(a) $C_3H_6O_3$ (b) C_2H_4O (c) $C_3H_4O_2$ (d) $C_2H_4O_3$

10. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? **(2018 Main)**

	Base	Acid	End point
(a)	Weak	Strong	Colourless to pink
(b)	Strong	Strong	Pinkish red to yellow
(c)	Weak	Strong	Yellow to pinkish red
(d)	Strong	Strong	Pink to colourless

11. From the following statements regarding H_2O_2 choose the incorrect statement. **(2015 Main)**
(a) It can act only as an oxidising agent
(b) It decomposed on exposure to light
(c) It has to be stored in plastic or wax lined glass bottles in dark
(d) It has to be kept away from dust

12. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is **(2007, 3M)**
(a) 3 (b) 4 (c) 5 (d) 6

13. In the standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is **(2001, 1M)**
(a) (molecular weight)/2 (b) (molecular weight)/6
(c) (molecular weight)/3 (d) same as molecular weight

14. The reaction, $3ClO\ (aq) \quad ClO_3^-\ (aq) + 2Cl\ (aq)$ is an example of **(2001)**
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction

15. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is **(2001, 1M)**
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

16. Among the following, the species in which the oxidation number of an element is + 6 **(2000)**
(a) MnO_4 (b) $Cr(CN)_6^3$
(c) NiF_6^2 (d) CrO_2Cl_2

17. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are **(1999)**
(a) 0, +1 and –2 (b) +2, +1 and –2
(c) 0, +1 and +2 (d) –2, +1 and –2

18. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic medium is **(1997)**
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

19. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is **(1997)**
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

20. For the redox reaction

$$MnO_4 + C_2O_4^2 + H^+ \qquad Mn^{2+} + CO_2 + H_2O$$

The correct coefficients of the reactants for the balanced reaction are **(1992)**

	MnO_4	$C_2O_4^2$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

21. The volume strength of 1.5 N H_2O_2 is **(1990, 1M)**
(a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0

22. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is **(1988)**
(a) +3 (b) +2
(c) +1 (d) –1

23. The equivalent weight of $MnSO_4$ is half of its molecular weight, when it converts to **(1988, 1M)**
(a) Mn_2O_3 (b) MnO_2
(c) MnO_4 (d) MnO_4^2

Objective Question II (More than one correct option)

24. For the reaction, $I \quad ClO_3 \quad H_2SO_4 \qquad Cl + HSO_4 \quad I_2$ the correct statement(s) in the balanced equation is/are **(2014 Adv)**
(a) stoichiometric coefficient of HSO_4 is 6
(b) iodide is oxidised
(c) sulphur is reduced
(d) H_2O is one of the products

Numerical Value Based Question

25. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2\ 6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $NiCl_2\ 6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is____
(Atomic weights in g mol ^{1} : H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59) **(2018 Adv.)**

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

26. **Statement I** In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

Statement II Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3. **(1991, 2M)**

Fill in the Blanks

27. The compound $YBa_2Cu_3O_7$, which shows super conductivity, has copper in oxidation state ………. Assume that the rare earth element yttrium is in its usual + 3 oxidation state. **(1994, 1M)**

Integer Answer Type Questions

28. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is **(2011)**

29. Among the following, the number of elements showing only one non-zero oxidation state is O, Cl, F, N, P, Sn, Tl, Na, Ti **(2010)**

30. A student performs a titration with different burettes and finds titrate values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titrate value is **(2010)**

Subjective Questions

31. Calculate the amount of calcium oxide required when it reacts with 852 g of P_4O_{10}. **(2005, 2M)**

32. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2. **(2001)**

33. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate? **(1999, 3M)**

34. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. **(1998, 5M)**

35. To a 25 mL H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution. **(1997, 5M)**

36. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL . A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the dilute solution, after complete extraction of the iodine required 12.80 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample. **(1996, 5M)**

37. A 20.0 cm^3 mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm^3.

A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. **(1995, 4M)**

38. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. **(1995, 3M)**

39. One gram of commercial $AgNO_3$ is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6 M HCl till all I ions are converted into ICl. It requires 50 mL of (M/10) KIO_3 solution, 20 mL of the same stock solution of KI requires 30 mL of (M/10) KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in the sample.

Reaction $KIO_3 + 2KI + 6HCl \qquad 3ICl + 3KCl + 3H_2O$ **(1992, 4M)**

40. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralisation. Calculate the percentage composition of the components of the mixture. **(1992, 5M)**

41. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. **(1991, 4M)**

42. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^2$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralised with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $C_2O_4^{2}$ in the compound. Write down the balanced redox reactions involved in the above titrations. **(1991, 5M)**

43. A mixture of $H_2C_2O_4$ (oxalic acid) and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralisation. In another experiment, 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture. **(1990, 5M)**

44. An organic compound *X* on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of *X* gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound *X* may be represented by two isomeric structures *Y* and *Z*. *Y* on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while *Z* on similar treatment gives ethanal. Find out the molecular formula of *X* and gives the structure of *Y* and *Z*. **(1989, 5M)**

45. An equal volume of a reducing agent is titrated separately with 1 M $KMnO_4$ in acid, neutral and alkaline medium. The volumes of $KMnO_4$ required are 20 mL in acid, 33.3 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reaction. Find out the volume of 1M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is titrated in acid medium. **(1989, 5M)**

46. A sample of hydrazine sulphate $(N_2H_6SO_4)$ was dissolved in 100 mL of water, 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it, required 20 mL of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution.

Reaction $4Fe^{3+} + N_2H_4 \qquad N_2 + 4Fe^{2+} + 4H^+$

$MnO_4 + 5Fe^{2+} + 8H^+ \qquad Mn^{2+} + 5Fe^{3+} + 4H_2O$

(1988, 3M)

47. 5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. 30 mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $Na_2CO_3 \; 10H_2O$ in 100 mL of water. Calculate the amount in gram of the sulphate ions in solution. **(1985, 4M)**

48. $2.68 \quad 10^{3}$ moles of a solution containing an ion A^{n+} require $1.61 \quad 10^{3}$ moles of MnO_4 for the oxidation of A^{n+} to AO_3 in acidic medium. What is the value of *n* ? **(1984, 2M)**

49. 4.08 g of a mixture of BaO and unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralisation. Identify the metal *M*. **(1983, 4M)**

Answers

Topic 1

1. (d)	**2.** (c)	**3.** (b)	**4.** (a)
5. (d)	**6.** (b)	**7.** (d)	**8.** (c)
9. (b)	**10.** (b)	**11.** (b)	**12.** (c)
13. (b)	**14.** (*)	**15.** (d)	**16.** (d)
17. (b)	**18.** (a)	**19.** (c)	**20.** (b)
21. (a)	**22.** (a)	**23.** (d)	**24.** (d)
25. (d)	**26.** (a)	**27.** (d)	**28.** (a)
29. (a)	**30.** (a)	**31.** (a)	**32.** (c)
33. (6.47kg)	**34.** (126 mg)	**35.** (495 g)	**36.** (4.14 g)
37. (0.4)	**38.** ($6.023 \quad 10^{24}$)	**39.** C-12 isotope	**40.** (9)
41. (8)	**42.** (8 mL)	**43.** (2)	**44.** ($5 \quad 10^{19}$ m^2)
45. (55.56 mol L^{1})	**46.** ($70.91 \quad 10^6$g)	**47.** ($4.3 \quad 10^{3}$)	**50.** (10.42)
51. (1.7 g)	**52.** (55.55 L)	**53.** ($9.9 \quad 10^{3}$)	
55. (i) 37.92, (ii) 0.065, (iii) 7.73m	**56.** (a) 0.6, (b) 24		
58. (i) 0.0179 g, (ii) 10.6 %	**59.** (0.437)	**61.** 20 %	

Topic 2

1. (d)	**2.** (b)	**3.** (a)	**4.** (a)
5. (d)	**6.** (*)	**7.** (b)	**8.** (c)
9. (d)	**10.** (c)	**11.** (a)	**12.** (d)
13. (b)	**14.** (c)	**15.** (a)	**16.** (d)
17. (a)	**18.** (b)	**19.** (a)	**20.** (a)
21. (b)	**22.** (c)	**23.** (b)	**24.** (a, b, d)
25. (2992)	**26.** (b)	**27.** 7 / 3	**28.** (5)
29. (2)	**30.** (3)	**31.** (1008 g)	**33.** (8.096 mL)
34. (0.062 M)	**35.** (1.334 V)	**39.** (85%)	**41.** ($1.04 \quad 10^4$)
42. (1:2)	**45.** (16.67 mL)	**46.** (6.5gL^{1})	**47.** (6.5376 g)
48. (2)	**49.** (Ca)		

Hints & Solutions

Topic 1 Mole Concept

1. **Key Idea** To find the mass of A and B in the given question, mole concept is used.

$$\text{Number of moles}(n) \quad \frac{\text{given mass }(w)}{\text{molecular mass }(M)}$$

Compound	Mass of A (g)	Mass of B (g)
AB_2	M_A	$2M_B$
A_2B_2	$2M_A$	$2M_B$

We know that,

$$\text{Number of moles }(n) \quad \frac{\text{given mass }(w)}{\text{molecular mass }(M)}$$

$$n \quad M \quad w \qquad \ldots(A)$$

Using equation (A), it can be concluded that

$$5(M_A \quad 2M_B) \quad 125 \quad 10^{\ 3}\text{ kg} \qquad \ldots\text{(i)}$$

$$10(2M_A \quad 2M_B) \quad 300 \quad 10^{\ 3}\text{ kg} \qquad \ldots\text{(ii)}$$

From equation (i) and (ii)

$$\frac{1}{2}\frac{(M_A \quad 2M_B)}{(2M_A \quad 2M_B)} \quad \frac{125}{300}$$

On solving the equation, we obtain

$$M_A \quad 5 \quad 10^{\ 3}$$

and $$M_B \quad 10 \quad 10^{\ 3}$$

So, the molar mass of $A(M_A)$ is
$5 \quad 10^{\ 3}$ kg mol $^{\ 1}$ and $B(M_B)$ is $10 \quad 10^{\ 3}$ kg mol $^{\ 1}$.

2. (a) $\underset{44\text{g}}{C_3H_8(g)} + \underset{160\text{g}}{5O_2(g)} \qquad 3CO_2(g) \quad 4H_2O(l)$

$$1\text{g of reactant} \quad \frac{160}{44}\text{ g of } O_2 \text{ consumed} \quad 3.64\text{ g}$$

(b) $\underset{124\text{g}}{P_4(s)} + \underset{160\text{g}}{5O_2(g)} \qquad P_4O_{10}(s)$

$$1\text{ g of reactant} \quad \frac{160}{124}\text{ g of } O_2 \text{ consumed} \quad 1.29\text{ g}$$

(c) $\underset{244\text{g}}{4Fe(s)} + \underset{96\text{g}}{3O_2(g)} \qquad 2Fe_2O_3(s)$

$$1\text{ g of reactant} \quad \frac{96}{224}\text{ g of } O_2 \text{ consumed} \quad 0.43\text{ g}$$

(d) $\underset{48\text{ g}}{2Mg(s)} + \underset{32\text{ g}}{O_2(g)} \qquad 2MgO(s)$

$$1\text{ g of reactant} \quad \frac{32}{48}\text{ g of } O_2 \text{ consumed} \quad 0.67\text{ g}$$

So, minimum amount of O_2 is consumed per gram of reactant (Fe) in reaction (c).

3. In eudiometry,

$$C_xH_y \quad x \quad \frac{y}{4} \quad O_2 \quad \xrightarrow[1\text{ atm}]{300\text{ K}} \quad x\,CO_2 \quad \frac{y}{2}H_2O$$

$$1\text{ mol} \quad x \quad \frac{y}{4}\text{ mol} \qquad x\text{ mol}$$

$$1\text{ mL} \quad x \quad \frac{y}{4}\text{ mL} \qquad x\text{ mL}$$

$$10\text{ mL} \quad x \quad \frac{y}{4} \quad 10\text{ mL} \qquad 10x\text{ mL}$$

Given, (i) $V_{CO_2} \quad 10x \quad 40\text{ mL} \quad x \quad 4$

(ii) $V_{O_2} \quad 10 \quad x \quad \frac{y}{4}\text{ mL} = 55\text{ mL}$

$$10 \quad 4 \quad \frac{y}{4} \quad 55 \qquad [\because x \quad 4]$$

$$40 \quad \frac{y \quad 10}{4} \quad 55$$

$$y \quad \frac{10}{4} \quad 15 \quad y \quad 15 \quad \frac{4}{10} \quad 6$$

So, the hydrocarbon (C_xH_y) is C_4H_6.

4. Given, volume $\quad 10\text{ mL}$

Molarity $\quad 1\text{ mM} \quad 10^{\ 3}\text{ M}$

Number of millimoles $\quad 10\text{ mL} \quad 10^{\ 3}\text{ M} \quad 10^{\ 2}$

Number of moles $\quad 10^{\ 5}$

Now, number of molecules

$$\text{Number of moles} \quad \text{Avogadro's number}$$

$$10^{\ 5} \quad 6 \quad 10^{23} \quad 6 \quad 10^{18}$$

Surface area occupied by $6 \quad 10^{18}$ molecules $\quad 0.24\text{ cm}^2$

Surface area occupied by 1 molecule

$$\frac{0.24}{6 \quad 10^{18}} \quad 0.04 \quad 10^{\ 18}\text{ cm}^2$$

As it is given that polar head is approximated as cube. Thus, surface area of cube $\quad a^2$, where

$$a \quad \text{edge length}$$

$$a^2 \quad 4 \quad 10^{\ 20}\text{ cm}^2$$

$$a \quad 2 \quad 10^{\ 10}\text{ cm} \quad 2\text{ pm}$$

5. **Key Idea** The reactant which is present in the lesser amount, i.e. which limits the amount of product formed is called limiting reagent.

When 56 g of $N_2 \quad 10$ g of H_2 is taken as a combination then dihydrogen (H_2) act as a limiting reagent in the reaction.

$$\underset{\substack{2 \quad 14\text{g} \\ 28\text{g}}}{N_2(g)} \quad \underset{\substack{3 \quad 2\text{g} \\ 6\text{g}}}{3H_2(g)} \qquad \underset{\substack{2(14 \quad 3)\text{ g} \\ 34\text{g}}}{2NH_3(g)} \qquad \ldots\text{(I)}$$

28 g N_2 requires 6 g H_2 gas.

56 g of N_2 requires $\frac{6\text{g}}{28\text{g}} \quad 56\text{g} \quad 12\text{g of } H_2$

12 g of H_2 gas is required for 56 g of N_2 gas but only 10 g of H_2 gas is present in option (a).
Hence, H_2 gas is the limiting reagent.
In option (b), i.e. 35 g of N_2 8 g of H_2.
As 28 g N_2 requires 6 g of H_2.

$$35\text{g } N_2 \text{ requires } \frac{6\text{ g}}{28\text{ g}} \quad 35\text{ g } H_2 \qquad 7.5\text{ g of } H_2.$$

Here, H_2 gas does not act as limiting reagent since 7.5 g of H_2 gas is required for 35 g of N_2 and 8 g of H_2 is present in reaction mixture. Mass of H_2 left unreacted 8 7.5 g of H_2.
0.5 g of H_2.
Similarly, in option (c) and (d), H_2 does not act as limiting reagent.
For 14 g of N_2 4 g of H_2.
As we know 28 g of N_2 reacts with 6 g of H_2.

$$14\text{ g of } N_2 \text{ reacts with } \frac{6}{28} \quad 14\text{ g of } H_2 \qquad 3\text{ g of } H_2.$$

For 28 g of N_2 6 g of H_2, i.e. 28 g of N_2 reacts with 6 g of H_2 (by equation I).

6. **Key Idea** The percentage composition of a compound is given by the formula.
% composition [Composition of a substance in a compound / Total composition total of compound] 100

In CH_4,
mole of carbon 1
mole of hydrogen 4

$$\% \text{ of carbon by mole in } CH_4 \quad \frac{1}{1 \quad 4} \quad 100 \quad 20\%$$

7. Mole fraction of solute

$$\frac{\text{number of moles of solute} + \text{ number of moles solvent}}{\text{number of moles of solute}}$$

$$_{\text{Solute}} \quad \frac{n_{\text{Solute}}}{n_{\text{Solute}} \quad n_{\text{Solvent}}} \quad \frac{\dfrac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{\dfrac{w_{\text{Solute}}}{Mw_{\text{Solute}}} \quad \dfrac{w_{\text{Solvent}}}{Mw_{\text{Solvent}}}}$$

Given, $w_{\text{Solute}} \quad w_{\text{NaOH}} \quad 8\text{ g}$

$Mw_{\text{Solute}} \quad Mw_{\text{NaOH}} \quad 40\text{g mol}^{1}$

$w_{\text{Solvent}} \quad w_{H_2O} \quad 18\text{g}$

$Mw_{\text{Solvent}} \quad 18\text{ g mol}^{1}$

$$_{\text{Solute}} \quad _{\text{NaOH}} \quad \frac{8/40}{\dfrac{8}{40} \quad \dfrac{18}{18}} \quad \frac{0.2}{0.2 \quad 1} \quad \frac{0.2}{1.2} \quad 0.167$$

$$\text{Now, molality } (m) \quad \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$\frac{\dfrac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{w_{\text{Solvent}}\text{(in g)}} \quad 1000 \quad \frac{\dfrac{8}{40}}{18} \quad 1000$$

$$\frac{0.2}{18} \quad 1000 \quad 11.11\text{ mol kg}^{1}$$

Thus, mole fraction of NaOH in solution and molality of the solution respectively are 0.167 and 11.11 mol kg^{1}.

8. Concentration of H_2O_2 is expressed in terms of volume strength, i.e. "volume of O_2 liberated by H_2O_2 at NTP". Molarity is connected to volume strength as:

$$\text{Molarity } (M) \quad \frac{x}{11.2} \text{ or } x \quad \text{Molarity} \quad 11.2$$

where, x volume strength
So, for 1 M H_2O_2, x 1 11.2 11.2
Among the given options, 11.35 is nearest to 11.2.

9.
$$\text{Molarity} \quad \frac{\text{Number of moles of solute } (n)}{\text{Volume of solution (in L)}}$$

$$\text{Also,} \quad n \quad \frac{w_B \text{ (g)}}{M_B \text{ (gmol}^{1})}$$

$$\text{Molarity} \quad \frac{w_B / M_B}{V}$$

Given, w_B mass of solute (B) in g
M_B Gram molar mass of B ($C_{12}H_{22}O_{11}$) 342 g mol^{1}
Molarity 0.1 M
Volume (V) 2 L

$$0.1 \quad \frac{w_B / 342}{2} \qquad w_B \quad 0.1 \quad 342 \quad 2\text{ g} \quad 68.4\text{ g}$$

10. $2\, C_{57}H_{110}O_6(s) + 163\, O_2(g) \qquad 110 H_2O(l) + 114\, CO_2(g)$
Molecular mass of $C_{57}H_{110}O_6$
2 (12 57 1 110 16 6) g 1780 g
Molecular mass of 110 H_2O 110 (2 16) = 1980 g
1780 g of $C_{57}H_{110}O_6$ produced 1980 g of H_2O.

$$445\text{g of } C_{57}H_{110}O_6 \text{ produced } \frac{1980}{1780} \quad 445\text{ g of } H_2O$$

495 of H_2O

11.
$$\text{Molality } (m) \quad \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in g)}} \quad 1000$$

$$\frac{\text{Mass of solute (in g)} \quad 1000}{\text{Molecular weight of solute} \atop \text{mass of solvent (in g)}}$$

$$\frac{w_{\text{Na}} \quad 1000}{M_{\text{Na}} \quad w_{H_2O}} \quad \frac{92 \quad 1000}{23 \quad 1000} \quad 4\text{ mol kg}^{1}$$

12. Given, abundance of elements by mass
oxygen 61.4%, carbon 22.9%, hydrogen 10% and nitrogen 2.6%
Total weight of person 75 kg

$$\text{Mass due to } {}^1\text{H} \quad \frac{75 \quad 10}{100} \quad 7.5\text{ kg}$$

^{1}H atoms are replaced by ^{2}H atoms,
Mass due to ^{2}H = (7.5 2) kg
Mass gain by person 7.5 kg

13.
$$\underset{1\text{ g}}{M_2CO_3} \quad 2HCl \qquad 2M\text{ Cl} \quad H_2O \quad \underset{0.01186 \text{ mole}}{CO_2}$$

Number of moles of M_2CO_3 reacted Number of moles of CO_2 evolved

$$\frac{1}{M} \quad 0.01186 \qquad [M \quad \text{molar mass of } M_2CO_3]$$

$$M \quad \frac{1}{0.01186} \quad 84.3\text{ g mol}^{1}$$

14. $\underset{75\text{ mL}}{C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g)} \quad \underset{30\text{ mL}}{xCO_2(g)} \quad \frac{y}{2}H_2O(l)$

O_2 used 20% of 375 75 mL

Inert part of air 80% of 375 300 mL

Total volume of gases CO_2 Inert part of air

30 300 330 mL

$$\frac{x}{1} \quad \frac{30}{15} \quad x \quad 2$$

$$\frac{x \quad \frac{y}{4}}{1} \quad \frac{75}{15} \quad x \quad \frac{y}{4} \quad 5$$

$$x \quad 2, \; y \quad 12 \qquad C_2H_{12}$$

15. We know the molecular weight of $C_8H_7SO_3Na$

12 8 1 7 32 16 3 23 206

we have to find, mole per gram of resin.

1g of $C_8H_7SO_3Na$ has number of mole

$$\frac{\text{weight of given resin}}{\text{Molecular, weight of resin}} \quad \frac{1}{206}\text{mol}$$

Now, reaction looks like

$$2C_8H_7SO_3Na \quad Ca^2 \qquad (C_8H_7SO_3)_2Ca \quad 2Na$$

$\because$ 2 moles of $C_8H_7SO_3Na$ combines with 1 mol Ca^2

1 mole of $C_8H_7SO_3Na$ will combine with $\frac{1}{2}$ mol Ca^2

$\frac{1}{206}$ mole of $C_8H_7SO_3$ Na will combine with

$$\frac{1}{2} \quad \frac{1}{206}\text{ mol } Ca^2 \quad \frac{1}{412}\text{ mol } Ca^2$$

16. Given, initial strength of acetic acid 0.06 N

Final strength 0.042 N; Volume 50 mL

Initial millimoles of CH_3COOH 0.06 50 3

Final millimoles of CH_3COOH 0.042 50 2.1

Millimoles of CH_3COOH adsorbed 3 2.1 0.9 mmol

0.9 60 mg 54 mg

17. $$\frac{n_{O_2}}{n_{N_2}} \quad \frac{\dfrac{(m_{O_2})}{(M_{O_2})}}{\dfrac{(m_{N_2})}{(M_{N_2})}}$$

where, m_{O_2} given mass of O_2, m_{N_2} given mass of N_2, M_{O_2} molecular mass of O_2, M_{N_2} molecular mass of N_2, n_{O_2} number of moles of O_2, n_{N_2} number of moles of N_2

$$\frac{m_{O_2}}{m_{N_2}} \quad \frac{28}{32} \quad \frac{1}{4} \quad \frac{28}{32} \quad \frac{7}{32}$$

18. From the formula, $M_f \quad \dfrac{M_1V_1 \quad M_2V_2}{V_1 \quad V_2}$

Given, V_1 750 mL, M_1 0.5 M

V_2 250 mL, M_2 2 M

$$\frac{750 \quad 0.5 \quad 250 \quad 2}{750 \quad 250} \quad \frac{875}{1000} \quad 0.875\text{ M}$$

19. Molarity $\dfrac{\text{Moles of solute}}{\text{Volume of solution (L)}}$

Moles of urea $\dfrac{120}{60}$ 2

Weight of solution Weight of solvent Weight of solute

1000 + 120 1120 g

Volume $\dfrac{1120\text{ g}}{1.15\text{ g / mL}} \quad \dfrac{1}{1000\text{mL / L}}$ 0.973 L

Molarity $\dfrac{2.000}{0.973}$ 2.05M

20. From the given relative abundance, the average weight of Fe can be calculated as

$$A \quad \frac{54 \quad 5 \quad 56 \quad 90 \quad 57 \quad 5}{100} = 55.95$$

21. 1.0 L of mixture X contain 0.01 mole of each $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$. Also, with $AgNO_3$, only $[Co(NH_3)_5SO_4]Br$ reacts to give AgBr precipitate as

$$\underset{1.0\text{ mol}}{[Co(NH_3)_5SO_4]Br} \quad \underset{\text{Excess}}{AgNO_3} \quad [Co(NH_3)_5SO_4]NO_3 + \underset{1.0\text{ mol}}{AgBr}$$

With $BaCl_2$, only $[Co(NH_3)_5Br]SO_4$ reacts giving $BaSO_4$ precipitate as

$$\underset{1.0\text{ mol}}{[Co(NH_3)_5Br]SO_4} \quad \underset{\text{Excess}}{BaCl_2} \quad [Co(NH_3)_5Br]Cl_2 + \underset{1\text{ mol}}{BaSO_4}$$

Hence, moles of Y and Z are 0.01 each.

22. Number of atoms Number of moles Avogadro's number (N_A)

Number of atoms in 24 g C $= \dfrac{24}{12} \quad N_A = 2N_A$

Number of atoms in 56 g of Fe $= \dfrac{56}{56}N_A \quad N_A$

Number of atoms in 27 g of Al $= \dfrac{27}{27}N_A \quad N_A$

Number of atoms in 108 g of Ag $= \dfrac{108}{108}N_A \quad N_A$

Hence, 24 g of carbon has the maximum number of atoms.

23. Mass of an electron = 9.108 10^{31} kg

$\because$ 9.108 10^{31} kg = 1.0 electron

$$1\text{ kg} \quad \frac{1}{9.108 \quad 10^{31}}\text{ electrons} \quad \frac{10^{31}}{9.108} \quad \frac{1}{6.023 \quad 10^{23}}$$

$$\frac{1}{9.108 \quad 6.023} \quad 10^8\text{ mole of electrons}$$

24. Phosphorus acid is a dibasic acid as :

O

H—P—OH only two replaceable hydrogens

OH

Therefore, normality molarity basicity 0.3 2 0.60

25. Molality is defined in terms of weight, hence independent of temperature. Remaining three concentration units are defined in terms of volume of solution, they depends on temperature.

26. Molality of a solution is defined as number of moles of solute present in 1.0 kg (1000 g) of solvent.

27. The balanced chemical reaction is

$$3BaCl_2 + 2Na_3PO_4 \qquad Ba_3(PO_4)_2 + 6NaCl$$

In this reaction, 3 moles of $BaCl_2$ combines with 2 moles of Na_3PO_4. Hence, 0.5 mole of of $BaCl_2$ require

$$\frac{2}{3} \quad 0.5 \quad 0.33 \text{ mole of } Na_3PO_4.$$

Since, available Na_3PO_4 (0.2 mole) is less than required mole (0.33), it is the limiting reactant and would determine the amount of product $Ba_3(PO_4)_2$.

$\because$ 2 moles of Na_3PO_4 gives 1 mole $Ba_3(PO_4)_2$

$$0.2 \text{ mole of } Na_3PO_4 \text{ would give } \frac{1}{2} \quad 0.2 = 0.1 \text{ mole } Ba_3(PO_4)_2$$

28. Unlike other metal carbonates that usually decomposes into metal oxides liberating carbon dioxide, silver carbonate on heating decomposes into elemental silver liberating mixture of carbon dioxide and oxygen gas as :

$$\underset{MW = 276\text{ g}}{Ag_2CO_3(s)} \xrightarrow{\text{Heat}} \underset{2 \quad 108 = 216\text{ g}}{2Ag\,(s)} + CO_2(g) + \frac{1}{2}O_2(g)$$

Hence, 2.76 g of Ag_2CO_3 on heating will give

$$\frac{216}{276} \quad 2.76 \quad 2.16\text{g Ag as residue.}$$

29. The balanced chemical reaction of zinc with sulphuric acid and NaOH are

$$Zn + H_2SO_4 \qquad ZnSO_4 + H_2(g)$$

$$Zn + 2NaOH + 2H_2O \qquad Na_2[Zn(OH)_4] + H_2\,(g)$$

Since, one mole of $H_2(g)$ is produced per mole of zinc with both sulphuric acid and NaOH respectively, hydrogen gas is produced in the molar ratio of 1:1 in the above reactions.

30. Number of molecules present in 36 g of water

$$\frac{36}{18} \quad N_A \quad 2N_A$$

Number of molecules present in 28 g of CO $\dfrac{28}{28} \quad N_A \quad N_A$

Number of molecules present in 46 g of C_2H_5OH $\dfrac{46}{46} \quad N_A = N_A$

Number of molecules present in 54 g of N_2O_5 $\dfrac{54}{108} \quad N_A = 0.5\,N_A$

Here, N_A is Avogadro's number. Hence, 36 g of water contain the largest $(2N_A)$ number of molecules.

31. In a neutral atom, atomic number represents the number of protons inside the nucleus and equal number of electrons around it. Therefore, the number of total electrons in molecule of CO_2

= electrons present in one carbon atom

+ 2 electrons present in one oxygen atom

$= 6 + 2 \quad 8 = 22.$

32. $\dfrac{\text{Weight of a compound in gram }(w)}{\text{Molar mass }(M)} = \text{Number of moles }(n)$

$$= \frac{\text{Number of molecules }(N)}{\text{Avogadro number }(N_A)}$$

$$\frac{w\,(O_2)}{32} \quad \frac{N\,(O_2)}{N_A} \qquad \ldots\text{(i)}$$

And $\dfrac{w\,(N_2)}{28} \quad \dfrac{N\,(N_2)}{N_A}$ …(ii)

Dividing Eq. (i) by Eq. (ii) gives

$$\frac{N\,(O_2)}{N\,(N_2)} \quad \frac{w\,(O_2)}{w\,(N_2)} \quad \frac{28}{32}$$

$$\frac{1}{4} \quad \frac{28}{32} \quad \frac{7}{32}$$

33. The equations of chemical reactions occurring during the process are

In the presence of oxygen

$$2PbS + 3O_2 \qquad 2PbO + 2SO_2 \qquad \ldots\text{(i)}$$

By self reduction

$$2PbO + PbS \qquad 3Pb + SO_2$$

Thus 3 moles of O_2 produces 3 moles of Pb

i.e. 32 3 96 g of O_2 produces 3 207 621 g of Pb

So 1000 g (1kg) of oxygen will produce

$$\frac{621}{96} \quad 1000 \quad 6468.75\text{ g}$$

$$6.4687\text{ kg} \quad 6.47\text{ kg}$$

Alternative Method

From the direct equation,

$$PbS \quad \underset{32\text{ g}}{O_2} \qquad \underset{207\text{ g}}{Pb} + SO_2$$

So, 32 g of O_2 gives 207 g of Pb

1 g of O_2 will give $\dfrac{207}{32}$ g of Pb

1000g of O_2 will give $\dfrac{207}{32} \quad 1000 = 6468.75$ g

$= 6.46875$ kg 6.47kg

34. The balanced equations are

(1) $2MnCl_2 \quad 5K_2S_2O_8 \quad 8H_2O$
$\qquad 2KMnO_4 \quad 4K_2SO_4 \quad 6H_2SO_4 \quad 4HCl$

(2) $2KMnO_4 \quad 5H_2C_2O_4 \quad 3H_2SO_4$
$\qquad K_2SO_4 \quad 2MnSO_4 \quad 8H_2O + 10CO_2$

Given, mass of oxalic acid added = 225mg

So, millimoles of oxalic acid added $= \dfrac{225}{90} \quad 2.5$

Now from equation 2

Millimoles of $KMnO_4$ used to react with oxalic acid=1 and

Millimoles of $MnCl_2$ required initially=1

Mass of $MnCl_2$ required initially $= 1 \quad (55 \quad 71) = 126$mg

Alternative Method

m moles of $MnCl_2$ $\quad m$ moles of $KMnO_4$ $\quad x$ (let)

and M_{eq} of $KMnO_4$ $\quad M_{eq}$ of oxalic acid

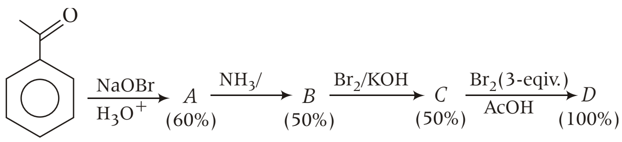
So, $\qquad x \quad 5 \quad \dfrac{225}{90} \quad 2$

Hence, $x \quad 1$

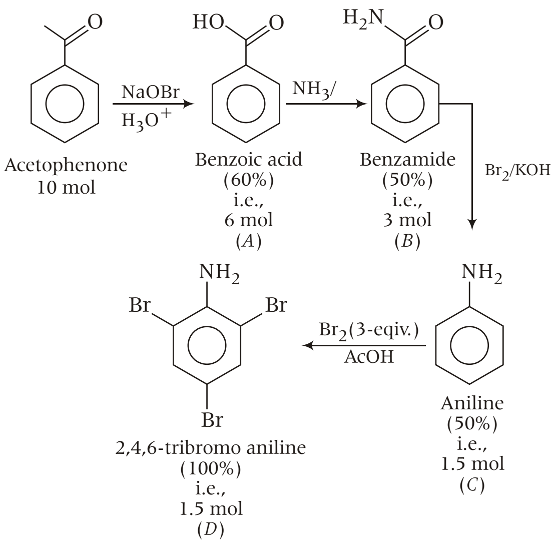
m moles of $MnCl_2 \quad 1$

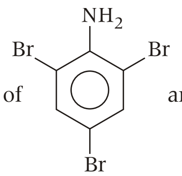
Hence mass of $MnCl_2 \quad (55 \quad 71) \quad 1 \quad 126$ mg.

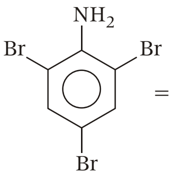
35. Given,

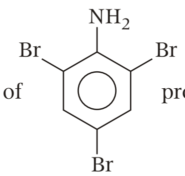


The products formed are



So, 1.5 mol of  are produced from 10 moles of acetophenone.

Molar mass of  = 240 + 14 + 4 + 72 = 330

Hence, amount of  produced is 330 × 1.5 = 495 g

36. Molar mass of $CuSO_4$ $5H_2O$

= 63.5 + 32 + 4   16 + 5   18

= 249.5 g

Also, molar mass represents mass of Avogadro number of molecules in gram unit, therefore

∵ 6.023 10^{23} molecules of $CuSO_4$ $5H_2O$ weigh 249.5 g

10^{22} molecules will weigh $\frac{249.5}{6.023 \quad 10^{23}}$ 10^{22} 4.14 g

37. Molarity $\frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$

$\frac{\text{Weight of solute}}{\text{Molar mass}} \quad \frac{1000}{\text{Volume in mL}}$

$\frac{3}{30} \quad \frac{1000}{250}$ 0.4 M

38. Considering density of water to be 1.0 g/mL, 18 mL of water is 18 g (1.0 mol) of water and it contain Avogadro number of molecules. Also one molecule of water contain

2   (one from each H-atom) + 8   (from oxygen atom)

= 10 electrons.

1.0 mole of H_2O contain   10   6.023 10^{23}

6.023 10^{24} electrons.

39. Carbon-12 isotope. According to modern atomic mass unit, one atomic mass unit (amu) is defined as one-twelfth of mass of an atom of C-12 isotope, i.e.

1 amu (u) $\frac{1}{12}$ weight of an atom of C-12 isotope.

40. Moles of solute, n_1 $\frac{w_1}{m_1}$; Moles of solvent, n_2 $\frac{w_2}{m_2}$

$_1$ (solute)   0.1 and $_2$ (solvent)   0.9

$\frac{1}{2} \quad \frac{n_1}{n_2} \quad \frac{w_1}{m_1} \quad \frac{m_2}{w_2} \quad \frac{}{9}$

Molarity $\frac{\text{Solute (moles)}}{\text{Volume (L)}} \quad \frac{w_1 \quad 1000 \quad 2}{m_1 \ (w_1 \quad w_2)}$

Note Volume $\frac{\text{Total mass of solution}}{\text{Density}} \quad \frac{w_1 \quad w_2}{2}$ mL

Molality $\frac{\text{Solute (moles)}}{\text{Solvent (kg)}} \quad \frac{w_1 \quad 1000}{m_1 \quad w_2}$

Given,   molarity   molality

hence, $\frac{2000\,w_1}{m_1 \ (w_1 \quad w_2)} \quad \frac{1000\ w_1}{m_1\ w_2}$

$\frac{w_2}{w_1 \quad w_2} \quad \frac{1}{2} \qquad w_1 \quad w_2 \quad 1$

$\frac{w_1\ m_2}{m_1\ w_2} \quad \frac{1}{9} \qquad \frac{m_1(\text{solute})}{m_2\ (\text{solvent})} \quad 9$

41. **PLAN** This problem can be solved by using concept of conversion of molarity into molality.

Molarity   3.2 M

Let volume of solution   1000 mL   Volume of solvent

Mass of solvent   1000   0.4   400 g

Since, molarity of solution is 3.2 molar

n_{solute} 3.2 mol

Molality (m) $\frac{3.2}{400/1000}$ 8

Hence, correct integer is (8).

42. Mass of HCl in 1.0 mL stock solution

1.25 $\frac{29.2}{100}$ 0.365 g

Mass of HCl required for 200 mL 0.4 M HCl

$$\frac{200}{1000} \quad 0.4 \quad 36.5 \quad 0.08 \quad 36.5 \text{ g}$$

0.365 g of HCl is present in 1.0 mL stock solution.

$$0.08 \quad 36.5 \text{ g HCl will be present in } \frac{0.08 \quad 36.5}{0.365} \quad 8.0 \text{ mL}$$

43. Partial pressure of N_2 $\quad$ 0.001 atm,

$$T \quad 298 \text{ K}, V \quad 2.46 \text{ dm}^3.$$

From ideal gas law : $pV \quad nRT$

$$n(N_2) \quad \frac{pV}{RT} \quad \frac{0.001 \quad 2.46}{0.082 \quad 298} \quad 10^{\ 7}$$

Number of molecules of N_2 $\quad 6.023 \quad 10^{23} \quad 10^{\ 7}$

$$= 6.023 \quad 10^{16}$$

Now, total surface sites available

$$= 6.023 \quad 10^{14} \quad 1000 = 6.023 \quad 10^{17}$$

$$\text{Surface sites used in adsorption} = \frac{20}{100} \quad 6.023 \quad 10^{17}$$

$$2 \quad 6.023 \quad 10^{16}$$

Sites occupied per molecules

$$= \frac{\text{Number of sites}}{\text{Number of molecules}} \quad \frac{2 \quad 6.023 \quad 10^{16}}{6.023 \quad 10^{16}} = 2$$

44. Initial millimol of CH_3COOH = 100 $\quad$ 0.5 = 50

millimol of CH_3COOH remaining after adsorption

$$100 \quad 0.49 \quad 49$$

millimol of CH_3COOH adsorbed = 50 – 49 = 1

number of molecules of CH_3COOH adsorbed

$$\frac{1}{1000} \quad 6.023 \quad 10^{23} \quad 6.023 \quad 10^{20}$$

$$\text{Area covered up by one molecule} \quad \frac{3.01 \quad 10^2}{6.02 \quad 10^{20}}$$

$$5 \quad 10^{\ 19} \text{ m}^2$$

45. Mass of 1.0 L water = 1000 g

$$\text{Molarity} = \frac{1000}{18} \quad 55.56 \text{ mol L}^{\ 1}$$

46. Volume of one cylinderical plant virus $\quad r^2 l$

$$3.14\,(75 \quad 10^{\ 8})^2 \quad 5000 \quad 10^{\ 8} \text{ cm}^3 \quad 8.83 \quad 10^{\ 17} \text{ cm}^3$$

$$\text{Mass of one virus} = \frac{\text{Volume of a virus}}{\text{Specific volume}}$$

$$\frac{8.83 \quad 10^{\ 17} \text{ cm}^3}{0.75 \text{ cm}^3 \text{ g}^{\ 1}} = 1.1773 \quad 10^{\ 16} \text{ g}$$

Molar mass of virus

$$\text{Mass of one virus} \quad \text{Avogadro's number}$$

$$1.1773 \quad 10^{\ 16} \quad 6.023 \quad 10^{23} \text{ g}$$

$$= 70.91 \quad 10^6 \text{ g}$$

47. Molar mass of Glauber's salt ($Na_2SO_4 \quad 10H_2O$)

$$23 \quad 2 \quad 32 \quad 64 \quad 10 \quad 18 \quad 322 \text{ g}$$

$$\text{Mole of } Na_2SO_4 \quad 10H_2O \text{ in 1.0 L solution} = \frac{80.575}{322} = 0.25$$

Molarity of solution = 0.25 M

Also, weight of 1.0 L solution = 1077.2 g

weight of Na_2SO_4 in 1.0 L solution $\quad 0.25 \quad 142 \quad 35.5$ g

Weight of water in 1.0 L solution $\quad 1077.2 - 35.5 \quad 1041.7$ g

$$\text{Molality} \quad \frac{0.25}{1041.7} \quad 1000 = 0.24 \text{ m}$$

$$\text{Mole fraction of } Na_2SO_4 \quad \frac{\text{Mole of } Na_2SO_4}{\text{Mole of } Na_2SO_4 \quad \text{Mole of water}}$$

$$\frac{0.25}{0.25 \quad \dfrac{1041.7}{18}}$$

$$4.3 \quad 10^{\ 3}.$$

48. Compound B forms hydrated crystals with $Al_2(SO_4)_3$. Also, B is formed with univalent metal on heating with sulphur. Hence, compound B must has the molecular formula M_2SO_4 and compound A must be an oxide of M which reacts with sulphur to give metal sulphate as

$$A + S \qquad \underset{B}{M_2SO_4}$$

∵ 0.321 g sulphur gives 1.743 g of M_2SO_4

32.1 g S (one mole) will give 174.3 g M_2SO_4

Therefore, molar mass of M_2SO_4 = 174.3 g

174.3 = 2 $\quad$ Atomic weight of M $\quad$ 32.1 + 64

Atomic weight of M = 39, metal is potassium (K)

K_2SO_4 on treatment with aqueous $Al_2(SO_4)_3$ gives potash-alum.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \qquad K_2SO_4Al_2(SO_4)_3 \quad 24H_2O$$

If the metal oxide A has molecular formula MO_x, two moles of it combine with one mole of sulphur to give one mole of metal sulphate as

$$2KO_x \quad S \qquad K_2SO_4$$

$x \quad 2$, i.e. A is KO_2.

49. The reaction involved is

$$3Pb(NO_3)_2 + Cr_2(SO_4)_3 \qquad 3PbSO_4(s) \quad + 2Cr(NO_3)_3$$

millimol of $Pb(NO_3)_2$ taken $\quad$ 45 $\quad$ 0.25 = 11.25

millimol of $Cr_2(SO_4)_3$ taken = 2.5

Here, chromic sulphate is the limiting reagent, it will determine the amount of product.

∵ 1 mole $Cr_2(SO_4)_3$ produces 3 moles $PbSO_4$.

2.5 millimol $Cr_2(SO_4)_3$ will produce 7.5 millimol $PbSO_4$.

Hence, mole of $PbSO_4$ precipitate formed = 7.5 $\quad 10^{\ 3}$

Also, millimol of $Pb(NO_3)_2$ remaining unreacted

$$11.25 - 7.50 = 3.75$$

Molarity of $Pb(NO_3)_2$ in final solution

$$\frac{\text{millimol of } Pb(NO_3)_2}{\text{Total volume}} \quad \frac{3.75}{70} = 0.054 \text{ M}$$

Also, millimol of $Cr(NO_3)_2$ formed

$$= 2 \quad \text{millimol of } Cr_2(SO_4)_3 \text{ reacted}$$

$$\text{Molarity of } Cr(NO_3)_2 = \frac{5}{70} \quad 0.071 \text{ M}$$

50. 93% H_2SO_4 solution weight by volume indicates that there is 93 g H_2SO_4 in 100 mL of solution.

If we consider 100 mL solution, weight of solution = 184 g

Weight of H_2O in 100 mL solution = 184 – 93 = 91 g

$$\text{Molality} \quad \frac{\text{Moles of solute}}{\text{Weight of solvent (g)}} \quad 1000$$

$$\frac{93}{98} \quad \frac{1000}{91} = 10.42$$

51. Heating below 600°C converts $Pb(NO_3)_2$ into PbO but to $NaNO_3$ into $NaNO_2$ as

$$\underset{330}{Pb(NO_3)_2} \qquad \underset{222}{PbO(s)} + 2NO_2 \quad + \frac{1}{2}O_2$$

MW : 330 222

$$\underset{85}{NaNO_3} \qquad \underset{69}{NaNO_2(s)} + \frac{1}{2}O_2$$

MW : 85 69

$$\text{Weight loss} \quad 5 \quad \frac{28}{100} \quad 1.4 \text{ g}$$

Weight of residue left 5 – 1.4 3.6 g

Now, let the original mixture contain x g of $Pb(NO_3)_2$.

∵ 330 g $Pb(NO_3)_2$ gives 222 g PbO

x g $Pb(NO_3)_2$ will give $\frac{222\,x}{330}$ g PbO

Similarly, 85 g $NaNO_3$ gives 69 g $NaNO_2$

$(5 - x)$ g $NaNO_3$ will give $\frac{69\,(5 \quad x)}{85}$ g $NaNO_2$

$$\text{Residue :} \quad \frac{222\,x}{330} \quad \frac{69\,(5 \quad x)}{85} = 3.6 \text{ g}$$

Solving for x gives, x 3.3 g $Pb(NO_3)_2$

$NaNO_3$ 1.7 g.

52. Reactions involved are

$$C_2H_6 + Br_2 \qquad C_2H_5Br + HBr$$

$$2C_2H_5Br + 2Na \qquad C_4H_{10} + 2NaBr$$

Actual yield of C_4H_{10} 55 g which is 85% of theoretical yield.

$$\text{Theoretical yield of } C_4H_{10} \quad \frac{55 \quad 100}{85} = 64.70 \text{ g}$$

Also, 2 moles (218 g) C_2H_5Br gives 58 g of butane.

64.70 g of butane would be obtained from

$$\frac{2}{58} \quad 64.70 \quad 2.23 \text{ moles } C_2H_5Br$$

Also yield of bromination reaction is only 90%, in order to have 2.23 moles of C_2H_5Br, theoretically

$$\frac{2.23 \quad 100}{90} \quad 2.48 \text{ moles of } C_2H_5Br \text{ required.}$$

Therefore, moles of C_2H_6 required = 2.48

Volume of C_2H_6 (NTP) required = 2.48 22.4 = 55.55 L.

53. Moles of sugar = $\frac{34.2}{342}$ 0.1

Moles of water in syrup = 214.2 – 34.2 = 180 g

$$\text{Therefore, (i) Molality} \quad \frac{\text{Moles of solute}}{\text{Weight of Solvent (g)}} \quad 1000$$

$$\frac{0.1}{180} \quad 1000 \quad 0.55$$

(ii) Mole fraction of sugar $\frac{\text{Mole of sugar}}{\text{Mole of sugar + Mole of water}}$

$$\frac{0.1}{0.1 \quad 10} \quad 9.9 \quad 10^{\;3}$$

54. From the given elemental composition, empirical formula can be derived as :

Element	**C**	**H**	**O**
Weight %	69.77	11.63	18.60
Mole %	5.81	11.63	1.1625 (obtained by dividing from M)
Simple ratio	5	10	1

Hence, empirical formula is $C_5H_{10}O$ and empirical formula weight is 86.

Since, empirical formula weight and molecular weight both are (86), empirical formula is the molecular formula also.

Also, the compound does not reduce Fehling's solution, therefore it is not an aldehyde, but it forms bisulphite, it must be a ketone.

Also, it gives positive iodoform test, it must be a methyl ketone.

$$C_3H_7—\overset{O}{C}—CH_3$$

Based on the above information, the compound may be one of the following :

$$\underset{\text{2-pentanone}}{CH_3CH_2CH_2—\overset{O}{C}—CH_3} \quad \text{or} \quad \underset{\text{3-methyl -2-butanone}}{CH_3 — \overset{CH_3}{CH}—\overset{O}{C}—CH_3}$$

55. (a) Let us consider 1.0 L solution for all the calculation.

(i) Weight of 1 L solution 1250 g

Weight of $Na_2S_2O_3$ 3 158 474 g

$$\text{Weight percentage of } Na_2S_2O_3 \quad \frac{474}{1250} \quad 100 \quad 37.92$$

(ii) Weight of H_2O in 1 L solution 1250 474 776 g

$$\text{Mole fraction of } Na_2S_2O_3 \quad \frac{3}{3 \quad \frac{776}{18}} \quad 0.065$$

$$\text{(iii) Molality of Na} \quad \frac{3 \quad 2}{776} \quad 100 \quad 7.73 \text{ m}$$

56. (a) After passing through red-hot charcoal, following reaction occurs

$$C(s) + CO_2(g) \qquad 2CO(g)$$

If the 1.0 L original mixture contain x litre of CO_2, after passing from tube containing red-hot charcoal, the new volumes would be :

$2x$ (volume of CO obtained from CO_2) 1

– x(original CO) 1 x 1.6 (given)

x 0.6

Hence, original 1.0 L mixture has 0.4 L CO and 0.6 L of CO_2, i.e. 40% CO and 60% CO_2 by volume.

(b) According to the given information, molecular formula of the compound is M_3N_2. Also, 1.0 mole of compound has 28 g of nitrogen. If X is the molar mass of compound, then :

$$X \quad \frac{28}{100} \quad 28$$

$$X \quad 100 \quad 3 \quad \text{Atomic weight of } M + 28$$

$$\text{Atomic weight of } M \quad \frac{72}{3} \quad 24$$

57. In the present case, $V \quad n$ ($\because$ all the volumes are measured under identical conditions of temperature and pressure) Hence, the reaction stoichiometry can be solved using volumes as :

$$C_xH_y(g) \quad x \quad \frac{y}{4} \quad O_2\,(g) \qquad xCO_2\,(g) \quad \frac{y}{2}\,H_2O\,(l)$$

volume of $CO_2(g) + O_2(g)$ (remaining unreacted) = 25

Volume of $CO_2(g)$ produced

= 10 mL (15 mL O_2 remaining)

$\because$ 1 mL C_xH_y produces x mL of CO_2

5 mL C_xH_y will produce 5 xmL of CO_2= 10 mL

$x \quad 2$

Also, 1 mL C_xH_y combines with $x \quad \frac{y}{4}$ mL of O_2

5 mL C_xH_y will combine with 5 $x \quad \frac{y}{4}$ mL of O_2

5 $x \quad \frac{y}{4}$ 15 (15 mL of O_2 out of 30 mL)

(remaining unreacted)

$y \quad 4$, hence hydrocarbon is C_2H_4.

58. Oxides of sodium and potassium are converted into chlorides according to following reactions :

$$Na_2O + 2HCl \qquad 2NaCl + H_2O$$
$$K_2O + 2HCl \qquad 2KCl + H_2O$$

Finally all the chlorides of NaCl and KCl are converted into AgCl, hence

moles of (NaCl + KCl) = moles of AgCl

(one mole of either NaCl or KCl gives one mole of AgCl)

Now, let the chloride mixture contain x g NaCl.

$$\frac{x}{58.5} \quad \frac{0.118 \quad x}{74.5} \quad \frac{0.2451}{143.5}$$

Solving for x gives $x \quad 0.0338$ g (mass of NaCl)

Mass of KCl $\quad 0.118 - 0.0338$

= 0.0842 g

Also, moles of $Na_2O = \frac{1}{2}$ moles of NaCl

$$\text{Mass of } Na_2O = \frac{1}{2} \quad \frac{0.0338}{58.5} \quad 62 \quad 0.0179\,\text{g}$$

$$\text{Similarly, mass of } K_2O = \frac{1}{2} \quad \frac{0.0842}{74.5} \quad 94 \quad 0.053\,\text{g}$$

$$\text{Mass \% of } Na_2O = \frac{0.0179}{0.5} \quad 100 \quad 3.58\%$$

$$\text{Mass \% of } K_2O = \frac{0.053}{0.5} \quad 100 \quad 10.6\,\%$$

59. From the vapour density information

Molar mass $\quad$ Vapour density $\quad 2$ ($\because$ Molar mass of $H_2 \quad 2$)

$38.3 \quad 2 \quad 76.6$

Now, let us consider 1.0 mole of mixture and it contains x mole of NO_2.

$$46x \quad 92\,(1 \quad x) \quad 76.6 \qquad x \quad 0.3348$$

Also, in 100 g mixture, number of moles $\frac{100}{76.6}$

$$\text{Moles of } NO_2 \text{ in mixture} \quad \frac{100}{76.6} \quad 0.3348 \quad 0.437$$

60. Most of the elements found in nature exist as a mixture of isotopes whose atomic weights are different. The atomic weight of an element is the average of atomic weights of all its naturally occurring isotopes.

61. Average atomic weight

$$\frac{\text{Percentage of an isotope} \quad \text{Atomic weight}}{100}$$

$$10.81 \quad \frac{10.01x \quad 11.01\,(100 \quad x)}{100} \qquad x \quad 20\%$$

Therefore, natural boron contains 20% (10.01) isotope and 80% other isotope.

Topic 2 Equivalent Concept, Neutralisation and Redox Titration

1. In disproportionation reactions, same element undergoes oxidation as well as reduction.

e.g.

Reduction

$$2\overset{+1}{Cu}Br \longrightarrow \overset{+2}{Cu}Br_2 + \overset{0}{Cu}$$

Oxidation

Here, CuBr get oxidised to $CuBr_2$ and also it get reduced to Cu. Other given reactions and their types are given below.

Reduction

$$2\,\overset{+7}{Mn}O_4^- \;+ 10I^- + 16\,H^+ \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O$$

Oxidation

In the given reaction, MnO_4 get oxidised to Mn^2 and I get reduced to I_2. It is an example of redox reaction. The reaction takes place in acidic medium.

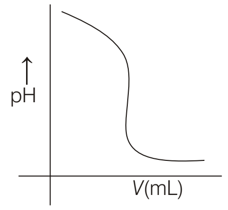
$$2KMnO_4 \qquad K_2MnO_4 \quad MnO_2 \quad O_2$$

The given reaction is an example of decomposition reaction. Here, one compound split into two or more simpler compounds, atleast one of which must be in elemental form.

$$2NaBr \quad Cl_2 \qquad 2NaCl \quad Br_2$$

The given reaction is an example of displacement reaction. In this reaction, an atom (or ion) replaces the ion (or atom) of another element from a compound.

2. The graph that shows the correct change of pH of the titration mixture in the experiment is



In this case, both the titrants are completely ionised.

$$HCl + NaOH \rightleftharpoons \overset{+}{N}a Cl + H_2O$$

As H is added to a basic solution, $[OH^{\ominus}]$ decreases and $[H\ \ ]$ increases. Therefore, pH goes on decreasing. As the equivalence point is reached, $[OH^{\ominus}]$ is rapidly reduced. After this point $[OH^{\ominus}]$ decreases rapidly and pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point. Most of them change their colour across this pH change.

3. 100 mL (cm^3) of hexane contains 0.27 g of fatty acid.
In 10 mL solution, mass of the fatty acid,

$$m \quad \frac{0.27}{100} \quad 10 \quad 0.027\,g$$

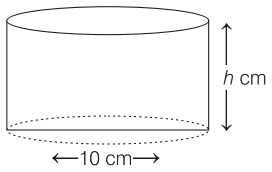
Density of fatty acid, $d \quad 0.9\,g\,cm^{\ \ 3}$

Volume of the fatty acid over the watch glass,

$$V \quad \frac{m}{d} \quad \frac{0.027}{0.9} \quad 0.03\ cm^3$$

Let, height of the cylindrical monolayer $\quad h$ cm

∵ Volume of the cylinder Volume of fatty acid



$$V \quad r^2 \quad h$$

$$h \quad \frac{V}{r^2} \quad \frac{0.03\,cm^3}{3 \quad (10)^2\,cm^2}$$

$$1 \quad 10^{\ \ 4}cm \qquad 1 \quad 10^{\ \ 6}\,m$$

4. The oxidation of a mixture of one mole of each of FeC_2O_4, $Fe_2\,(C_2O_4)_3$ $FeSO_4$ and $Fe_2\,(SO_4)_3$ in acidic medium with $KMnO_4$ is as follows :

$$FeC_2O_4 \quad KMnO_4 \qquad Fe^{3+} \quad CO_2 \quad Mn^{2} \qquad \ldots(i)$$

$$Fe_2(C_2O_4)_3 \quad KMnO_4 \qquad Fe^{3+} \quad CO_2 \quad Mn^{2} \qquad \ldots(ii)$$

$$FeSO_4 \quad KMnO_4 \qquad Fe^{3+} \quad SO_4^{2} \quad Mn^{2} \qquad \ldots(iii)$$

Change in oxidation number of Mn is 5. Change in oxidation number of Fe in (i), (ii) and (iii) are 3, 6, 1, respectively.

$$n_{eq}KMnO_4 \quad n_{eq}[FeC_2O_4 \quad Fe_2\,(C_2O_4)_3 \quad FeSO_4]$$

$$n \quad 5 \quad 1 \quad 3 \quad 1 \quad 6 \quad 1 \quad 1$$

$$n \quad 2$$

5. Given, $W_{Ca(HCO_3)_2} \quad 0.81\,g$

$$W_{Mg\,(HCO_3)_2} \quad 0.73\,g$$

$$M_{Ca(HCO_3)_2} \quad 162\,g\,mol^{\ \ 1},$$

$$M_{Mg(HCO_3)_2} \quad 146\ mol^{\ \ 1}$$

$$V_{H_2O} \quad 100mL$$

Now, $\quad n_{eq}(CaCO_3) \quad n_{eq}[Ca(HCO_3)_2] \quad n_{eq}[Mg(HCO_3)_2]$

$$\frac{W}{100} \quad 2 \quad \frac{0.81}{162} \quad 2 \quad \frac{0.73}{146} \quad 2$$

$$\frac{W}{100} \quad 0.005 \quad 0.005$$

$$W \quad 0.01 \quad 100 \quad 1$$

Thus, hardness of water sample $\quad \frac{1}{100} \quad 10^6 \quad 10{,}000$ ppm

6. The reaction takes place as follows,

$$H_2C_2O_4 + 2NaOH \qquad Na_2C_2O_4 + 2H_2O$$

Now, 50 mL of 0.5 M $H_2C_2O_4$ is needed to neutralize 25 mL of NaOH.

$$\text{Meq of } H_2C_2O_4 = \text{Meq of NaOH}$$

$$50 \quad 0.5 \quad 2 \quad 25 \quad M_{NaOH} \quad 1$$

$$M_{NaOH} \quad 2M$$

Now, $\quad$ molarity $\quad \frac{\text{Number of moles}}{\text{Volume of solution (in L)}}$

$$\frac{\text{Weight / molecular mass}}{\text{Volume of solution (in L)}}$$

$$2 \quad \frac{w_{NaOH}}{40} \quad \frac{1000}{50}$$

$$w_{NaOH} = \frac{2 \quad 40 \quad 50}{1000} \quad 4g$$

Thus, (*) none option is correct.

7. The reaction of HCl with Na_2CO_3 is as follows:

$$2HCl \quad Na_2CO_3 \qquad 2NaCl \quad H_2O \quad CO_2$$

We know that, M_{eq} of HCl $\quad M_{eq}$ of Na_2CO_3

$$\frac{25}{1000} \quad 1 \quad M_{HCl} \quad \frac{30}{1000} \quad 0.1 \quad 2$$

$$M_{HCl} \quad \frac{30 \quad 0.2}{25} \quad \frac{6}{25}M$$

The reaction of HCl with NaOH is as follows:

$$NaOH \quad HCl \qquad NaCl \quad H_2O$$

Also, M_{eq} of HCl $\quad M_{eq}$ of NaOH

$$\frac{6}{25} \quad 1 \quad \frac{V}{1000} \quad \frac{30}{1000} \quad 0.2 \quad 1$$

$$V \quad 25\,mL$$

8. Reaction of oxalate with permanganate in acidic medium.

$$5C_2O_4^{2} \quad 2MnO_4 \qquad 10CO_2 \quad 2Mn^{2} \quad 8H_2O$$

n-factor :	(4 3) 2 2		(7 2) 5		
Number of mole	5		2		10

$5C_2O_4^{2-}$ ions transfer $10e$ to produce 10 molecules of CO_2.

So, number of electrons involved in producing 10 molecules of CO_2 is 10. Thus, number of electrons involved in producing 1 molecule of CO_2 is 1.

9. We can calculate the simplest whole number ratio of C and H from the data given, as

Element	Relative mass	Molar mass	Relative mole	Simplest whole number ratio
C	6	12	$\frac{6}{12}$ 0.5	$\frac{0.5}{0.5}$ 1
H	1	1	$\frac{1}{1}$ 1	$\frac{1}{0.5}$ 2

Alternatively this ratio can also be calculated directly in the terms of x and y as

$\frac{12x}{y}$ $\frac{6}{1}$ (given and molar mass of C 12, H 1)

Now, after calculating this ratio look for condition 2 given in the question i.e. quantity of oxygen is half of the quantity required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. We can calculate number of oxygen atoms from this as consider the equation.

$$C_xH_y \quad x \quad \frac{y}{4}\, O_2 \qquad xCO_2 \quad \frac{y}{2} H_2O$$

Number of oxygen atoms required $2 \quad x \quad \frac{y}{4} \qquad 2x \quad \frac{y}{2}$

Now given, $z \quad \frac{1}{2} \quad 2x \quad \frac{y}{2} \qquad x \quad \frac{y}{4}$

Here we consider x and y as simplest ratios for C and H so now putting the values of x and y in the above equation.

$$z \quad x \quad \frac{y}{4} \qquad 1 \quad \frac{2}{4} \qquad 1.5$$

Thus, the simplest ratio figures for x, y and z are x 1, y 2 and z 1.5

Now, put these values in the formula given i.e. $C_xH_yO_z$ $C_1H_2O_{1.5}$

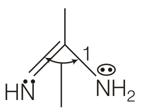
So, empirical formula will be $[C_1H_2O_{1.5}]$ 2 $C_2H_4O_3$

10. Methyl orange show Pinkish colour towards more acidic medium and yellow orange colour towards basic or less acidic media. Its working pH range is

Pinkish Red ← 3.9 –4.5 → Yellow orange

Weak base have the pH range greater than 7. When methyl orange is added to this weak base solution it shows yellow orange colour.

Now when this solution is titrated against strong acid the pH move towards more acidic range and reaches to end point near 3.9 where yellow orange colour of methyl orange changes to Pinkish red resulting to similar change in colour of solution as well.



In conjugation

11. H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is 1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state –2.

H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

12. n-factor of dichromate is 6.

Also, n-factor of Mohr's salt is 1 as :

$$\underset{\text{Mohr's salt}}{FeSO_4(NH_4)_2SO_4 \; 6H_2O} \xrightarrow{O.A} Fe^{3+}$$

∵ 1 mole of dichromate = 6 equivalent of dichromate.

6 equivalent of Mohr's salt would be required.

Since, n-factor of Mohr's salt is 1, 6 equivalent of it would also be equal to 6 moles.

Hence, 1 mole of dichromate will oxidise 6 moles of Mohr's salt.

13. The following reaction occur between $S_2O_3^{2}$ and $Cr_2O_7^{2}$:

$$26H^+ + 3S_2O_3^{2} + 4Cr_2O_7^{2} \qquad 6SO_4^{2} \quad 8Cr^{3+} + 13H_2O$$

Change in oxidation number of $Cr_2O_7^{2}$ per formula unit is 6 (it is always fixed for $Cr_2O_7^{2}$).

Hence, equivalent weight of $K_2Cr_2O_7 = \frac{\text{Molecular weight}}{6}$

14. It is an example of disproportionation reaction because the same species (ClO) is being oxidised to ClO_3 as well as reduced to Cl .

15. Oxalic acid dihydrate $H_2C_2O_4$ $2H_2O$: mw = 126

It is a dibasic acid, hence equivalent weight = 63

$$\text{Normality} \quad \frac{6.3}{63} \quad \frac{1000}{250} = 0.4\text{ N}$$

$$N_1V_1 \quad N_2V_2$$

$$0.1 \quad V_1 \quad 0.4 \quad 10$$

Hence, $\qquad V_1 \quad 40\text{ mL}$

16. In MnO_4, oxidation state of Mn is +7

In $Cr(CN)_6^{3}$, oxidation state of Cr is +3

In NiF_6^{2} , Ni is in + 4 oxidation state.

In CrO_2Cl_2, oxidation state of Cr is +6.

17. In S_8, oxidation number of S is 0, elemental state.

In S_2F_2, F is in – 1 oxidation state, hence S is in + 1 oxidation state.

In H_2S, H is in +1 oxidation state, hence S is in – 2 oxidation state.

18. The balanced redox reaction is :

$$3MnO_4 \quad 5FeC_2O_4 \quad 24H \qquad 3Mn^{2+} + 5Fe^{3+} + 10CO_2 \quad 12H_2O$$

∵ 5 moles of FeC_2O_4 require 3 moles of $KMnO_4$

1 mole of FeC_2O_4 will require $\frac{3}{5}$ mole of $KMnO_4$.

19. The balanced chemical reaction is :

$$2MnO_4 + 5SO_3^{2} + 6H^+ \qquad 2Mn^{2+} \quad 5SO_4^{2} + 3H_2O$$

∵ 5 moles SO_3^{2} reacts with 2 moles of $KMnO_4$

1 mole of SO_3^{2} will react with $\frac{2}{5}$ mole $KMnO_4$.

20. The balanced redox reaction is :

$$2MnO_4 \quad 5C_2O_4^{2} + 16H^+ \qquad 2Mn^{2+} \quad 10CO_2 \quad 16H_2O$$

Hence, the coefficients of reactants in balanced reaction are 2, 5 and 16 respectively.

21. Volume strength of H_2O_2 Normality 5.6 1.5 5.6 8.4 V

22. In $Ba(H_2PO_2)_2$, oxidation number of Ba is +2. Therefore,

H_2PO_2 : 2 (+1) + x + 2 (2) 1

x 1

23. Equivalent weight in redox system is defined as :

$$E \quad \frac{\text{Molar mass}}{n\text{-factor}}$$

Here n-factor is the net change in oxidation number per formula unit of oxidising or reducing agent. In the present case, n-factor is 2 because equivalent weight is half of molecular weight. Also,

***n*-factor** $MnSO_4$ $\frac{1}{2}Mn_2O_3$ 1 (+ 2 + 3)

$MnSO_4$ MnO_2 2 (+ 2 + 4)

$MnSO_4$ MnO_4 5 (+ 2 + 7)

$MnSO_4$ MnO_4^2 4 (+ 2 + 6)

Therefore, $MnSO_4$ converts to MnO_2.

24. **PLAN** This problem includes concept of redox reaction. A redox reaction consists of oxidation half-cell reaction and reduction half-cell reaction. Write both half-cell reactions, i.e. oxidation half-cell reaction and reduction half-cell reaction.Then balance both the equations.

Now determine the correct value of stoichiometry of H_2SO_4.

Oxidation half-reaction, 2 I I_2 2e ...(i)

Here, I is converted into I_2. Oxidation number of I is increasing from –1 to 0 hence, this is a type of oxidation reaction.

Reduction half-reaction

6H ClO_3 6e Cl $3H_2O$ ...(ii)

- Here, H_2O releases as a product. Hence, option (d) is correct.

  Multiplying equation (i) by 3 and adding in equation (ii)

  6I ClO_3 6H Cl $3I_2 + 3H_2O$

  6I ClO_3 $6H_2SO_4$ Cl $3I_2$ $3H_2O$ $6HSO_4$

- Stoichiometric coefficient of HSO_4 is 6.

  Hence, option (a), (b) and (d) are correct.

25. Balanced equations of reactions used in the problem are as follows

(i) $(NH_4)_2SO_4$ (1 mol, 132 g) $Ca(OH)_2$ $CaSO_4$ $2H_2O$ (1 mol, 172 g) $2NH_3$ (2 mol, (2 17) = 34 g)

(ii) $NiCl_2$ $6H_2O$ (1 mol, 238 g) $6NH_3$ (6 mol, 102 g) $[Ni(NH_3)_6]$ Cl_2 (1 mol, 232 g) $6H_2O$

Now, in Eq. (i)

if, 1584 g of ammonium sulphate is used.

i.e., 1584 g $(NH_4)_2SO_4$ $\frac{1584}{132}$ 12 mol

So, according to the Eq. (i) given above 12 moles of $(NH_4)_2SO_4$ produces

(a) 12 moles of gypsum

(b) 24 moles of ammonia

Here, 12 moles of gypsum 12 172 2064 g

and 24 moles of NH_3 24 17 408 g

Further, as given in question,

24 moles of NH_3 produced in reaction (i) is completly utilised by 952g or 4 moles of $NiCl_2$ $6H_2O$ to produce 4 moles of $[Ni(NH_3)_6]$ Cl_2.

So, 4 moles of $[Ni(NH_3)_6]$ Cl_2 4 232 928gms

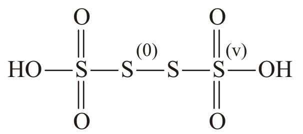
Hence, total mass of gypsum and nickel ammonia coordination compound $[Ni(NH_3)_6]$ Cl_2 2064 928 2992

26. Both assertion and reason are factually true but the reason does not exactly explain the assertion. The correct explanation is, methyl orange and phenolphthalein changes their colour at different pH.

27. If x is the oxidation state of Cu then :

3 2 2 3x 7 (2) 0 x $\frac{7}{3}$

28. $Na_2S_4O_6$ is a salt of $H_2S_4O_6$ which has the following structure



Difference in oxidation number of two types of sulphur = 5

29. Only F and Na show only one non-zero oxidation state.

O O , O^2 , O^2 ;

Cl 1 to 7

N 3 to 5

P 3 to 5

Sn 2, 4

Tl 1, 3 (rare but does exist)

Ti 2, 3, 4

30. Average titrate value is 25.15, but the number of significant figure cannot be greater than the same in either of them being manipulated.

31. The balanced reaction is

$6CaO + P_4O_{10}$ $2Ca_3(PO_4)_2$

Moles of P_4O_{10} $\frac{852}{284}$ 3

Moles of CaO required 3 6 18

Mass of CaO required 18 56 = 1008 g

32. Meq of oxalate 10 0.2 2 4

Meq of MnO_2 formed Meq of oxalate 4

Meq of $KMnO_4$ in 20 mL 4

Normality of H_2O_2 20 4

Normality of H_2O_2 0.20 N

Molarity of H_2O_2 $\frac{0.20}{2}$ 0.10 M

The balanced reactions are

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4$ $2MnSO_4 + 5O_2 + K_2SO_4 + 8H_2O$

$MnO_2 + Na_2C_2O_4 + 2H_2SO_4$ $MnSO_4 + Na_2SO_4 + 2CO_2 + 2H_2O$

33. The balanced chemical reaction is

$$CuCO_3 \quad H_2SO_4 \qquad CuSO_4 \quad H_2O \quad CO_2$$

$$\text{millimol of } CuCO_3 \quad \frac{0.5 \quad 1000}{123.5} = 4.048$$

Millimol of H_2SO_4 required 4.048

$\because$ Millimol Molarity Volume (in mL)

$$\text{Volume} \quad \frac{4.048}{0.50} \quad 8.096 \text{ mL}$$

34. The redox reaction involved are

$$IO_3 \;+ 5I \;+ 6H^+ \qquad 3I_2 + 3H_2O$$

$$I_2 \;+ 2S_2O_3^2 \qquad 2I \;+ S_4O_6^2$$

$$\text{millimol of } KIO_3 \text{ used} \quad \frac{0.1}{214} \quad 1000 \quad 0.467$$

millimol of I_2 formed 3 0.467 1.4

millimol of $Na_2S_2O_3$ consumed 2 1.4 2.8

$$\text{Molarity of } Na_2S_2O_3 \quad \frac{2.8}{45} \quad 0.062 \text{ M}$$

35. Meq of H_2O_2 Meq of I_2 Meq of $Na_2S_2O_3$

If N is normality of H_2O_2, then

$$N \quad 25 \quad 0.3 \quad 20$$

$$N \quad 0.24$$

Volume strength N 5.6 1.334 V

36. Let the original sample contains x millimol of Fe_3O_4 and y millimol of Fe_2O_3. In the first phase of reaction,

$$Fe_3O_4 \quad I \qquad 3Fe^{2+} \quad I_2 \;(n\text{-factor of } Fe_3O_4 \quad 2)$$

$$Fe_2O_3 \quad I \qquad 2Fe^{2+} \quad I_2 \;(n\text{-factor of } Fe_2O_3 \quad 2)$$

Meq of I_2 formed Meq (Fe_3O_4 Fe_2O_3)
Meq of hypo required

$$2x \quad 2y \quad 11 \quad 0.5 \quad 5 \quad 27.5 \qquad \ldots\text{(i)}$$

Now, total millimol of Fe^{2+} formed $3x$ $2y$. In the reaction

$$Fe^{2+} + MnO_4 \;+ H^+ \qquad Fe^{3+} + Mn^{2+}$$

n-factor of Fe^{2+} 1

$$\text{Meq of } MnO_4 \quad \text{Meq of } Fe^{2+}$$

$$3x \quad 2y \quad 12.8 \quad 0.25 \quad 5 \quad 2 \quad 32 \qquad \ldots\text{(ii)}$$

Solving Eqs. (i) and (ii), we get

$$x \quad 4.5 \text{ and } y \quad 9.25$$

$$\text{Mass of } Fe_3O_4 \quad \frac{4.5}{1000} \quad 232 = 1.044 \text{ g}$$

$$\%\text{ mass of } Fe_3O_4 \quad \frac{1.044}{3} \quad 100 = 34.80\%$$

$$\text{Mass of } Fe_2O_3 \quad \frac{9.25}{1000} \quad 160 = 1.48 \text{ g}$$

$$\%\text{ mass of } Fe_2O_3 \quad \frac{1.48}{3} \quad 100 \quad 49.33\%$$

37. The reaction involved in the explosion process is

$$\underset{x\text{ mL}}{CO(g)} + \underset{\frac{x}{2}\text{ mL}}{\frac{1}{2}O_2(g)} \qquad \underset{x\text{ mL}}{CO_2(g)}$$

$$\underset{y\text{ mL}}{CH_4(g)} + \underset{2y\text{ mL}}{2O_2(g)} \qquad \underset{y\text{ mL}}{CO_2(g)} + 2H_2O(l)$$

The first step volume contraction can be calculated as :

$$x \quad \frac{x}{2} \quad y \quad 2y \quad (x \quad y) \quad 13$$

$$x \quad 4y \quad 26 \qquad \ldots\text{(i)}$$

The second volume contraction is due to absorption of CO_2.

Hence, $x \quad y \quad 14$ ...(ii)

Now, solving equations (i) and (ii),

x 10 mL, y 4 mL and volume of He = 20 – 14 = 6 mL

$$\text{Vol \% of CO} = \frac{10}{20} \quad 100 \quad 50\%$$

$$\text{Vol \% of } CH_4 = \frac{4}{20} \quad 100 = 20\%$$

Vol % of He = 30%

38. The redox reaction involved is :

$$H_2O_2 + 2I \;+ 2H^+ \qquad 2H_2O + I_2$$

If M is molarity of H_2O_2 solution, then

$$5M \quad \frac{0.508 \quad 1000}{254} \;(\because 1 \text{ mole } H_2O_2 \quad 1 \text{ mole } I_2)$$

$$M \quad 0.4$$

Also, n-factor of H_2O_2 is 2, therefore normality of H_2O_2 solution is 0.8 N.

Volume strength = Normality 5.6 0.8 5.6 = 4.48 V

39. The reaction is

$$KIO_3 \quad 2KI + 6HCl \qquad 3ICl + 3KCl \;+ 3H_2O$$

KIO_3 required for 20 mL original KI solution = 3 millimol.

7.5 millimol KIO_3 would be required for original 50 mL KI.

Original 50 mL KI solution contain 15 millimol of KI.

After $AgNO_3$ treatment 5 millimol of KIO_3 is required, i.e. 10 millimol KI is remaining.

5 millimol KI reacted with 5 millimol of $AgNO_3$.

$$\text{Mass of } AgNO_3 \quad \frac{5}{1000} \quad 170 = 0.85 \text{ g}$$

Mass percentage of $AgNO_3$ = 85%

40. CO_2 is evolved due to following reaction :

$$2NaHCO_3 \qquad Na_2CO_3 + H_2O + CO_2$$

$$\text{Moles of } CO_2 \text{ produced} \quad \frac{pV}{RT}$$

$$\frac{750}{760} \quad \frac{123.9}{1000} \quad \frac{1}{0.082 \quad 298}$$

$$5 \quad 10^{\;3}$$

Moles of $NaHCO_3$ in 2 g sample 2 5 $10^{\;3}$ = 0.01

millimol of $NaHCO_3$ in 1.5 g sample

$$\frac{0.01}{2} \quad 1.5 \quad 1000 = 7.5$$

Let the 1.5 g sample contain x millimol Na_2CO_3, then

$$2x \quad 7.5 \quad \text{millimol of HCl} = 15$$

$$x \quad 3.75$$

Mass of $NaHCO_3$ $\frac{7.5 \quad 84}{1000} = 0.63$ g

Mass of $Na_2CO_3 = \frac{3.75 \quad 106}{1000} = 0.3975$ g

% mass of $NaHCO_3 = \frac{0.63}{1.50} \quad 100 = 42$ %

% mass of Na_2CO_3 $\frac{0.3975}{1.5} \quad 100$

$= 26.5\%$

41. Mass of $Fe_2O_3 = 0.552$ g

millimol of Fe_2O_3 $\frac{0.552}{160} \quad 1000 = 3.45$

During treatment with Zn-dust, all Fe^{3+} is reduced to $Fe^{\;+}$, hence

millimol of $Fe^{\;+}$ (in 100 mL) = 3.45 2 = 6.90

In 25 mL aliquot, $\frac{6.90}{4} = 1.725$ millimol Fe^{2+} ion.

Finally Fe^{2+} is oxidised to Fe^{3+}, liberating one electron per Fe^{2+} ion. Therefore, total electrons taken up by oxidant.

$1.725 \quad 10^{\;3} \quad 6.023 \quad 10^{23}$

$1.04 \quad 10^{21}$

42. With $KMnO_4$, oxalate ion is oxidised only as :

$5C_2O_4^2 \quad 2MnO_4 + 16H^+ \qquad 2Mn^{2+} + 10CO_2 + 8H_2O$

Let, in the given mass of compound, x millimol of $C_2O_4^2$ ion is present, then

Meq of $C_2O_4^2$ Meq of MnO_4

$2x \quad 0.02 \quad 5 \quad 22.6 \qquad x \quad 1.13$

At the later stage, with I , Cu^{2+} is reduced as :

$2Cu^{2+} + 4I \qquad 2CuI + I_2$

and $I_2 + 2S_2O_3^2 \qquad 2I + S_4O_6^2$

Let there be x millimol of Cu^{2+}.

Meq of Cu^{2+} Meq of I_2 = meq of hypo

$x \quad 11.3 \quad 0.05 = 0.565$

Moles of Cu^{2+} : moles of $C_2O_4^2$ 0.565 : 1.13 1 : 2

43. Let us consider 10 mL of the stock solution contain x millimol oxalic acid $H_2C_2O_4$ and y millimol of $NaHC_2O_4$.

When titrated against NaOH, basicity of oxalic acid is 2 while that of $NaHC_2O_4$ is 1.

$2x \quad y \quad 3 \quad 0.1 \quad 0.3$ … (i)

When titrated against acidic $KMnO_4$, n-factors of both oxalic acid and $NaHC_2O_4$ would be 2.

$2x \quad 2y \quad 4 \quad 0.1 \quad 0.4$ … (ii)

Solving equations (i) and (ii) gives

$y \quad 0.1, x \quad 0.1$

In 1.0 L solution, mole of $H_2C_2O_4$ $\frac{0.1}{1000} \quad 100 \quad 0.01$

Mole of $NaHC_2O_4$ $\frac{0.1}{1000} \quad 100 = 0.01$

Mass of $H_2C_2O_4$ 90 0.01 = 0.9 g

Mass of $NaHC_2O_4$ 112 0.01 = 1.12 g

44. Mass of chlorine in 1.0 g $X = \frac{35.5}{143.5} \quad 2.9 = 0.717$ g

Now, the empirical formula can be derived as :

	C	H	Cl
% wt :	24.24	4.04	71.72
Mole :	2	4	2
Simple ratio :	1	2	1

Empirical formula = CH_2Cl.

Because X can be represented by two formula of which one gives a dihydroxy compound with KOH indicates that X has two chlorine atoms per molecule.

$X \quad C_2H_4Cl_2$ with two of its structural isomers.

$Cl—CH_2—CH_2—Cl$ (I) and $CH_3—CHCl_2$ (II)

On treatment with KOH, I will give ethane-1, 2-diol, hence it is Y. Z on treatment with KOH will give ethanal as

$ClCH_2CH_2Cl + OH \qquad \underset{OH \quad OH}{CH_2—CH_2}$ (Y)

$CH_3CHCl_2 + KOH \qquad \underset{\text{Unstable}}{CH_3CH(OH)_2} \xrightarrow{-H_2O} \underset{(Z)}{CH_3CHO}$

45. Let the n-factor of $KMnO_4$ in acid, neutral and alkaline media are N_1, N_2 and N_3 respectively. Also, same volumes of reducing agent is used everytime, same number of equivalents of $KMnO_4$ would be required every time.

$20N_1 \quad \frac{100}{3}N_2 \quad 100N_3 \qquad N_1 \quad \frac{5}{3}N_2 \quad 5N_3$

Also, n-factors are all integer and greater than or equal to one but less than six, N_3 must be 1.

$N_1 \quad 5, N_2 \quad 3$

In acid medium MnO_4 Mn^{2+}

In neutral medium MnO_4 Mn^{4+}

In alkaline medium MnO_4 Mn^{6+}

meq of $K_2Cr_2O_7$ required = 100

$100 = 1 \quad 6 \quad V$ (n-factor = 6)

$V \quad 100/6 = 16.67$ mL

46. Meq of MnO_4 required $20 \quad \frac{1}{50} \quad 5 \quad 2$

Meq of Fe^2 present in solution = 2

millimol of Fe^2 present in solution = 2 (n-factor = 1)

Also,

∵ 4 millimol of Fe^2 are formed from 1 millimol N_2H_4

2 millimol Fe^2 from $\frac{1}{4} \quad 2 \quad \frac{1}{2}$ millimol N_2H_4

Therefore, molarity of hydrazine sulphate solution

$\frac{1}{2} \quad \frac{1}{10} \quad \frac{1}{20}$

In 1 L solution $\frac{1}{20}$ mol $N_2H_6SO_4$ is present.

Amount of $N_2H_6SO_4$ $\quad \frac{1}{20} \quad 130 \quad 6.5$ gL ^{1}

47. Molecular weight of $Na_2CO_3 \;\; 10H_2O = 286$

Molarity of carbonate solution $\quad \frac{1}{286} \quad \frac{1000}{100} = 0.035$

Normality of carbonate solution $\quad 2 \quad 0.035 = 0.07$ N

In acid solution : Normality of HNO_3 $\quad \frac{8 \quad 5}{2000} = 0.02$

Normality of HCl $= \frac{5 \quad 4.8}{2000} \quad 0.012$

Let normality of H_2SO_4 in final solution be N.

$(N \quad 0.02 \quad 0.012) \quad 30 \quad 0.07 \quad 42.9$

$N \quad 0.0681$

Gram equivalent of SO_4^{2} in 2 L solution $\quad 2 \quad 0.0681$

0.1362

Mass of SO_4^{2} in solution $= 0.1362 \quad \frac{96}{2} = 6.5376$ g

48. For the oxidation of A^{n+} as :

$A^{n+} \qquad AO_3 \quad n\text{-factor} = 5 - n$

Gram equivalent of $A^{n+} = 2.68 \quad 10^{\;3} \, (5 \quad n)$

Now equating the above gram equivalent with gram equivalent of $KMnO_4$:

$2.68 \quad 10^{\;3} \, (5 \quad n) \quad 1.61 \quad 10^{\;3} \quad 5$

$n \quad 2$

49. During heating MCO_3 is converted into MO liberating CO_2 while BaO is remaining unreacted :

$$MCO_3(s) \xrightarrow{\text{Heat}} MO(s) + CO_2(g) \quad 0.44 \text{ g} = 0.01 \text{ mol}$$
$$\underset{4.08\text{ g}}{\underline{BaO(s)}} \quad \underset{3.64\text{ g}}{\underline{BaO(s)}}$$

From the decomposition information, it can be deduced that the original mixture contained 0.01 mole of MCO_3 and the solid residue, obtained after heating, contain 0.01 mole (10 millimol) of MO.

Also, millimol of HCl taken initially = 100

millimol of NaOH used in back-titration $\quad 16 \quad 2.5 = 40$

millimol of HCl reacted with oxide residue = 60

HCl reacts with oxides as :

$$\underset{10\text{ millimol}}{MO} + \underset{20\text{ millimol}}{2HCl} \qquad MCl_2 \qquad H_2O$$

$$BaO + 2HCl \qquad BaCl_2 + H_2O$$

60 – 20 = 40 millimol

Therefore, the residue contain 20 millimol of BaO.

Also, molar mass of BaO = 138 + 16

= 154

Mass of BaO $\quad \frac{154 \quad 20}{1000} = 3.08$ g

Mass of $MCO_3 = 4.08 - 3.08 = 1.0$ g

$\because$ 0.01 mole of MCO_3 weight 1.0 g

1 mole of MCO_3 = 100 g

100 = (Atomic weight of metal) + (12 + 3 16)

Atomic weight of metal = 40, i.e. Ca

Download Chapter Test
http://tinyurl.com/y2r7vwy5 *or*

2

Atomic Structure

Topic 1 Preliminary Developments and Bohr's Model

Objective Questions I (Only one correct option)

1. Which one of the following about an electron occupying the 1*s*-orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0) **(2019 Main, 9 April II)**

(a) The electron can be found at a distance $2a_0$ from the nucleus.

(b) The magnitude of the potential energy is double that of its kinetic energy on an average.

(c) The probability density of finding the electron is maximum at the nucleus.

(d) The total energy of the electron is maximum when it is at a distance a_0 from the nucleus.

2. If p is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength , then for 1.5 p momentum of the photoelectron, the wavelength of the light should be

(Assume kinetic energy of ejected photoelectron to be very high in comparison to work function) **(2019 Main, 8 April II)**

(a) $\frac{4}{9}$ (b) $\frac{3}{4}$

(c) $\frac{2}{3}$ (d) $\frac{1}{2}$

3. What is the work function of the metal, if the light of wavelength 4000 Å generates photoelectron of velocity $6 \quad 10^5$ ms ^{1} from it?

(Mass of electron $9 \quad 10^{31}$ kg

Velocity of light $3 \quad 10^8$ ms ^{1}

Planck's constant $6.626 \quad 10^{34}$ Js

Charge of electron $1.6 \quad 10^{19}$ JeV ^{1}) **(2019 Main, 12 Jan I)**

(a) 4.0 eV (b) 2.1 eV

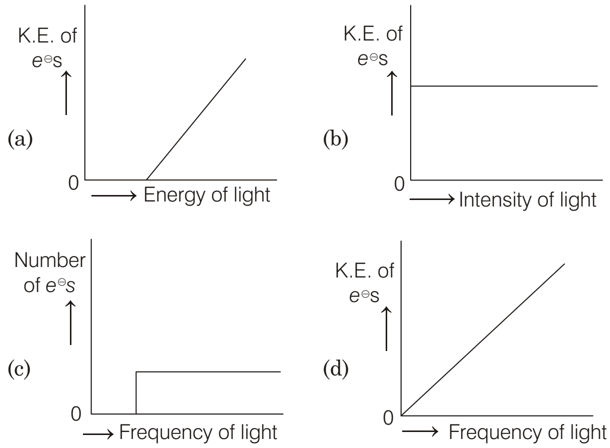
(c) 0.9 eV (d) 3.1 eV

4. The ground state energy of hydrogen atom is 13.6 eV. The energy of second excited state of He ion in eV is **(2019 Main, 10 Jan II)**

(a) 54.4 (b) 3.4

(c) 6.04 (d) 27.2

5. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? **(2019 Main, 10 Jan I)**



6. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of $h/$ (where, is wavelength associated with electron wave) is given by **(2016 Main)**

(a) 2 meV (b) $\sqrt{meV}$

(c) $\sqrt{2meV}$ (d) meV

7. Rutherford's experiment, which established the nuclear model of the atom, used a beam of **(2002, 3M)**

(a) -particles, which impinged on a metal foil and got absorbed

(b) -rays, which impinged on a metal foil and got scattered

(c) helium atoms, which impinged on a metal foil and got scattered

(d) helium nuclei, which impinged on a metal foil and got scattered

8. Rutherford's alpha particle scattering experiment eventually led to the conclusion that **(1986, 1M)**
(a) mass and energy are related
(b) electrons occupy space around the nucleus
(c) neutrons are burried deep in the nucleus
(d) the point of impact with matter can be precisely determined

9. The radius of an atomic nucleus is of the order of **(1985, 1M)**
(a) 10^{10} cm (b) 10^{13} cm
(c) 10^{15} cm (d) 10^{8} cm

10. Bohr's model can explain **(1985, 1M)**
(a) the spectrum of hydrogen atom only
(b) spectrum of an atom or ion containing one electron only
(c) the spectrum of hydrogen molecule
(d) the solar spectrum

11. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (is **(1984, 1M)**
(a) $e, p, n,$ (b) $n, p, e,$
(c) $n, p, \ , e$ (d) $n, \ p, e$

12. Rutherford's scattering experiment is related to the size of the **(1983, 1M)**
(a) nucleus (b) atom (c) electron (d) neutron

13. Rutherford's experiment on scattering of -particles showed for the first time that the atom has **(1981, 1M)**
(a) electrons (b) protons
(c) nucleus (d) neutrons

Objective Questions II
(One or more than one correct option)

14. The energy of an electron in the first Bohr orbit of H-atom is –13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) **(1988)**
(a) 3.4 eV (b) 4.2 eV (c) 6.8 eV (d) 6.8 eV

15. The atomic nucleus contains **(1988, 1M)**
(a) protons (b) neutrons
(c) electrons (d) photons

16. The sum of the number of neutrons and proton in the isotope of hydrogen is **(1986, 1M)**
(a) 6 (b) 5 (c) 4 (d) 3

17. When alpha particles are sent through a thin metal foil, most of them go straight through the foil, because **(1984, 1M)**
(a) alpha particles are much heavier than electrons
(b) alpha particles are positively charged
(c) most part of the atom is empty space
(d) alpha particles move with high velocity

18. Many elements have non-integral atomic masses, because
(a) they have isotopes **(1984, 1M)**
(b) their isotopes have non-integral masses
(c) their isotopes have different masses
(d) the constituents, neutrons, protons and electrons, combine to give fractional masses

Match the Columns

19. According to Bohr's theory,
E_n Total energy K_n Kinetic energy
V_n Potential energy r^n Radius of nth orbit
Match the following : **(2006, 6M)**

	Column I		Column II
A.	$V_n/K_n = ?$	p.	0
B.	If radius of nth orbit E_n^x , x ?	q.	– 1
C.	Angular momentum in lowest orbital	r.	– 2
D.	$\frac{1}{r^n}$ Z^y, y ?	s.	1

Fill in the Blanks

20. The light radiations with discrete quantities of energy are called .... **(1993, 1M)**

21. The mass of a hydrogen is …… kg. **(1982, 1M)**

22. Isotopes of an element differ in the number of …… in their nuclei. **(1982, 1M)**

23. Elements of the same mass number but of different atomic numbers are known as …… . **(1983, 1M)**

Subjective Questions

24. With what velocity should an -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{13} m from the nucleus of the copper atom ? **(1997 (C), 3M)**

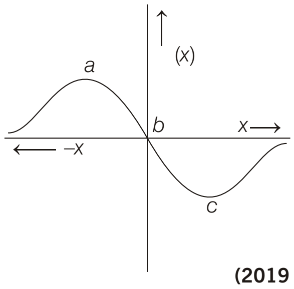
Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

Objective Questions I (Only one correct option)

1. Among the following, the energy of $2s$-orbital is lowest in **(2019 Main, 12 April II)**

(a) K (b) H (c) Li (d) Na

2. The electrons are more likely to be found



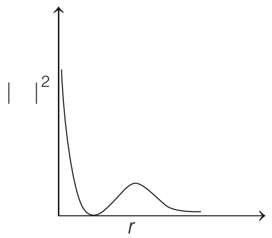
(2019 Main, 12 April I)

(a) in the region a and c (b) in the region a and b
(c) only in the region a (d) only in the region c

3. The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are **(2019 Main, 10 April II)**

(a) Lyman and Paschen (b) Brackett and Pfund
(c) Paschen and Pfund (d) Balmer and Brackett

4. The graph between $|\quad|^2$ and r (radial distance) is shown below. This represents **(2019 Main, 10 April I)**



(a) $1s$-orbital (b) $2p$-orbital
(c) $3s$-orbital (d) $2s$-orbital

5. For any given series of spectral lines of atomic hydrogen, let $\bar{\ } \quad \bar{\ }_{max} \quad \bar{\ }_{min}$ be the difference in maximum and minimum frequencies in cm ^{1}. The ratio $\bar{\ }_{Lyman} / \bar{\ }_{Balmer}$ is **(2019 Main, 9 April I)**

(a) 27 : 5 (b) 5 : 4 (c) 9 : 4 (d) 4 : 1

6. The quantum number of four electrons are given below:

I. $n \quad 4, l \quad 2, m_l \quad 2, m_s \quad \frac{1}{2}$

II. $n \quad 3, l \quad 2, m_l \quad 1, m_s \quad \frac{1}{2}$

III. $n \quad 4, l \quad 1, m_l \quad 0, m_s \quad \frac{1}{2}$

IV. $n \quad 3, l \quad 1, m_l \quad 1, m_s \quad \frac{1}{2}$

The correct order of their increasing energies will be **(2019 Main, 8 April I)**

(a) IV < III < II < I (b) I < II < III < IV
(c) IV < II < III < I (d) I < III < II < IV

7. If the de-Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to 1.5 a_0 (a_0 is Bohr radius), then the value of n/Z is **(2019 Main, 12 Jan II)**

(a) 1.0 (b) 0.75 (c) 0.40 (d) 1.50

8. The de-Broglie wavelength ( ) associated with a photoelectron varies with the frequency ( ) of the incident radiation as, [$_0$ is threshold frequency] **(2019 Main, 11 Jan II)**

(a) $\frac{1}{(\quad _0)^{\frac{1}{4}}}$ (b) $\frac{1}{(\quad _0)^{\frac{3}{2}}}$

(c) $\frac{1}{(\quad _0)}$ (d) $\frac{1}{(\quad _0)^{\frac{1}{2}}}$

9. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals? **(2019 Main, 9 Jan II)**

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
II. For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
III. According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2}$.
IV. The plot of $\quad vs\ r$ for various azimuthal quantum numbers, shows peak shifting towards higher r value.

(a) I, III (b) II, III (c) I, II (d) I, IV

10. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose? [$R_H \quad 1 \quad 10^5$ cm^{-1}, $h \quad 6.6 \quad 10^{\ 34}$ Js, $c \quad 3 \quad 10^8$ ms ^{1}] **(2019 Main, 11 Jan I)**

(a) Paschen, 5 3 (b) Paschen, 3
(c) Lyman, 1 (d) Balmer, 2

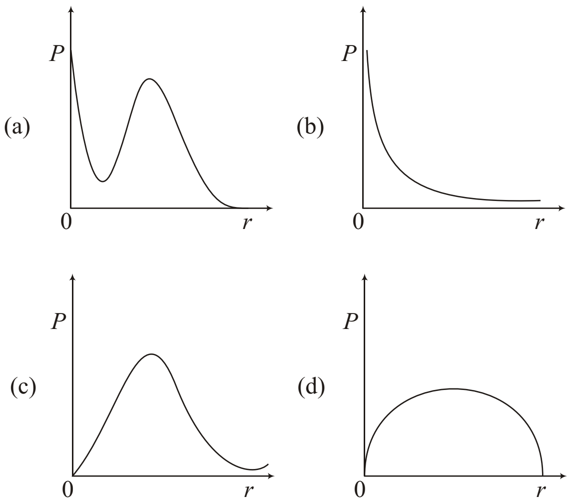
11. For emission line of atomic hydrogen from $n_i \quad 8$ to $n_f \quad n$, the plot of wave number ( ) against $\frac{1}{n^2}$ will be (The Rydberg constant, R_H is in wave number unit) **(2019 Main, 9 Jan I)**

(a) non linear
(b) linear with slope R_H
(c) linear with slope R_H
(d) linear with intercept R_H

12. The radius of the second Bohr orbit for hydrogen atom is (Planck's constant (h) 6.6262 10 ^{34} Js; mass of electron 9.1091 10 ^{31} kg ; charge of electron (e) 1.60210 10 ^{19} C; permitivity of vacuum $(\ _0)$ 8.854185 10 ^{12}kg ^{1}m ^{3}A^{2}) **(2017 Main)**

(a) 1.65 Å (b) 4.76 Å (c) 0.529 Å (d) 2.12 Å

13. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is 4 r^2dr. The qualitative sketch of the dependence of P on r is **(2016 Adv.)**



14. Which of the following is the energy of a possible excited state of hydrogen? **(2015 Main)**

(a) + 13.6 eV (b) – 6.8 eV
(c) –3.4 eV (d) + 6.8 eV

15. The correct set of four quantum numbers for the valence electrons of rubidium atom (Z 37) is **(2013 Main)**

(a) 5, 0, 0, $\frac{1}{2}$ (b) 5, 1, 0, $\frac{1}{2}$
(c) 5, 1, ,1, $\frac{1}{2}$ (d) 5, 0, 1, $\frac{1}{2}$

16. Energy of an electron is given by

$$E \quad 2.178 \quad 10^{18}\ \text{J} \quad \frac{Z^2}{n^2}$$

(2013 Main)

Wavelength of light required to excite an electron in an hydrogen atom from level n 1 to n 2 will be (h 6.62 10 ^{34} Js and c 3.0 10^8 ms ^{1})

(a) 1.214 10 ^{7} m (b) 2.816 10 ^{7} m
(c) 6.500 10 ^{7} m (d) 8.500 10 ^{7} m

17. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] **(2012)**

(a) $\frac{h^2}{4\ ^2ma_0^2}$ (b) $\frac{h^2}{16\ ^2ma_0^2}$ (c) $\frac{h^2}{32\ ma_0^2}$ (d) $\frac{h^2}{64\ ^2ma_0^2}$

18. The number of radial nodes in 3s and 2p respectively are **(2005, 1M)**

(a) 2 and 0 (b) 0 and 2
(c) 1 and 2 (d) 2 and 1

19. Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom? **(2004, 1M)**

(a) n 2, Li^2 (b) n 2, Be^3
(c) n 2, He (d) n 3, Li^2

20. If the nitrogen atom had electronic configuration 1s^7, it would have energy lower than that of the normal ground state configuration 1s^2 2s^2 2p^3, because the electrons would be closer to the nucleus, yet 1s^7 is not observed, because it violates **(2002, 3M)**

(a) Heisenberg uncertainty principle
(b) Hund's rule
(c) Pauli exclusion principle
(d) Bohr postulate of stationary orbits

21. The quantum numbers $\frac{1}{2}$ and $\frac{1}{2}$ for the electron spin represent **(2001, 1M)**

(a) rotation of the electron in clockwise and anti-clockwise direction respectively
(b) rotation of the electron in anti-clockwise and clockwise direction respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

22. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order **(2001, 1M)**

(a) 10 ^{10} m (b) 10 ^{20} m
(c) 10 ^{30} m (d) 10 ^{40} m

23. The number of nodal planes in a p_x orbital is **(2001, 1M)**

(a) one (b) two
(c) three (d) zero

24. The electronic configuration of an element is 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1. This represents its **(2000, 1M)**

(a) excited state (b) ground state
(c) cationic form (d) anionic form

25. The electrons, identified by quantum numbers n and l, (i) n 4, l 1, (ii) n 4, l 0, (iii) n 3, l 2, (iv) n 3, l 1 can be placed in order of increasing energy, from the lowest to highest, as **(1999, 2M)**

(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

26. The energy of an electron in the first Bohr orbit of H-atom is –13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) **(1998, 2M)**

(a) –3.4 eV (b) – 4.2 eV (c) – 6.8 eV (d) + 6.8 eV

27. For a d-electron, the orbital angular momentum is **(1997, 1M)**

(a) $\sqrt{6}\ \frac{h}{2}$ (b) $\sqrt{2}\ \frac{h}{2}$ (c) $\frac{h}{2}$ (d) 2 $\frac{h}{2}$

28. The first use of quantum theory to explain the structure of atom was made by **(1997, 1M)**
(a) Heisenberg (b) Bohr
(c) Planck (d) Einstein

29. Which of the following has the maximum number of unpaired electrons ? **(1996, 1M)**
(a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}

30. The orbital angular momentum of an electron in $2s$-orbital is **(1996, 1M)**
(a) $\frac{1}{2}\ \frac{h}{2}$ (b) zero
(c) $\frac{h}{2}$ (d) $\sqrt{2}\ \frac{h}{2}$

31. Which of the following relates to photons both as wave motion and as a stream of particles ? **(1992, 1M)**
(a) Interference (b) $E \quad mc^2$
(c) Diffraction (d) $E \quad h$

32. Which of the following does not characterise X-rays ? **(1992, 1M)**
(a) The radiation can ionise gases
(b) It causes ZnS to fluoresce
(c) Deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays

33. The correct set of quantum numbers for the unpaired electron of chlorine atom is **(1989, 1M)**

	n	l	m		n	l	m
(a)	2	1	0	(b)	2	1	1
(c)	3	1	1	(d)	3	0	0

34. The correct ground state electronic configuration of chromium atom is **(1989, 1M)**
(a) $[Ar]\,3d^5\,4s^1$ (b) $[Ar]\,3d^4\,4s^2$
(c) $[Ar]\,3d^6\,4s^0$ (d) $[Ar]\,4d^5\,4s^1$

35. The outermost electronic configuration of the most electronegative element is **(1988, 90, 1M)**
(a) ns^2np^3 (b) ns^2np^4
(c) ns^2np^5 (d) ns^2np^6

36. The orbital diagram in which the Aufbau principle is violated **(1988, 1M)**

(a) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$

(b) $\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

(c) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

(d) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

37. The wavelength of a spectral line for an electronic transition is inversely related to **(1988, 1M)**
(a) the number of electrons undergoing the transition
(b) the nuclear charge of the atom
(c) the difference in the energy of the energy levels involved in the transition
(d) the velocity of the electron undergoing the transition

38. The ratio of the energy of a photon of 200 Å wavelength radiation to that of 4000 Å radiation is **(1986, 1M)**
(a) $\frac{1}{4}$ (b) 4
(c) $\frac{1}{2}$ (d) 2.

39. Which one of the following sets of quantum numbers represents an impossible arrangement? **(1986, 1M)**

	n	l	m	s
(a)	3	2	–2	$\frac{1}{2}$
(b)	4	0	0	$\frac{1}{2}$
(c)	3	2	–3	$\frac{1}{2}$
(d)	5	3	0	$\frac{1}{2}$

40. Electromagnetic radiation with maximum wavelength is **(1985, 1M)**
(a) ultraviolet (b) radio wave
(c) X-ray (d) infrared

41. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon? **(1984, 1M)**
(a) $3s$ (b) $2p$
(c) $2s$ (d) $1s$

42. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z \quad 37$) is **(1984, 1M)**
(a) 5, 0, 0, $\frac{1}{2}$ (b) 5, 1, 0 , $\frac{1}{2}$
(c) 5, 1, 1, $\frac{1}{2}$ (d) 6, 0, 0, $\frac{1}{2}$

43. The principal quantum number of an atom is related to the **(1983, 1M)**
(a) size of the orbital
(b) spin angular momentum
(c) orientation of the orbital in space
(d) orbital angular momentum

44. Any p-orbital can accommodate upto **(1983, 1M)**
(a) four electrons
(b) six electrons
(c) two electrons with parallel spins
(d) two electrons with opposite spins

Objective Questions II
(One or more than one correct option)

45. The ground state electronic configuration of nitrogen atom can be represented by **(1999, 3M)**

(a) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}$

(b) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow}\ \boxed{\downarrow}\ \boxed{\uparrow}$

(c) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow}\ \boxed{\downarrow}\ \boxed{\downarrow}$

(d) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\downarrow}\ \boxed{\downarrow}\ \boxed{\downarrow}$

46. Which of the following statement (s) is (are) correct ? **(1998, 2M)**

(a) The electronic configuration of Cr is [Ar] $3d^5\ 4s^1$ (atomic number of Cr = 24)

(b) The magnetic quantum number may have a negative value

(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (atomic number of Ag = 47)

(d) The oxidation state of nitrogen in HN_3 is – 3

47. An isotone of ${}^{76}_{32}Ge$ is **(1984, 1M)**

(a) ${}^{77}_{32}Ge$ (b) ${}^{77}_{33}As$

(c) ${}^{77}_{34}Se$ (d) ${}^{78}_{34}Se$

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Both Statement I and Statement II are correct; Statement II is the correct explanation of Statement I

(b) Both Statement I and Statement II are correct; Statement II is not the correct explanation of Statement I

(c) Statement I is correct; Statement II is incorrect

(d) Statement I is incorrect; Statement II is correct

48. Statement I The first ionisation energy of Be is greater than that of B.

Statement II $2p$-orbital is lower in energy than $2s$. **(2000)**

Passage Based Questions

The hydrogen-like species Li^{2} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

49. The state S_1 is **(2010)**

(a) $1s$ (b) $2s$ (c) $2p$ (d) $3s$

50. Energy of the state S_1 in units of the hydrogen atom ground state energy is **(2010)**

(a) 0.75 (b) 1.50 (c) 2.25 (d) 4.50

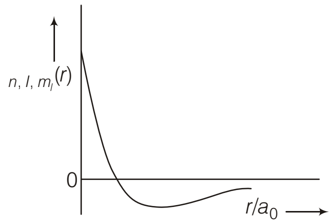
51. The orbital angular momentum quantum number of the state S_2 is **(2010)**

(a) 0 (b) 1 (c) 2 (d) 3

Match the Columns

Answer Q. 52, Q. 53 and Q. 54 by appropriately matching the information given in the three columns of the following table.

The wave function, $_{n}, l, m_l$ is a mathematical function whose value depends upon spherical polar coordinates $(r, \ \ ,\ \ )$ of the electron and characterised by the quantum number n, l and m_l. Here r is distance from nucleus, is colatitude and is azimuth. In the mathematical functions given in the Table, Z is atomic number and a_0 is Bohr radius. **(2017 Adv.)**

Column 1	*Column 2*	*Column 3*
(I) 1s-orbital	(i) $_{n,l,m_l}\ \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{Zr}{a_0}}$	(P) 
(II) 2s-orbital	(ii) One radial node	(Q) Probability density at nucleus $\frac{1}{a_0^3}$
(III) $2p_z$-orbital	(iii) $_{n,l\ m_l}\ \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{\frac{Zr}{a_0}} \cos$	(R) Probability density is maximum at nucleus
(IV) $3d_z^2$-orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from n 2 state to n 4 state is $\frac{27}{32}$ times the energy needed to excite electron from n 2 state to n 6 state

52. For He ion, the only **INCORRECT** combination is

(a) (I) (i) (S) (b) (II) (ii) (Q) (c) (I) (iii) (R) (d) (I) (i) (R)

53. For the given orbital in Column 1, the Only **CORRECT** combination for any hydrogen-like species is

(a) (II) (ii) (P) (b) (I) (ii) (S) (c) (IV) (iv) (R) (d) (III) (iii) (P)

54. For hydrogen atom, the only **CORRECT** combination is

(a) (I) (i) (P) (b) (I) (iv) (R) (c) (II) (i) (Q) (d) (I) (i) (S)

55. Match the entries in Column I with the correctly related quantum number(s) in Column II. **(2008, 6M)**

	Column I		Column II
A.	Orbital angular momentum of the electron in a hydrogen-like atomic orbital.	p.	Principal quantum number
B.	A hydrogen-like one-electron wave function obeying Pauli's principle.	q.	Azimuthal quantum number
C.	Shape, size and orientation of hydrogen-like atomic orbitals.	r.	Magnetic quantum number
D.	Probability density of electron at the nucleus in hydrogen-like atom.	s.	Electron spin quantum number

Fill in the Blanks

56. The outermost electronic configuration of Cr is .... **(1994, 1M)**

57. 8 g each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of .... **(1989, 1M)**

58. The uncertainty principle and the concept of wave nature of matter were proposed by .... and ....respectively. **(1988, 1M)**

59. Wave functions of electrons in atoms and molecules are called .... **(1993, 1M)**

60. The $2p_{x,}$ $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their .... **(1993, 1M)**

61. When there are two electrons in the same orbital, they have …… spins. **(1983, 1M)**

True/False

62. In a given electric field, -particles are deflected more than -particles in spite of -particles having larger charge. **(1993, 1M)**

63. The electron density in the XY-plane in $3d_{x^2 \quad y^2}$ orbital is zero. **(1986, 1M)**

64. The energy of the electron in the $3d$-orbital is less than that in the $4s$-orbital in the hydrogen atom. **(1983, 1M)**

65. Gamma rays are electromagnetic radiations of wavelengths of $10^{\ \ 6}$ to $10^{\ \ 5}$ cm. **(1983, 1M)**

66. The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$. **(1982, 1M)**

Integer Answer Type Questions

67. Not considering the electronic spin, the degeneracy of the second excited state ($n \quad 3$) of H-atom is 9, while the degeneracy of the second excited state of H is **(2015 Adv.)**

68. In an atom, the total number of electrons having quantum numbers **(2014 Adv.)**

$$n \quad 4, |m_l| \quad 1 \text{ and } m_s \quad \frac{1}{2} \text{ is}$$

69. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de-Broglie wavelength of He gas at 73°C is 'M' times that of the de-Broglie wavelength of Ne at 727°C. M is **(2013 Adv.)**

70. The work function ( ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is **(2011)**

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
(eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

71. The maximum number of electrons that can have principal quantum number, $n \quad 3$ and spin quantum number, $m_s \quad 1/2$, is **(2011)**

Subjective Questions

72. (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given, $r \quad a_0$).

(b) Find de-Broglie wavelength of the electron in first Bohr orbit.

(c) Find the orbital angular momentum of $2p$-orbital in terms of $h/2$ units. **(2005, 2M)**

73. (a) The Schrodinger wave equation for hydrogen atom is

$$_{2s} \quad \frac{1}{4(2\ \ )^{1/2}} \ \frac{1}{a_0}^{3/2} \quad 2 \quad \frac{r}{a_0} \quad e^{\ r/2a_0}$$

where, a_0 is Bohr's radius. Let the radial node in $2s$ be at r_0. Then, find r in terms of a_0.

(b) A base ball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of base ball. **(2004, 2M)**

74. The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. Find the corresponding wavelength for He^+ ion. **(2003, 2M)**

75. Calculate the energy required to excite 1 L of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ $mol^{\ 1}$. **(2000)**

76. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. **(1997 (C), 2M)**

77. Consider the hydrogen atom to be proton embedded in a cavity of radius a_0 (Bohr's radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. **(1996, 2M)**

78. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. **(1996, 1M)**

79. Iodine molecule dissociates into atoms after absorbing light to 4500Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms.
(Bond energy of $I_2 = 240$ kJ mol^{-1}) **(1995, 2M)**

80. Find out the number of waves made by a Bohr's electron in one complete revolution in its 3rd orbit. **(1994, 3M)**

81. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? **(1993, 3M)**

82. Estimate the difference in energy between 1st and 2nd Bohr's orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $l = 3.0 \quad 10^{-8}$ m? Which hydrogen atom-like species does this atomic number correspond to? **(1993, 5M)**

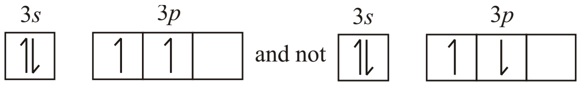
83. According to Bohr's theory, the electronic energy of hydrogen atom in the nth Bohr's orbit is given by :

$$E_n \quad \frac{21.7 \quad 10^{19}}{n^2} \text{ J}$$

Calculate the longest wavelength of electron from the third Bohr's orbit of the He^+ ion. **(1990, 3M)**

84. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2 ? **(1985, 2M)**

85. Give reason why the ground state outermost electronic configuration of silicon is **(1985, 2M)**



86. The electron energy in hydrogen atom is given by $E_n \quad \frac{21.7 \quad 10^{12}}{n^2}$ erg. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? **(1984, 3M)**

87. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr's orbit, $n = 2$ returns to the orbit, $n = 1$ in the hydrogen atom. The ionisation potential of the ground state hydrogen atom is $2.17 \quad 10^{11}$ erg per atom. **(1982, 4M)**

88. The energy of the electron in the second and third Bohr's orbits of the hydrogen atom is $5.42 \quad 10^{12}$ erg and $2.41 \quad 10^{12}$ erg respectively. Calculate the wavelength of the emitted light when the electron drops from the third to the second orbit. **(1981, 3M)**

Answers

Topic 1

1. (d)	**2.** (a)	**3.** (b)	**4.** (c)
5. (d)	**6.** (c)	**7.** (d)	**8.** (b)
9. (b)	**10.** (b)	**11.** (d)	**12.** (a)
13. (c)	**14.** (a)	**15.** (a,b)	**16.** (d)
17. (a,c)	**18.** (a,c)	**19.** A r; B q; C p, D s	
20. (photons)	**21.** (1.66 10^{-27} kg)		**22.** (neutrons)
23. (isobars)	**24.** 6.3 10^6		

Topic 2

1. (a)	**2.** (a)	**3.** (a)	**4.** (d)
5. (c)	**6.** (c)	**7.** (b)	**8.** (d)
9. (d)	**10.** (b)	**11.** (c)	**12.** (d)
13. (c)	**14.** (c)	**15.** (a)	**16.** (a)
17. (c)	**18.** (a)	**19.** (b)	**20.** (c)
21. (d)	**22.** (c)	**23.** (a)	**24.** (b)
25. (a)	**26.** (a)	**27.** (a)	**28.** (b)
29. (d)	**30.** (b)	**31.** (a)	**32.** (c)
33. (c)	**34.** (a)	**35.** (c)	**36.** (b)
37. (c)	**38.** (d)	**39.** (c)	**40.** (b)
41. (d)	**42.** (a)	**43.** (a)	**44.** (d)
45. (a,d)	**46.** (a,b,c)	**47.** (b,d)	**48.** (c)
49. (b)	**50.** (c)	**51.** (b)	**52.** (c)
53. (a)	**54.** (d)		

55. A q; B p, q, r, s C p, q, r D p, q, r

56. Cr [Ar] $3d^5$, $4s^1$ **57.** 1 : 16

58. Heisenberg, de-Broglie. **59.** orbital

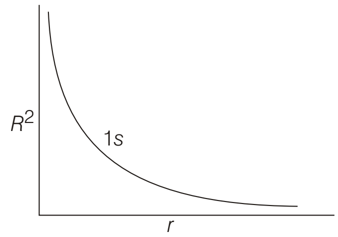
60. Orientation in space **61.** opposite

62. True	**63.** False	**64.** True	**65.** False
66. False	**67.** (3)	**68.** (6)	**69.** (5)
70. (4.14 eV)	**71.** (9)	**74.** (22.8 nm)	**75.** (98.44 kJ)
76. (63.56 V)	**78.** (2.725 10^6 M ^{1})		
79. (2.16 10^{20} J/atom)		**83.** (471 nm)	**84.** (10)
86. (3.66 10^{5} cm)	**87.** (1220 Å)	**88.** (660 nm)	

Hints & Solutions

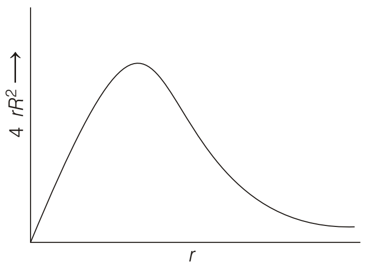
Topic 1 Preliminary Developments and Bohr's Model

1. Statement (d) is incorrect. For 1*s*-orbital radial probability density (R^2) against *r* is given as:



For 1*s*-orbital, probability density decreases sharply as we move away from the nucleus.

The radial distribution curves obtained by plotting radial probability functions *vs r* for 1*s*-orbital is



The graph initially increases and then decreases. It reaches a maximum at a distance very close to the nucleus and then decreases. The maximum in the curve corresponds to the distance at which the probability of finding the electron in maximum.

2. The expression of kinetic energy of photo electrons,

$$\text{KE} \quad \frac{1}{2}mv^2 \quad E \quad E_0$$

When, KE $\quad E_0$, the equation becomes,

$$\text{KE} \quad \frac{1}{2}mv^2 \quad E$$

$$\frac{1}{2}mv^2 \quad \frac{hc}{} \quad \frac{p^2}{2m^2} \quad \frac{hc}{}$$

$$hc \quad 2m^2 \quad \frac{1}{p^2} \qquad \frac{1}{p^2}$$

$E \quad \frac{hc}{}$ energy of incident light.

E_0 threshold energy or work functions,

$$\frac{1}{2}mv^2 \quad \frac{1}{2} \quad \frac{(mv)^2}{m^2} \quad \frac{1}{2} \quad \frac{p^2}{m^2}$$

$\because p$ momentum mv

As per the given condition,

$$\frac{\ \ _2}{_1} \quad \frac{p_1}{p_2}^{\ 2}$$

$$\frac{\ \ _2}{} \quad \frac{p}{1.5 \quad p}^{\ 2} \quad \frac{2}{3}^{\ 2} \quad \frac{4}{9}$$

$$_2 \quad \frac{4}{9} \qquad \qquad \because p_1^{\ 1} \quad p$$

3. Work function of metal ( ) $\quad h \ _0$

where, $_0$ threshold frequency

Also, $\quad \frac{1}{2}m_e v^2 \quad h \quad h \ _0$

or $\quad \frac{1}{2}m_e v^2 \quad h$ …(i)

$\frac{1}{2}m_e v^2 \quad \frac{hc}{}$ …(ii)

Given : $\quad$ 4000 Å $\quad 4000 \quad 10^{\ 10}$m

$v \quad 6 \quad 10^5 \text{ ms}^{\ 1}$,

$m_e \quad 9 \quad 10^{\ 31}$kg, $c \quad 3 \quad 10^8 \text{ ms}^{\ 1}$

$h \quad 6.626 \quad 10^{\ 34}$ Js

Thus, on substituting all the given values in Eq. (i), we get

$$\frac{1}{2} \quad 9 \quad 10^{\ 31}\text{ kg} \quad (6 \quad 10^5 \text{ ms}^{\ 1})^2$$

$$\frac{6.626 \quad 10^{\ 34}\text{J s} \quad 3 \quad 10^8 \text{ ms}^{\ 1}}{4000 \quad 10^{\ 10}\text{m}}$$

$1.62 \quad 10^{\ 21}\text{ kgm}^2\text{s}^{\ 2} \quad 4.96 \quad 10^{\ 19}$ J

$3.36 \quad 10^{\ 19}$ J $\qquad$ [1 kg m^{2}s$^{\ 2}$ $\quad$ 1J]

2.1 eV

4. The ground state energy of H-atom is $\quad$ 13.6 eV.

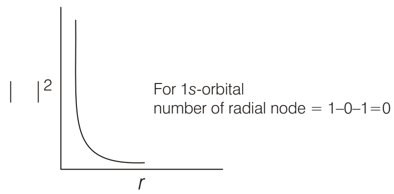
For second excited state, $n \quad 2 \quad 1 \quad 3$

$$E_3(\text{He} \ ) \quad 13.6 \quad \frac{Z^2}{n^2}\text{ eV} \qquad [\because \text{for He} \ , Z \quad 2]$$

$$13.6 \quad \frac{2^2}{3^2}\text{eV} \quad 6.04 \text{ eV}$$

5. For photoelectric effect,

(i) $\quad$ KE $\quad E \quad E_0$



where,

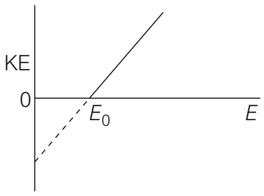
KE $\quad$ Kinetic energy of ejected electrons.

$E \quad$ Energy of incident light $\quad h$

$E_0 \quad$ Threshold energy $\quad h \ _0$

Frequency of incident light

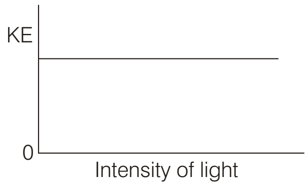
$_0 \quad$ Threshold frequency



Slope 1, intercept E_0

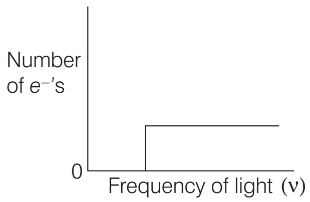
So, option (a) is correct.

(ii) KE of ejected electrons does not depend on the intensity of incident light.



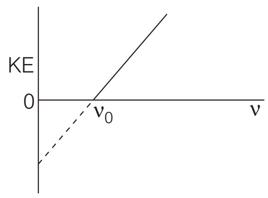
So, option (b) is correct.

(iii) When, number of ejected electrons is plotted with frequency of light, we get



So, option (c) is also correct.

(iv) KE $h \quad h_0$



Slope h, intercept h_0. So, option (d) is not correct.

6. **Plan** As you can see in options, energy term is mentioned hence, we have to find out relation between $h/$ and energy. For this, we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron ( ) $\frac{h}{p}$

$$p \quad \frac{h}{} \qquad \text{...(i)}$$

Kinetic energy of an electron eV

As we know that, KE $\frac{p^2}{2m}$

$$\text{eV} \quad \frac{p^2}{2m} \quad \text{or } p \quad \sqrt{2meV} \qquad \text{...(ii)}$$

From equations (i) and (ii), we get $\frac{h}{} \quad \sqrt{2meV}$

7. Rutherford used -particle (He^2 nuclei) in his experiment.

8. According to Rutherford's model, there is a heavily positively charged nucleus and negatively charged electrons occupies space around it in order to maintain electro-neutrality.

9. Radius of a nucleus is in the order of $10^{\ 13}$ cm, a fact.

10. Bohr's model is applicable to one-electron system only.

11. Neutron has no charge, hence e/m is zero for neutron. Next, -particle (He^{2+}) has very high mass compared to proton and electron, therefore very small e/m ratio. Proton and electron have same charge (magnitude) but former is heavier, hence has smaller value of e/m.

$$\frac{e}{m} : n \qquad p \quad e$$

12. The negligibly small size of nucleus compared to the size of atom was first established in Rutherford's experiment.

13. The most important findings of Rutherford's experiment is discovery of nucleus.

14. Energy of electron in H-atom is determined by the expression:

$$E_n \quad \frac{13.6}{n^2}\text{ eV} \qquad \text{where, } n \quad 1, 2, 3, ...$$

In excited states, $E_2 \quad \frac{13.6}{4} \quad 3.4$ eV

$$E_3 \quad \frac{13.6}{9} \quad 1.51 \text{ eV etc.}$$

15. Nucleus is composed of neutrons and protons.

16. The isotopes of hydrogen are $_1H^2$ and $_1H^3$.

17. Alpha particles passes mostly undeflected when sent through thin metal foil mainly, because

(i) it is much heavier than electrons.

(ii) most part of atom is empty space.

18. Many elements have several isotopes. For such elements, atomic mass is average of the atomic masses of different isotopes, which is usually non-integral.

19. A. $V_n \quad \frac{1}{4\ _0} \frac{Ze^2}{r}$

$$K_n \quad \frac{1}{8\ _0} \frac{Ze^2}{r}$$

$$\frac{V_n}{K_n} \quad 2 \quad \text{(r)}$$

B. $E_n \quad \frac{Ze^2}{8\ _0 r} \quad r^{\ 1}$

$$x \quad 1 \quad \text{(q)}$$

C. Angular momentum $\sqrt{l(l \quad 1)}\frac{h}{2} \quad 0$ in 1s-orbital (p).

D. $r_n \quad \frac{a_0 n^2}{Z} \quad \frac{1}{r_n} \quad Z$ (s)

20. Photons have quantised energy.

21. Mass of one H-atom $\frac{10^{\ 3}}{6.023 \quad 10^{23}}$ kg = 1.66 $10^{\ 27}$ kg

22. Isotopes have different number of neutrons.

23. Isobars have same mass number but different atomic numbers.

24. When -particle stop at 10 ^{13}m from nucleus, kinetic energy is zero, i.e. whole of its kinetic energy at the starting point is now converted into potential energy.

Potential energy of this -particle can be determined as

$$\boxed{\text{PE} \quad \frac{Z_1 \quad Z_2e^2}{(4 \quad _0)\, r}}$$

$$(Z_1 \quad 2, Z_2 \quad 29, \; _0 \quad 8.85 \quad 10^{\;12}\text{ J}^{\;1}\text{ C}^2\text{ m}^{\;1},$$
$$r \quad 10^{\;13}\text{m})$$

$$|\,\text{PE}\,| = \frac{2 \quad 29 \quad (1.6 \quad 10^{\;19})^2}{4 \quad 3.14 \quad 8.85 \quad 10^{\;12} \quad 10^{\;13}}\text{ J}$$

$$1.33 \quad 10^{\;13}\text{ J}$$

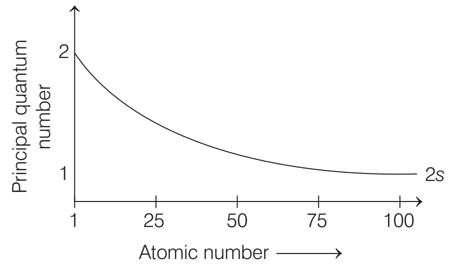
= kinetic energy of -particle at t 0

$$\text{KE} \quad \frac{1}{2}mv^2 \quad 1.33 \quad 10^{\;13}$$

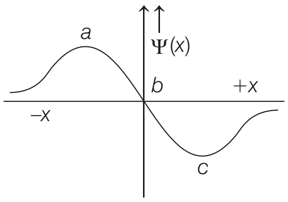
$$v \quad \sqrt{\frac{2 \quad 1.33 \quad 10^{\;13}}{4 \quad 1.66 \quad 10^{\;27}}} \quad 6.3 \quad 10^6\text{ ms}^{\;1}$$

Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

1. The energy of 2*s*-orbital is lowest in K(potassium). An orbital gets larger as the principal quantum number *n* increases. Correspondingly, the energy of the electron in such an orbital becomes less negative, meaning that the electron is less strongly bound and has less energy. The graph of principal quantum number with atomic number is



2. The electrons are more likely to be found in the region *a* and *c*. At *b*, wave function becomes zero and is called radial nodal surface or simply node.



The graph between wavefunction ( ) and distance (r) from the nucleus helps in determining the shape of orbital.

3. According to Rydberg's equation,

$$\frac{1}{\;} \quad \frac{R_H}{hc}\;\frac{1}{n_1^2} \quad \frac{1}{n_2^2} \quad \text{or} \quad \frac{1}{\;} \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2}$$

For shortest wavelength, i.e. highest energy spectral line, n_2 will be ( ).

For the given spectral series, ratio of the shortest wavelength of two spectral series can be calculated as follows :

(a) $\frac{\;_L}{\;_P} \quad \frac{\frac{1}{3^2} \quad \frac{1}{\;^2}}{\frac{1}{1^2} \quad \frac{1}{\;^2}} \quad \frac{\frac{1}{9} \quad 0}{1 \quad 0} \quad \frac{1}{9}$

(b) $\frac{\;_{Bk}}{\;_{Pf}} \quad \frac{\frac{1}{5^2} \quad \frac{1}{\;^2}}{\frac{1}{4^2} \quad \frac{1}{\;^2}} \quad \frac{1}{25} \quad \frac{16}{1} \quad \frac{16}{25}$

(c) $\frac{\;_P}{\;_{Pf}} \quad \frac{\frac{1}{5^2} \quad \frac{1}{\;^2}}{\frac{1}{3^2} \quad \frac{1}{\;^2}} \quad \frac{1}{25} \quad \frac{9}{1} \quad \frac{9}{25}$

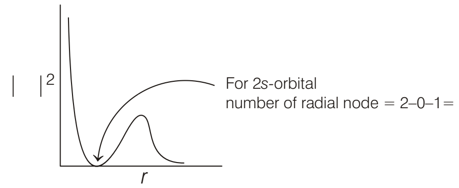
(d) $\frac{\;_B}{\;_{Bk}} \quad \frac{\frac{1}{4^2} \quad \frac{1}{\;^2}}{\frac{1}{2^2} \quad \frac{1}{\;^2}} \quad \frac{1}{16} \quad \frac{4}{1} \quad \frac{1}{4}$

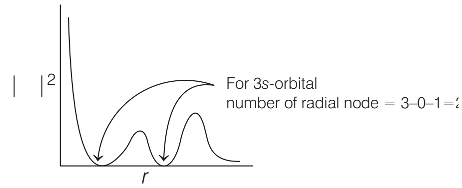
Note Lyman L (n_1 1), Balmer B (n_1 2)

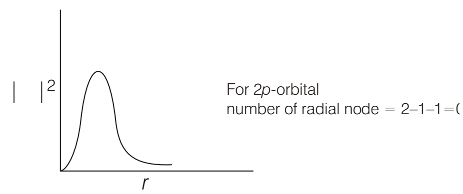
Paschen P (n_1 3), Brackett Bk (n_1 4)

Pfund Pf (n_1 5)

4. The graphs between | |^2 and r are radial density plots having (n l 1) number of radial nodes. For 1s, 2s, 3s and 2 p-orbitals these are respectively.







Thus, the given graph between | |^2 and r represents 2s-orbital.

5. For any given series of spectral lines of atomic hydrogen.

Let $\bar{\ } \quad \bar{\ }_{max} \quad \bar{\ }_{min}$ be the difference in maximum and minimum frequencies in cm ^{1}.

For Lyman series,

$$\bar{\ } \quad \bar{\ }_{max} \quad \bar{\ }_{min}$$

General formula:

$$\bar{\ } \quad 109677 \quad \frac{1}{n_i^2} \quad \frac{1}{n_f^2}$$

For Lyman $n_1 \quad 1, n_2 \quad 2, 3, \ldots$

$$\bar{\ }_{max} \quad 109{,}677 \quad \frac{1}{1} \quad \frac{1}{\ } \quad 109{,}677 \quad \frac{1}{1} \quad 0$$

$$109{,}677$$

$$\bar{\ }_{min} \quad 109{,}677 \quad \frac{1}{1} \quad \frac{1}{(2)^2}$$

$$\bar{\ }_{Lyman} \quad \bar{\ }_{max} \quad \bar{\ }_{min}$$

$$109{,}677 \quad \frac{109{,}677 \quad 3}{4} \quad \frac{109{,}677}{4}$$

For Balmer series,

$$\bar{\ }_{max} \quad 109{,}677 \quad \frac{1}{(2)^2} \quad \frac{1}{\ } \quad \frac{109677}{4}$$

$$\bar{\ }_{min} \quad 109{,}677 \quad \frac{1}{(2)^2} \quad \frac{1}{(3)^2} \quad \frac{109677 \quad 5}{36}$$

$$\bar{\ } \quad \bar{\ }_{max} \quad \bar{\ }_{min}$$

$$\bar{\ }_{Balmer} \quad \frac{109{,}677}{4} \quad \frac{109{,}677}{36} \quad 5 \quad 109{,}677 \quad \frac{1}{9}$$

$$\frac{\bar{\ }_{Lyman}}{\bar{\ }_{Balmer}} \quad \frac{109{,}677/4}{109{,}677/9}$$

$$\frac{\bar{\ }_{Lyman}}{\bar{\ }_{Balmer}} \quad \frac{9}{4}$$

The ratio of $\frac{\bar{\ }_{Lyman}}{\bar{\ }_{Balmer}}$ is 9 : 4.

6. Smaller the value of ($n \quad l$), smaller the energy. If two or more sub-orbits have same values of ($n \quad l$), sub-orbits with lower values of n has lower energy. The ($n \quad l$) values of the given options are as follows :

I. $n \quad 4, l \quad 2; n \quad l \quad 6$
II. $n \quad 3, l \quad 2; n \quad l \quad 5$
III. $n \quad 4, l \quad 1, n \quad l \quad 5$
IV. $n \quad 3, l \quad 1, n \quad l \quad 4$

Among II and III, $n \quad 3$ has lower value of energy. Thus, the correct order of their increasing energies will be

IV < II < III < I

7. Number of waves $\frac{\text{Circumference}}{\text{Wavelength}} \qquad n \quad \frac{2 \quad r}{\ }$

$$2 \quad r \quad n \qquad \text{...(i)}$$

Also, we know that radius (r) of an atom is given by

$$r \quad \frac{a_0 n^2}{Z}$$

Thus, Eq. (i) becomes

$$2 \quad a_0 \frac{n^2}{Z} \quad n \qquad \text{...(ii)}$$

$$2 \quad a_0 \frac{n^2}{Z} \quad n\,(1.5 \quad a_0) \text{ [Given, } \quad 1.5 \quad a_0]$$

$$\frac{n}{Z} \quad \frac{1.5 \quad a_0}{2 \quad a_0} \quad \frac{1.5}{2} \quad 0.75$$

8. de-Broglie wavelength ( ) for electron is given by

$$\frac{h}{\sqrt{2\,m\,\text{K.E}}} \qquad \text{...(i)}$$

Also, according to photoelectric effect

$$\text{KE} \quad h \quad h_{\ 0}$$

On substituting the value of KE in Eq (i), we get

$$\frac{h}{\sqrt{2m \quad (h \quad h_{\ 0})}}$$

$$\frac{1}{(\qquad)^{1/2}}$$

9. (I) Angular momentum, $mvr \quad \frac{nh}{2}$

$$mvr \quad n$$

distance from the nucleus

(II) This statement is incorrect as size of an orbit

Azimuthal quantum number (l)

($\because n \quad$ constant)

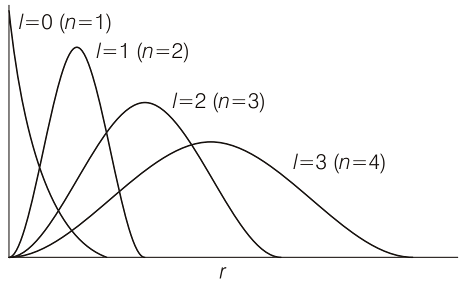
(III) This statement is incorrect as at ground state,

$$n \quad 1, l \quad 0$$

Orbital angular momentum (wave mechanics)

$$\sqrt{l\,(l \quad 1)}\,\frac{h}{2} \quad 0 \qquad [\because l \quad 0]$$

(IV) The given plot is



10. $E \quad hc \quad \frac{1}{\ } \quad hc \quad R_H \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2} \quad Z^2$

$$\frac{1}{n_1^2} \quad \frac{1}{n_2^2} \quad \frac{hc}{R_H \quad Z^2 \quad hc} \qquad \text{[for H, atom } Z \quad 1]$$

$$\frac{1}{R_H} \quad \frac{1}{(1 \quad 10^{7} \text{ m}^{\ 1})} \quad \frac{1}{(900 \quad 10^{\ 9} \text{ m})}$$

$$\frac{1}{n_1^2} \quad \frac{1}{n_2^2} \quad \frac{1}{9}$$

So, in option (b) $\frac{1}{3^2} \quad \frac{1}{\ ^2} \quad \frac{1}{9} \quad 0 \quad \frac{1}{9} \qquad n_1 \quad 3, \; n_2$

11. According to Rydberg's formula,

wave number $(\bar{\nu}) = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$

Given, $n_i = n$, $n_f = 8$ [$\because$ it is the case of emission]

$$\bar{\nu} = R_H (1)^2 \left(\frac{1}{n^2} - \frac{1}{8^2}\right)$$

$$\bar{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{64}\right) = \frac{R_H}{n^2} - \frac{R_H}{64}$$

On comparing with equation of straight line, $y = mx + c$, we get

Slope $= R_H$, intercept $= -\frac{R_H}{64}$.

Thus, plot of wave number $(\bar{\nu})$ against $\frac{1}{n^2}$ will be linear with slope $(-R_H)$.

12. Bohr radius $(r_n) \propto \varepsilon_0 n^2 h^2$

$$r_n = \frac{n^2h^2}{4\pi^2 me^2 kZ}$$

$$k = \frac{1}{4\pi\varepsilon_0}$$

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi me^2 Z} = n^2 \frac{a_0}{Z}$$

where, $m =$ mass of electron

$e =$ charge of electron

$h =$ Planck's constant

$k =$ Coulomb constant

$$r_n = \frac{n^2 \times 0.53}{Z} \text{ Å}$$

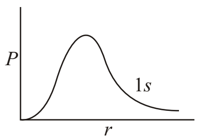
Radius of n^{th} Bohr orbit for H-atom

$= 0.53\, n^2$ Å [$Z = 1$ for H-atom]

Radius of 2^{nd} Bohr orbit for H-atom

$= 0.53 \times (2)^2 = 2.12$ Å

13. This graph shows the probability of finding the electron within shell at various distances from the nucleus (radial probability). The curve shows the maximum, which means that the radial probability is greatest for a given distance from the nucleus. This distance is equal to Bohr's radius $= a_0$



(a) It is for 2*s*-orbital.
(b) It is radial wave function for 1*s*.
(c) Correct
(d) Probability cannot be zero at a certain distance from nucleus.

14. $E_n = -\frac{13.6}{n^2}$ eV where, $n = 1, 2, 3 \ldots$

In excited states, $E_2 = -\frac{13.6}{4} = -3.4$ eV

15. Given, atomic number of Rb, $Z = 37$

Thus, its electronic configuration is $[\text{Kr}]5s^1$. Since, the last electron or valence electron enter in 5*s* subshell.

So, the quantum numbers are $n = 5$, $l = 0$, (for *s*-orbital) $m = 0$ ($\because m = -l$ to $+l$), $s = +1/2$ or $-1/2$.

16. Given, in the question $E = -2.178 \times 10^{-18}\text{ J}\left(\frac{Z^2}{n^2}\right)$

For hydrogen $Z = 1$,

So, $E_1 = -2.178 \times 10^{-18}\text{ J}\left(\frac{1}{1^2}\right)$

$E_2 = -2.178 \times 10^{-18}\text{ J}\left(\frac{1}{2^2}\right)$

Now, $E_1 - E_2$

i.e. $\Delta E = 2.178 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{hc}{\lambda}$

$$\lambda = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{2.178 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)}$$

$$= 1.21 \times 10^{-7}\text{ m}$$

17. According to Bohr's model,

$$mvr = \frac{nh}{2\pi} \Rightarrow (mv)^2 = \frac{n^2h^2}{4\pi^2r^2}$$

$$\text{KE} = \frac{1}{2}mv^2 = \frac{n^2h^2}{8\pi^2r^2m} \quad \ldots\text{(i)}$$

Also, Bohr's radius for H-atom is, $r = n^2 a_0$

Substituting 'r' in Eq. (i) gives

$$\text{KE} = \frac{h^2}{8\pi^2n^2a_0^2m} \text{ when } n = 2,\ \text{KE} = \frac{h^2}{32\pi^2a_0^2 m}$$

18. The number of radial nodes is given by expression $(n - l - 1)$.

For 3*s*, number of nodes $= 3 - 0 - 1 = 2$

For 2*p*, number of nodes $= 2 - 1 - 1 = 0$

19. Expression for Bohr's orbit is, $r_n = \frac{a_0n^2}{Z} = a_0$

when $n = 2$, $Z = 4$.

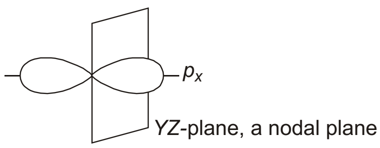
20. $1s^7$ violate Pauli exclusion principle, according to which an orbital cannot have more than two electrons.

21. $+\frac{1}{2}$ and $-\frac{1}{2}$ just represents two quantum mechanical spin states which have no classical analogue.

22. Using the de-Broglie's relationship :

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{0.2 \times \frac{5}{60 \times 60}} = 2.3 \times 10^{-30}\text{ m}$$

23. Nodal plane is an imaginary plane on which probability of finding an electron is minimum. Every *p*-orbital has one nodal plane :



24. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ is ground state electronic configuration of Cr.

25. (i) n 4, l 1 $4p$-orbital
(ii) n 4, l 0 $4s$-orbital
(iii) n 3, l 2 $3d$-orbital
(iv) n 3, l 1 $3d$-orbital

According to Aufbau principle, energies of above mentioned orbitals are in the order of

(iv) $3p <$ (ii) $4s <$ (iii) $3d <$ (i) $4p$

26. The energy of an electron in a Bohr atom is expressed as

$$E_n \quad \frac{kZ^2}{n^2} \qquad \text{where, } k \text{ Constant, } Z \text{ Atomic number, } n \text{ Orbit number}$$

13.6 eV for H (n 1)

when n 2, $E_2 \quad \frac{13.6}{2^2}$ eV= 3.40 eV

(n can have only integral value 1, 2, 3,……)

27. The orbital angular momentum (L) $\sqrt{l(l \quad 1)}\,\frac{h}{2}$

$$\sqrt{6}\,\frac{h}{2} \quad (l \quad 2 \text{ for } d\text{-orbital})$$

28. Bohr first made use of quantum theory to explain the structure of atom and proposed that energy of electron in an atom is quantised.

29. Mg^2 $1s^2\ 2s^2 2p^6$ no unpaired electron

Ti^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ one unpaired electron

V^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ two unpaired electrons

Fe^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ four unpaired electrons

30. Expression for orbital angular momentum (L) is

$$L \quad \sqrt{l(l \quad 1)}\,\frac{h}{2} \quad 0 \quad \text{for } 2s\text{-electrons}$$

$\because$ For s-orbital, l 0.

31. Diffraction is property of wave, $E \quad mc^2$ determine energy of particle and $E \quad h$ determine energy of photon. Interference phenomena is exhibited by both matter and waves.

32. X-rays is electrically neutral, not deflected in electric or magnetic fields.

33. Cl (17) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$$

The last, unpaired electron has, n 3, l 1(p) and m can have any of the three value (1, 0, 1).

34. Cr (24) $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{Ar}}\ 3d^5\ 4s^1$

The above configuration is exception to Aufbau's principle.

35. Fluorine, a halogen, is the most electronegative atom, has the electronic configuration $2s^2 2p^5$ (valence shell).

36. Option (b) is wrong representation according to aufbau principle. A high energy atomic orbital ($2p$) cannot be filled unless the low energy orbital ($2s$) is completely occupied.

37. Transition energy (E) $kZ^2 \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2} \quad \frac{hc}{}$

i.e. $E \quad \frac{1}{}$

38. $$E \quad \frac{hc}{}$$

$$\frac{E_1}{E_2} \quad \frac{2}{1} \quad 2$$

39.

n	l	m	s
3	2	3	$\frac{1}{2}$

This is the wrong set of quantum number because $|m|$ cannot be greater than l.

40. The wavelength order is

X-ray < ultraviolet < infrared < radio wave

41. When electron jumps to lower orbit photons are emitted while photons are absorbed when electron jumps to higher orbit. $1s$-orbital is the lower most, electron in this orbital can absorb photons but cannot emit.

42. The valence shell configuration of Rubidium (Rb) is

$$[\text{Kr}]\,5s^1 \qquad n \quad 5, l \quad 0, m \quad 0, s \quad \frac{1}{2} \text{ or } \frac{1}{2}$$

43. The principal quantum number 'n' represents orbit number hence, determine the size of orbitals.

44. According to Pauli exclusion principle, an atomic orbital can accommodate at the most, two electrons, with opposite spins.

45. Both (a) and (d) are correct. The three electrons in the $2p$-orbitals must have same spin, no matter up spin or down spin.

46. (a) Cr = [Ar] $3d^5 4s^1$, an exception to aufbau principle.

(b) For a given value of l, m can have any value from (l to l), so can have negative value.

(c) Ag is in copper group with $d^{10}s^1$ configuration, i.e. 46 electrons are spin paired.

47. Isotones have same number of neutrons.

${}_{32}Ge^{76}$, ${}_{33}As^{77}$ and ${}_{34}Se^{78}$ have same number (44) of neutrons, hence they are isotones.

48. Assertion is correct $Be(1s^2, 2s^2)$ has stable electronic configuration, removing an electron require more energy than the same for $B(2p^1)$. Reason is incorrect (Aufbau principle).

49. S_1 is spherically symmetrical state, i.e. it correspond to a s-orbital. Also, it has one radial node.

Number of radial nodes $n \quad l \quad l$

$n \quad 0 \quad 1 \quad 1$

n 2 i.e. S_1 $2s$-orbital.

50. Ground state energy of electron in H-atom (E_H)

$$E_H \quad \frac{kZ^2}{n^2} \quad k \ (Z \quad 1, n \quad 1)$$

For S_1 state of Li^{2} ,

$$E \quad \frac{k(3)^2}{2^2} \quad \frac{9}{4} k \quad 2.25\, k$$

51. In S_2 state, $E(Li^{2}\ )\quad K$ (given)

$$K \quad \frac{qk}{n^2}$$

$$n \quad 3$$

Since, S_2 has one radial node.

$$3 \quad l \quad 1 \quad 1$$

$$l \quad 1$$

52. In the wave function ( ) expression for 1*s*-orbital of He , there should be no angular part. Hence (iii) can't be true for $_{1s}$ of He .

53. Correct : 2*s* orbital has one radial node.

No of radial node $n \quad l \quad 1 \quad 2 \quad 0 \quad 1 \quad 1$

Also, when radial part of wave function ( ) is plotted against "*r*", wave function changes its sign at node.

54. *i* is the correct expression of wave function for 1*s*-orbital of hydrogenic system.

55. A. Orbital angular momentum

$$(L) \quad \sqrt{l(l \quad 1)}\ \frac{h}{2}$$

i.e. *L* depends on azimuthal quantum number only.

B. To describe a one electron wave function, three quantum numbers *n*, *l* and *m* are needed. Further to abide by Pauli exclusion principle, spin quantum number(*s*) is also needed.

C. For shape, size and orientation, only *n*, *l* and *m* are needed.

D. Probability density (^{2}) can be determined if *n*, *l* and *m* are known.

56. Cr [Ar] $3d^5 4s^1$

57. 1 : 16

58. Heisenberg proposed uncertainty principle and de-Broglie proposed wave nature of electron.

59. orbital

60. $2p_x, 2p_y$ and $2p_z$ have different orientation in space.

61. Two electrons in same orbital must have opposite spin.

62. Very large mass of alpha particles than beta particles is responsible for less deflection in former case.

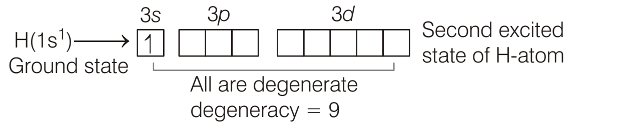
63. $3d_{x^2 \quad y^2}$ orbital lies in *XY*-plane.

64. Aufbau principle.

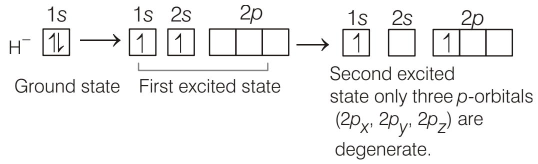
65. This is the wavelength of infrared radiation.

66. Cr $3d^5 4s^1$.

67. In an one electron (hydrogenic) system, all orbitals of a shell remains degenerate, hence in second excited state, the degeneracy of H-atom is nine



In case of many electrons system, different orbitals of a shell are non-degenerate. Hence,



68. **PLAN** This problem is based on concept of quantum number. Follow the following steps to solve this problem.
Write all possible orbitals having combination of same principal, azimuthal, magnetic and spin quantum number.

Then count the all possible electrons having given set of quantum numbers.

For $n \quad 4$, the total number of possible orbitals are

4*s*	4*p*			4*d*					4*f*						
0	–1	0	+1	–2	–1	0	+1	+2	–3	–2	–1	0	+1	+2	+3

According to question $|m_l| \quad 1$, i.e. there are two possible values of m_l, i.e. +1 and –1 and one orbital can contain maximum two electrons one having $s \quad \frac{1}{2}$ and other having $s \quad 1/2$.

So, total number of orbitals having $\{|m_l| \quad 1\} \quad 6$

Total number of electrons having

$$\{|m_l| \quad 1 \text{ and } m_s \quad \frac{1}{2}\} \quad 6$$

69. **PLAN** $KE \quad \frac{1}{2}mv^2 \quad \frac{3}{2}RT$

$$m^2v^2 \quad 2m\text{KE} \qquad mv \quad \sqrt{2m\text{KE}}$$

$$\text{(wavelength)} \quad \frac{h}{mv} \quad \frac{h}{\sqrt{2m\text{KE}}} \quad \frac{h}{\sqrt{2m(T)}}$$

where, T Temperature in Kelvin

$$(\text{He at } \ 73\ \text{C} \quad 200\ \text{K}) \quad \frac{h}{\sqrt{2 \quad 4 \quad 200}}$$

$$(\text{Ne at } 727°\text{C} \quad 1000\ \text{K}) \quad \frac{h}{\sqrt{2 \quad 20 \quad 1000}}$$

$$\frac{(\text{He})}{(\text{Ne})} \quad M \quad \sqrt{\frac{2 \quad 20 \quad 1000}{2 \quad 4 \quad 200}} \quad 5$$

Thus, $M \quad 5$

70. Energy of photon

$$\frac{hc}{\ }\text{J} = \frac{hc}{e}\text{eV} \quad \frac{6.625 \quad 10^{-34} \quad 3 \quad 10^8}{300 \quad 10^{-9} \quad 1.602 \quad 10^{-19}} \quad 4.14 \text{ eV}$$

For photoelectric effect to occur, energy of incident photons must be greater than work function of metal. Hence, only Li, Na, K and Mg have work functions less than 4.14 V.

71. When $n = 3$, $l = 0, 1, 2$ i.e. there are $3s$, $3p$ and $3d$-orbitals. If all these orbitals are completely occupied as

$$\boxed{\uparrow\downarrow}\quad \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\quad \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$$

Total 18 electrons, 9 electrons with $s \quad +\frac{1}{2}$ and 9 with

$$s \quad -\frac{1}{2}.$$

Alternatively In any nth orbit, there can be a maximum of $2n^2$ electrons. Hence, when $n = 3$, number of maximum electrons = 18. Out of these 18 electrons, 9 can have spin $-\frac{1}{2}$ and remaining nine with spin $\frac{1}{2}$.

72. (a) $mvr \quad \frac{nh}{2}$

$$v \quad \frac{nh}{2 \quad mr} \quad \frac{6.625 \quad 10^{\quad 34}}{2 \quad 3.14 \quad 9.1 \quad 10^{\quad 31} \quad 0.529 \quad 10^{\quad 10}}$$

$$2.18 \quad 10^6 \text{ ms}^{\quad 1}$$

(b) $$\frac{h}{mv} \quad \frac{6.625 \quad 10^{\quad 34}}{9.1 \quad 10^{\quad 31} \quad 2.18 \quad 10^6} \quad 0.33 \quad 10^{\quad 9} \text{ m}$$

(c) Orbital angular momentum

$$(L) \quad \sqrt{l(l \quad 1)}\,\frac{h}{2} \quad \sqrt{2}\,\frac{h}{2}$$

[$\because$ For p-orbital, $l \quad 1$]

73. (a) At radial node, $\;^2$ must vanishes, i.e.

$$^2_{2s} \quad 0 \quad \left(\frac{1}{4\sqrt{2}}\right)^2 \left(2 \quad \frac{r_0}{a_0}\right)^2 e^{\quad \frac{r_0}{a_0}}$$

$$2 \quad \frac{r_0}{a_0} \quad 0 \qquad r_0 \quad 2a_0$$

(b) $$\frac{h}{mv} \quad \frac{6.625 \quad 10^{\quad 34}}{100 \quad 10^{\quad 3} \quad 100} \quad 6.625 \quad 10^{\quad 35} \text{ m}$$

$$6.625 \quad 10^{\quad 25} \text{ Å (negligibly small)}$$

74. The general Rydberg's equation is

$$\bar{\ } \quad \frac{1}{\ } \quad R(Z)^2 \left(\frac{1}{n_1^2} \quad \frac{1}{n_2^2}\right)$$

$$\frac{1}{\ } \quad Z^2$$

$$\frac{(\text{He}^+)}{(\text{H})} \quad \frac{Z(\text{H})^2}{Z(\text{He}^+)^2} \quad \frac{1}{4}$$

$$(\text{He}^+) \quad \frac{(\text{H})}{4} \quad \frac{91.2}{4} \text{ nm} = 22.8 \text{ nm}$$

75. Moles of $H_2 \quad \frac{pV}{RT} \quad \frac{1 \quad 1}{0.082 \quad 298} \quad 0.0409$

Bond energy $\quad 0.0409 \quad 436 \quad 17.84$ kJ

Number of H-atoms produced after dissociation

$$2 \quad 0.0409 \quad 6.023 \quad 10^{23} \quad 4.93 \quad 10^{22}$$

Transition energy/atom $\quad 2.18 \quad 10^{\quad 18}\left(1 \quad \frac{1}{4}\right)$ J

$$\frac{3}{4} \quad 2.18 \quad 10^{\quad 18} \text{ J}$$

Total transition energy

$$\frac{3}{4} \quad 2.18 \quad 10^{\quad 18} \quad 4.93 \quad 10^{22} \text{ J}$$

$$80.60 \quad 10^3 \text{ J} = 80.60 \text{ kJ}$$

Therefore, total energy required

= dissociation energy + transition energy

(17.84 + 80.60) kJ = 98.44 kJ

76. If accelerated by potential difference of V volt, then

$$\frac{1}{2}mv^2 \quad eV$$

$$\frac{p^2}{2m} \quad eV, \text{ here } p \quad \text{momentum } (mv)$$

Using de-Broglie equation, $\quad \frac{h}{p} \quad \frac{h}{\sqrt{2meV}}$

$$1.54 \quad 10^{\quad 10} \quad \frac{6.625 \quad 10^{\quad 34}}{(2 \quad 9.1 \quad 10^{\quad 31} \quad 1.6 \quad 10^{\quad 19}\; V)^{1/2}}$$

Solving for V gives : $V \quad 63.56$ V.

77. The work done in the given neutralisation process is

$$W \quad \int_{a_0} F\,dr \text{ and } F \quad \frac{e^2}{4 \quad _0 r^2}$$

$$W \quad \frac{e^2}{4 \quad _0}\left[\frac{1}{r}\right]_{a_0} \quad \frac{e^2}{4 \quad _0 r} \quad \text{Total energy } (E)$$

Now, if 'V' is magnitude of potential energy, then according to given information, kinetic energy (E_k) is $V/2$. Therefore,

$$E \quad V \quad \frac{V}{2} \quad \text{(PE is always negative)}$$

$$\frac{V}{2}$$

$$V \quad 2E \quad \frac{e^2}{2 \quad _0 r}$$

78. The Rydberg's equation for H-atom is

$$\frac{1}{\ } \quad \bar{\ } \text{ (wave number) } \quad R_H\left(\frac{1}{n_1^2} \quad \frac{1}{n_2^2}\right)$$

For Balmer series, $n_1 \quad 2$ and $n_2 \quad 3, 4, 5, \ldots,$

For shortest $\;$, n_2 has to be maximum, i.e. infinity. Then

$$\bar{\ } \quad R_H\left(\frac{1}{4} \quad \frac{1}{\ }\right) \quad \frac{R_H}{4} \quad \frac{1.09 \quad 10^7}{4} \quad 2.725 \quad 10^6 \text{ m}^{\quad 1}$$

79. After breaking of the bond of I_2 molecule, the remaining energy would be distributed uniformly to iodine atoms as their kinetic energy, i.e.

E (energy of photon) Bond energy 2 kinetic energy

$$\frac{6.625 \quad 10^{34} \quad 3 \quad 10^8}{4500 \quad 10^{10}} \quad \frac{240 \quad 10^3}{6.023 \quad 10^{23}} \quad 2 \quad E_k$$

$$E_k \quad 2.16 \quad 10^{20} \text{ J/atom}$$

80. The Bohr de-Broglie relationship is

$$2 \quad r \quad n \qquad \text{circumference of Bohr's orbit.}$$

i.e. number of complete waves formed in one complete revolution of electron in any Bohr orbit is equal to orbit number, hence three.

81. The expression for transition wavelength is given by Rydberg's equation :

$$\frac{1}{} \quad R_H Z^2 \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2}$$

Equating the transition wavelengths of H-atom and He^+ ion,

$$R_H \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2} \qquad R_H \quad \frac{4}{2^2} \quad \frac{4}{4^2}$$

Equating termwise on left to right of the above equation gives $n_1 \quad 1$ and $n_2 \quad 2$

82. For H-atom, the energy of a stationary orbit is determined as

$$E_n \quad \frac{k}{n^2} \quad \text{where, } k \quad \text{constant } (2.18 \quad 10^{18} \text{ J})$$

$$E\,(n \quad 2 \text{ to } n \quad 1) \quad k \quad 1 \quad \frac{1}{4} \quad \frac{3}{4}k$$

$$= 1.635 \quad 10^{18} \text{ J}$$

For a H-like species, energy of stationary orbit is determined as

$$E_n \quad \frac{kZ^2}{n^2}$$

where, Z atomic number

$$E \quad kZ^2 \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2}$$

$$\frac{1}{} \quad \frac{E}{hc} \quad \frac{k}{hc}Z^2 \quad \frac{1}{1} \quad \frac{1}{4} \qquad R_H \, Z^2 \quad \frac{3}{4}$$

$$Z^2 \quad \frac{4}{3R_H} \quad \frac{4}{3 \quad 1.097 \quad 10^7 \quad 3 \quad 10^{8}} \quad 4.05$$

$$Z \quad 2 \, (He^+)$$

83. For H-like species, the energy of stationary orbit is expressed as $E(X) \quad Z^2 \quad E(H)$

For He^+ ($Z \quad 2$)

$$E \quad \frac{4 \quad 21.7 \quad 10^{19}}{n^2} \text{ J}$$

For longest wavelength transition from 3rd orbit, electron must jump to 4th orbit and the transition energy can be determined as

$$E \quad 4 \quad 21.7 \quad 10^{19} \quad \frac{1}{9} \quad \frac{1}{16} \text{ J} \quad 4.22 \quad 10^{19} \text{ J}$$

Also, $\because \quad E \quad \frac{hc}{}$

$$\frac{hc}{E} \quad \frac{6.625 \quad 10^{34} \quad 3 \quad 10^8}{4.22 \quad 10^{19}} \text{ m}$$

$$471 \quad 10^{9} \text{ m} = 471 \text{ nm}$$

84. Ten, the given value of n and l correspond to $3d$-orbital which has five fold degeneracy level.

85. The 2nd configuration is against Hund's rule of maximum multiplicity which states that the singly occupied degenerate atomic orbitals must have electrons of like spins.

86. The required transition is $n_1 \quad 2$ to n_2 and corresponding transition energy is

$$E \quad 21.7 \quad 10^{12} \quad \frac{1}{n_1^2} \quad \frac{1}{n_2^2} \text{ erg}$$

$$\frac{21.7}{4} \quad 10^{12} \text{ erg} \quad 5.425 \quad 10^{12} \text{ erg}$$

The longest wavelength that can cause above transition can be determined as :

$$\frac{hc}{E} \quad \frac{6.625 \quad 10^{34} \quad 3 \quad 10^8}{5.425 \quad 10^{12} \quad 10^{7}}$$

$$3.66 \quad 10^{7} \text{ m} = 3.66 \quad 10^{5} \text{ cm}$$

87. Ionisation potential of H-like species

$$E_1 \quad 2.17 \quad 10^{11} \text{ erg}$$

$$E \quad 2.17 \quad 10^{11} \quad 1 \quad \frac{1}{2^2} \quad 10^{7} \text{J}$$

$$1.6275 \quad 10^{18} \text{ J} \qquad \frac{hc}{E}$$

$$\frac{6.625 \quad 10^{34} \quad 3 \quad 10^8}{1.6275 \quad 10^{18}} \text{ m}$$

$$122 \quad 10^{9} \text{ m} = 1220 \text{ Å}$$

88. Transition energy $[\ 2.41 \quad (\ 5.42)] \quad 10^{12}$ erg

$$3.01 \quad 10^{12} \text{ erg}$$

$$3.01 \quad 10^{19} \text{ J} \qquad [\because \ 1 \text{ erg} = 10^{7} \text{ J}]$$

Also, $E \quad \frac{hc}{}$

$$\frac{6.625 \quad 10^{34} \quad 3 \quad 10^8}{3.01 \quad 10^{19}} \text{ m}$$

$$660 \quad 10^{9} \text{ m} \quad 660 \text{ nm}$$

3

Periodic Classification and Periodic Properties

Topic 1 History and Periodic Classification

Objective Question I (Only one correct option)

1. The IUPAC symbol for the element with atomic number 119 would be **(2019 Main, 8 April II)**

(a) unh (b) uue
(c) uun (d) une

2. The element with $Z = 120$ (not yet discovered) will be an/a **(2019 Main, 12 Jan I)**

(a) transition metal (b) inner-transition metal
(c) alkaline earth metal (d) alkali metal

3. The statement that is not correct for the periodic classification of elements, is **(1992, 1M)**

(a) the properties of elements are the periodic functions of their atomic numbers
(b) non-metallic elements are lesser in number than metallic elements
(c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
(d) for transition elements the *d*-subshells are filled with electrons monotonically with increase in atomic number

Objective Question II
(One or more than one correct option)

4. The statements that is/are true for the long form of the periodic table is/are **(1988, 1M)**

(a) it reflects the sequence of filling the electrons in the order of sub-energy level *s*, *p*, *d* and *f*
(b) it helps to predict the stable valency states of the elements
(c) it reflects tends in physical and chemical properties of the elements
(d) it helps to predict the relative ionicity of the bond between any two elements

Topic 2 Periodic Properties

Objective Questions I (Only one correct option)

1. The group number, number of valence electrons and valency of an element with atomic number 15, respectively, are **(2019 Main, 12 April I)**

(a) 16, 5 and 2 (b) 15, 5 and 3
(c) 16, 6 and 3 (d) 15, 6 and 2

2. The element having greatest difference between its first and second ionisation energy, is **(2019 Main, 9 April I)**

(a) Ca (b) Sc
(c) Ba (d) K

3. The correct option with respect to the Pauling electronegativity values of the elements is **(2019 Main, 11 Jan II)**

(a) P > S (b) Si < Al
(c) Te > Se (d) Ga < Ge

4. The correct order of the atomic radii of C, Cs, Al and S is **(2019 Main, 11 Jan I)**

(a) C < S < Al < Cs (b) C < S < Cs < Al
(c) S < C < Cs < Al (d) S < C < Al < Cs

5. In general, the properties that decrease and increase down a group in the periodic table, respectively are **(2019 Main, 9 Jan I)**

(a) electronegativity and atomic radius
(b) electronegativity and electron gain enthalpy
(c) electron gain enthalpy and electronegativity
(d) atomic radius and electronegativity

6. The ionic radii (in Å) of N^{3} ,O^{2} and F respectively are **(2015 Main)**

(a) 1.36, 1.40 and 1.71 (b) 1.36, 1.71 and 1.40
(c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40

7. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **(2015 Main)**
(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

8. Which among the following is the most reactive? **(2015 Main)**
(a) Cl_2 (b) Br_2
(c) I_2 (d) ICl

9. Which one has the highest boiling point?
(a) He (b) Ne (c) Kr (d) Xe

10. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be **(2013 Main)**
(a) 2.55 eV (b) 5.1 eV
(c) 10.2 eV (d) 2.55 eV

11. Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar? **(2013 Main)**
(a) Ca < S < Ba < Se < Ar (b) S < Se < Ca < Ba < Ar
(c) Ba < Ca < Se < S < Ar (d) Ca < Ba < S < Se < Ar

12. Identify the least stable ion amongst the following. **(2002, 3M)**
(a) Li^+ (b) Be
(c) B (d) C

13. The set representing the correct order of first ionisation potential is **(2001, 1M)**
(a) K Na Li (b) Be Mg Ca
(c) B C N (d) Ge Si C

14. The correct order of radii is **(2000, 1M)**
(a) N < Be < B (b) F $< O^2 < N^3$
(c) Na < Li < K (d) Fe^{3+} Fe^{2+} Fe^{4+}

15. The incorrect statement among the following. **(1997(C), 1M)**
(a) The first ionisation potential of Al is less than the first ionisation potential of Mg
(b) The second ionisation potential of Mg is greater than the second ionisation potential of Na
(c) The first ionisation potential of Na is less than the first ionisation potential of Mg
(d) The third ionisation potential of Mg is greater than third ionisation potential of Na

16. Which of the following has the maximum number of unpaired electrons ? **(1996, 1M)**
(a) Mg^2 (b) Ti^3
(c) V^3 (d) Fe^2

17. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionisation energy is **(1990, 1M)**
(a) [Ne] $3s^2\ 3p^1$ (b) [Ne] $3s^2\ 3p^3$
(c) [Ne] $3s^2\ 3p^2$ (d) [Ar] $3d^{10}\ 4s^2\ 4p^3$

18. Which one of the following is the smallest in size? **(1989, 1M)**
(a) N^3 (b) O^2
(c) F (d) Na^+

19. The first ionisation potential of Na, Mg, Al and Si are in the order **(1988, 1M)**
(a) Na Mg>Al Si (b) Na Mg Al Si
(c) Na < Mg<Al>Si (d) Na Mg Al<Si

20. The electronegativity of the following elements increases in the order **(1987, 1M)**
(a) C, N, Si, P (b) N, Si, C, P
(c) Si, P, C, N (d) P, Si, N, C

21. Atomic radii of fluorine and neon in Angstrom units are respectively given by **(1987, 1M)**
(a) 0.72, 1.60 (b) 1.60, 1.60
(c) 0.72, 0.72 (d) None of these

22. The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by **(1987, 1M)**
(a) 14.6, 13.6 (b) 13.6, 14.6
(c) 13.6, 13.6 (d) 14.6, 14.6

23. The hydration energy of Mg^2 is larger than that of **(1984, 1M)**
(a) Al^3 (b) Na (c) Be^2 (d) Mg^3

24. The element with the highest first ionisation potential is **(1982, 1M)**
(a) boron (b) carbon
(c) nitrogen (d) oxygen

25. The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is **(1981, 1M)**
(a) C > N > O > F (b) O > N > F > C
(c) O > F > N > C (d) F > O > N > C

Objective Questions II

(One or more than one correct option)

26. The option(s) with only amphoteric oxides is(are) **(2017 Adv.)**
(a) NO, B_2O_3, PbO, SnO_2 (b) Cr_2O_3, CrO, SnO, PbO
(c) Cr_2O_3, BeO, SnO, SnO_2 (d) ZnO, Al_2O_3, PbO, PbO_2

27. Ionic radii of **(1999, 3M)**
(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl < {}^{37}Cl$
(c) $K^+ > Cl$ (d) $P^{3+} > P^{5+}$

28. The first ionisation potential of nitrogen and oxygen atoms are related as follows. **(1989, 1M)**
(a) The ionisation potential of oxygen is less than the ionisation potential of nitrogen
(b) The ionisation potential of nitrogen is greater than the ionisation potential of oxygen
(c) The two ionisation potential values are comparable
(d) The difference between the two ionisation potential is too large

29. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because **(1989, 1M)**
(a) the hydration energy of sodium sulphate is more than its lattice energy
(b) the lattice energy of barium sulphate is more than its hydration energy
(c) the lattice energy has no role to play in solubility
(d) the hydration energy of sodium sulphate is less than its lattice energy

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

30. **Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II The reaction between nitrogen and oxygen requires high temperature. **(2015 Main)**

31. **Statement I** Pb^{4} compounds are stronger oxidising agents than Sn compounds.
Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **(2008, 3M)**

32. **Statement I** Band gap in germanium is small.
Statement II The energy spread of each germanium atomic energy level is infinitesimally small. **(2007, 3M)**

33. **Statement I** The first ionisation energy of Be is greater than that of B.
Statement II $2p$-orbital is lower in energy than $2s$. **(2000, (S), 1M)**

34. **Statement I** F-atom has a less negative electron affinity than Cl-atom.
Statement II Additional electrons are repelled more effectively by $3p$-electrons in Cl-atom than by $2p$-electrons in F-atom. **(1998, 2M)**

Fill in the Blanks

35. Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+}. The stability of the lower oxidation state is due to …… . **(1997, 1M)**

36. Ca^{2} has a smaller ionic radius than K because it has .... **(1993, 1M**

37. On Mulliken scale, the average of ionisation potential and electron affinity is known as .... **(1985, 1M)**

38. The energy released when an electron is added to a neutral gaseous atom is called …… . **(1982, 1M)**

True/False

39. The basic nature of the hydroxides of group 13 (III B) decreases progressively down the group. **(1993, 1M)**

40. The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. **(1993, 1M)**

41. In group IA of alkali metals, the ionisation potential decreases down the group. Therefore, lithium is a poor reducing agent. **(1987, 1M)**

42. The softness of group IA metals increases down the group with increasing atomic number. **(1986, 1M)**

Subjective Questions

43. Arrange the following ions in order of their increasing radii $Li^{+}, Mg^{2+}, K^{+}, Al^{3+}$. **(1997, 1M)**

44. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation. **(1996, 2M**

45. Arrange the following as stated :
"Increasing order of ionic size'' $N^{3-}, Na^{+}, F , O^{2} , Mg^{2+}$ **(1991, 1M)**

46. Explain the following :
"The first ionisation energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionisation energy.'' **(1989, 2M)**

47. Arrange the following in the order of their increasing size: Cl , S^{2} , Ca^{2+}, Ar **(1986, 1M)**

48. Arrange the following in order of their
(i) decreasing ionic size $Mg^{2+}, O^{2} , Na^{+}, F$
(ii) increasing first ionisation energy Mg, Al, Si, Na
(iii) increasing bond length F_2, N_2, Cl_2, O_2 **(1985, 3M)**

Answers

Topic 1

1. (b)	**2.** (c)	**3.** (d)	**4.** (b,c,d)

Topic 2

1. (b)	**2.** (d)	**3.** (d)	**4.** (a)
5. (a)	**6.** (c)	**7.** (b)	**8.** (d)
9. (d)	**10.** (b)	**11.** (c)	**12.** (b)
13. (b)	**14.** (b)	**15.** (b)	**16.** (d)
17. (b)	**18.** (d)	**19.** (a)	**20.** (c)
21. (a)	**22.** (a)	**23.** (b)	**24.** (c)
25. (c)	**26.** (a,b)	**27.** (d)	**28.** (a,b,c)
29. (a,b)	**30.** (a)	**31.** (c)	**32.** (c)
33. (c)	**34.** (c)		

35. (inert pair effect)
36. (higher effective nuclear charge)
37. (electronegativity) **38.** (electron affinity)

39. F	**40.** F	**41.** F	**42.** T

Hints & Solutions

Topic 1 History and Periodic Classification

1. Atomic number (119) = $\underset{\text{un}}{1}\ \underset{\text{un}}{1}\ \underset{\text{en}}{9}$

So, symbol of the element uue

Name of the element ununennium

It is expected to be *s*-block element an alkali metal and the first element in eighth period. It is the lightest element that has not yet been synthesised.

2. The element with Z 120 will be an alkaline earth metal. Recently, oganesson (Og) with atomic number 118 is named by IUPAC is a noble gas and placed just two place before 120. So, the general electronic configuration is represented as [noble gas]ns^2 and element with Z 120 exist as an alkaline earth metal.

3. (a) **Correct statement** According to Moseley's law, the properties of elements are the periodic function of their atomic numbers.

(b) **Correct statement** The whole *s*-block, *d*-block, *f*-block and heavier *p*-block elements are metal.

(c) **Correct statement** Trend is not regular, Be has higher first ionisation energy than B, nitrogen has higher first ionisation energy than oxygen.

(d) **Inccorrect statement** *d*-subshells are not filled monotonically, regularity break at chromium and copper.

4. (a) **Incorrect** Electrons are not filled in sub-energy levels *s*, *p*, *d* and *f* in the same sequence.

(b) **Correct** Number of valence shell electrons usually determine the stable valency state of an element.

(c) **Correct** Physical and chemical properties of elements are periodic function of atomic number which is the basis of modern, long form of periodic table.

(d) **Correct** Relative ionicity of the bond between any two elements is function of electronegativity difference of the bonded atoms which in turn has periodic trend in long form of periodic table.

Topic 2 Periodic Properties

1. The group number, number of valence electrons and valency of an element with atomic number 15 are 15, 5 and 3 respectively. Modern periodic table is based on the atomic number. Number of valence electrons present in an atom decides the group number. Electronic configuration of element having atomic number 15 $1s^2\ 2s^2\ 2p^6\ \underbrace{3s^2\ 3p^3}_{\text{Valence electrons}}$

As five electrons are present in valence shell, its group number is 15. Valency of element having atomic number 15 is +3 (8 5 3).

2. The electronic configuration of given elements are as follows :

K(19) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^1$

Mg(12) = $1s^2\ 2s^2\ 2p^6\ 3s^2$

Sr(38) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$

Sc(21) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^2\ 3d^1$

First ionisation enthalpy (I.E.) of K is lowest among the given options. Here, the energy required to remove an electron from $4s^1$ is least as only one electron is present in the outermost shell. I.E. (I) is comparatively high for Mg and Sr and two electrons (fully-filled) are placed in *s*-orbital. Second ionisation enthalpy of K is highest among the given options.

Now, removal of an electron occur from p^6 (fully-filled). So, high energy is required to remove the electron. From the above discussion, it can be concluded that $(\text{I.E}_2\ \ \text{I.E}_1)$ value is maximum for K (potassium).

3. The electronegativity values of given elements on the Pauling scale can be shown as follows:

Period No.	Group 13	Group 14	Group 15	Group 16
3	Al (1.5)	Si (1.8)	P (2.1)	S (2.5)
4	Ga (1.6)	Ge (1.8)		Se (2.4)
5				Te (2.01)

On moving from left to right across a period, i.e. from Ga to Se, the effective nuclear charge increases and size decreases.

As a result, the value of electronegativity increases due to increase in the attraction between the outer electrons and the nucleus. Whereas on moving down the group, (i.e. from Se to Te), the atomic size increases.

As a result, the force of attraction between the outer electron and the nucleus decreases. Hence, the electronegativity decreases.

4.

Element	Period No.	Group No.
C	2nd	14
Al	3rd	13 Along the period atomic radius decreases, so, radii : Al > S.
S	3rd	16
Cs	6th	1

With the addition of a new shell, period number as well as atomic radius increases. It is because of the successive addition of one extra shell of electrons. So, the order of the atomic radii of the given elements will be: C < S < Al < Cs

5. The summary of variation of periodic properties is given in table below:

S.No.	Periodic property	Variation	
		Along a period	Along a group
1.	Atomic radius	Decreases	Increases
2.	Electron gain enthalpy	Increases	Decreases
3.	Electronegativity	Increases	Decreases

Thus, electronegativity decreases and atomic radius increases down a group in the periodic table.

6. Number of electrons in N^3 , 7 3 10

Number of electrons in O^2 8 2 10

Number of electrons in F 9 1 10

Since, all the three species have each 10 electrons, hence they are isoelectronic species.

It is considered that, in case of isoelectronic species as the negative charge increases, ionic radii increases and therefore the value of ionic radii are

N^{3} 1.71 (highest among the three)

O^{2} 1.40 F 1.36 (lowest among the three)

Time Saving Technique There is no need to mug up the radius values for different ions. This particular question can be solved through following time saving.

Trick The charges on the ions indicate the size as N^{3} O^{2} F . Thus, you have to look for the option in which the above trend is followed. Option(c) is the only one in which this trend is followed. Hence, it is the correct answer.

7. As we move down the group, size of metal increases. Be has lower size while SO_4^2 has bigger size, that's why $BeSO_4$ breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest of the metals, i.e Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time Saving Technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy. Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, $BeSO_4$ is the right response.

8. Cl_2, Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas, I and Cl have different electronegativities and bond between them are polarised and reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique In this type of question of halogen, only go through the polarity of the molecules. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

9. As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe.

Therefore, more amount of energy is required to break these forces, thus boiling point also increases from He and Xe.

10. Na Na e First IE

Na^+ e Na

Electron gain enthalpy of Na^+ is reverse of (IE)

Because reaction is reverse so $H(eq)$ 5.1 eV

11. Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as

Group No. 2	16	18
Ca	S	Ar
Ba	Se	

Thus, the order of increasing H_{IE_1} is Ba Ca Se S Ar

12. Be is the least stable ion, Be ($1s^2 2s^2$) has stable electronic configuration, addition of electron decreases stability.

13. In a group, ionisation energy decreases down the group

Be > Mg > Ca

14. Among isoelectronic species, greater the negative charge, greater the ionic size, hence F $< O^2 < N^3$.

15. (a) **Correct statement** In a period, element of 2nd group has higher first ionisation potential than element of group 13.

(b) **Incorrect statement** Mg^+ require less energy for further ionisation than Na^+ because of noble gas configuration of Na^+.

(c) **Correct statement** Ionisation energy increases from left to right in a period.

16. Mg^{2+} $1s^2\ 2s^2\ 2p^6$ no unpaired electron

Ti^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ one unpaired electron

V^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ two unpaired electrons

Fe^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ four unpaired electrons

17. [Ne] $3s^2\ 3p^3$ has highest ionisation energy, periodic trend.

18. Among isoelectronic species, the relation in size is

cation < neutral < anion

Hence, Na^+ has smallest size.

19. Ionisation energy increases from left to right in a period. However, exception occur between group 2 and group 13 elements on account of stability of electronic configuration of valence shell.

Group 2 = [⇅] $\overset{IE}{>}$ Group 13 = [⇅] [↿| |]

ns^2 ns^2 np^1

The desired order is Na < Mg > Al < Si

20. Electronegativity increases from left to right in a period and decreases from top to bottom in a group. Variation is more rapid in group than in a period, hence the desired order is

Electronegativity : Si < P < C < N

21. Atomic radius of noble gases are greater than halogens of same period, hence (a) is the correct answer.

22. First ionisation energy of oxygen is less than that of nitrogen on the ground of stability of valence shell configuration, hence (a) is the correct answer.

23. Hydration energy depends on charge of ion and ionic radius. Higher the charge, greater the hydration energy. On the other hand, smaller the size, greater the hydration energy. Charge is considered first for comparison. Hence, Mg^{2+} has higher hydration energy than Na^+.

24. Nitrogen has highest ionisation potential due to exceptional stability of its valence shell configuration mentioned in question 21.

25. For second ionisation potential, electron will have to be removed from valence shell of the following ions:

C^+ ($5e$) = $1s^2$ $2s^2$ [↿| |] $2p$

N^+ ($6e$) = $1s^2$ $2s^2$ [↿|↿|] $2p$

O^+ ($7e$) = $1s^2$ $2s^2$ [↿|↿|↿] $2p$

F^+ ($8e$) = $1s^2$ $2s^2$ [⇅|↿|↿] $2p$

In general, ionisation energy increases from left to right in a period. However, exception occur between adjacent atoms in a period, greater amount energy is required for removal of electron from completely half-filled or completely filled orbital than the same for adjacent atom with either less than completely half-filled or less than completely filled orbital. Therefore, ionisation potential of O^+ is greater than that of F^+. Also ionisation potential of N^+ is greater than C^+ but less than both O^+ and F^+ (periodic trend). Hence, overall order is 2nd IP : O > F > N > C.

26. (c) is incorrect because NO is neutral oxide.
(d) is incorrect because CrO is basic oxide.

27. (a) $Ti^{4+} > Mn^{7+}$ is the correct order of size due to lower positive charge on Ti^{4+}.
(b) $^{37}Cl \;=\; ^{37}Cl$: Isotopes with same charge have same size because isotopes differ in compositions of nuclei which do not affect the atomic/ionic radius.
(c) $K^+ < Cl$ is the correct order. Among isoelectronic species, anion has greater size than cation.
(d) $P^{3+} > P^{5+}$ is the correct order. For the same elements, lower the positive charge, larger the ions.

28. (a) and (b) are infact the same statements and both are correct. N has slightly greater ionisation energy than oxygen which is against periodic trend. This exception is due to completely half-filled ($2p^3$) orbital in nitrogen that makes ionisation slightly difficult than oxygen.
(c) Also correct : Although N has greater first ionisation potential than oxygen, two values of ionisation potentials are comparable since they are adjacent in a period, i.e. electrons are removed from same orbit during ionisation.
(d) Incorrect – opposite to (c). of the bonded atoms which in turn has periodic trend in long form of periodic table.

29. (a) **Correct** For greater solubility, hydration energy must be greater than lattice energy.
(b) **Correct** Greater lattice energy discourage dissolution of a salt.
(c) **Incorrect** When a salt dissolve, energy is required to break the lattice, which comes from hydration process.
(d) **Incorrect** Explained in (A).

30. Statement I and II are true and Statement II is the correct explanation of statement I.

31. Statement I is true. Stronger oxidising agent is one which itself can easily be reduced. Pb^{4+} is unstable, due to inert pair effect, can easily be reduced to stable Pb^{2+}, hence a stronger oxidising agent than Sn^{4+}.

Statement II is false. Due to inert pair effect, the higher oxidation states of group 14 elements becomes less stable for heavier member.

32. Both statements I and II are true and Statement II is the correct explanation of statement I.

33. Statement I is true Be has higher first ionisation energy than B which is against periodic trend.

Statement II is false $2s$-orbital is lower in energy than $2p$, Aufbau's principle.

34. Statement I is true; Statement II is false.

F atom has slightly lower affinity for the electron than chlorine. It is due to the reason that additional electrons are repelled more effectively by $2p$-electrons in F than by $3p$-electrons in Cl-atom.

35. Inert pair effect-favours lower oxidation state.

36. Higher effective nuclear charge due to greater p/e ratio.

37. Electronegativity $\dfrac{\text{IP + EA}}{2}$ (Mulliken formula)

38. Electron affinity–definition.

39. Basic nature of hydroxides increases down a group.

40. Cl has maximum electron affinity, hence the correct order is Cl > F > Br

41. Ionisation potential decreases down the group but this is not the only criteria of reducing power.

42. In a group, size increases from top to bottom.

43. $Li^+ < Al^{3+} < Mg^{2+} < K^+$. Size decreases from left to right in a period and it increases from top to bottom in a group. Variation is more pronounced in group than in period.

44. Zn $3d^{10}4s^2$, Cu $3d^{10}4s^1$

The first ionisation energy is greater for Zn but reverse is true for 2nd ionisation energy.

45. Ionic size $Mg^{2+} < Na^+ < F \quad O^2 \quad N^3$

Already explained in question 1 (i).

46. The first ionisation energy of carbon is greater than the same of boron as predicted from periodic trend. However, for 2nd

$B^+ = 1s^2 \underset{2s^2}{\boxed{\uparrow\downarrow}}$; more stable than $C^+ = 1s^2\ 2s^2 \underset{2p^1}{\boxed{\uparrow}\boxed{}\boxed{}}$

ionisation trend is reversed due to stability of completely filled $2s$-orbital of B^+ :

47. Size $Ca^{2+} < Ar < Cl \;< S^2$. Explained in (i), question 6.

48. (i) Mg^{2+}, O^2 , Na^+ and F are all isoelectronic, has 10 electrons each. Among isoelectronic species, the order of size is cation < neutral < anion.
Also, between cations, higher the charge, smaller the size and between anions, greater the negative charge, larger the size. Therefore, the decreasing order of ionic radii : $O^2 \quad F \quad Na \quad Mg^2$

(ii) First ionisation energy increases from left to right in a period. However, exception occur between group 2 and 13 and group 15 and 16 where trend is reversed on the grounds of stability of completely filled and completely half-filled orbitals. Therefore,
Ionisation energy (1st) : Na < Al < Mg < Si

(iii) If the atoms are from same period, bond length is inversely proportional to bond order. In a group, bond length is related directly to atomic radius. Therefore,
bond length $N_2 < O_2 < F_2 < Cl_2$

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4

Chemical Bonding

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding

Objective Questions I (Only one correct option)

1. The isoelectronic set of ions is **(2019 Main, 10 April I)**
   (a) F , Li^+, Na^+ and Mg^{2+}
   (b) N^3 , Li^+, Mg^{2+} and O^2
   (c) Li , Na^+, O^2 and F
   (d) N^3 , O^2 , F and Na^+
2. Which of the following compounds contain(s) no covalent bond(s)?
   KCl, PH_3, O_2, B_2H_6, H_2SO_4 **(2018 Main)**
   (a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
   (c) KCl (d) KCl, B_2H_6
3. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is **(2015 Main)**
   (a) ion-ion interaction (b) ion-dipole interaction
   (c) London force (d) hydrogen bond
4. The nodal plane in the -bond of ethene is located in
   (a) the molecular plane **(2002, 3M)**
   (b) a plane parallel to the molecular plane
   (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon -bond at right angle
   (d) a plane perpendicular to the molecular plane which contains the carbon-carbon -bond
5. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is **(2000, 1M)**
   (a) H_2O because of hydrogen bonding
   (b) H_2Te because of higher molecular weight
   (c) H_2S because of hydrogen bonding
   (d) H_2Se because of lower molecular weight
6. Arrange the following compounds in order of increasing dipole moment, toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV) **(1996, 1M)**
   (a) I < IV < II < III (b) IV < I < II < III
   (c) IV < I < III < II (d) IV < II < I < III
7. The number and type of bonds between two carbon atoms in CaC_2 are **(1996, 1M)**
   (a) one sigma ( ) and one pi ( ) bonds
   (b) one sigma ( ) and two pi ( ) bonds
   (c) one sigma ( ) and one half pi ( ) bonds
   (d) one sigma ( ) bond
8. The molecule which has zero dipole moment is **(1989, 1M)**
   (a) CH_2Cl_2 (b) BF_3 (c) NF_3 (d) ClO_2
9. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be **(1980, 1M)**
   (a) X Y (b) X Y (c) X Y (d) X Y
10. Which of the following compound is covalent? **(1980, 1M)**
    (a) H_2 (b) CaO
    (c) KCl (d) Na_2S
11. The total number of electrons that take part in forming the bonds in N_2 is **(1980, 1M)**
    (a) 2 (b) 4 (c) 6 (d) 10
12. The compound which contains both ionic and covalent bonds is **(1979, 1M)**
    (a) CH_4 (b) H_2 (c) KCN (d) KCl

Objective Questions II
(One or more than one correct option)

13. Dipole moment is shown by **(1986, 1M)**
    (a) 1, 4-dichlorobenzene (b) *cis*-1, 2-dichloroethene
    (c) *trans*-1, 2-dichloroethene (d) *trans*-1, 2-dichloro-2- pentene

Numerical Value

14. Among the species given below, the total number of diamagnetic species is____
    H atom, NO_2 monomer, O_2 (superoxide), dimeric sulphur in vapour phase, Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4 **(2018 Adv.)**

Assertion and Reason

Read the following questions and answer as per the direction given below:

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I

(c) Statement I is correct; Statement II is incorrect

(d) Statement I is incorrect; Statement II is correct

15. **Statement I** LiCl is predominantly a covalent compound.

Statement II Electronegativity difference between Li and Cl is too small. **(1998, 2M)**

Fill in the Blank

16. There are …… bonds in a nitrogen molecule. **(1982, 1M)**

True/False

17. All molecules with polar bonds have dipole moment. **(1985, $\frac{1}{2}$ M)**

18. Linear overlapping of two atomic *p*-orbitals leads to a sigma bond. **(1983, 1M)**

Subjective Questions

19. Arrange the following ions in order of their increasing radii: Li , Mg^{2} , K , Al^{3} . **(1997, 1M)**

20. Between Na and Ag , which is stronger Lewis acid and why? **(1997, 3M)**

21. In the reaction, I + I_2 I_3, which is the Lewis acid? **(1997, 1M)**

22. Explain the difference in the nature of bonding in LiF and LiI. **(1996, 2M)**

23. The dipole moment of KCl is 3.336 10^{29} C-m which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl in this molecule is 2.6 10^{10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. **(1993, 2M)**

24. Give reasons in two or three sentences only for the following :

"Hydrogen peroxide acts as an oxidising as well as a reducing agent.'' **(1992, 1M)**

25. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case. **(1978, 2M)**

Topic 2 VBT, Hybridisation and VSEPR Theory

Objective Questions I (Only one correct option)

1. The correct statements among I to III are :

I. Valence bond theory cannot explain the color exhibited by transition metal complexes.

II. Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.

III. Valence bond theory cannot distinguish ligands as weak and strong field ones. **(2019 Main, 9 April II)**

(a) II and III only
(b) I, II and III
(c) I and II only
(d) I and III only

2. The correct statement about ICl_5 and ICl_4 is **(2019 Main, 8 April II)**

(a) ICl_5 is square pyramidal and ICl_4 is tetrahedral
(b) ICl_5 is square pyramidal and ICl_4 is square planar
(c) Both are isostructural
(d) ICl_5 is trigonal bipyramidal and ICl_4 is tetrahedral

3. The ion that has sp^3d^2 hybridisation for the central atom, is **(2019 Main, 8 April II)**

(a) $[ICl_2]$ (b) $[BrF_2]$
(c) $[ICl_4]$ (d) $[IF_6]$

4. The size of the iso-electronic species Cl , Ar and Ca^{2} is affected by **(2019 Main, 8 April I)**

(a) azimuthal quantum number of valence shell
(b) electron-electron interaction in the outer orbitals
(c) principal quantum number of valence shell
(d) nuclear charge

5. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? **(2019 Main, 9 Jan II)**

(a) O_2 O_2^+ (b) N_2 N_2^+
(c) O_2 O_2^{2} (d) NO NO^+

6. Total number of lone pair of electron in I_3 ion is **(2018 Main)**

(a) 3 (b) 6
(c) 9 (d) 12

7. The group having isoelectronic species is **(2017 Main)**

(a) O^{2} , F , Na^+, Mg^{2+} (b) O , F , Na, Mg^+
(c) O^{2} , F , Na, Mg^{2+} (d) O , F , Na^+, Mg^{2+}

8. The correct statement for the molecule, CsI_3 is **(2014 Main)**

(a) it is a covalent molecule
(b) it contains Cs and I_3 ions
(c) it contains Cs^{3+} and I ions
(d) it contains Cs , I and lattice I_2 molecule

9. The species having pyramidal shape is **(2010)**
(a) SO_3 (b) BrF_3 (c) SiO_3^2 (d) OSF_2

10. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is **(2010)**
(a) 1 and diamagnetic (b) 0 and diamagnetic
(c) 1 and paramagnetic (d) 0 and paramagnetic

11. The species having bond order different from that in CO is
(a) NO (b) NO **(2007, 3M)**
(c) CN (d) N_2

12. Among the following, the paramagnetic compound is **(2007, 3M)**
(a) Na_2O_2 (b) O_3 (c) N_2O (d) KO_2

13. Which of the following contains maximum number of lone pairs on the central atom? **(2005, 1M)**
(a) ClO_3 (b) XeF_4 (c) SF_4 (d) I_3

14. Number of lone pair(s) in $XeOF_4$ is/are **(2004, 1M)**
(a) 0 (b) 1 (c) 2 (d) 3

15. Which of the following are isoelectronic and isostructural ?
$NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$ **(2003, 1M)**
(a) NO_3^-, CO_3^2 (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

16. Among the following, the molecule with the highest dipole moment is **(2003, 1M)**
(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

17. Which of the following molecular species has unpaired electron (s)? **(2002, 3M)**
(a) N_2 (b) F_2 (c) O_2^- (d) O_2^{2-}

18. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3.
(a) N : tetrahedral, sp^3 ; B: tetrahedral, sp^3 **(2002, 3M)**
(b) N : pyramidal, sp^3; B: pyramidal, sp^3
(c) N: pyramidal, sp^3; B: planar, sp^2
(d) N: pyramidal, sp^3; B: tetrahedral, sp^3

19. The correct order of hybridisation of the central atom in the following species NH_3, $[PtCl_4]^2$, PCl_5 and BCl_3 is
(a) dsp^2, dsp^3, sp^2 and sp^3 **(2001, 1M)**
(b) sp^3, dsp^2, sp^3d and sp^2
(c) dsp^2, sp^2, sp^3 and dsp^3
(d) dsp^2, sp^3, sp^2 and dsp^3

20. The common features among the species CN^-, CO and NO^+ are **(2001, 1M)**
(a) bond order three and isoelectronic
(b) bond order three and weak field ligands
(c) bond order two and acceptors
(d) isoelectronic and weak field ligands

21. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3 and NH_4^+ are **(2000, 1M)**
(a) sp, sp^3 and sp^2 respectively
(b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively
(d) sp^2, sp^3 and sp respectively

22. In the compound CH_2 CH CH_2 CH_2 C CH, the C_2 C_3 bonds is of **(1999, 2M)**
(a) sp - sp^2 (b) sp^3 - sp^3
(c) sp - sp^3 (d) sp^2 - sp^3

23. The geometry of H_2S and its dipole moment are **(1999, 2M)**
(a) angular and non-zero (b) angular and zero
(c) linear and non-zero (d) linear and zero

24. The geometry and the type of hybrid orbital present about the central atom in BF_3 is **(1998, 2M)**
(a) linear, sp (b) trigonal planar, sp^2
(c) tetrahedral, sp^3 (d) pyramidal, sp^3

25. Which one of the following compounds has sp^2- hybridisation? **(1997, 1M)**
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

26. Among KO_2, AlO_2, BaO_2 and NO_2^+, unpaired electron is present in **(1997 C, 1M)**
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2
(c) Only KO_2 (d) Only BaO_2

27. The cyanide ion CN and N_2 are isoelectronic, but in contrast to CN , N_2 is chemically inert because of **(1997 C, 1M)**
(a) low bond energy
(b) absence of bond polarity
(c) unsymmetrical electron distribution
(d) presence of more number of electron in bonding orbitals

28. Among the following species, identify the isostructural pairs.
$NF_3, NO_3, BF_3, H_3O^+, N_3H$ **(1996, 1M)**
(a) $[NF_3, NO_3]$ and $[BF_3, H_3O^+]$
(b) $[NF_3, N_3H]$ and $[NO_3, BF_3]$
(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(d) $[NF_3, H_3O^+]$ and $[N_3H, BF_3]$

29. Which one of the following molecules is planar? **(1996, 1M)**
(a) NF_3 (b) NCl_3 (c) PH_3 (d) BF_3

30. The maximum possible number of hydrogen bonds a water molecule can form is **(1992, 1M)**
(a) 2 (b) 4 (c) 3 (d) 1

31. The type of hybrid orbitals used by the chlorine atom in ClO_2 is **(1992, 1M)**
(a) sp^3 (b) sp^2
(c) sp (d) None of these

32. The molecule which has pyramidal shape is **(1989, 1M)**
(a) PCl_3 (b) SO_3
(c) CO_3^{2-} (d) NO_3^-

33. Which of the following is paramagnetic? **(1989, 1M)**
(a) O_2^- (b) CN^-
(c) CO (d) NO^+

34. The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane respectively will be about **(1988, 1M)**
(a) 120 and 109.5 (b) 90 and 109.5
(c) 109° and 90 (d) 109.5 and 120

35. The molecule that has linear structure is **(1988, 1M)**
(a) CO_2 (b) NO_2 (c) SO_2 (d) SiO_2

36. The species in which the central atom uses sp^2-hybrid orbitals in its bonding is **(1988, 1M)**
(a) PH_3 (b) NH_3 (c) CH_3^+ (d) SbH_3

37. Of the following compounds, which will have a zero dipole moment ? **(1987, 1M)**
(a) 1, 1-dichloroethylene
(b) *cis*-1, 2-dichloroethylene
(c) *trans*-1, 2-dichloroethylene
(d) None of the above

38. The hybridisation of sulphur in sulphur dioxide is **(1986, 1M)**
(a) *sp* (b) sp^3
(c) sp^2 (d) dsp^2

39. The bond between two identical non-metal atoms has a pair of electrons **(1986, 1M)**
(a) unequally shared between the two
(b) transferred fully from one atom to another
(c) with identical spins
(d) equally shared between them

40. On hybridisation of one *s* and one *p*-orbital we get
(a) two mutually perpendicular orbitals **(1984, 1M)**
(b) two orbitals at 180
(c) four orbitals directed tetrahedrally
(d) three orbitals in a plane

41. Carbon tetrachloride has no net dipole moment because of
(a) its planar structure **(1983, 1M)**
(b) its regular tetrahedral structure
(c) similar sizes of carbon and chlorine atoms
(d) similar electron affinities of carbon and chlorine

42. The ion that is isoelectronic with CO is **(1982, 1M)**
(a) CN (b) O_2
(c) O_2 (d) N_2

43. Among the following, the linear molecule is **(1982, 1M)**
(a) CO_2 (b) NO_2
(c) SO_2 (d) ClO_2

44. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number 21) are
(a) pure p (b) sp-hybridised **(1981, 1M)**
(c) sp^2-hybridised (d) sp^3-hybridised

Objective Questions II

(One or more than one correct option)

45. The molecules that will have dipole moment are **(1992, 1M)**
(a) 2, 2-dimethyl propane (b) *trans*-2-pentene
(c) *cis*-3-hexene (d) 2,2,3,3-tetramethyl butane

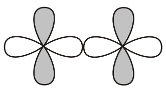
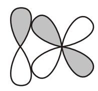
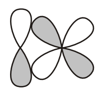
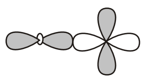
46. Which of the following have identical bond order?
(a) CN^- (b) O_2^- **(1992, 1M)**
(c) NO^+ (d) CN^+

47. The linear structure assumed by **(1991, 1M)**
(a) $SnCl_2$ (b) CS_2 (c) NO_2^+ (d) NCO^-

48. CO_2 is isostructural with **(1986, 1M)**
(a) $HgCl_2$ (b) C_2H_2 (c) $SnCl_2$ (d) NO_2

Match the Columns

49. Match the orbital overlap figures shown in Column I with the description given in Column II and select the correct answer using the codes given below the Columns. **(2014 Adv.)**

	Column I		Column II
A.		1.	*p-d* antibonding
B.		2.	*d-d* bonding
C.		3.	*p-d* bonding
D.		4.	*d-d* antibonding

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	2	1	(b)	1	2	3	4
(c)	2	3	1	4	(d)	4	1	2	3

50. Match each of the diatomic molecules in Column I with its property/properties in Column II. **(2009)**

	Column I		ColumnII
A.	B_2	p.	Paramagnetic
B.	N_2	q.	Undergoes oxidation
C.	O_2	r.	Undergoes reduction
D.	O_2	s.	Bond order 2
		t.	Mixing of '*s*' and '*p*' orbitals

Codes

	A	B	C	D
(a)	q, r, s	p, r, t, s	q, r, t	p, q, t
(b)	p, q, r, t	q, r, s, t	p, q, r, t	p, r, s, t
(c)	q, r, s, t	p, q, r	r, s, t	p, q, r, t
(d)	p, q, s, t	p, q, s	p, t	q, r, t

Fill in the Blanks

51. Among N_2O, SO_2, I_3^+ and I_3^-, the linear species are …… and …… **(1997 C, 1M)**

52. When N_2 goes to N_2, the N N bond distance … , and when O_2 goes to O_2 the O O bond distance …… **(1996, 1M)**

53. The two types of bonds present in B_2H_6 are covalent and …… **(1994, 1M)**

54. The kind of delocalisation involving sigma bond orbitals is called................ **(1994, 1M)**

55. The valence atomic orbitals on C in silver acetylide is ....hybridised. **(1990, 1M)**

56. The shape of CH_3 is …… . **(1990, 1M)**

57. …… hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. **(1982, 1M)**

58. Pair of molecules which forms strongest intermolecular hydrogen bonds is ……… . (SiH_4 and SiF_4, acetone and $CHCl_3$, formic acid and acetic acid) **(1981, 1M)**

59. The angle between two covalent bonds is maximum in …… . (CH_4, H_2O, CO_2) **(1981, 1M)**

True/False

60. The dipole moment of CH_3F is greater than that of CH_3Cl. **(1993, 1M)**

61. H_2O molecule is linear. **(1993, 1M)**

62. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. **(1990, 1M)**

63. sp^3 hybrid orbitals have equal s and p character. **(1987, 1M)**

64. In benzene, carbon uses all the three p-orbitals for hybridisation. **(1987, 1M)**

65. $SnCl_2$ is a non-linear molecule. **(1985, $\frac{1}{2}$M)**

Integer Type Questions

66. The sum of the number of lone pairs of electrons on each central atom in the following species is

$[TeBr_6]^2$, $[BrF_2]$, SNF_3 and $[XeF_3]$

(Atomic numbers : N 7, F 9, S 16, Br 35, Te 52, Xe 54) **(2017 Adv.)**

67. Among the triatomic molecules/ions $BeCl_2$, N_3, N_2O, NO_2, O_3, SCl_2, ICl_2 , I_3 and XeF_2, the total number of linear molecules(s)/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbital(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe 54] **(2015 adv.)**

68. A list of species having the formula XZ_4 is given below **(2014 Adv.)**

XeF_4, SF_4, SiF_4, BF_4 , BrF_4 , $[Cu(NH_3)_4]^2$, $[FeCl_4]^2$, $[CoCl_4]^2$ and $[PtCl_4]^2$

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

69. The total number of lone-pair of electrons in melamine is **(2013 Adv.)**

70. Based on VSEPR theory, the number of 90° F—Br—F angles in BrF_5 is **(2010)**

Subjective Questions

71. Predict whether the following molecules are isostructural or not. Justify your answer.

(i) NMe_3 (ii) $N(SiMe_3)_3$ **(2005, 2M)**

72. On the basis of ground state electronic configuration, arrange the following molecules in increasing O—O bond length order. KO_2, O_2, $O_2[AsF_6]$ **(2004, 2M)**

73. Draw the shape of XeF_4 and OSF_4 according to VSEPR theory. Show the lone pair of electrons on the central atom. **(2004, Main, 2M)**

74. Using VSEPR theory, draw the shape of PCl_5 and BrF_5. **(2003, 2M)**

75. Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2, indicating the location of lone pair(s) of electrons. **(2000, 3M)**

76. Interpret the non-linear shape of H_2S molecule and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic number : H = 1, P = 15, S = 16, Cl = 17) **(1998, 4M)**

77. Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are the oxidation states of O and F ? **(1997, 3M)**

78. Write the Lewis dot structural formula for each of the following. Give also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is given below in the case of H_3O^+ and NH_3.

```
   H          H
 H O H      H N H
```

Lewis dot structure   Neutral molecule **(1983, 4M)**

(i) O_2^2 (ii) CO_3^2 (iii) CN (iv) NCS

Topic 3 Resonance, LCAO, MOT, Other Bonding Types

Objective Questions I (Only one correct option)

1. During the change of O_2 to O_2, the incoming electron goes to the orbital. **(2019 Main, 10 April I)**

(a) $2p_x$ (b) $^*2p_x$ (c) $2p_y$ (d) $^*2p_z$

2. HF has highest boiling point among hydrogen halides, because it has **(2019 Main, 9 April II)**

(a) lowest ionic character
(b) strongest van der Waals' interactions
(c) strongest hydrogen bonding
(d) lowest dissociation enthalpy

3. Among the following species, the diamagnetic molecule is **(2019 Main, 9 April II)**

(a) CO (b) B_2 (c) NO (d) O_2

4. Among the following, the molecule expected to be stabilised by anion formation is C_2, O_2, NO, F_2. **(2019 Main, 9 April I)**

(a) C_2 (b) F_2
(c) NO (d) O_2

5. Among the following molecules/ions, C_2^2 , N_2^2 , O_2^2 , O_2

Which one is diamagnetic and has the shortest bond length? **(2019 Main, 8 April II)**

(a) C_2^2 (b) O_2 (c) O_2^2 (d) N_2^2

6. Two pi and half sigma bonds are present in **(2019 Main, 10 Jan I)**

(a) O_2 (b) N_2 (c) N_2 (d) O_2

7. According to molecular orbital theory, which of the following is true with respect to Li_2 and Li_2? **(2019 Main, 9Jan I)**

(a) Both are unstable
(b) Li_2 is unstable and Li_2 is stable
(c) Both are stable
(d) Li_2 is stable and Li_2 is unstable

8. According to molecular orbital theory, which of the following will not be a viable molecule? **(2018 Main)**

(a) He_2^2 (b) He_2 (c) H_2 (d) H_2^2

9. Which of the following species is not paramagnetic? **(2017 Main)**

(a) NO (b) CO (c) O_2 (d) B_2

10. Assuming $2s$-$2p$ mixing is not operative, the paramagnetic species among the following is **(2014 Adv.)**

(a) Be_2 (b) B_2 (c) C_2 (d) N_2

11. Stability of the species Li_2, Li_2 and Li_2 increases in the order of **(2013 Main)**

(a) Li_2 Li_2 Li_2 (b) Li_2^- Li_2 Li_2
(c) Li_2 Li_2 Li_2 (d) Li_2 Li_2 Li_2

12. In which of the following pairs of molecules/ions both the species are not likely to exist? **(2013 Main)**

(a) H_2^+, He_2^2 (b) H_2, He_2^2 (c) H_2^2 , He_2 (d) H_2, He_2^{2+}

13. Hyperconjugation involves overlap of which of the following orbitals? **(2008, 3M)**

(a) - (b) - p (c) p - p (d) -

14. According to MO theory, **(2004, 1M)**

(a) O_2^+ is paramagnetic and bond order greater than O_2
(b) O_2 is paramagnetic and bond order less than O_2
(c) O_2 is diamagnetic and bond order is less than O_2
(d) O_2 is diamagnetic and bond order is more than O_2

15. Molecular shape of SF_4, CF_4 and XeF_4 are **(2000, 1M)**

(a) the same, with 2, 0 and 1 lone pair of electrons respectively
(b) the same, with 1, 1 and 1 lone pair of electrons respectively
(c) different, with 0, 1 and 2 lone pair of electrons respectively
(d) different, with 1, 0 and 2 lone pair of electrons respectively

16. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl—E—Cl is in order **(1999, 2M)**

(a) B > P = As = Bi (b) B > P > As > Bi
(c) B < P = As = Bi (d) B < P < As < Bi

17. The correct order of increasing C O bond length of CO, CO_3^2 , CO_2 is **(1999, 2M)**

(a) CO_3^2 < CO_2 < CO (b) CO_2 < CO_3^{2-} < CO
(c) CO < CO_3^{2-} < CO_2 (d) CO < CO_2 < CO_3^{2-}

18. Which contains both polar and non-polar bonds? **(1997, 1M)**

(a) NH_4Cl (b) HCN (c) H_2O_2 (d) CH_4

19. Which one among the following does not have the hydrogen bond? **(1983, 1M)**

(a) Phenol (b) Liquid NH_3
(c) Water (d) HCl

Objective Question II
(One or more than one correct option)

20. According to molecular orbital theory, which of the following statements is(are) correct? **(2016 adv.)**

(a) C_2^2 is expected to be diamagnetic
(b) O_2^2 is expected to have a longer bond length than O_2
(c) N_2 and N_2 have the same bond order
(d) He_2 has the same energy as two isolated He atoms

21. Hydrogen bonding plays a central role in which of the following phenomena? **(2014 Adv.)**

(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene

22. Which one of the following molecules is expected to exhibit diamagnetic behaviour? **(2013 Main)**

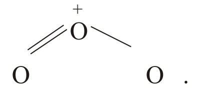
(a) C_2 (b) N_2 (c) O_2 (d) S_2

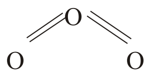
Assertion and Reason

Read the following questions and answer as per the direction given below:

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
(c) Statement I is correct; Statement II is incorrect.
(d) Statement I is incorrect; Statement II is correct.

23. Statement I The electronic structure of O_3 is



Statement II  structure is not allowed because octet around O cannot be expanded. **(1998, 2M)**

Match the Columns

24. Match the reactions in Column I with nature of the reactions/type of the products in Column II. **(2007, 6M)**

	Column I		Column II
A.	O_2 $O_2 + O_2^2$	1.	Redox reaction
B.	CrO_4^2 $+ H^+$	2.	One of the products has trigonal planar structure
C.	MnO_4 $+ NO_2$ $+ H^+$	3.	Dimeric bridged tetrahedral metal ion
D.	NO_3 $+ H_2SO_4$ $+ Fe^{2+}$	4.	Disproportionation

Codes

	A	B	C	D		A	B	C	D
(a)	2	1, 4	3	4	(b)	1, 4	3	1, 2	1
(c)	2	3	1	4	(d)	3	4	2, 3	1

Integer Questions

25. Among $H_2, He_2, Li_2, Be_2, B_2, C_2, N_2, O_2$ and F_2, the number of diamagnetic species is
(Atomic numbers : H 1, He 2, Li 3, Be 4, B 5, C 6, N 7, O 8, F 9) **(2017 Adv.)**

Subjective Questions

26. Write the MO electron distribution of O_2. Specify its bond order and magnetic property. **(2000, 3M)**

27. Arrange the following as stated.
"Increasing strength of hydrogen bonding (X H X)."
O, S, F, Cl, N **(1991, 1M)**

28. What effect should the following resonance of vinyl chloride have on its dipole moment? **(1987, 1M)**

$CH_2{=}CH$ Cl CH_2^- C HCl

Answers

Topic 1

1. (d)	**2.** (c)	**3.** (b)	**4.** (a)
5. (a)	**6.** (b)	**7.** (b)	**8.** (b)
9. (a)	**10.** (a)	**11.** (c)	**12.** (c)
13. (b, d)	**14.** (1)	**15.** (c)	**16.** (2)
17. F	**18.** T	**23.** (80.2%)	

Topic 2

1. (d)	**2.** (b)	**3.** (c)	**4.** (d)
5. (d)	**6.** (c)	**7.** (a)	**8.** (d)
9. (d)	**10.** (a)	**11.** (a)	**12.** (d)
13. (d)	**14.** (b)	**15.** (a)	**16.** (a)
17. (c)	**18.** (a)	**19.** (b)	**20.** (a)
21. (b)	**22.** (d)	**23.** (a)	**24.** (b)
25. (b)	**26.** (c)	**27.** (b)	**28.** (c)
29. (d)	**30.** (b)	**31.** (a)	**32.** (a)
33. (a)	**34.** (a)	**35.** (a)	**36.** (c)
37. (c)	**38.** (c)	**39.** (d)	**40.** (b)
41. (b)	**42.** (a)	**43.** (a)	**44.** (c)
45. (b, c)	**46.** (a, c)	**47.** (b, c, d)	**48.** (a, b)

49. (c) A 2; B 3; C 1; D 4
50. (b) A p, q, r, t; B q, r, s, t; C p, q, r, t; D p, r, s, t
51. N_2O, I_3 **52.** increases, decreases
53. three centre bond-two electrons
54. hyperconjugation
55. *sp* **56.** Triangular planar **57.** sp^3
58. HCOOH and CH_3COOH **59.** CO_2 **60.** F
61. F **62.** F **63.** F **64.** F
65. T **66.** (6) **68.** (4) **69.** (6)

Topic 3

1. (b)	**2.** (c)	**3.** (a)	**4.** (a)
5. (a)	**6.** (c)	**7.** (d)	**8.** (d)
9. (b)	**10.** (c)	**11.** (b)	**12.** (c)
13. (b)	**14.** (a)	**15.** (d)	**16.** (b)
17. (a)	**18.** (c)	**19.** (d)	**20.** (a, c)
21. (a, b, d)	**22.** (a,b)	**23.** (a)	

24. (b) A 1, 4; B 3; C 1, 2; D 1 **25.** (6)

Hints & Solutions

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding

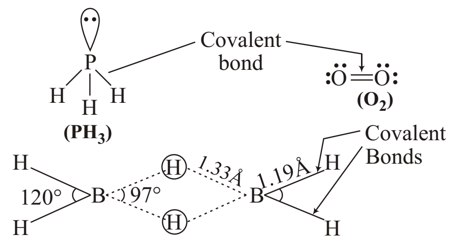
1. **Key Idea** Isoelectronic species contains same number of electrons.

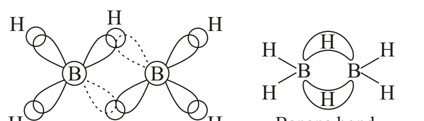
The species with its atomic number and number of electrons are as follows :

Species (ions)	At. no. (Z)	No. of electrons
N^{3}	7	7 3 10
O^{2}	8	8 2 10
F	9	9 1 10
Na	11	11 1 10
Li	3	3 1 2
Mg^{2}	12	12 2 10

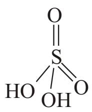
Thus, option (d) contains isoelectronic set of ions.

2. KCl is the only ionic compound. The structure of PH_3, O_2, B_2H_6 and H_2SO_4 are given below





Banana bond



Sulphuric acid
(H_2SO_4)

All bond between S and O atom are covalent bonds.

3. Ion-ion interaction is dependent on the square of distance, i.e.

ion-ion interaction $\frac{1}{r^2}$

Similarly, ion-dipole interaction $\frac{1}{r^3}$

London force $\frac{1}{r^6}$ and dipole-dipole interaction $\frac{1}{r^3}$

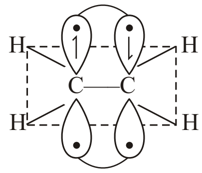
Superficially it seems as both ion-dipole interaction and hydrogen bonding vary with the inverse cube of distance between the molecules but when we look at the exact expressions of field (force) created in two situations, it comes as

$$|E| \text{or} |F| \quad \frac{2|P|}{4 \quad r^3} \qquad \text{(In case of ion-dipole interaction)}$$

$$\text{and } F \quad \frac{2q^2r - 4q^2a}{4 \quad {}_0 r^3} \qquad \text{(In case of dipole-dipole interaction)}$$

From the above, it is clear that the ion-dipole interaction is the better answer as compared to dipole-dipole interaction, i.e. hydrogen bonding.

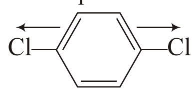
4.



Pi bond is formed by the p-orbitals whose lobes have minima in the plane of molecule, hence molecular plane is the nodal plane of pi-bond.

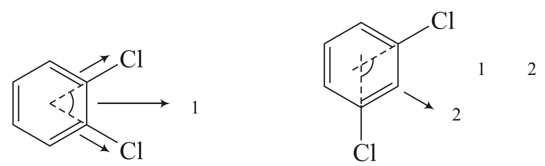
5. H-bond is the strongest intermolecular force.
All are different with 1, 0 and 2 lone pairs of electrons at central atom.

6. p-dichlorobenzene is non-polar.



p-dichlorobenzene

The two dipole vectors cancelling each other giving zero resultant dipole moment. o-dichlorobenzene has greater dipole moment than *meta*-isomer.



(o-dichlorobenzene)
dipole vectors are at 60° angle

(m-dichlorobenzene)
dipole vectors are at 120° angle

Toluene is less polar than both *ortho* and *para* dichlorobenzene. Therefore, the increasing order of dipole moment is

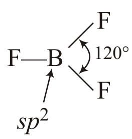
p-dichlorobenzene (IV) < toluene (I) < m-dichlorobenzene (II) < o-dichlorobenzene (III)

7. The carbide (C_2^{2}) ion has the following bonding pattern:

$:\bar{C} \quad \bar{C}:$ one sigma and two pi bonds.

8. BF_3 has triangular planar arrangement.

Three identical vectors acting in outward direction at equal angles in a plane cancel each other giving zero resultant, hence non-polar.



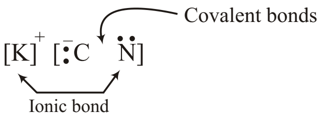
9. Strongly electropositive, univalent X will form an 1 : 1 ionic compound with strongly electronegative, univalent Y.

$$X \quad Y \qquad X \quad Y$$

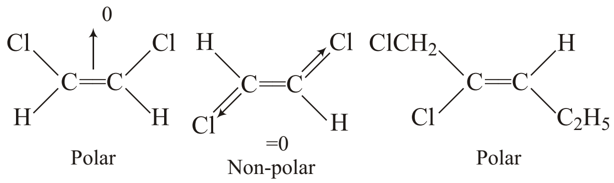
10. H_2 is a covalent, diatomic molecule with a sigma covalent bond between two hydrogen atoms.

11. N_2 has triple bond and each covalent bond is associated with one pair of electrons, therefore, six electrons are involved in forming bonds in N_2.

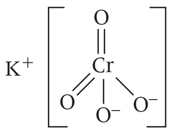
12. In KCN, the bonding between potassium ion and cyanide ion is ionic while carbon and nitrogen are covalently bonded in cyanide ion as:



13. 1,4-dichlorobenzene is non-polar, individual dipole vectors cancel each other.

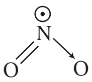


14. Among the given species only K_2CrO_4 is diamagnetic as central metal atom Cr in it has $[Ar]3d^0$ electronic configuration i.e., all paired electrons. The structure and oxidation state of central metal atom of this compound are as follows

Structure , **Oxidation state** Cr^{6+}

Rest all the compounds are **paramagnetic**. Reasons for their paramagnetism are given below

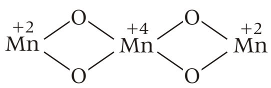
(i) H-atom have $1s^1$ electronic configuration, i.e. 1 unpaired electron.

(ii) NO_2, i.e.  in itself is **an odd electron species.**

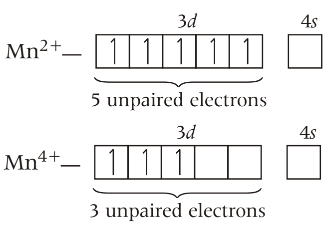
(iii) O_2 (Superoxide) has one unpaired electron in * molecular orbital.

(iv) S_2 in vapour phase has O_2 like electronic configuration i.e., have 2 unpaired electrons in * molecular orbitals.

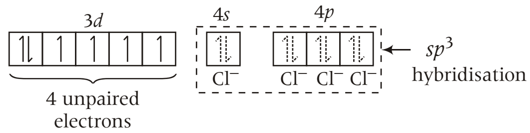
(v) Mn_3O_4 has following structure



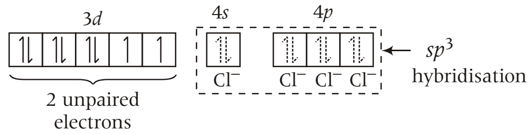
Thus, Mn is showing +2 and +4 oxidation states. The outermost electronic configuration of elemental Mn is $3d^5 4s^2$. Hence, in both the above oxidation states it has unpaired electrons as



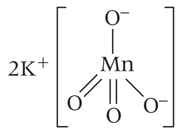
(vi) $(NH_4)_2FeCl_4$ has Fe as central metal atom with +2 oxidation state. The electronic configuration of Fe^{2+} in the complex is



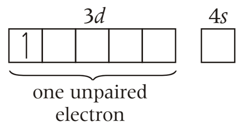
(vii) $(NH_4)_2NiCl_4$ has Ni as central metal atom with +2 oxidation state. The electronic configuration of Ni^{2+} in the complex is



(viii) In K_2MnO_4 central metal atom Mn has +6 oxidation state with following structure



Electronic configuration of Mn^{6+} is



15. Statement I is correct but Statement II is incorrect. The covalency in LiCl is due to small size of Li ion which brings about large amount of polarisation in bond.

16. These are 2 -bonds in a nitrogen molecule.

17. The resultant of individual bond dipoles may or may not be non-zero.

18. Linear overlapping of *p*-orbitals form sigma bond while sidewise overlapping of two *p*-orbitals forms a pi bond.

19. $Li^+ < Al^{3+} < Mg^{2+} < K^+$

20. Ag^+ is stronger Lewis acid because it can easily accommodate lone pair of electrons from Lewis base. On the other hand, Na^+ has noble gas configuration, cannot accept lone pair of electron, not at all a Lewis acid.

21. I_2 is Lewis acid because I coordinate its one lone pair to I_2.

22. Both LiF and LiI are expected to be ionic compounds. However , LiI is predominantly covalent because of small size of Li^+ and large size of iodide ion. A smaller cation and a larger anion introduces covalency in ionic compound.

23. Dipole moment is calculated theoretically as

$$q \quad d$$

Here, $q \quad 1.6 \quad 10^{19}$ C and $d \quad 2.6 \quad 10^{10}$ m

$$_{\text{Theo}} \quad 1.6 \quad 10^{19} \quad 2.6 \quad 10^{10} \quad 4.16 \quad 10^{29}\text{cm}$$

$$\% \text{ ionic character} \quad \frac{_{\text{obs}}}{_{\text{Theo}}} \quad 100 \quad \frac{3.336 \quad 10^{29}}{4.16 \quad 10^{29}} \quad 100$$

$= 80.2\%$

24. In hydrogen peroxide (H_2O_2), oxygen is in –1 oxidation state, can be oxidised to O_2 (zero oxidation state) or can be reduced to H_2O (–2 oxidation state of oxygen).

Hence, H_2O_2 can act as both oxidising agent and reducing agent. With strong oxidising agent like $KMnO_4$, H_2O_2 acts as a reducing agent while with strong reducing agent like $H_2C_2O_4$, it acts as an oxidising agent.

25. (i) **Melting points** Ionic compounds have higher melting points than covalent compounds.

(ii) **Boiling points** Ionic compounds have higher boiling points than covalent compounds.

(iii) **Solubility** Ionic compounds have greater solubility in water than a covalent compound.

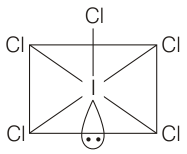
(iv) **Conductivity in aqueous solution** Ionic compounds have greater electrical conductivity in aqueous solution while covalent compounds are usually non-conducting.

Topic 2 VBT, Hybridisation and VSEPR Theory

1. Among the given statements, correct statements are I and III only. Valence bond theory (VBT) cannot explain the colour exhibited by transition metal complexes. This theory cannot distinguish ligands as weak and strong field ones.

2. For ICl_5

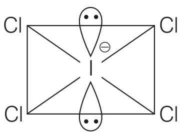
$$H \quad \frac{1}{2}(7 \quad 5 \quad 0 \quad 0) \quad 6\ (sp^3d^2)$$



sp^3d^2 hybridised
Geometry : Octahedral
Shape / Structure : Square pyramidal

For $\ddot{I}Cl_4$

$$H \quad \frac{1}{2}(7 \quad 4 \quad 0 \quad 1) \quad 6\ (sp^3d^2)$$



sp^3d^2 hybridised
Geometry : Octahedral
Shape/Structure : Square planar

So, ICl_5 and ICl_4 are isolobal but not isostructural.

3. **Key Idea** The hybridisation for a central atom in a species can be calculated using formula

$$H \quad \frac{1}{2}(V \quad M \quad C \quad A)$$

where, H No. of hybridised orbitals used by central atoms.
V No. of valence electrons of the central atom.
M No. of mono-valent atoms (bonded).
C No. of cationic (positive) charge.
A No. of anionic (negative) charge.

The hybridisation of given species are as follows :

- For $[ICl_2]$ and $[BrF_2]$

$$H \quad \frac{1}{2}(7 \quad 2 \quad 0 \quad 1) \quad 5\ (sp^3d)$$

- For $[ICl_4]$,

$$H \quad \frac{1}{2}(7 \quad 4 \quad 0 \quad 1) \quad 6\ (sp^3d^2)$$

- For $[IF_6]$,

$$H \quad \frac{1}{2}(7 \quad 6 \quad 0 \quad 1) \quad 7\ (sp^3d^3)$$

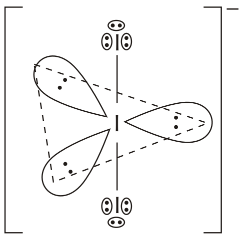
4. The radius of isoelectronic species is inversely proportional to their nuclear charge or atomic number (Z). Thus, greater the value of Z, lesser the radii of isoelectronic species.

5.

Species	**Valence MOs**	**Bond Order** $\frac{N_b \quad N_a}{2}$	**Paramagnetic/ Diamagnetic Nature**
NO(15e)	$[8e\ ]\ 2p_x^2 \quad 2p_y^2\ 2p_z^2$ $*2p_x^1 \quad *2p_y^0 \quad * \quad pz^0$	$\frac{6 \quad 1}{2}$ 2.5	Paramagnetic
NO (14e)	$[8e\ ]\ 2p_x^2 \quad 2p_y^2\ 2p_z^2$ $*2p_x^0 \quad *2p_y^0\ *2p_z^0$	$\frac{6 \quad 0}{2}$ 3	Diamagnetic
N_2(14e)	$[8e\ ]\ 2p_x^2 \quad 2p_y^2 \quad p_z^2$ $*2p_x^0 \quad *2p_y^0,\ 2p_z^0$	$\frac{6 \quad 0}{2}$ 3	Diamagnetic
N_2 (13e)	$[8e\ ]\ 2p_x^2 \quad 2p_y^2\ 2p_z1$ $*2p_x^0 \quad *2p_y^0\ *2pz_0$	$\frac{5 \quad 0}{2}$ 2.5	Paramagnetic
O_2(16e)	$[8e\ ]\ 2p_z^2\ 2p_x^2 \quad 2p_y^2$ $*2p_x^1 \quad *2p_y^1\ *2p_z^0$	$\frac{6 \quad 2}{2}$ 2	Paramagnetic
O_2 (15e)	$[8e\ ]\ 2p_z^2\ 2p_x^2 \quad 2p_y^2$ $*2p_x^1 \quad *2p_y^0\ *2p_z^0$	$\frac{6 \quad 1}{2}$ 2.5	Paramagnetic
O_2^2 (18e)	$[8e\ ]\ 2p_z^2\ 2p_x^2 \quad 2p_y^2$ $*2p_x^2 \quad *2p_y^2\ *2p_z^0$	$\frac{6 \quad 4}{2}$ 1	Diamagnetic

So, only in the conversion of NO NO^+, the bond order has increased (2.5 3) and paramagnetic character has changed to diamagnetic.

6. The structure of I_3 ion is



Hence, 9 is the correct answer.

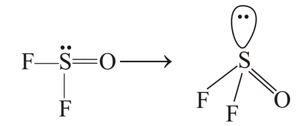
7. Isoelectronic species are those which contains same number of electrons.

Species	Atomic number	Number of electrons
O^{2}	8	10
F	9	10
Na	11	10
Mg^{2}	12	10
O	8	9
Na	11	11
Mg	12	11

Option (a) is correct which contains isoelectronic species O^{2} , F , Na , Mg^{2} .

8. I_3 is an ion made up of I_2 and I which has linear shape.
While Cs is an alkali metal cation.

9.



S is sp^3 hybridised Pyramidal

SO_3 is planar (S is sp^2 hybridised), BrF_3 is T-shaped and SiO_3^2 is planar (Si is sp^2 hybridised).

10. For molecules lighter than O_2, the increasing order of energies of molecular orbitals is

$$1s\ {}^*1s\ \ 2s\ {}^*2s\ \ \begin{matrix}2p_y\\2p_z\end{matrix}\ \ 2p_x\ {}^*2p_x\ \ \begin{matrix}{}^*2p_y\\{}^*2p_z\end{matrix}.....$$

where, $2p_y$ and $2p_z$ are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in B_2, electronic arrangement would be

$$1s^2\ {}^*1s^2\ \ 2s^2\ {}^*2s^2\ \ \begin{matrix}2p_y^2\\2p_z\end{matrix}...$$

No unpaired electron-diamagnetic.

$$\text{Bond order}\ \ \frac{\text{bonding electrons}\quad\text{antibonding electrons}}{2}$$

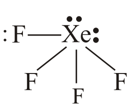
$$\frac{6\quad 4}{2}\quad 1$$

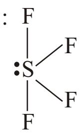
11. The bond order of CO = 3. NO^+, CN and N_2 are isoelectronic with CO, have the same bond order as CO. NO ($16e$) has bond order of 2.

12. O_2 in KO_2 has 17 electrons, species with odd electrons are always paramagnetic.

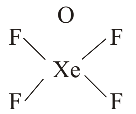
13. ClO_3 : O Cl O one lone pair at Cl.

O

XeF_4 :  two lone pairs at Xe.

SF_4 :  one lone pair at S.

I_3 : I I I three lone pairs at central iodine.

14.  At central atom (Xe), there is one lone pair.

15. NO_3 and CO_3^2 both have 32 electrons, central atom sp^2 hybridised, triangular planar.

16. CH_3Cl has the highest dipole moment.

17. O_2 has odd number(17) of electrons, therefore it must contain at least one unpaired electron.

18.

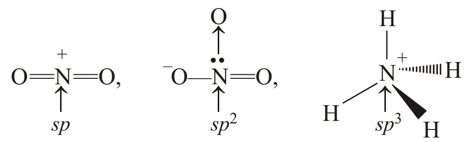
F H

F B N H Both 'B' and 'N' sp^3 tetrahedral.

F H

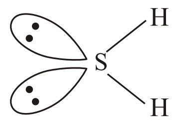
19. NH_3 sp^3, $[PtCl_4]^2$ dsp^2, PCl_5 sp^3d, BCl_3 sp^2

20. All three have 14 electrons (iso electronic) with bond order of three.

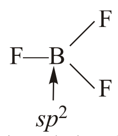
21. 

22. $\overset{1}{C}H_2{=}\overset{2}{C}H\ \ \overset{3}{C}H_2\ \ \overset{4}{C}H_2\ \ \overset{5}{C}\ \ \overset{6}{C}H$
Hybridisation at C_2 sp^2 and at C_3 sp^3.

23. H_2S has sp^3 hybridised sulphur, therefore, angular in shape with non-zero dipole moment.

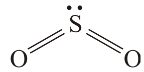


(Non-linear, polar molecule)

24. 

(Trigonal planar)

25. Sulphur in SO_2 is sp^2-hybridised.



Electron pair 2 (-bonds) + 1 (lone pair) = 3
Hybridisation sp^2
Carbon in CO_2 is sp-hybridised, N in N_2O is sp-hybridised, carbon in CO is sp-hybridised.

26. Molecular orbital electronic configuration are

$$KO_2\ (O_2\ ):\ 1s^2\ {}^*1s^2\ \ 2s^2\ {}^*2s^2\ \ 2p_x^2 \left|\begin{array}{c} 2p_y^2 \\ 2p_z^2 \end{array}\right| \begin{array}{c} {}^*2p_y^2 \\ {}^*2p_z^1 \end{array}\Bigg|\ {}^*2p_x^0$$

Has one unpaired electron in $^*2p$ orbital.

AlO_2 has both oxygen in O^2 state, therefore, no unpaired electron is present.

$BaO_2\ (O_2^2\ )$

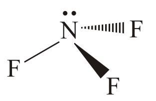
$$1s^2\ {}^*1s^2\ \ 2s^2\ {}^*2s^2\ \ 2p_x^2 \left|\begin{array}{c} 2p_y^2 \\ 2p_z^2 \end{array}\right| \begin{array}{c} {}^*2p_y^2 \\ {}^*2p_z^2 \end{array}\Bigg|\ {}^*2p_x^0$$

Has no unpaired electron.

NO_2 has [O═N═O] bonding, hence no unpaired electron.

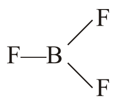
27. N_2 is a neutral, non-polar, inert molecule while CN is a highly polar, highly active ion.

28. NF_3 :



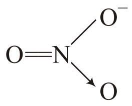
Pyramidal (N-sp^3)

BF_3 :



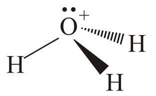
Triangular planar (B-sp^2)

NO_3^- :



Triangular planar (N-sp^2)

H_3O^+ :



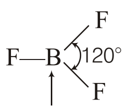
Pyramidal (O-sp^3)

N_3H $\overline{N}$ N   N   H

Central nitrogen is *sp*-hybridised

Therefore, NF_3, H_3O and BF_3, NO_3 pairs have same shape.

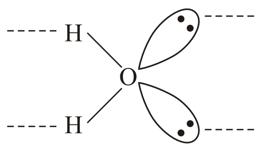
29. BF_3 has triangular planar arrangement.



sp^2-hybridised

There identical vectors acting in outward direction, at equal angles in a plane, cancel each other giving zero resultant, hence non-polar.

30. A water molecule can form at the most four H-bonds.



Four sites of H-bonding

31. O Cl═O

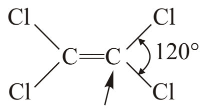
electron pairs at Cl = 2 (-bonds) + 2 (lone-pairs) = 4

Hybridisation at Cl = sp^3

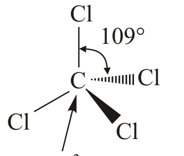
32. PCl_3 has sp^3-hybridised phosphorus, with one lone pair. Therefore, molecule has pyramidal shape like ammonia.

33. O_2 has odd number of electrons, hence it is paramagnetic.

34.



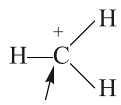
sp^2-hybridised



sp^3-hybridised

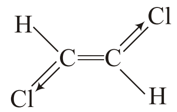
35. CO_2 is linear because carbon is *sp*-hybridised.

36. In CH_3^+, there are only three electron pairs around carbon atom giving sp^2-hybridisation state.



sp^2-hybridised

37. Dipole vectors in *trans*-1, 2-dichloroethylene are at 180° and directed in opposite direction, cancelling each other.



dipole moment = 0

38. In SO_2, the Lewis-dot structure is

O═ S ═O

Electron pairs at S 2 (-bonds) + 1 (lone-pair) 3

sp^2 hybridised.

NOTE

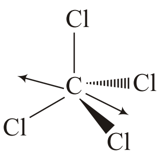
-bonded electrons are not present in hybrid orbitals, therefore not counted in electron pairs. Rather bonds are formed by lateral overlapping of pure *p*-orbitals.

39. Bonds between identical non-metal is purely covalent due to same electronegativities of the bonded atoms. Hence, the bonded atoms have equal holds on the shared pair of electrons.

40. Hybridisation of one '*s*' and one '*p*' orbitals gives two *sp* hybrid orbitals oriented linearly at 180°.

s   *p*   2*sp* hybrid orbitals

41. CCl_4 has a regular tetrahedral shape.



Net dipole = 0

42. CO has a total of 14 electrons and CN also has 14 electrons.

C (6e) + N (7e) + e   CN (14e)

43. CO_2 is a linear molecule because of *sp*-hybridisation around carbon atom.

44. For non-polar MX_3, it must have triangular planar arrangement, i.e. there should be sp^2-hybridisation around *M*.

45. H_3C C CH_3 (with CH_3 above and CH_3 below C)
Symmetric, non-polar

H_3C(H)C=C(H)(CH_2CH_3)
Polar

CH_3H_2C(H)C=C(CH_2CH_3)(H)
Polar

H_3C C C CH_3 (with CH_3 CH_3 above and CH_3 CH_3 below)
Symmetric, non-polar

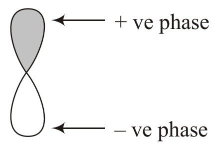
46. CN and NO^+ are isoelectronic, have the same bond order of 3.

47. S=C=S (Linear) O=N=O (Linear) O C N (Linear)

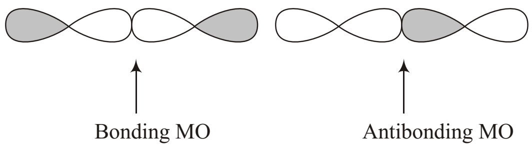
Cl–Sn–Cl (Bent) O=S=O (Bent)

48. CO_2, $HgCl_2$, C_2H_2 are all linear.

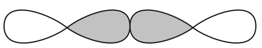
49. **PLAN** This problem includes basic concept of bonding. It can be solved by using the concept of molecular orbital theory.

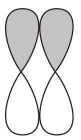


Any orbital has two phase +ve and –ve. In the following diagram, +ve phase is shown by darkening the lobes and –ve by without darkening the lobes.

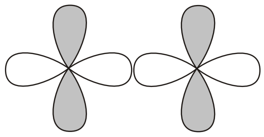


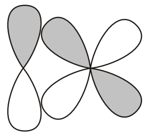
When two same phase overlap with each other, it forms bonding molecular orbital otherwise antibonding.

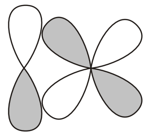

-bond

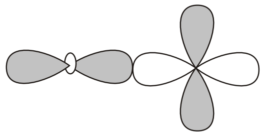

-bond

On the basis of above two concepts, correct matching can be done as shown below:

A.  *d-d* bonding

B.  *p-d* bonding

C.  *p-d* antibonding

D.  *d-d* antibonding

A 2, B 3, C 1, D 4

Hence, (c) is the correct option.

50. (A) B_2 : $1s^2\ {}^*1s^2\quad 2s^2\ {}^*2s^2 \left|\begin{matrix} 2p_y^1 \\ 2p_z^1 \end{matrix}\right|$ paramagnetic.

Bond order $\frac{6\quad 4}{2}$ 1

Bond is formed by mixing of *s* and *p* orbitals.

B_2 undergoes both oxidation and reduction as

$B_2 + O_2 \xrightarrow{\text{Heat}} B_2O_3$ (Oxidation)

$B_2 + H_2 \quad B_2H_6$ (Reduction)

(B) N_2 : $1s^2\ {}^*1s^2\quad 2s^2\ {}^*2s^2\quad 2p_x^2 \left|\begin{matrix} 2p_y^2 \\ 2p_z^2 \end{matrix}\right|$ diamagnetic.

Bond order $\frac{10\quad 4}{2}$ 3 2

N_2 undergoes both oxidation and reduction as

$N_2 + O_2 \quad NO$

$N_2 + 3H_2 \xrightarrow{\text{Catalyst}} NH_3$

In N_2, bonds are formed by mixing of *s* and *p* orbitals.

(C) O_2 : $1s^2\ {}^*1s^2\quad 2s^2\ {}^*2s^2\quad 2p_x^2 \left|\begin{matrix} 2p_y^2 \\ 2p_z^2 \end{matrix}\right| \left.\begin{matrix} {}^*2p_y^2 \\ {}^*2p_z^1 \end{matrix}\right| {}^*2p_x^0$

Paramagnetic with bond order 1.5. O_2 undergoes both oxidation and reduction and bond involves mixing of *s* and *p*-orbitals.

(D) O_2 : $1s^2\ {}^*1s^2\quad 2s^2\ {}^*2s^2\quad 2p_x^2 \left|\begin{matrix} 2p_y^2 \\ 2p_z^2 \end{matrix}\right| \left.\begin{matrix} {}^*2p_y^1 \\ {}^*2p_z^1 \end{matrix}\right| {}^*2p_x^0$

Paramagnetic with bond order 2.

O_2 undergoes reduction and the bond involves mixing of *s* and *p*-orbitals.

51. N_2O and I_3 are linear species.

52. Bond order in N_2 is 3 while same in N_2^+ is 2.5, hence bond distance increases as N_2 goes to N_2^+.
Bond order in O_2 is 2 while same in O_2^+ is 2.5, hence bond distance decreases as O_2 goes to O_2^+.

53. Three centred-2 electrons.

54. Hyperconjugation involves delocalisation of -electrons.

55. *sp*-hybridised.

56. Triangular planar. Carbon in CH_3^+ is sp^2 hybridised.

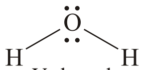
57. sp^3-hybrid orbital holding the lone pair is involved in formation of ammonium ion.

58. H C(O) OH and CH_3 C(O) OH . Both are capable of forming H-bonds.

59. CO_2, it is 180°.

60. Dipole moment ( ) *q.d*
Since electronegativity of F and Cl are very close, it is the internuclear distance (*d*) that decides dipole moment here. Hence, C Cl bond has greater dipole moment the C-F bond.

61. H_2O is V-shaped molecule.



V-shaped

62. False

63. In sp^3-hybrid orbital, there is 25 % *s*-character and 75 % *p*-character.

64. Carbon in benzene is sp^2-hybridised, i.e. uses only two of its *p*-orbitals in hybridisation.

65. Sn in $SnCl_2$ has sp^2-hybridisation.

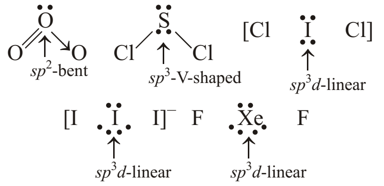
66.

S.N.	Species	No. of -bonds with central atom	No. of L.P at central atom
(i)	In $[TeBr_6]^2$	6	1
(ii)	In $[BrF_2]$	2	2
(iii)	In SNF_3	4	0
(iv)	In $[XeF_3]$	3	3

67. Cl Be Cl   N N N$^-$
sp   *sp*

N N O   O N O
sp   *sp*

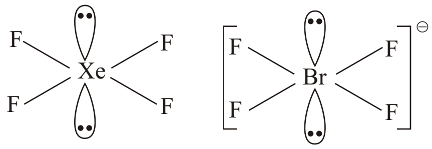
All the above mentioned molecules/ions have *sp*-hybridised central atom and no one pair at central atom, hence linear also.
Others are :

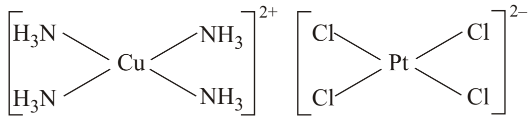


[Although ICl_2^-, I_3^- and XeF_2 all also are linear but in them *d*-orbital contribute in hybridisation.]

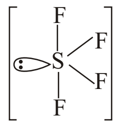
68. **PLAN** This problem includes concept of hybridisation using VBT, VSEPR theory, etc.,

XeF_4, BrF_4 ,$[Cu(NH_3)_4]^2$,$[PtCl_4]^2$ are square planar as shown below:

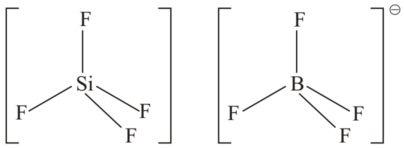


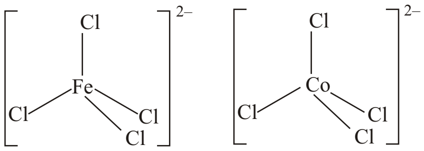


SF_4 (*See-saw*) as shown below:



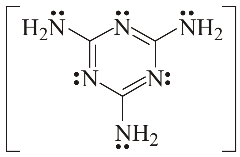
SiF_4, BF_4 , $[FeCl_4]^2$, $[CoCl_4]^2$ are tetrahedral as shown below:





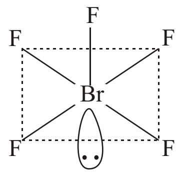
Hence, correct integer is 4.

69. **PLAN** Melamine is a heterocyclic compound.



Each nitrogen atom has one pair of lone pair. Thus, in all six lone pairs.

70.

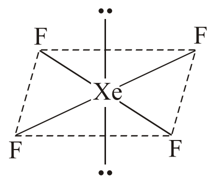


Lone pair would push the Br—F bond pairs in upward direction and all Br—F bond angles will contract.

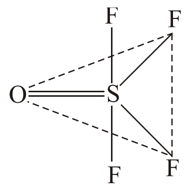
71. No, (i) NMe_3 is pyramidal while (ii) $N(SiMe_3)_3$ is planar. In the latter case, *p* -*d* back bonding between N and Si makes N sp^2-hybridised.

72. Bond order : O_2 1.5, O_2 = 2, O_2^+ = 2.5
Bond length : O_2^+ < O_2 < O_2

73.

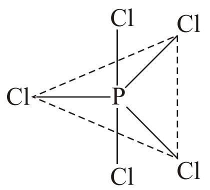


Square planar

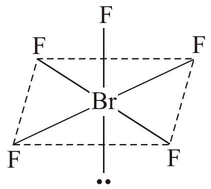


Trigonal bipyramidal

74.

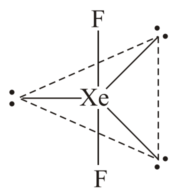


Trigonal bipyramidal
(P is sp^3d-hybridised)

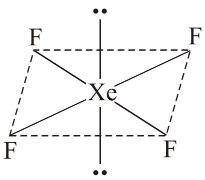


Square pyramidal
(Br is sp^3d^2-hybridised)

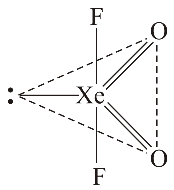
75.



Linear



Square planar

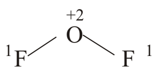


See-saw shaped

76. In H_2S, S is sp^3-hybridised with two lone pairs of electrons on it giving V-shaped (water like) shape. In PCl_3, P is sp^3-hybridised with one lone pair of electrons on it. Therefore, PCl_3 is pyramidal in shape.

77. F O F

Electron pair P 2 2 4
Hybridisation sp^3



V-shaped

78. (i) O_2^{2} : O O ^{2} and Cl Cl (Cl_2)

O ^{2}

(ii) CO_3^{2} : C and F B F (BF_3)

O O F

(iii) CN : C N and C O (CO)

(iv) NCS : S C N and Cl C N (ClCN)

Topic 3 Resonance, LCAO, MOT, Other Bonding Types

1. The change of O_2 to O_2 can be as follows:

O_2 (16 e^-) [Dioxygen] → Energy $\xrightarrow{+e^-}$ O_2^- (17 e^-) [Super-oxide] → Energy

$[8e^-]$ $2p_z^2$ $2p_x^2$ $= 2p_y^2\,{}^*2p_x^1 = {}^*2p_y^1$ (Half-filled anti-bonding *-MOs)

$[8e^-]$ $2p_z^2$ $2p_x^2 = 2p_y^2\,{}^*2p_x^2 = {}^*2p_y^1$

So, in the formation of O_2 from O_2, the 17th electron goes to the $^*2p_x$ or $^*2p_y$ molecular orbital (anti-bonding) which is half-filled in O_2.

2. HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding. Here, the hydrogen bond exists between hydrogen of one molecule and fluorine atom of another molecule as shown below.

$\ldots \overset{+}{H}$ $F\ldots\overset{+}{H}$ $F\ldots H$ F

In this molecule, hydrogen bond behaves like a bridge between two atoms that holds one atom by covalent bond and the other by hydrogen bond.

3. **Key Idea** Magnetic nature can be detected by molecular orbital theory. Presence of unpaired electrons means paramagnetic and absence of unpaired electrons means diamagnetic in nature.

Among the given options, CO is a diamagnetic molecule. It can be proved by molecular orbital (MO) theory. The electronic configuration of given diatomic molecules are given below.

- CO (Number of electrons 14)

Electronic configuration $1s^2, {}^*1s^2, 2s^2, {}^*2s^2, p_z^2, 2p_x^2 \quad 2p_y^2$

Since, there is no unpaired electron in the CO molecule, so it is diamagnetic.

- NO (Number of electrons 15)

Electronic configuration $1s^2, {}^*1s^2, 2s^2, {}^*2s^2, 2p_z^2, 2p_x^2 \quad 2p_y^2, {}^*2p_x^1 \quad {}^*2p_y^0$

Since, NO has one unpaired electron in $^*2p_x^1$ orbital, so it is paramagnetic.

- B_2 (Number of electrons 10)

Electronic configuration $1s^2, {}^*1s^2, 2s^2, {}^*2s^2, 2p_x^1 \quad p_y^1$

Since, two unpaired electrons are present in $2p_x^1$ and $2p_y^1$ orbital. So, it is paramagnetic.

- O_2 (Number of electrons 16)

Electronic configuration $1s^2, {}^*1s^2, 2s^2, {}^*2s^2, 2pz^2, 2p_x^2 \quad 2p_y^2, {}^*2p_x^1 \quad {}^*2p_y^1$

Since, two unpaired electrons are present in $^*2p_x^1$ and $^*2p_y^1$ orbital. So, it is also paramagnetic.

4. C_2 will be stabilised after forming anion. The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. After forming anion (i.e. C_2^-), the electronic configuration is

- $C_2 : (\ 1s)^2(\ ^*1s)^2(\ 2s)^2(\ ^*2s)^2(\ 2p_x^2\quad 2p_y^2)(\quad p_z^1)$ or $KK(\ 2s)^2(\ ^*2s)^2(\ 2p_x^2\quad 2p_y^2).\ 2p_z^1$

Bond order $\frac{1}{2}(N_b\quad N_a)\quad \frac{1}{2}(9\quad 4)\quad 2.5$

For other options such as F_2, O_2, NO , the electronic configurations are as follows :

$F_2\ :(\ 1s)^2(\ ^*1s)^2(\ 2s)^2(\ ^*2s)^2(\ 2p_z)^2(\ 2p_x^2\quad 2p_y^2)(\ ^*2p_x^2\quad ^*2p_y^2)(\ ^*2p_z^1)$

Bond order $1/2(N_b\quad N_a)\quad 1/2(10\quad 9)\quad 0.5$

- $O_2 :(\ 1s)^2(\ ^*1s)^2(\ 2s)^2(\ ^*2s)^2(\ 2p_z)^2(\ 2p_x^2\quad 2p_y^2)(\ ^*2p_x^2\quad ^*2p_y^1)$

Bond order $\frac{1}{2}(N_b\quad N_a)\quad \frac{1}{2}(10\quad 7)\quad 1.5$

- $NO :(\ 1s)^2(\ ^*1s)^2(\ 2s)^2(\ ^*2s)^2(\ 2p_z)^2(\ 2p_x^2\quad 2p_y^2)(\ ^*2p_x^1\quad ^*2p_y^1)$

Bond order $\frac{1}{2}(N_b\quad N_a)\quad \frac{1}{2}(10\quad 6)\quad 2$

The value of bond order of C_2 is highest among the given options. Bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.
The bond length decreases as bond order increases. As a result, stability of a molecule increases.

5.

Species	**MO energy order**	**Bond order** (BO)	***n*, number of unpaired *e***	**Magnetic character**
$C_2^2\ (14e\ )$	$[8\bar{e}]\ 2p_x^2\quad 2p_y^2\ 2p_z^2$	$\frac{6\quad 0}{2}\quad 3$	0	Diamagnetic
$O_2(16e\ )$	$[8\bar{e}]\ 2p_z^2\ 2p_x^2\quad 2p_y^2\ ^*2p_x^1\quad ^*2p_y^1$	$\frac{6\quad 2}{2}\quad 2$	2	Paramagnetic
$O_2^2\ (18e\ )$	$[8\bar{e}]\ 2p_z^2\ 2p_x^2\quad 2p_y^2\ ^*2p_x^2\quad ^*2p_y^2$	$\frac{6\quad 4}{2}\quad 1$	0	Diamagnetic
$N_2^2\ (16e\ )$	$[8\bar{e}]\ 2p_x^2\quad 2p_y^2\ 2p_z^2\ ^*2p_x^1\quad ^*2p_y^1$	$\frac{6\quad 2}{2}\quad 2$	2	Paramagnetic

Bond length $\frac{1}{\text{BO (Bond order)}}$. So order of bond length $\underset{(BO\quad 3)}{C_2^2}\quad \underset{(BO\quad 2)}{O_2}\quad N_2^2\quad \underset{(BO\quad 1)}{O_2^2}$

The diamagnetic species with shortest bond length is C_2^2 (option-a).

6. The energy order of MOs of the given species are as follows:

$O_2(16e\ \text{'s})\quad 1s^2,\ ^*1s^2,\ 2s^2,\ ^*2s^2,\ 2p_z^2,$
$2p_x^2\quad 2p_y^2,\ ^*2p_x^1\quad ^*2p_y^1,$

$O_2\ (15e\ \text{'s})\quad 1s^2,\ ^*1s^2,\ 2s^2,\ ^*2s^2,\ 2p_z^2,$
$2p_x^2\quad 2p_y^2,\ ^*2p_x^1\quad ^*2p_y^0$

$N_2(14e\ \text{'s})\quad 1s^2\ ^*1s^2,\ 2s^2,\ ^*2s^2$
$2p_x^2\quad 2p_y^2,\ 2p_z^2$

$N_2\ (13e\ \text{'s})\quad 1s^2\ ^*1s^2\quad s^2\ ^*2s^2$
$2p_x^2\quad 2p_z^2\ 2p_z^1$

Thus, in case of N_2, two -bonds and half -bond are present in the bonding MOs.

7. Considering molecular orbital theory (MOT) :
The electronic configuration of $Li_2\ (Z\quad 5)\quad 1s^2,\ ^*1s^2,\ 2s^1$

Bond order (BO) $\frac{N_b\quad N_a}{2}\quad \frac{3\quad 2}{2}\quad \frac{1}{2}$

The electronic configuration of $Li_2(Z\quad 7)\quad 1s^2,\ ^*1s^2,\quad s^2,\quad s^1$

Bond order (BO) $\frac{N_b\quad N_a}{2}\quad \frac{4\quad 3}{2}\quad \frac{1}{2}$

For the species having the same value of BO, the specie having lesser number of antibonding electrons $[N_a]$ will be more stable.

Here, N_a of Li_2^+ (2) N_a of Li_2 (3). So, their order of stability will be Li_2 Li_2.

8. **Key Idea** *According to M.O.T, the viability of any molecule can be judged through the calculation of bond order.*

Electronic	Configuration	Bond order
He_2	$1s^2$ $\overset{*}{1s^1}$	$\frac{2 \quad 1}{2}$ 0.5
H_2	$1s^2$ $\overset{*}{1s^1}$	$\frac{2 \quad 1}{2}$ 0.5
H_2^2	$1s^2$ $\overset{*}{1s^2}$	$\frac{2 \quad 2}{2}$ 0
He_2^2	$1s^2$	$\frac{2 \quad 0}{2}$ 1

The molecule having zero bond order will not be viable hence, H_2^2 (option d) is the correct answer.

9. To identify the magnetic nature we need to check the molecular orbital configuration. If all orbitals are fully occupied, species is diamagnetic while when one or more molecular orbitals is/are singly occupied, species is paramagnetic.

(a) NO (7 8 15) $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$,
$2p_x^2$ $2p_y^2$, $2p_z^2$, $^*2p_x^1$ $^*2p_y^0$

One unpaired electron is present. Hence, it is paramagnetic.

(b) CO (6 8 14) $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$,
$2p_x^2$ $2p_y^2$ $2p_z^2$

No unpaired electron is present. Hence, it is diamagnetic.

(c) O_2 (8 8 16) $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$, $2p_z^2$,
$2p_x^2$ $2p_x^2$, $^*2p_x^1$ $^*2p_y^1$

Two unpaired electrons are present.
Hence, it is paramagnetic.

(d) B_2(5 5) $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$, $2p_x^1$ $2p_y^1$

Two unpaired electrons are present.
Hence, it is paramagnetic.

10. **PLAN** This problem can be solved by using the concept involved in molecular orbital theory. Write the molecular orbital electronic configuration keeping in mind that there is no 2*s*-2*p* mixing, then if highest occupied molecular orbital contain unpaired electron then molecule is paramagnetic otherwise diamagnetic.

Assuming that no 2*s*-2*p* mixing takes place the molecular orbital electronic configuration can be written in the following sequence of energy levels of molecular orbitals

$1s$, $^*1s$, $2s$, $^*2s$, $2p_z$, $2p_x$ $2p_y$, $^*2p_x$ $^*2p_y$, $^*2p_z$

(a) Be_2 $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$ (diamagnetic)

(b) B_2 $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$, $2p_z^2$, $\begin{matrix} 2p_x^0 \\ 2p_y^0 \end{matrix}$ (diamagnetic)

(c) C_2 $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$, $2p_z^2$, $\begin{matrix} 2p_x^1, \\ 2p_y^1 \end{matrix}$

$\begin{matrix} ^*2p_x^0, \\ ^*2p_y^0 \end{matrix}$ $^*2p_z^0$ (paramagnetic)

(d) N_2 $1s^2$, $^*1s^2$, $2s^2$, $^*2s^2$, $2p_z^2$, $\begin{matrix} 2p_x^2, \\ 2p_y^2 \end{matrix}$

$\begin{matrix} ^*2p_x^0, \\ ^*2p_y^0 \end{matrix}$ $^*2p_z^0$ (diamagnetic)

Hence, (c) is the correct choice.

11. Li_2 (3 3 6) $1s^2$, $^*1s^2$, $2s^2$

Bond order $\frac{N_b \quad N_a}{2}$ $\frac{4 \quad 2}{2}$ 1

Li_2 (3 3 1 5) $1s^2$, $^*1s^2$, $2s^1$

Bond order $\frac{3 \quad 2}{2}$ $\frac{1}{2}$ 0.5

Li_2 (3 3 1 7) $1s^2$, $^*1s^2$, $2s^2$ $^*2s^1$

Bond order $\frac{4 \quad 3}{2}$ $\frac{1}{2}$ 0.5

Stability order is Li_2 Li_2 Li_2 (because Li_2 has more number of electrons in antibonding orbitals which destabilises the species).

12. Species having zero or negative bond order do not exist.

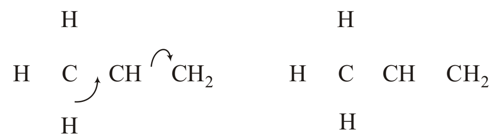
H_2^2 (1 1 2 0) $1s^0$

Bond order 0

He_2 (2 2 4) $1s^2$, $^*1s^2$

Bond order $\frac{N_b \quad N_a}{2}$ $\frac{2 \quad 2}{2}$ 0

So, both H_2^2 and He_2 do not exist.

13. 

(I) (II)

I and II are hyperconjugation structures of propene and involves -electrons of C—H bond and *p*-orbitals of pi bond in delocalisation.

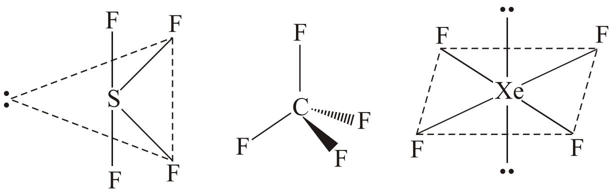
14. O_2^+ (15*e*) : $1s^2$ $^*1s^2$ $2s^2$ $^*2s^2$ $2p_x^2$ $\begin{vmatrix} 2p_y^2 \\ 2p_z^2 \end{vmatrix}$ $\begin{vmatrix} ^*2p_y^1 \\ ^*2p_z^0 \end{vmatrix}$ $^*2p_x^0$

Bond order $\frac{10 \quad 5}{2}$ 2.5; paramagnetic.

O_2 (16*e*) : $1s^2$ $^*1s^2$ $2s^2$ $^*2s^2$ $2p_x^2$ $\begin{vmatrix} 2p_y^2 \\ 2p_z^2 \end{vmatrix}$ $\begin{vmatrix} ^*2p_y^1 \\ ^*2p_z^1 \end{vmatrix}$ $^*2p_x$

Bond order $\frac{10 \quad 6}{2}$ 2

Hence, (a) is the correct answer.

15. 

See-saw shape molecule Tetrahedral Square planar

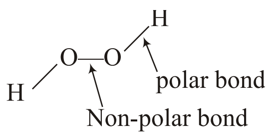
16. When E B in BCl_3, bond angle is 120°. When E P, As or Bi in ECl_3, hybridisation at E will be sp^3. Also, if central atoms are from same group, bond angle decreases down the group provided all other things are similar. Hence, the order of bond angles is $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$

17. Bond length $\frac{1}{\text{Bond order}}$

Bond order : $CO_2 = 2$, $CO = 3$, CO_3^2 $1 \ \frac{1}{3} \ \frac{4}{3}$

Therefore, order of bond length is CO_3^2 $CO_2 < CO$

18. H_2O_2



19. HCl does not form hydrogen bond. For formation of hydrogen bond, atleast one hydrogen atom must be bonded to one of the three most electronegative atom O , N and F.

20.

Species	Electrons	MOEC	N_B	N_A	BO	Magnetic character
C_2^2	14	$1s^2$, $*1s^2$, $2s^2$, $*2s^2$, $2p_x^2$ $2p_y^2$, $2p_z^2$	10	4	3	Diamagnetic
O_2^2	14	As above according to number of electrons	10	4	3	Diamagnetic
O_2	16		10	6	2	Paramagnetic
N_2	13		9	4	2.5	Paramagnetic
N_2	15		10	5	2.5	Paramagnetic
He_2	3		2	1	0.5	Paramagnetic

Thus, (a) is correct.

(b) Bond order O_2^2 O_2 thus,

Bond length of O_2^{2+} O_2 thus, incorrect.

(c) N_2^+ and N_2 have same bond order thus correct.

(d) He_2 with bond order 0.5 is more stable thus, less energy than isolated He atoms. Thus, (d) is incorrect.

21. **PLAN** This problem can be solved by using concept of H-bonding and applications of H-bonding.

22. C_2 (6 6 12) $s^2, {}^*1s^2, 2s^2, {}^*2s^2, 2p_x^2 \ 2p_y^2$

Since, all the electrons are paired, it is a diamagnetic species.

N_2 (7 7 14) $1s^2, {}^*1s^2, 2s^2,$

${}^*2s^2 \ 2p_x^2 \ 2p_y^2, 2p_z^2$

It is also a diamagnetic species because of the absence of unpaired electrons.

O_2 (8 8 16)

or S_2 $1s^2, {}^*1s^2, 2s^2, 2s^2,$

$2p_z^2, 2p_x^2 \ 2p_y^2 \ {}^*2p_x^1 \ {}^*2p_y^1$

Due to the presence of two unpaired electrons, O_2 and S_2 both are paramagnetic molecules.

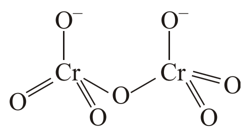
23. Statement I is correct, given structure is one of the resonance structure of ozone.

Statement II is also correct because oxygen cannot expand its octet. It is also the explanation for the given structure of ozone.

24. (A) In the reaction : O_2 $O_2 + O_2^2$

Oxygen on reactant side is in $\frac{1}{2}$ oxidation state. In product side, one of the oxygen is in zero oxidation state, i.e. oxidised while the other oxygen is in –1 oxidation state, i.e. reduced. Hence, in the above reaction, oxygen ($O^{1/2}$) is simultaneously oxidised and reduced disproportionated.

(B) In acidic medium, CrO_4^2 is converted into $Cr_2O_7^2$ which is a dimeric, bridged tetrahedral.



(C) MnO_4 NO_2 H^+ $Mn^{2+} + NO_3$

The above is a redox reaction and a product NO_3 has trigonal planar structure.

(D) NO_3 $H_2SO_4 + Fe^{2+}$ $Fe^+ + NO$

The above is a redox reaction.

25. $H_2, Li_2, Be_2, C_2, N_2$ and F_2 are diamagnetic according to molecular orbital theory.

26. $O_2 : \ 1s^2 \ {}^*1s^2 \ 2s^2 \ {}^*2s^2 \ 2p_x^2 \left| \begin{matrix} 2p_y^2 \\ 2p_z^2 \end{matrix} \right| \begin{matrix} {}^*2p_y^1 \\ {}^*2p_z^1 \end{matrix}$

Bond order $\frac{10 \quad 6}{2}$ 2, paramagnetic.

27. Strength of hydrogen bonding in X—H—X depends on electronegativity as well as size of X. X with higher electronegativity and smaller size forms stronger H-bond. Hence, increasing order of strength of H-bond is

$$S < Cl < N < O < F$$

28. Resonance in vinyl chloride increases polar character of the molecule.

Download Chapter Test
http://tinyurl.com/y3mna4bw *or*

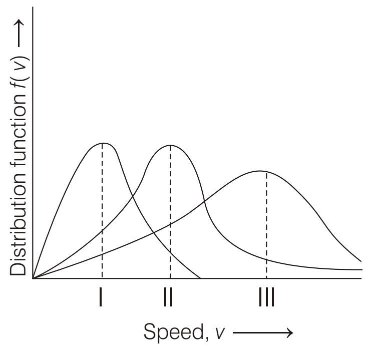
5

States of Matter

Topic 1 Gaseous State

Objective Questions I (Only one correct option)

1. Points I, II and III in the following plot respectively correspond to (v_{mp} : most probable velocity) **(2019 Main, 10 April II)**



(a) v_{mp} of H_2 (300 K); v_{mp} of N_2(300 K); v_{mp} of O_2(400 K)
(b) v_{mp} of O_2(400 K); v_{mp} of N_2(300 K); v_{mp} of H_2(300 K)
(c) v_{mp} of N_2(300 K); v_{mp} of O_2(400 K); v_{mp} of H_2(300 K)
(d) v_{mp} of N_2(300 K); v_{mp} of H_2(300 K); v_{mp} of O_2(400 K)

2. Consider the following table.

Gas	a/(k Pa dm^{6}mol $^{\;1}$)	b/(dm^{3}mol $^{\;1}$)
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and b are van der Waals' constants. The correct statement about the gases is **(2019 Main, 10 April I)**

(a) gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D
(b) gas C will occupy more volume than gas A; gas B will be more compressible than gas D
(c) gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D
(d) gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D

3. At a given temperature T, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as, $p \quad \frac{RT}{V \quad b}$ at T.

Here, b is the van der Waals' constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) *vs* p? **(2019 Main, 9 April II)**

(a) Xe (b) Ar
(c) Kr (d) Ne

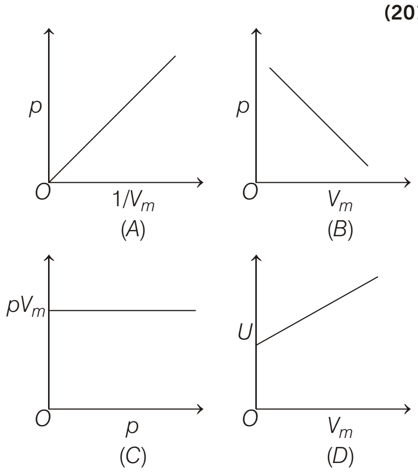
4. Consider the van der Waals' constants, a and b, for the following gases.

Gas	Ar	Ne	Kr	Xe
a/(atm dm^6 mol $^{\;2}$)	1.3	0.2	5.1	4.1
b/(10 $^{\;2}$ dm^3 mol $^{\;1}$)	3.2	1.7	1.0	5.0

Which gas is expected to have the highest critical temperature ? **(2019 Main, 9 April I)**

(a) Kr (b) Xe
(c) Ar (d) Ne

5. The combination of plots which does not represent isothermal expansion of an ideal gas is **(2019 Main, 12 Jan II)**



(a) (A) and (C) (b) (B) and (C)
(c) (B) and (D) (d) (A) and (D)

6. An open vessel at 27ºC is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is **(2019 Main, 12 Jan II)**

(a) 750 K (b) 500 K
(c) 750ºC (d) 500ºC

7. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are **(2019 Main, 12 Jan I)**

(a) $p_A \quad 2p_B$ (b) $2p_A \quad 3p_B$
(c) $p_A \quad 3p_B$ (d) $3p_A \quad 2p_B$

8. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at T 298.15 K and p 1 bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet?
[Molar mass of $NaHCO_3$ 84 g mol ^{1}] **(2019 Main, 11 Jan I)**

(a) 8.4 (b) 0.84 (c) 16.8 (d) 33.6

9. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume $10 m^3$ at 1000 K. Given R is the gas constant in JK ^{1} mol ^{1}, x is **(2019 Main, 9 Jan I)**

(a) $\frac{2R}{4 \quad R}$ (b) $\frac{4 \quad R}{2R}$ (c) $\frac{4 \quad R}{2R}$ (d) $\frac{2R}{4 \quad R}$

10. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is **(2016 Main)**

(a) $2p_i \frac{T_1}{T_1 \quad T_2}$ (b) $2p_i \frac{T_2}{T_1 \quad T_2}$

(c) $2p_i \frac{T_1T_2}{T_1 \quad T_2}$ (d) $p_i \frac{T_1T_2}{T_1 \quad T_2}$

11. If Z is a compressibility factor, van der Waals' equation at low pressure can be written as **(2014 Main)**

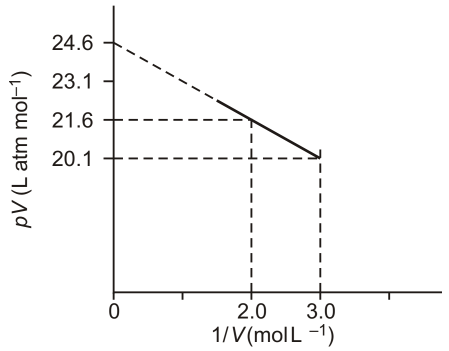
(a) $Z \quad 1 \quad \frac{RT}{pb}$ (b) $Z \quad 1 \quad \frac{a}{VRT}$

(c) $Z \quad 1 \quad \frac{pb}{RT}$ (d) $Z \quad 1 \quad \frac{pb}{RT}$

12. For gaseous state, if most probable speed is denoted by C^*, average speed by $\bar{C}$ and root square speed by C, then for a large number of molecules, the ratios of these speeds are **(2013 Main)**

(a) $C^* : \bar{C} : C \quad 1.225 : 1.128 : 1$
(b) $C^* : \bar{C} : C \quad 1.128 : 1.225 : 1$
(c) $C^* : \bar{C} : C \quad 1 : 1.128 : 1.225$
(d) $C^* : \bar{C} : C \quad 1 : 1.225 : 1.128$

13. For one mole of a van der Waals' gas when b 0 and T 300 K, the pV vs $1/V$ plot is shown below. The value of the van der Waals' constant a (atm L mol ^{2}) **(2012)**

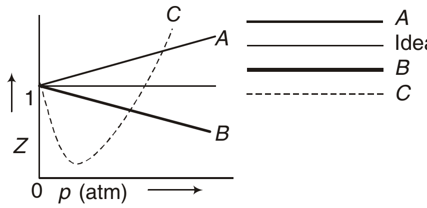


(a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

14. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is **(2009)**

(a) nb (b) n^2a/V^2
(c) (n^2a/V^2) (d) nb

15. The given graph represent the variations of Z (compressibility factor (Z) $\frac{pV}{nRT}$) *versus* p, for three real gases A, B and C. Identify the only incorrect statement. **(2006, 5M)**



(a) For the gas A, a 0 and its dependence on p is linear at all pressure
(b) For the gas B, b 0 and its dependence on p is linear at all pressure
(c) For the gas C, which is typical real gas for which neither a nor b 0 . By knowing the minima and the point of intersection, with Z 1, a and b can be calculated
(d) At high pressure, the slope is positive for all real gases

16. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of rate of diffusion of helium to methane is **(2005)**

(a) 2.0 (b) 1.0
(c) 0.5 (d) 4.0

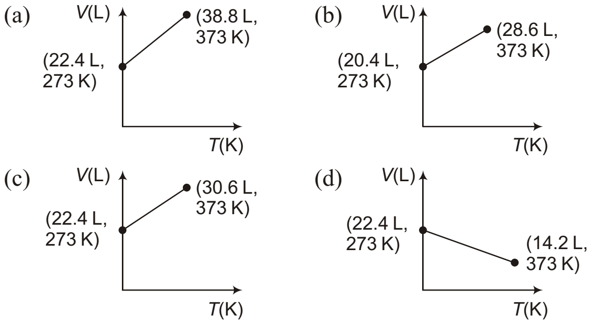
17. For a monatomic gas kinetic energy E. The relation with rms velocity is **(2004, 1M)**

(a) $u \quad \frac{2E}{m}^{1/2}$ (b) $u \quad \frac{3E}{2m}^{1/2}$

(c) $u \quad \frac{E}{2m}^{1/2}$ (d) $u \quad \frac{E}{3m}^{1/2}$

18. Positive deviation from ideal behaviour takes place because of **(2003, 1M)**
(a) molecular interaction between atom and $pV/nRT \quad 1$
(b) molecular interaction between atom and $pV/nRT \quad 1$
(c) finite size of atoms and $pV/nRT \quad 1$
(d) finite size of atoms and $pV/nRT \quad 1$

19. Which of the following volume (V) temperature (T) plots represents the behaviour of one mole of an ideal gas at the atmospheric pressure? **(2002, 3M)**



20. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as **(2001, S, 1M)**
(a) d^2 (b) d (c) $\sqrt{d}$ (d) $1/\sqrt{d}$

21. The compressibility of a gas is less than unity at STP. Therefore, **(2000, 1M)**
(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L
(c) $V_m = 22.4$ L (d) $V_m = 44.8$ L

22. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas **(2000, 1M)**
(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\ T(N_2)$

23. A gas will approach ideal behaviour at **(1999, 2M)**
(a) low temperature and low pressure
(b) low temperature and high pressure
(c) high temperature and low pressure
(d) high temperature and high pressure

24. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B is given by (where, p and M are pressures and molecular weights of gases A and B respectively) **(1998, 2M)**
(a) $\frac{p_A}{p_B} \quad \frac{M_A}{M_B}^{\frac{1}{2}}$ (b) $\frac{M_A}{M_B} \quad \frac{p_A}{p_B}^{\frac{1}{2}}$
(c) $\frac{p_A}{p_B} \quad \frac{M_B}{M_A}^{\frac{1}{2}}$ (d) $\frac{M_A}{M_B} \quad \frac{p_B}{p_A}^{\frac{1}{2}}$

25. The compressibility factor for an ideal gas is **(1997, 1M)**
(a) 1.5 (b) 1.0 (c) 2.0 (d)

26. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is **(1996, 1M)**
(a) 4 (b) 2 (c) 1 (d) $\frac{1}{4}$

27. Equal weights of ethane and hydrogen are mixed in an empty container at 25 C. The fraction of the total pressure exerted by hydrogen is **(1993, 1M)**
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

28. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with rise of temperature due to **(1992, 1M)**
(a) increase in average molecular speed
(b) increase rate of collisions amongst molecules
(c) increase in molecular attraction
(d) decrease in mean free path

29. According to kinetic theory of gases, for a diatomic molecule **(1991, 1M)**
(a) the pressure exerted by the gas is proportional to mean velocity of the molecule
(b) the pressure exerted by the gas is proportional to the root mean velocity of the molecule
(c) the root mean square velocity of the molecule is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature

30. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is **(1990, 1M)**
(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0

31. The density of neon will be highest at **(1990, 1M)**
(a) STP (b) 0 C, 2 atm
(c) 273 C, 1 atm (d) 273 C, 2 atm

32. The value of van der Waals' constant a for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol ^{2} respectively. The gas which can most easily be liquefied is
(a) O_2 (b) N_2 (c) NH_3 (d) CH_4

33. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be **(1988, 1M)**
(a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube

34. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular forces is **(1988, 1M)**
(a) $(V \quad b)$ (b) RT (c) $p + \frac{a}{V^2}$ (d) $(RT)^{1}$

35. The average velocity of an ideal gas molecule at 27 C is 0.3 m/s. The average velocity at 927 C will be **(1986, 1M)**
(a) 0.6 m/s (b) 0.3 m/s (c) 0.9 m/s (d) 3.0 m/s

36. Rate of diffusion of a gas is **(1985, 1M)**
(a) directly proportional to its density
(b) directly proportional to its molecular weight
(c) directly proportional to the square root of its molecular weight
(d) inversely proportional to the square root of its molecular weight

37. Equal weights of methane and hydrogen are mixed in an empty container at 25 C. The fraction of the total pressure exerted by hydrogen is **(1984, 1M)**

(a) $\frac{1}{2}$ (b) $\frac{8}{9}$ (c) $\frac{1}{9}$ (d) $\frac{16}{17}$

38. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules **(1984, 1M)**

(a) are above the inversion temperature
(b) exert no attractive forces on each other
(c) do work equal to loss in kinetic energy
(d) collide without loss of energy

39. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is

(a) two times that of a hydrogen molecule **(1982, 1M)**
(b) same as that of a hydrogen molecule
(c) four times that of a hydrogen molecule
(d) half that of a hydrogen molecule

40. Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **(1981, 1M)**

(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3}\ \frac{273}{298}$

41. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is **(1981, 1M)**

(a) critical temperature (b) Boyle temperature
(c) inversion temperature (d) reduced temperature

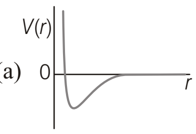
42. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is **(1981, 1M)**

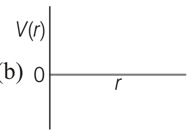
(a) 1.085 : 1 (b) 1 : 1.086 (c) 2 : 1.086 (d) 1.086 : 2

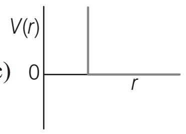
Objective Questions II

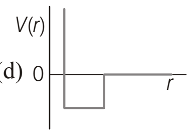
(One or more than one correct option)

43. One mole of a monoatomic real gas satisfies the equation $p(V \quad b) = RT$ where, b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for gas is given by **(2015 Adv.)**

(a)


(b)


(c)


(d)


44. According to kinetic theory of gases **(2011)**

(a) collisions are always elastic
(b) heavier molecules transfer more momentum to the wall of the container
(c) only a small number of molecules have very high velocity
(d) between collisions, the molecules move in straight lines with constant velocities

45. A gas described by van der Waals' equation **(2008, 4M)**

(a) behaves similar to an ideal gas in the limit of large molar volumes
(b) behaves similar to an ideal gas in the limit of large pressures
(c) is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature
(d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

46. If a gas is expanded at constant temperature **(1986, 1M)**

(a) the pressure decreases
(b) the kinetic energy of the molecules remains the same
(c) the kinetic energy of the molecules decreases
(d) the number of molecules of the gas increases

Numerical Value Based Question

47. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Fig. 1). If the old partition is replaced by a new partition which can slide and conduct heat but does not allow the gas to leak across (Fig. 2), the volume (in m^3) of the compartment A after the system attains equilibrium is ____.

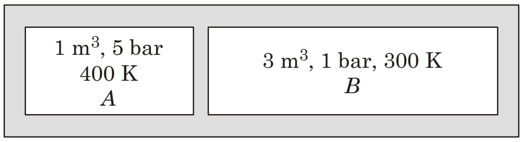


Fig. 1

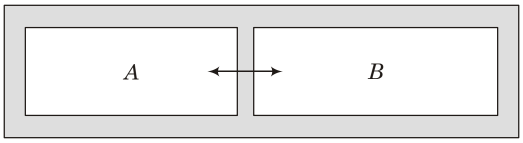


Fig. 2 **(2018 Adv)**

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

48. **Statement I** The pressure of a fixed amount of an ideal gas is proportional to its temperature.

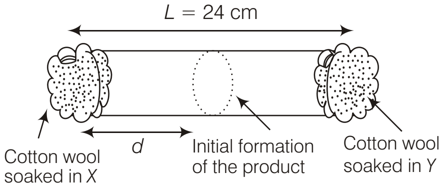
Statement II Frequency of collisions and their impact both increase in proportion to the square root of temperature. **(2000)**

49. **Statement I** The value of van der Waals' constant 'a' is larger for ammonia than for nitrogen.

Statement II Hydrogen bonding is present in ammonia. **(1998)**

Passage Based Questions

Passage



X and Y are two volatile liquids with molar weights of 10 g mol ^{1} and 40 g mol ^{1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length L 24 cm, as shown in the figure.
The tube is filled with an inert gas at 1 atm pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance d cm from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours. **(2014 Adv.)**

50. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to
(a) larger mean free path for X as a compared of that of Y
(b) larger mean free path for Y as compared to that of X
(c) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas
(d) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas

51. The value of d in cm (shown in the figure), as estimated from Graham's law, is
(a) 8 (b) 12 (c) 16 (d) 20

Match the Columns

52. Match the gases under specified conditions listed in Column I with their properties/laws in Column II.

	Column I		Column II
A.	Hydrogen gas (p 200 atm, T 273 K)	p.	compressibility factor 1
B.	Hydrogen gas ($p \sim 0, T$ 273 K)	q.	attractive forces are dominant
C.	CO_2 (p 1 atm, T 273 K)	r.	pV nRT
D.	Real gas with very large molar volume	s.	$p(V$ $nb)$ nRT

(2007, 6M)

Fill in the Blanks

53. The absolute temperature of an ideal gas is …… to/than the average kinetic energy of the gas molecules. **(1997, 1M)**

54. 8 g each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of …… . **(1989, 1M)**

55. The value of pV for 5.6 L of an ideal gas is .... RT, at NTP. **(1987, 1M)**

56. The rate of diffusion of a gas is .... proportional to both .... and square root of molecular mass. **(1986, 1M)**

57. C_p C_V for an ideal gas is …… **(1984, 1M)**

58. The total energy of one mole of an ideal monoatomic gas at 27 C is …… cal. **(1984, 1M)**

True / False

59. A mixture of ideal gases is cooled up to liquid helium temperature (4.22 K) to form an ideal solution. **(1996, 1M)**

60. In the van der Waals' equation, $p \quad \frac{n^2a}{V^2} \quad (V \quad nb) \quad nRT$
the constant 'a' reflects the actual volume of the gas molecules. **(1993, 1M)**

61. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. **(1985, 1/2 M)**

62. Kinetic energy of a molecule is zero at 0°C. **(1985, 1/2 M)**

Integer Answer Type Questions

63. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ... **(2016 Adv.)**

64. A closed vessel with rigid walls contains 1 mole of $^{238}_{92}U$ and 1 mole of air at 298 K. Considering complete decay of $^{238}_{92}U$ to $^{206}_{82}Pb$, the ratio of the final pressure to the initial pressure of the system at 298 K is **(2015 Adv.)**

65. If the value of Avogadro number is 6.023   10 ^{23} mol ^{1} and the value of Boltzmann constant is 1.380   10 ^{23} JK ^{1}, then the number of significant digits in the calculated value of the universal gas constant is **(2014 Adv.)**

66. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm at 0 C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0 C is close to **(2011)**

Subjective Questions

67. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is **(2009)**

68. The average velocity of gas molecules is 400 m s ^{1}, find the rms velocity of the gas. **(2003, 2M)**

69. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.
(i) Determine, (a) molecular weight (b) molar volume (c) compression factor (Z) of the vapour and (d) which forces among the gas molecules are dominating, the attractive or the repulsive?
(ii) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of a molecule. **(2002, 5M)**

70. The compression factor (compressibility factor) for one mole of a van der Waals' gas at 0 C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'. **(2001, 5M)**

71. Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waals' constant a = 3.592 dm^6 atm $mol^{\ 2}$. Assume that the volume occupied by CO_2 molecules is negligible. **(2000)**

72. (i) One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pin-hole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

(ii) The pressure exerted by 12 g of an ideal gas at temperature t C in a vessel of volume V litre is one atm. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V.
(Molecular weight of the gas = 120) **(1999, 5M)**

73. Using van der Waals' equation, calculate the constant a when two moles of a gas confined in a four litre flask exert a pressure of 11.0 atm at a temperature of 300 K. The value of b is 0.05 L mol^{-1}. **(1998, 4M)**

74. An evacuated glass vessel weighs 50.0 g when empty 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas. **(1998, 3M)**

75. A mixture of ideal gases is cooled up to liquid helium temperature (4.22 K) to form an ideal solution. Is this statement true or false ? Justify your answer in not more than two lines. **(1996, 1M)**

76. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$) which is attained at 1200 C, is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (atomic weight of Kr = 84) **(1995, 4M)**

77. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 L at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. **(1995, 4M)**

78. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 C, the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to the n-butane with normal boiling point of 0 C. **(1994, 3M)**

89. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? **(1994, 2M)**

80. A gas bulb of 1 L capacity contains 2.0 10^{21} molecules of nitrogen exerting a pressure of 7.57 10^3 Nm^{-2}. Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of the most probable speed to root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature. **(1993, 4M)**

81. At room temperature, the following reaction proceed nearly to completion. $2NO + O_2 \quad 2NO_2 \quad N_2O_4$

The dimer, N_2O_4, solidifies at 262 K. A 250 mL flask and a 100 mL flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm.

The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally). **(1992, 4M)**

82. At 27 C, hydrogen is leaked through a tiny hole into a vessel for 20 min. Another unknown gas at the same temperature and pressure as that of hydrogen is leaked through same hole for 20 min. After the effusion of the gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 L. What is the molecular weight of the unknown gas? **(1992, 3M)**

83. Calculate the volume occupied by 5.0 g of acetylene gas at 50 C and 740 mm pressure. **(1991, 2M)**

84. The average velocity at T_1 K and the most probable at T_2 K of CO_2 gas is 9.0 10^4 cm s^{-1}. Calculate the value of T_1 and T_2 **(1990, 4M)**

85. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm at 27 C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up. **(1987, 5M)**

86. Calculate the root mean square velocity of ozone kept in a closed vessel at 20 C and 82 cm mercury pressure. **(1985, 2M)**

87. Give reasons for the following in one or two sentences.

(i) Equal volumes of gases contain equal number of moles. **(1984, 1M)**

(ii) A bottle of liquor ammonia should be cooled before opening the stopper. **(1983, 1M)**

88. Oxygen is present in one litre flask at a pressure of 7.6 $10^{\ 10}$ mm Hg. Calculate the number of oxygen molecules in the flask at 0 C. **(1983, 2M)**

89. When 2 g of a gas A is introduced into an evacuated flask kept at 25 C, the pressure is found to be one atmosphere. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$. **(1983, 2M)**

90. At room temperature, ammonia gas at 1 atm pressure and hydrogen chloride gas at p atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one metre length and of uniform cross-section.

Ammonium chloride is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of p ? **(1982, 4M)**

91. Calculate the average kinetic energy, in joule per molecule in 8.0 g of methane at 27°C. **(1982, 2M)**

92. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 min when the contained oxygen leaked through a small hole. The bulb was then evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min. **(1981, 3M)**

93. A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. 1 L of the vapour of the hydrocarbon at 127°C and 1 atm pressure weighs 2.8 g. Find the molecular formula of the hydrocarbon. **(1980, 3M)**

94. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas ? **(1979, 2M)**

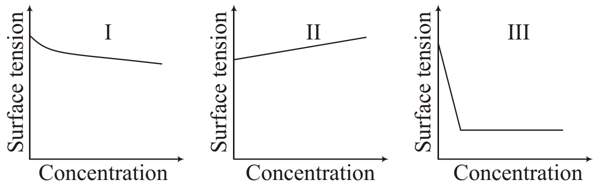
95. 4.215 g of a metallic carbonate was heated in a hard glass tube, the CO_2 evolved was found to measure 1336 mL at 27°C and 700 mm of Hg pressure. What is the equivalent weight of the metal ? **(1979, 3M)**

96. Calculate the density of NH_3 at 30°C and 5 atm pressure. **(1978, 2M)**

Topic 2 Liquid State

Objective Questions I (Only one correct option)

1. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3Na^+$ at room temperature. **(2016 Adv.)**



The correct assignment of the sketches is

	I	II	III
(a)	KCl	CH_3OH	$CH_3(CH_2)_{11}OSO_3\ Na^+$
(b)	$CH_3(CH_2)_{11}OSO_3\ Na^+$	CH_3OH	KCl
(c)	KCl	$CH_3(CH_2)_{11}OSO_3\ Na^+$	CH_3OH
(d)	CH_3OH	KCl	$CH_3(CH_2)_{11}OSO_3\ Na^+$

2. At 100°C and 1 atm if the density of the liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm ^{3}, then the volume occupied by water molecules in 1 L of steam at this temperature is **(2000, 1M)**

(a) 6 cm^3 (b) 60 cm^3
(c) 0.6 cm^3 (d) 0.06 cm^3

3. The critical temperature of water is higher than that of O_2 because the H_2O molecule has **(1997)**

(a) fewer electrons than O_2
(b) two covalent bonds
(c) V-shape
(d) dipole moment

4. A liquid is in equilibrium with its vapour at it's boiling point. On the average, the molecules in the two phases have equal

(a) inter-molecular forces (b) potential energy
(c) kinetic energy (d) total energy

Answers

Topic 1

1. (c)	**2.** (b)	**3.** (a)	**4.** (a)
5. (c)	**6.** (b)	**7.** (b)	**8.** (a)
9. (b)	**10.** (b)	**11.** (b)	**12.** (c)
13. (c)	**14.** (b)	**15.** (b)	**16.** (a)
17. (a)	**18.** (a)	**19.** (c)	**20.** (d)
21. (b)	**22.** (c)	**23.** (c)	**24.** (c)
25. (b)	**26.** (c)	**27.** (d)	**28.** (a)
29. (d)	**30.** (a)	**31.** (b)	**32.** (c)
33. (b)	**34.** (c)	**35.** (a)	**36.** (d)
37. (b)	**38.** (b)	**39.** (b)	**40.** (a)
41. (b)	**42.** (a)	**43.** (c)	**44.** (a)
45. (a,c)	**46.** (a,b)	**47.** (2.22)	**48.** (d)
49. (a)	**50.** (d)	**51.** (c)	

52. A p,s; B r; C p, q; D r

53. less	**54.** 1 : 16	**55.** 0.25	
56. inversely, time		**57.** R	**58.** 900
59. F	**60.** F	**61.** F	**62.** F
63. (4)	**64.** (9)	**65.** (4)	**66.** (7 L)
67. (4)	**68.** 435 ms ^{1}	**70.** (1025)	**71.** (0.99 atm)
73. (6.46)	**74.** (123 g mol ^{1})		**76.** (0.14)
78. (2.46 m^3)	**79.** (8:1)	**80.** (407 ms ^{1})	**81.** (0.221 atm)
82. (1020 g mol ^{1})	**83.** (5.23 L)	**85.** (10)	
86. (390.2 ms ^{1})	**88.** (2.7 10^{10} g mol ^{1})		
89. (1 : 3)	**90.** (2.20 atm)	**91.** (6.2 10 ^{21} J/molecule)	
94. (41.32g)	**95.** (12.15)	**96.** (3.42 gL ^{1})	

Topic 2

1. (d)	**2.** (c)	**3.** (d)	**4.** (c)

Hints & Solutions

Topic 1 Gaseous State

1. **Key Idea** From kinetic gas equation,

Most probable velocity (v_{mp}) $\sqrt{\frac{2RT}{M}}$

where, R gas constant, T temperature,

M molecular mass

$$v_{mp} \quad \sqrt{\frac{2RT}{M}}, \text{ i.e. } v_{mp} \quad \sqrt{\frac{T}{M}}$$

Gas	M	T(K)	$\sqrt{T/M}$
H_2	2	300	$\sqrt{300/2}$ $\sqrt{150}$ ...III (Highest)
N_2	28	300	$\sqrt{300/28}$ $\sqrt{10.71}$ ...I (Lowest)
O_2	32	400	$\sqrt{400/32}$ $\sqrt{12.5}$ ... II

So,

I. corresponds to v_{mp} of N_2 (300 K)

II. corresponds to v_{mp} of O_2 (400 K)

III. corresponds to v_{mp} of H_2 (300 K)

2. For 1 mole of a real gas, the van der Waals' equation is

$$p \quad \frac{a}{V^2} \quad (V \quad b) \quad RT$$

The constant 'a' measures the intermolecular force of attraction of gas molecules and the constant 'b' measures the volume correction by gas molecules after a perfectly inelastic binary collision of gas molecules.

For gas A and gas C given value of 'b' is $0.05196 \, dm^3 \, mol^{\ 1}$. Here,

a intermolecular force of attraction

compressibility real nature

$\frac{1}{\text{volume occupied}}$

Value of a/(kPa $dm^6 \, mol^{\ 1}$) for gas A (642.32) > gas C (431.91)

So, gas C will occupy more volume than gas A. Similarly, for a given value of a say 155.21 kPa $dm^6 \, mol^{\ 1}$ for gas B and gas D

$\frac{1}{b}$ intermolecular force of attraction

compressibility real nature

$\frac{1}{\text{volume accupied}}$

b/($dm^3 \, mol^{\ 1}$) for gas B (0.04136) < Gas D (0.4382)

So, gas B will be more compressible than gas D.

3. Noble gases such as Ne, Ar, Xe and Kr found to deviate from ideal gas behaviour.

Xe gas will exhibit steepest increase in plot of Z *vs* p.

Equation of state is given as:

$$p \quad \frac{RT}{(V \quad b)} \quad p(V \quad b) \quad RT$$

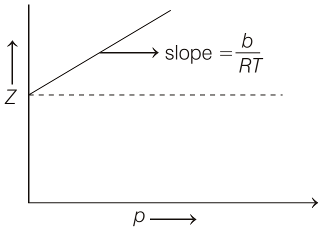
$$pV \quad pb \quad RT \qquad pV \quad RT \quad pb$$

$$\frac{pV}{RT} \quad 1 \quad \frac{pb}{RT}$$

As, $\quad Z \quad \frac{pV}{RT}$

so, $\quad Z \quad 1 \quad \frac{pb}{RT} \qquad y \quad c \quad mx$

The plot of z *vs* p is found to be



The gas with high value of b will be steepest as slope is directly proportional to b. b is the van der Waals' constant and is equal to four times the actual volume of the gas molecules. Xe gas possess the largest atomic volume among the given noble gases (Ne, Kr, Ar). Hence, it gives the steepest increase in the plot of Z (compression factor) *vs* p.

4. Critical temperature is the temperature of a gas above which it cannot be liquefied what ever high the pressure may be. The kinetic energy of gas molecules above this temperature is sufficient enough to overcome the attractive forces. It is represented as T_c.

$$T_c \quad \frac{8a}{27Rb}$$

For Ar, $\quad T_c \quad \frac{8 \quad 1.3}{27 \quad 8.314 \quad 3.2} \quad 0.0144$

For Ne, $\quad T_c \quad \frac{8 \quad 0.2}{27 \quad 8.314 \quad 1.7} \quad 0.0041$

For Kr, $\quad T_c \quad \frac{8 \quad 5.1}{27 \quad 8.314 \quad 1.0} \quad 0.18$

For Xe, $\quad T_c \quad \frac{8 \quad 4.1}{27 \quad 8.314 \quad 5.0} \quad 0.02$

The value of T_c is highest for Kr (Krypton).

5. In isothermal expansion, $pV_m \quad K$ (constant)

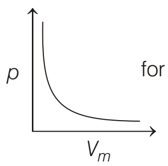
This relation is plotted in graph 'C'

Likewise, $\quad p \quad \frac{K}{V_m}$

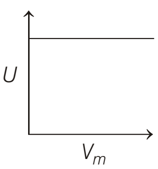
This relation is plotted in graph "A".

Thus, graph B and D are incorrect.

For them the correct graphs are:



for graph B and



for graph D

6. Given, temperature (T_1) 27 C 273 27 300 K

Volume of vessel constant

Pressure in vessel constant

Volume of air reduced by $\frac{2}{5}$ so the remaining volume of air is $\frac{3}{5}$.

Let at T_1 the volume of air inside the vessel is n so at T_2 the volume of air will be $\frac{3}{5}n$.

Now, as p and V are constant, so

$$n \quad T_1 \quad \frac{3}{5} n \, T_2 \qquad \text{...(i)}$$

Putting the value of T_1 in equation (i) we get,

$$n \quad 300 \quad \frac{3}{5} n \quad T_2$$

or
$$T_2 \quad 300 \quad \frac{5}{3} \quad 500 \text{ K}$$

7. Given, $Z_A = 3Z_B$

Compressibility factor $(Z) = \frac{pV}{nRT}$ [for real gases]

On substituting in equation (i), we get

$$\frac{p_A V_A}{n_A R T_A} \quad \frac{3 p_B V_B}{n_B R T_B} \qquad \text{...(ii)}$$

Also, it is given that

$$V_A = 2V_B,\ n_A = n_B \text{ and } T_A = T_B$$

Eq. (ii) becomes

$$\frac{p_A \quad 2V_B}{n_B R T_B} \quad \frac{3 p_B V_B}{n_B R T_B}$$

$$2p_A = 3p_B$$

8. $\underset{2\text{ mol}}{2NaHCO_3} \quad \underset{1\text{ mol}}{H_2C_2O_4} \qquad \underset{2\text{ mol}}{2CO_2} \quad Na_2C_4O_4 \quad H_2O$

In the reaction, number of mole of CO_2 produced.

$$n \quad \frac{pV}{RT} \quad \frac{1 \text{ bar} \quad 0.25 \quad 10^{\quad 3} \text{ L}}{0.082 \text{ L atm K}^{\quad 1}\text{mol}^{\quad 1} \quad 298.15 \text{ K}}$$

$$1.02 \quad 10^{\quad 5} \text{ mol}$$

Number of mole of $NaHCO_3$ $\frac{\text{Weight of } NaHCO_3}{\text{Molecular mass of } NaHCO_3}$

$$w_{NaHCO_3} \quad 1.02 \quad 10^{\quad 5} \quad 84 \quad 10^3 \text{ mg}$$

$$0.856 \text{ mg}$$

$$NaHCO_3\,\% \quad \frac{0.856}{10} \quad 100 \quad 8.56\%$$

9. From the ideal gas equation,

$$pV \quad nRT \qquad \text{...(i)}$$

Given: p 200 Pa, V 10m^3, T 1000 K

n_A 0.5 moles, n_B x moles

On substituting the given values in equation (i), we get

$$200 \quad 10 \quad (n_A \quad n_B) \quad R \quad 1000$$

$$0.5 \quad x \quad \frac{200 \quad 10}{R \quad 1000}$$

$$\frac{1}{2} \quad x \quad \frac{2}{R} \quad \frac{2}{R} \quad \frac{1}{2} \quad \frac{4 \quad R}{2R}$$

10. Initially,

Number of moles of gases in each container $\frac{p_i V}{RT_1}$

Total number of moles of gases in both containers $2\frac{p_i V}{RT_1}$

After mixing, number of moles in left chamber $\frac{p_f V}{RT_1}$

Number of moles in right chamber $\frac{p_f V}{RT_2}$

Total number of moles $\frac{p_f V}{RT_1} \quad \frac{p_f V}{RT_2} \quad \frac{p_f V}{R} \quad \frac{1}{T_1} \quad \frac{1}{T_2}$

As total number of moles remains constant.

Hence, $\frac{2p_i V}{RT_1} \quad \frac{p_f V}{RT_1} \quad \frac{p_f V}{RT_2} \qquad p_f \quad 2p_i \quad \frac{T_2}{T_1 \quad T_2}$

11. **PLAN** To solve this problem, the stepwise approach required, i.e.

(*i*) Write the van der Waals' equation, then apply the condition that at low pressure, volume become high,

i.e. $V \quad b \sim V$

(*ii*) Now calculate the value of compressibility factor (Z).
$[Z \quad pV / RT]$

According to van der Waals' equation,

$$p \quad \frac{a}{V^2} \quad (V \quad b) \quad RT$$

At low pressure, $p \quad \frac{a}{V^2} \quad V \quad RT$

$$pV \quad \frac{a}{V} \quad RT \text{ or } pV \quad RT \quad \frac{a}{V}$$

Divide both side by RT, $\frac{pV}{RT} \quad 1 \quad \frac{a}{RTV}$

12. C^* Most probable speed $\sqrt{\frac{2RT}{M}}$

$\overline{C}$ Average speed $\sqrt{\frac{8RT}{M}}$

C Root square speed corrected as root means square speed, i.e.

rms $\sqrt{\frac{3RT}{M}}$ and as we know $\overset{*}{C} \quad \overline{C} \quad C$

$$\overset{*}{C} : \overline{C} : C \quad 1 : \sqrt{\frac{4}{p}} : \sqrt{\frac{3}{2}} \quad 1 : 1.128 \ : \ 1.225$$

NOTE

As no option correspond to root square speed, it is understood as misprint. It should be root mean square speed.

13. The van der Waals' equation of state is

$$p \quad \frac{n^2 a}{V^2} \quad (V \quad nb) \quad nRT$$

For one mole and when b 0, the above equation condenses to

$$p \quad \frac{a}{V^2} \quad V \quad RT$$

$$pV \quad RT \quad \frac{a}{V} \qquad \ldots(i)$$

Eq. (i) is a straight equation between pV and $\frac{1}{V}$ whose slope is 'a'. Equating with slope of the straight line given in the graph.

$$a \quad \frac{20.1 \quad 21.6}{3 \quad 2} \quad 1.5$$

$$a \quad 1.5$$

14. In the van der Waals' equation

$$p \quad \frac{n^2 a}{V^2} \quad (V \quad nb) \quad nRT$$

The additional factor in pressure, i.e. $\frac{n^2 a}{V^2}$ corrects for intermolecular force while b corrects for molecular volume.

15. Option (b) is incorrect statement because at high pressure slope of the line will change from negative to positive.

16. $\frac{r_{(He)}}{r_{(CH_4)}} \quad \sqrt{\frac{16}{4}} \quad 2:1$

17. Kinetic energy $(E) \quad \frac{3}{2}kT$

RMS speed $(u) \quad \sqrt{\frac{3kT}{m}}$

$$u \quad \sqrt{\frac{2E}{m}}$$

18. Positive deviation corresponds to $Z \quad 1$

$\because \; Z \quad \frac{pV}{nRT}$, for positive deviation, $\frac{pV}{nRT} \quad 1.$

19. Option (b) and (d) are ruled out on the basis that at the initial point of 273 K, 1 atm, for 1.0 mole volume must be 22.4 L, and it should increase with rise in temperature.
Option (a) is ruled out on the basis that initial and final points are not connected by the ideal gas equation $V \quad T$, i.e. V/T do not have the same value at the two points.
In option (c), at the initial point, the volume is 22.4 L as required by ideal gas equation and (V/T) have the same value at both initial and final points.

20. Root mean square velocity $(u_{rms}) \quad \sqrt{\frac{3RT}{M}}$

Also, $\qquad p \; M \quad dRT$

Substituting for RT/M in u_{rms} expression gives,

$$u_{rms} \quad \sqrt{\frac{3p}{d}} \qquad u_{rms} \quad \frac{1}{\sqrt{d}}$$

21. Compressibility factor $(Z) \quad \frac{V}{V_{id}} \quad 1$ (given)

$$V \quad 22.4 \text{ L}$$

$\because \qquad V_{id}$ (1 mol) $\quad 22.4$ L at STP

22. Root mean square speed $u_{rms} \quad \sqrt{\frac{3RT}{M}}$

$$\frac{u_{rms}(H_2)}{u_{rms}(N_2)} \quad \sqrt{7} \quad \sqrt{\frac{T(H_2)}{2} \quad \frac{28}{T(N_2)}}$$

$$7 \quad \frac{14T\,(H_2)}{T\,(N_2)}$$

$$T(N_2) \quad 2T(H_2) \text{ i.e. } T(H_2) \quad T(N_2)$$

23. At high temperature and low pressure, the gas volume is infinitely large and both intermolecular force as well as molecular volume can be ignored. Under this condition postulates of kinetic theory applies appropriately and gas approaches ideal behaviour.

24. Rate of effusion $\quad p_i;\, p_i \quad$ Partial pressure of ith component

$$\sqrt{\frac{1}{M}}$$

25. Compressibility factor $(Z) \quad \frac{V}{V_{ideal}} \quad 1$

$\because \qquad$ For ideal gas $V \quad V_{ideal}$

26. Expression of rms is, $u_{rms} \quad \sqrt{\frac{3RT}{M}}$

$$\frac{u_{rms}\,(H_2 \text{ at } 50\text{ K})}{u_{rms}\,(O_2 \text{ at } 800\text{ K})} \quad \frac{\sqrt{\frac{3R \quad 50}{2}}}{\sqrt{\frac{3R \quad 800}{32}}}$$

$$\sqrt{\frac{50}{2} \quad \frac{32}{800}} \quad 1$$

27. Let x g of each gas is mixed.

Mole of ethane $\quad \frac{x}{30}$

Mole of hydrogen $\quad \frac{x}{2}$

Mole fraction of hydrogen $\quad \frac{\frac{x}{2}}{\frac{x}{2} \quad \frac{x}{30}} \quad \frac{15}{16}$

$$\frac{\text{Partial pressure of } H_2}{\text{Total pressure}} \quad \text{Mole fraction of hydrogen}$$

$$15:16$$

28. Average speed $\quad \sqrt{\frac{8RT}{M}}$

i.e. at constant volume, for a fixed mass, increasing temperature increases average speeds and molecules collide more frequently to the wall of container leading to increase in gas pressure.

29. The mean translational kinetic energy ( ) of an ideal gas is $\frac{3}{2}k_B T;\, T \quad$ Absolute temperature, i.e. $\quad T$

30. $\frac{r_{CH_4}}{r_X} \quad 2 \quad \sqrt{\frac{M_X}{16}} \qquad M_X \quad 64$

31. The ideal gas equation, $pV \quad nRT \quad \frac{w}{M}RT$

$$pM \quad \frac{w}{V} \quad RT \quad dRT \qquad (d \quad \text{density})$$

$$d \quad \frac{pM}{RT}$$

i.e. density will be greater at low temperature and high pressure.

32. The ease of liquefication of a gas depends on their intermolecular force of attraction which in turn is measured in terms of van der Waals' constant *a*. Hence, higher the value of *a*, greater the intermolecular force of attraction, easier the liquefication.

In the present case, NH_3 has highest *a*, can most easily be liquefied.

33. HCl will diffuse at slower rate than ammonia because rate of effusion $\quad \frac{1}{\sqrt{M}}$.

Therefore, ammonia will travel more distance than HCl in the same time interval and the two gas will first meet nearer to HCl end.

34. In van der Waals' equation of state

$$p \quad \frac{a}{V^2} \quad (V \quad b) \quad RT \qquad \text{(For 1 mole)}$$

The first factor $(p \quad a/V^2)$ correct for intermolecular force while the second term $(V \quad b)$ correct for molecular volume.

35. Expression for average velocity is $u_{av} \quad \sqrt{\frac{8RT}{M}}$

For the same gas but at different temperature

$$\frac{u_{avg}(T_1)}{u_{avg}(T_2)} \quad \sqrt{\frac{T_1}{T_2}} \quad \sqrt{\frac{300}{1200}} \quad \frac{1}{2}$$

$$u_{av}\ (927\ \ C) \quad 2 \quad u_{av}\ (27\ \ C) \quad 0.6\ \text{ms}^{\ \ 1}$$

36. Rate of effusion $\quad \frac{1}{\sqrt{M}}$,

37. Let *x* grams of each hydrogen and methane are mixed,

$$\text{Moles of } H_2 \quad \frac{x}{2}$$

$$\text{Moles of } CH_4 \quad \frac{x}{16}$$

$$\text{Mole fraction of } H_2 \quad \frac{\frac{x}{2}}{\frac{x}{2} \quad \frac{x}{16}} \quad \frac{8}{9}$$

$$\frac{\text{Partial pressure of } H_2}{\text{Total pressure}} \quad \text{Mole fraction of } H_2 \quad \frac{8}{9}$$

38. According to postulates of kinetic theory, there is no intermolecular attractions or repulsions between the molecules of ideal gases.

39. According to kinetic theory, average kinetic energy $(E) \quad \frac{3}{2}k_BT$

where, k_B is Boltzmann's constant. Since, it is independent of molar mass, it will be same for He and H_2 at a given temperature.

40. If *x* g of both oxygen and methane are mixed then :

$$\text{Mole of oxygen} \quad \frac{x}{32}$$

$$\text{Mole of methane} \quad \frac{x}{16}$$

$$\text{Mole fraction of oxygen} \quad \frac{\frac{x}{32}}{\frac{x}{32} \quad \frac{x}{16}} \quad \frac{1}{3}$$

According to law of partial pressure

Partial pressure of oxygen (p_{O_2}) Mole fraction Total pressure

$$\frac{p_{O_2}}{p} \quad \frac{1}{3}$$

41. It is the Boyle temperature T_B. At Boyle temperature, the first virial coefficient (B) vanishes and real gas approaches ideal behaviour.

$$T_B \quad \frac{a}{Rb}$$

Here, *a* and *b* are van der Waals' constants.

42. The two types of speeds are defined as;

$$\text{Root mean square speed } (u_{rms}) \quad \sqrt{\frac{3RT}{M}}$$

$$\text{Average speed } (u_{av}) \quad \sqrt{\frac{8RT}{M}}$$

For the same gas, at a given temperature, *M* and *T* are same, therefore

$$\frac{u_{rms}}{u_{av}} \quad \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{M}}$$

$$\sqrt{3} : \sqrt{\frac{8}{\ }} \quad \sqrt{3} : \sqrt{2.54} \quad 1.085 : 1$$

43. Equation of state $p(V \quad b) \quad RT$ indicates absence of intermolecular attraction or repulsion, hence interatomic potential remains constant on increasing ' ' in the beginning. As the molecules come very close, their electronic and nuclear repulsion increases abruptly.

44. (a) According to a postulate of kinetic theory of gases, collision between the molecules as well as with the wall of container is perfectly elastic in nature.

(b) If a gas molecule of mass *m* moving with speed *u* collide to the wall of container, the change in momentum is $p = -2mu$. Therefore, heavier molecule will transfer more momentum to the wall as there will be greater change in momentum of the colliding gas molecule. However, this is not postulated in kinetic theory.

(c) According to Maxwell-Boltzmann distribution of molecular speed, very few molecules have either very high or very low speeds. Most of the molecules moves in a specific, intermediate speed range.

(d) According to kinetic theory of gases, a gas molecule moves in straight line unless it collide with another molecule or to the wall of container and change in momentum is observed only after collision.

45. Option (a) is correct because in the limit of large volume, both intermolecular force and molecular volume becomes negligible in comparison to volume of gas.

Option (b) is wrong statement because in the limit of large pressure $Z \quad 1$.

Option (c) is correct statement. For a van der Waals' gas, van der Waals' constants a and b are characteristic of a gas, independent of temperature.

Option (d) is wrong statement because Z can be either less or greater than unity, hence real pressure can be less or greater than ideal pressure.

46. Pressure is inversely proportional to volume at constant temperature, hence (a) is correct.

Average kinetic energy of a gas is directly proportional to absolute temperature, hence (b) is correct.

Expansion at constant temperature cannot change the number of molecules, hence (d) is incorrect.

47. Given $p_1 \quad 5\,\text{bar}, V_1 \quad 1\,\text{m}^3, T_1 \quad 400\,\text{K}$

So, $\qquad n_1 \quad \frac{5}{400R} \qquad$ (from $pV \quad nRT$)

Similarly, $p_2 \quad 1\,\text{bar}, V_2 \quad 3\,\text{m}^3, T_2 \quad 300\,\text{K}, n_2 \quad \frac{3}{300R}$

Let at equilibrium the new volume of A will be $(1 \quad x)$

So, the new volume of B will be $(3 \quad x)$

Now, from the ideal gas equation.

$$\frac{p_1V_1}{n_1RT_1} \quad \frac{p_2V_2}{n_2RT_2}$$

and at equilibrium (due to conduction of heat)

$$\frac{p_1}{T_1} \quad \frac{p_2}{T_2}$$

So, $\qquad \frac{V_1}{n_1} \quad \frac{V_2}{n_2}$ or $V_1n_2 \quad V_2n_1$

After putting the values

$$(1 \quad x)\frac{3}{300R} \quad (3 \quad x)\frac{5}{400R} \text{ or } (1 \quad x) \quad \frac{(3 \quad x)5}{4}$$

or $\quad 4(1 \quad x) \quad 15 \quad 5x$ or $\quad 4 \quad 4x \quad 15 \quad 5x \quad$ or $x \quad \frac{11}{9}$

Hence, new volume of A i.e., $(1 \quad x)$ will comes as $1 \quad \frac{11}{9} \quad \frac{20}{9}$ or 2.22.

48. Assertion is incorrect because besides amount, pressure also depends on volume. However, reason is correct because both frequency of collisions and impact are directly proportional to root mean square speed which is proportional to square root of absolute temperature

49. a is the measure of intermolecular force of attraction. Greater the intermolecular force of attraction (H-bond in the present case) higher the value of a.

50. X is a lighter gas than Y, hence X has greater molecular speed. Due to greater molecular speed of X, it will have smaller mean free path and greater collision frequency with the incrt gas molecules. As a result X will take more time to travel a given distance along a straight line. Hence X and Y will meet at a distance smaller than one calculated from Graham's law.

Hence, (d) is the correct choice.

51. **PLAN** This problem can be solved by using the concept of Graham's law of diffusion according to which rate of diffusion of non-reactive gases under similar conditions of temperature and pressure are inversely proportional to square root of their density.

$$\text{Rate of diffusion} \quad \frac{1}{\sqrt{\text{molar weight of gas}}}$$

Let distance covered by X is d, then distance covered by Y is $24 - d$.

If r_X and r_Y are the rate of diffusion of gases X and Y,

$$\frac{r_X}{r_Y} \quad \frac{d}{24 \quad d} \quad \sqrt{\frac{40}{10}} \quad 2$$

[∵ Rate of diffusion $\quad$ distance travelled]

$$d \quad 48 \quad 2d$$

$$3d \quad 48 \qquad d \quad 16\,\text{cm}$$

Hence, (c) is the correct choice.

52. A. At $p \quad 200$ atm, very high pressure, $Z \quad 1$. Also, at such a high pressure, the pressure correction factor $\frac{n^2a}{V^2}$ can be ignored in comparison to p.

B. At $P \sim 0$, gas will behave like an ideal gas, $pV \quad nRT$.

C. CO_2 ($p \quad 1$ atm, $T \quad 273$ K), $Z \quad 1$.

D. At very large molar volume, real gas behaves like an ideal gas.

53. Less; $E \quad \frac{3}{2}RT$

54. 1 : 16, KE $\quad \frac{3}{2}nRT$. At same temperature, KE (total) $\quad n$.

55. 0.25 RT because at NTP, 5.6 L $\quad \frac{1}{4}$ mole.

56. Inversely, time.

57. For an ideal gas, $C_p \quad C_V \quad R$

58. At 27°C, $E \quad \frac{3}{2}RT \quad \frac{3}{2} \quad 2 \quad 300 \quad 900$ cal

59. An ideal gas cannot be liquefied because there exist no intermolecular attraction between the molecules of ideal gas.

60. a is the measure of intermolecular force.

61. In a close container, gas exert uniform pressure everywhere in the container.

62. KE $\quad \frac{3}{2}RT$ where, T is absolute temperature (in Kelvin).

63. (DC) Diffusion coefficient $\quad$ (mean free path) $\quad U_{\text{mean}}$

Thus (DC) $\quad U_{\text{mean}}$

But, $\qquad \frac{RT}{\sqrt{2}\,N_0 \quad p} \qquad \frac{T}{p}$

and $\qquad U_{\text{mean}} \quad \sqrt{\frac{8RT}{M}}$

$$U_{\text{mean}} \quad \sqrt{T}$$

$$\text{DC} \quad \frac{(T)^{3/2}}{p}$$

$$\frac{(\text{DC})_2}{(\text{DC})_1}(x) \quad \frac{p_1}{p_2}\quad \frac{T_2}{T_1}^{3/2} \qquad \frac{p_1}{2p_1} \quad \frac{4T_1}{T_1}^{3/2}$$

$$\frac{1}{2}\ (8) \quad 4$$

64. ${}_{92}U^{238} \qquad {}_{82}Pb^{206} \quad 8\ {}_2He^4(g) \quad 6 \quad {}_1$

n(gas)[Initial] 1 (air)

n(gas) [Final] 8 (He) 1 (air) 9

At constant temperature and volume;

$$p \quad n.$$

So, $\dfrac{p_f}{p_i} \quad \dfrac{n_f}{n_i} \quad \dfrac{9}{1} \quad 9$

65. **PLAN** This problem can be solved by using the concept involved in calculation of significant figure.

Universal gas constant, $R \quad kN_A$

where, k Boltzmann constant

and N_A Avogadro's number

$R \quad 1.380 \quad 10^{\ \ 23} \quad 6.023 \quad 10^{23}$ J/Kmol

$8.31174 \ \tilde{}\ 8.312$

Since, k and N_A both have four significant figures, so the value of R is also rounded off upto 4 significant figures.

[When number is rounded off, the number of significant figure is reduced, the last digit is increased by 1 if following digits 5 and is left as such if following digits is 4.]

Hence, correct integer is (4).

66. Since, the external pressure is 1.0 atm, the gas pressure is also 1.0 atm as piston is movable. Out of this 1.0 atm partial pressure due to unknown compound is 0.68 atm.

Therefore, partial pressure of He

1.00 – 0.68 = 0.32 atm.

Volume $\dfrac{n(\text{He})RT}{p(\text{He})} \quad \dfrac{0.1 \quad 0.082 \quad 273}{0.32} \quad 7$ L

Volume of container = Volume of He.

67. Given,

$$u_{\text{rms}} \quad u_{\text{mps}}$$

$$\sqrt{\frac{3RT}{M(X)}} \quad \sqrt{\frac{2RT}{M(Y)}}$$

$$\frac{3R \quad 400}{40} \quad \frac{2R \quad 60}{M(Y)}$$

$$M(Y) \quad 4$$

68. $\dfrac{u_{\text{av}}}{u_{\text{rms}}} \quad \sqrt{\dfrac{8RT}{M}} : \sqrt{\dfrac{3RT}{M}} \quad \sqrt{\dfrac{8}{3}}$

$u_{\text{rms}} \quad \sqrt{\dfrac{3}{8}}\, u_{\text{av}} \quad \sqrt{\dfrac{3 \quad 3.14}{8}} \quad 400 \quad 434$ ms $^{\ 1}$

69. $\dfrac{r_{\text{gas}}}{r_{O_2}} \quad 1.33 = \sqrt{\dfrac{32}{M_{\text{gas}}}}$

(i) (a) M_{gas} 18 g mol $^{\ 1}$

(b) $V_m \quad \dfrac{18}{0.36} \quad 50$ L mol $^{\ 1}$

(c) $Z \quad \dfrac{pV}{RT} \quad \dfrac{1 \quad 50}{0.082 \quad 500} \quad 1.22$

(d) $\because \quad Z \quad 1$, repulsive force is dominating.

(ii) $\overline{E}_k \quad \dfrac{3}{2}k_BT \quad \dfrac{3}{2} \quad 1.38 \quad 10^{\ \ 23} \quad 1000$ J $\quad 2.07 \quad 10^{\ \ 20}$ J

70. In case of negligible molecular volume, $b \quad 0$. For 1 mole of gas

$$p \quad \frac{a}{V^2} \quad V \quad RT$$

$$pV \quad \frac{a}{V} \quad RT$$

$$\frac{pV}{RT} \quad \frac{a}{VRT} \quad 1 \qquad\qquad \because \frac{pV}{RT} \quad Z$$

$$Z \quad \frac{a}{\dfrac{ZRT}{p} \quad RT} \quad 1 \qquad Z \quad \frac{ap}{ZR^2T^2} \quad 1$$

$$a \quad \frac{ZR^2T^2(1 \quad Z)}{p} \quad \frac{0.5\,(0.082 \quad 273)^2\,(1 \quad 0.5)}{100}$$

$$a \quad 1.25 \text{ atm L}^2 \text{ mol}^{\ \ 2}$$

71. In case of negligible molecular volume, $b \quad 0$ and van der Waals' equation reduces to

$$p \quad \frac{n^2a}{V^2} \quad V \quad nRT$$

$$p \quad \frac{RT}{V} \quad \frac{a}{V^2} \qquad\qquad (n \quad 1 \text{ mole})$$

$$\frac{0.082 \quad 273}{22.4} \quad \frac{3.592}{(22.4)^2} \quad 0.99 \text{ atm}$$

72. (i) For the same amount of gas being effused

$$\frac{r_1}{r_2} \quad \frac{t_2}{t_1} \quad \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}}$$

$$\frac{57}{38} \quad \frac{0.8}{1.6}\sqrt{\frac{M_2}{28}}$$

$$M_2 \quad 252 \text{ g mol}^{\ \ 1}$$

Also, one molecule of unknown xenon-fluoride contain only one Xe atom [M (Xe) = 131], formula of the unknown gas can be considered to be XeF_n.

$131 \quad 19n \quad 252;\ n \quad 6.3$, hence the unknown gas is XeF_6.

(ii) For a fixed amount and volume, $p \quad T$

$$\frac{1}{1.1} \quad \frac{T}{T \quad 10} \quad \text{where, } T \quad \text{Kelvin temperature}$$

$$T \quad 100 \text{ K} \quad t \quad 273$$

$$t \quad 173 \ \text{C}$$

$$\text{Volume} \quad \frac{nRT}{p} \quad \frac{12}{120} \quad \frac{0.082 \quad 100}{1} \quad 0.82 \text{ L}$$

73. The van der Waals' equation is

$$p \quad \frac{n^2a}{V^2} \quad (V \quad nb) \quad nRT$$

$$a \quad \frac{V^2}{n^2} \quad \frac{nRT}{V \quad nb} \quad p \quad \frac{(4)^2}{(2)^2} \quad \frac{2 \quad 0.082 \quad 300}{4 \quad 2\,(0.05)} \quad 11$$

$$6.46 \text{ atm L}^2 \text{ mol}^{\ 2}$$

74. Mass of liquid 148 50 98 g

$$\text{Volume of liquid} \quad \frac{98}{0.98} \quad 100 \text{ mL} = \text{volume of flask}$$

mass of gas 50.5 50 = 0.50 g

Now applying ideal gas equation : $pV \quad \frac{w}{M} \quad RT$

$$M \quad \frac{wRT}{pV} \quad \frac{0.5 \quad 0.082 \quad 300}{1 \quad 0.1} \quad 123 \text{ g mol}^{\ 1}$$

75. False, ideal gas cannot be liquefied as there is no intermolecular attraction between the molecules of ideal gas. Hence, there is no point of forming ideal solution by cooling ideal gas mixture.

76. If ‘ ’ is the degree of dissociation, then at equilibrium

$$Cl_2 \rightleftharpoons 2Cl$$

Moles 1 2 Total 1

From diffusion information

$$\frac{r_{(mix)}}{r_{(Kr)}} \quad 1.16 \quad \sqrt{\frac{84}{M\,(\text{mix})}}$$

$$M_{(mix)} \quad 62.4$$

$$M_{(mix)} \quad \frac{71}{1} \quad 62.4$$

$$0.14$$

77. The total moles of gaseous mixture $\frac{pV}{RT} \quad \frac{1 \quad 40}{0.082 \quad 400}$

$$1.22$$

Let the mixture contain x mole of ethane. Therefore,

$$\underset{x}{C_2H_6} + \frac{7}{2} O_2 \qquad 2CO_2 + 3H_2O$$

$$\underset{1.22 \quad x}{C_2H_4} + 3O_2 \qquad 2CO_2 + 2H_2O$$

Total moles of O_2 required $\frac{7}{2}x \quad 3(1.22 \quad x) \quad \frac{x}{2} \quad 3.66$

$$\frac{130}{32} \quad \frac{x}{2} \quad 3.66$$

x 0.805 mole ethane and 0.415 mole ethene.

$$\text{Mole fraction of ethane} \quad \frac{0.805}{1.22} \quad 0.66$$

Mole fraction of ethene 1 0.66 0.34

78. Weight of butane gas in filled cylinder 29 14.8 kg

14.2 kg

During the course of use, weight of cylinder reduces to 23.2 kg

Weight of butane gas remaining now

23.2 14.8 = 8.4 kg

Also, during use, V (cylinder) and T remains same.

Therefore, $\frac{p_1}{p_2} \quad \frac{n_1}{n_2}$

$$p_2 \quad \frac{n_2}{n_1} \quad p_1 \quad \frac{8.4}{14.2} \quad 2.5 \qquad \text{Here, } \frac{n_2}{n_1} \quad \frac{w_2}{w_1}$$

1.48 atm

Also, pressure of gas outside the cylinder is 1.0 atm.

$$pV \quad nRT$$

$$V \quad \frac{nRT}{p} \quad \frac{(14.2 \quad 8.4) \quad 10^3}{58} \quad \frac{0.082 \quad 30}{1} \text{ L}$$

$$2460 \text{ L} \quad 2.46 \text{ m}^3$$

79. $\frac{r_{He}}{r_{CH_4}} \quad \frac{n_{He}}{n_{CH_4}} \sqrt{\frac{M_{CH_4}}{M_{He}}} \quad \frac{4}{1}\sqrt{\frac{16}{4}} \quad 8$

Initial ratio of rates of effusion gives the initial composition of mixture effusing out. Therefore, $n(\text{He}) : n(CH_4) \quad 8:1$

80. Number of moles $\frac{2 \quad 10^{21}}{6 \quad 10^{23}} \quad 0.33 \quad 10^{\ 2}$

$$p \quad 7.57 \quad 10^3 \text{ Nm}^{\ 2}$$

Now, $pV \quad nRT$

$$T \quad \frac{pV}{nR} \quad \frac{7.57 \quad 10^3 \quad 10^{\ 3}}{0.33 \quad 10^{\ 2} \quad 8.314} \quad 276 \text{ K}$$

$$u_{rms} \quad \sqrt{\frac{3RT}{M}} \quad \sqrt{\frac{3 \quad 8.314 \quad 276}{28 \quad 10^{\ 3}}} \text{ m s}^{\ 1} \quad 496 \text{ ms}^{\ 1}$$

Also, $\frac{u_{mps}}{u_{rms}} \quad 0.82$

$$u_{mps} \quad 0.82 \quad u_{rms} \quad 0.82 \quad 496 \text{ ms}^{\ 1} = 407 \text{ ms}^{\ 1}$$

81. First we calculate partial pressure of NO and O_2 in the combined system when no reaction taken place.

$$pV \quad \text{constant} \qquad p_1V_1 \quad p_2V_2$$

$$p_2(\text{NO}) \quad \frac{1.053 \quad 250}{350} \quad 0.752 \text{ atm}$$

$$p_2(O_2) \quad \frac{0.789 \quad 100}{350} \quad 0.225 \text{ atm}$$

Now the reaction stoichiometry can be worked out using partial pressure because in a mixture.

$$p_i \quad n_i$$

	2NO	+ O_2	$2NO_2$	N_2O_4
Initial	0.752 atm	0.225 atm	0	0
Final	0.302	0	0	0.225 atm

Now, on cooling to 220 K, N_2O_4 will solidify and only unreacted NO will be remaining in the flask.

$\because$
$$p \quad T$$

$$\frac{p_1}{p_2} \quad \frac{T_1}{T_2}$$

$$\frac{0.302}{p_2} \quad \frac{300}{220}$$

$$p_2(\text{NO}) \quad 0.221 \text{ atm}$$

82. Total moles of gas in final mixture $\frac{pV}{RT} \quad \frac{6 \quad 3}{0.082 \quad 300} \quad 0.731$

$\because$ Mole of H_2 in the mixture 0.70

Mole of unknown gas (X) 0.031

Because both gases have been diffused for same time

$$\frac{r(H_2)}{r(X)} \quad \frac{0.70}{0.031} \quad \sqrt{\frac{M}{2}}$$

$$M \quad 1020 \text{ g mol}^{\ 1}$$

83. $$V \quad \frac{nRT}{p}$$

For acetylene gas, $5\text{ g} \quad \frac{5}{26}\text{ mol}$

$$p \quad 740\text{ mm} = \frac{740}{760}\text{ atm}$$

$$T \quad 50 \quad \text{C} = 323\text{ K}$$

Substituting in ideal gas equation

$$V \quad \frac{5}{26} \quad \frac{0.082 \quad 323}{74} \quad 76 \quad 5.23\text{ L}$$

84. u_{av} (average velocity) $\sqrt{\frac{8RT_1}{M}}$

$$\frac{9 \quad 10^4}{100}\text{ ms}^{\ 1} \quad \sqrt{\frac{8 \quad 8.314\ T_1}{3.14 \quad 44 \quad 10^{\ 3}}}$$

$$T_1 \quad 1682.5\text{ K}$$

Also, for the same gas

$$\frac{u_{\text{av}}}{u_{\text{mps}}} \quad \sqrt{\frac{8RT_1}{M}} : \sqrt{\frac{2RT_2}{M}} \quad \sqrt{\frac{8T_1}{} \quad \frac{1}{2T_2}} \quad \sqrt{\frac{4T_1}{T_2}}$$

$$1 \quad \sqrt{\frac{4T_1}{T_2}}$$

$$T_2 \quad \frac{4T_1}{} \quad \frac{4 \quad 1682.5}{3.14} \quad 2142\text{ K}$$

Hence, $\quad T_1 \quad 1682.5\text{ K}, T_2 \quad 2142\text{ K}$

85. Volume of balloon $\frac{4}{3} \quad r^3 \quad \frac{4}{3} \quad 3.14 \quad \left(\frac{21}{2}\right)^3 \text{cm}^3$

$$= 4847\text{ cm}^3 \quad 4.85\text{ L}$$

Now, when volume of $H_2(g)$ in cylinder is converted into NTP volume, then

$$\frac{p_1V_1}{T_1} \quad \frac{p_2V_2}{T_2}$$

$$\frac{20 \quad 2.82}{300} \quad \frac{1 \quad V_2}{273}, V_2 \quad \text{NTP volume}$$

$$V_2 \quad 51.324\text{ L}$$

Also, the cylinder will not empty completely, it will hold 2.82 L of $H_2(g)$ when equilibrium with balloon will be established. Hence, available volume of $H_2(g)$ for filling into balloon is

$$51.324 \quad 2.82 = 48.504\text{ L}$$

Number of balloons that can be filled $\frac{48.504}{4.85} \quad 10$

86. $u_{\text{rms}} \quad \sqrt{\frac{3RT}{M}} \quad \sqrt{\frac{3 \quad 8.314 \quad 293}{48 \quad 10^{\ 3}}} = 390.2\text{ ms}^{\ 1}$

87. (i) $NH_3(l)$ is highly volatile, a closed bottle of $NH_3(l)$ contains large number of molecules in vapour phase maintaining high pressure inside the bottle. When the bottle is opened, there is chances of bumping of stopper. To avoid bumping, bottle should be cooled that lowers the pressure inside.

(ii) According to Avogadro's hypothesis, "Under identical conditions of pressure and temperature, equal volume of ideal gases contain equal number of molecules."

88. Number of moles $(n) \quad \frac{pV}{RT}$

and $\quad n \quad \frac{N\text{ (Number of molecules)}}{N_A\text{ (Avogadro number)}}$

$$N \quad nN_A \quad \frac{pV}{RT} \quad N_A$$

$$\frac{7.6 \quad 10^{\ 10}}{760} \quad \frac{1}{0.082 \quad 273} \quad 6.023 \quad 10^{23}$$

$$2.7 \quad 10^{10}\text{ molecules}$$

89. From the given information, it can be easily deduced that in the final mixture,

partial pressure of $A \quad 1.0$ atm

partial pressure of $B \quad 0.5$ atm

Also $\quad n_A \quad \frac{p_AV}{RT} \quad \frac{V}{RT}$

$$n_B \quad \frac{p_BV}{RT} \quad \frac{0.5\ V}{RT}$$

$$\frac{n_B}{n_A} \quad \frac{1}{2} \quad \frac{w_B}{M_B} \quad \frac{M_A}{w_A} \quad \frac{3}{2} \quad \frac{M_A}{M_B}$$

$$M_A : M_B \quad 1:3$$

90. Rate of effusion $(r) \quad \frac{p}{\sqrt{M}}$

$$\frac{r(NH_3)}{r(HCl)} \quad \frac{1}{\sqrt{17}} \quad \frac{\sqrt{36.5}}{p} \quad \frac{40}{60} \quad \frac{1}{p}\sqrt{\frac{36.5}{17}}$$

$$p \quad \frac{3}{2}\sqrt{\frac{36.5}{17}} \quad 2.20\text{ atm}$$

91. KE $\quad \frac{3}{2}k_BT : k_B \quad$ Boltzmann's constant

$$\frac{3}{2} \quad 1.38 \quad 10^{\ 23} \quad 300\text{ J} \quad 6.21 \quad 10^{\ 21}\text{ J/molecule}$$

92. Rate of effusion is expressed as $\frac{dp}{dt} \quad \frac{kp}{\sqrt{M}}$

$k \quad$ constant, $p \quad$ instantaneous pressure

$$\frac{dp}{p} \quad \frac{k\ dt}{\sqrt{M}}$$

Integration of above equation gives $\ln \frac{p_0}{p} \quad \frac{kt}{\sqrt{M}}$

Using first information : $\ln \frac{2000}{1500} \quad \frac{k47}{\sqrt{32}}$

$$k \quad \frac{\sqrt{32}}{47}\ln\frac{4}{3} \qquad \text{...(i)}$$

Now in mixture, initially gases are taken in equal mole ratio, hence they have same initial partial pressure of 2000 mm of Hg each.

After 74 min :

For $O_2 \quad \ln\frac{2000}{p_{O_2}} \quad \frac{74k}{\sqrt{32}}$

Substituting k from Eq. (i) gives

$$\ln\frac{2000}{p_{O_2}} \quad \frac{74}{\sqrt{32}} \quad \frac{\sqrt{32}}{47}\ln\frac{4}{3}$$

$$\ln \frac{2000}{p_{O_2}} \quad \frac{74}{47} \ln \frac{4}{3}$$

Solving gives $p\,(O_2)$ at 74 min   1271.5 mm

For unknown gas : $\ln \dfrac{2000}{p_g} \quad \dfrac{74\,k}{\sqrt{79}}$

Substituting k from (i) gives

$$\ln \frac{2000}{p_g} \quad \frac{74}{\sqrt{79}} \quad \frac{\sqrt{32}}{47} \ln \frac{4}{3}$$

Solving gives : p_g 1500 mm

After 74 min, $p(O_2) : p(g)$ 1271.5 : 1500

Also, in a mixture, partial pressure   number of moles

$n(O_2) : n(g)$ 1 : 1.18

93. First we determine empirical formula as

	C	H
Weight	10.5	1
Mole	$\frac{10.5}{12}$ 0.875	1
Simple ratio	1	1/0.875 = 1.14
Whole no.	7	8

Empirical formula C_7H_8

From gas equation : $pV \quad \dfrac{w}{M} \quad RT$

$$M \quad \frac{wRT}{pV} \quad \frac{2.8 \quad 0.082 \quad 400}{1 \quad 1} \quad 91.84 \quad 92$$

∵ Molar mass (M) is same as empirical formula weight.

Molecular formula = Empirical formula C_7H_8

94. For same p and V, $n \quad \dfrac{1}{T}$

$$\frac{n(\text{gas})}{n(H_2)} \quad \frac{T\,(H_2)}{T\,(\text{gas})}$$

$$n(H_2) \quad \frac{0.184}{2} \quad 0.092$$

$$n(\text{gas}) \quad \frac{290}{298} \quad 0.092 = 0.0895$$

∵ 0.0895 mole of gas weigh 3.7 g

1 mole of gas will weigh $\dfrac{3.7}{0.0895}$ 41.32 g

95. Moles of CO_2 can be calculated using ideal gas equation as :

$$n \quad \frac{pV}{RT} \quad \frac{700}{760} \quad \frac{1336}{1000} \quad \frac{1}{0.082 \quad 300} \quad 0.05$$

Also, the decomposition reaction is :

$$\underset{0.05\ \text{mol}}{MCO_3} \qquad \underset{0.05\ \text{mol}}{MO + CO_2}$$

∵ 0.05 mole MCO_3 4.21 5 g

1.0 mole MCO_3 $\dfrac{4.215}{0.05}$ = 84.3 g (molar mass)

84.3   MW of M + 12 + 48

Molecular weight of metal   24.3

∵ Metal is bivalent, equivalent weight

$\dfrac{\text{Molecular weight}}{2}$ 12.15

96. The ideal gas equation :

$$pV \quad nRT \quad \frac{w}{M} RT$$

$$pM \quad \frac{w}{V} RT \quad dRT \text{ where, 'd' is density.}$$

$$d \quad \frac{pM}{RT} \quad \frac{5 \quad 17}{0.082 \quad 303} \quad 3.42 \text{ g L}^{1}.$$

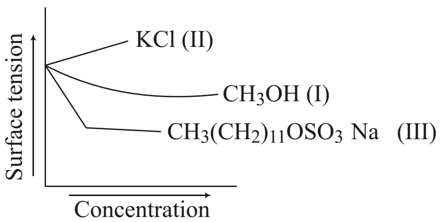
Topic 2 Liquid State

1. I (CH_3OH) : Surface tension decreases as concentration increases.

II (KCl) : Surface tension increases with concentration for ionic salt.

III [$CH_3(CH_2)_{11}OSO_3\ Na^+$] : It is an anionic detergent.

There is decrease in surface tension before micelle formation, and after CMC (Critical Micelle Concentration) is attained, no change in surface tension.



2. Let us consider, 1.0 L of liquid water is converted into steam .

Volume of $H_2O\,(l)$ 1 L, mass   1000 g

Volume of 1000 g steam $\dfrac{1000}{0.0006}$ cm^3

∵ Volume of molecules in $\dfrac{1000}{0.0006}$ cm^3 steam = 1000 cm^3

Volume of molecules in

1000 cm^3 steam = $\dfrac{1000}{1000}$ 0.0006   1000 = 0.60 cm^3

3. Critical temperature is directly proportional to intermolecular force of attraction. H_2O is a polar molecule, has greater intermolecular force of attraction than O_2, hence higher critical temperature.

4. At liquid-vapour equilibrium at boiling point, molecules in two phase posses the same kinetic energy.

6

Chemical and Ionic Equilibrium

Topic 1 Chemical Equilibrium

Objective Questions I (Only one correct option)

1. The incorrect match in the following is **(2019 Main, 12 April II)**

(a) $G \quad 0, K \quad 1$ (b) $G \quad 0, K \quad 1$
(c) $G \quad 0, K \quad 1$ (d) $G \quad 0, K \quad 1$

2. In which one of the following equilibria, $K_p \quad K_c$? **(2019 Main, 12 April II)**

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

3. For the reaction,

$2SO_2(g) \quad O_2(g) \qquad 2SO_3(g), \quad H \quad 57.2$ kJ mol ^{1} and $K_c \quad 1.7 \quad 10^{16}$. Which of the following statement is incorrect? **(2019 Main, 10 April II)**

(a) The equilibrium constant decreases as the temperature increases
(b) The addition of inert gas at constant volume will not affect the equilibrium constant
(c) The equilibrium will shift in forward direction as the pressure increases
(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required

4. For the following reactions, equilibrium constants are given :

$$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 \quad 10^{52}$$
$$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 \quad 10^{129}$$

The equilibrium constant for the reaction,

$$2SO(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ is}$$ **(2019 Main, 8 April II)**

(a) 10^{25} (b) 10^{77} (c) 10^{154} (d) 10^{181}

5. In a chemical reaction, $A \quad 2B \overset{K}{\rightleftharpoons} 2C \quad D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is **(2019 Main, 12 Jan I)**

(a) $\frac{1}{4}$ (b) 16 (c) 1 (d) 4

6. Two solids dissociate as follows:

$$A(s) \rightleftharpoons B(g) \quad C(g); \; K_{p_1} \quad x \text{ atm}^2$$
$$D(s) \rightleftharpoons C(g) \quad E(g); \; K_{p_2} \quad y \text{ atm}^2$$

The total pressure when both the solids dissociate simultaneously is **(2019 Main, 12 Jan I)**

(a) $\sqrt{x \quad y}$ atm (b) $x^2 \quad y^2$ atm
(c) $(x \quad y)$ atm (d) $2(\sqrt{x \quad y})$ atm

7. Consider the reaction,

$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{total}$ at equilibrium) **(2019 Main, 11 Jan I)**

(a) $\frac{3^{3/2}K_p^{1/2}P^2}{4}$ (b) $\frac{3^{3/2}K_p^{1/2}P^2}{16}$

(c) $\frac{K_p^{1/2}P^2}{16}$ (d) $\frac{K_p^{1/2}P^2}{4}$

8. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327 C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327 C is ($R = 0.082$ atm mol ^{1}K ^{1}, molar mass of S 32 g mol ^{1}, molar mass of N 14 g mol ^{1}) **(2019 Main, 10 Jan II)**

(a) $0.242 \quad 10^{4}$ atm^2 (b) 0.242 atm^2
(c) $4.9 \quad 10^{3}$ atm^2 (d) $1 \quad 10^{4}$ atm^2

9. The values of $\frac{K_p}{K_C}$ for the following reactions at 300 K are, respectively (At 300 K, $RT \quad 24.62$ dm^3 atm mol ^{1})

$$N_2(g) \quad O_2(g) \rightleftharpoons 2NO(g)$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(2019 Main, 10 Jan I)

(a) 1, 24.62 dm^3 atm $mol^{\ 1}$, 606.0 dm^6 atm^2 $mol^{\ 2}$
(b) 1, 24.62 dm^3 atm $mol^{\ 1}$, 1.65 $10^{\ 3}$ $dm^{\ 6}$ $atm^{\ 2}$ mol^2
(c) 24.62 dm^3 atm $mol^{\ 1}$, 606.0 dm^6 $atm^{\ 2}$ mol^2, 1.65 $10^{\ 3}$ $dm^{\ 6}$ $atm^{\ 2}$ mol^2
(d) 1, 4.1 $10^{\ 2}$ $dm^{\ 3}$atm ^{1} mol, 606 dm^6 atm^2 $mol^{\ 2}$

10 Consider the following reversible chemical reactions,

$$A_2(g) \quad B_2(g) \xrightleftharpoons{K_1} 2AB(g) \qquad \ldots\text{(i)}$$

$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) \quad 3B_2(g) \qquad \ldots\text{(ii)}$$

The relation between K_1 and K_2 is **(2019 Main, 9 Jan II)**

(a) $K_2 \quad K_1^3$
(b) $K_1K_2 \quad 3$
(c) $K_2 = K_1^{\ 3}$
(d) $K_1K_2 \quad \frac{1}{3}$

11. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS from H_2S is 1.0 $10^{\ 7}$ and that of S^2 from HS ions is 1.2 $10^{\ 13}$ then the concentration of S^2 ions in aqueous solution is : **(2018 Main)**

(a) 5 $10^{\ 8}$
(b) 3 $10^{\ 20}$
(c) 6 $10^{\ 21}$
(d) 5 $10^{\ 19}$

12. The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1 M each, then equilibrium concentration of D (in mol $L^{\ 1}$) will be **(2016 Main)**

(a) 0.818
(b) 1.818
(c) 1.182
(d) 0.182

13. The standard Gibbs energy change at 300 K for the reaction, $2A \rightleftharpoons B \quad C$ is 2494. 2 J. At a given time, the composition of the reaction mixture is $[A] \quad \frac{1}{2}$, $[B] \quad 2$ and $[C] \quad \frac{1}{2}$. The reaction proceeds in the

(R 8.314 JK / mol, e = 2.718) **(2015, Main)**

(a) forward direction because $Q \quad K_c$
(b) reverse direction because $Q \quad K_c$
(c) forward direction because $Q \quad K_c$
(d) reverse direction because $Q \quad K_c$

14. For the reaction, $SO_2(g) \quad \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

if $K_p \quad K_C(RT)^x$ where, the symbols have usual meaning, then the value of x is (assuming ideality) **(2014 Main)**

(a) 1
(b) $\frac{1}{2}$
(c) $\frac{1}{2}$
(d) 1

15. The species present in solution when CO_2 is dissolved in water are **(2006 Main)**

(a) CO_2, H_2CO_3, HCO_3, CO_3^2
(b) H_2CO_3, CO_3^2
(c) HCO_3, CO_3^2
(d) CO_2, H_2CO_3

16. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition? **(2006, 3M)**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics, the entropy must increases in the direction of spontaneous reaction
(b) The condition for equilibrium is $G(N_2)$ + $3G(H_2)$ = $2G(NH_3)$ where, G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent
(c) The catalyst will increase the rate of forward reaction by and that of backward reaction by
(d) Catalyst will not alter the rate of either of the reaction

17. Ag $NH_3 \rightleftharpoons [Ag(NH_3)]^+$; K_1 3.5 $10^{\ 3}$

$[Ag(NH_3)] \quad NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; K_2 1.7 $10^{\ 3}$

then the formation constant of $[Ag(NH_3)_2]$ is **(2006, 3M)**

(a) 6.08 $10^{\ 6}$
(b) 6.08 10^6
(c) 6.08 $10^{\ 9}$
(d) None of these

18. Consider the following equilibrium in a closed container

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation ( )? **(2002, 3M)**

(a) Neither K_p nor changes
(b) Both K_p and change
(c) K_p changes but does not change
(d) K_p does not change but changes

19. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is expressed by $K_p \quad \frac{4x^2p}{(1 \quad x^2)}$, where, p pressure, x extent of decomposition. Which one of the following statement is true? **(2001, 1M)**

(a) K_p increases with increase of p
(b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in p and x

20. When two reactants, A and B are mixed to give products, C and D, the reaction quotient, (Q) at the initial stages of the reaction **(2000)**

(a) is zero
(b) decreases with time
(c) is independent of time
(d) increases with time

21. For the reversible reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 500 C, the value of K_p is 1.44 10^{-5} when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol/L is **(2000, S, 1M)**

(a) $\dfrac{1.44 \quad 10^{\;5}}{(0.082 \quad 500)^{\;2}}$ (b) $\dfrac{1.44 \quad 10^{\;5}}{(8.314 \quad 773)^{\;2}}$

(c) $\dfrac{1.44 \quad 10^{\;5}}{(0.082 \quad 773)^{2}}$ (d) $\dfrac{1.44 \quad 10^{-5}}{(0.082 \quad 773)^{\;2}}$

22. For the chemical reaction,

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

the amount of X_3Y at equilibrium is affected by **(1999, 2M)**

(a) temperature and pressure
(b) temperature only
(c) pressure only
(d) temperature, pressure and catalyst

23. For the reaction ,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$

at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by **(1998)**

(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of $CO(g)$

24. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is **(1996, 1M)**

(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

25. An example of a reversible reaction is **(1985, 1M)**

(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \quad PbI_2(s) + 2NaNO_3(aq)$
(b) $AgNO_3(aq) + HCl(aq) \quad AgCl(s) + HNO_3(aq)$
(c) $2Na(s) + 2H_2O(l) = 2NaOH(aq) + H_2(g)$
(d) $KNO_3(aq) + NaCl(aq) \quad KCl(aq) \quad NaNO_3(aq)$

26. Pure ammonia is placed in a vessel at a temperature where its dissociation constant ( ) is appreciable. At equilibrium,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$ **(1984, 1M)**

(a) K_p does not change significantly with pressure
(b) does not change with pressure
(c) concentration of NH_3 does not change with pressure
(d) concentration of hydrogen is less than that of nitrogen

27. For the reaction, $H_2(g) \quad I_2(g) \rightleftharpoons 2HI(g)$

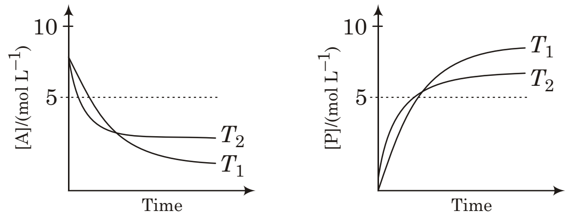
the equilibrium constant K_p changes with **(1981, 1M)**

(a) total pressure
(b) catalyst
(c) the amount of H_2 and I_2 present
(d) temperature

Objective Questions II

(One or more than one correct option)

28. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.



If $T_2 \quad T_1$, the correct statement(s) is are

(Assume $H^\ominus$ and $S^\ominus$ are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2 / T_1. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.) **(2018 Adv.)**

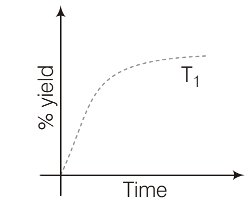
(a) $H^\ominus \quad 0, \; S^\ominus \quad 0$ (b) $G^\ominus \quad 0, \; H^\ominus \quad 0$

(c) $G^\ominus \quad 0, \; S^\ominus \quad 0$ (d) $G^\ominus \quad 0, \; S^\ominus \quad 0$

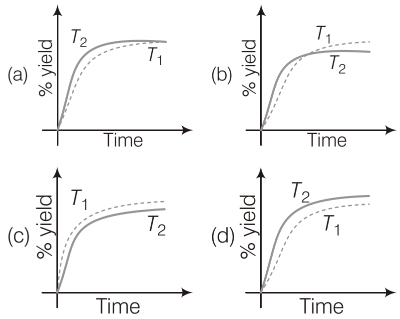
29. The % yield of ammonia as a function of time in the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad H < 0$ **(2015 adv.)**

at (p, T_1) is given below.



If this reaction is conducted at (p, T_1), with $T_2 > T_1$ the % yield by of ammonia as a function of time is represented by



30. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a (HA) is **(2013 Adv.)**

(a) $1 \quad 10^{\;4}$ (b) $1 \quad 10^{\;5}$

(c) $1 \quad 10^{\;6}$ (d) $1 \quad 10^{\;3}$

31. The equilibrium $2\,Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$ in aqueous medium at 25 C shifts towards the left in the presence of **(2011)**

(a) NO_3 (b) Cl (c) SCN (d) CN

32. For the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ the forward reaction at constant temperature is favoured by **(1991, 1M)**

(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

33. The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25 C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct? **(1989, 1M)**

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) None of the above

34. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, **(1986, 1M)**

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

35 For the gas phase reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \qquad (\ H \quad 32.7 \text{ kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by **(1984, 1M)**

(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

Fill in the Blanks

36. For a gaseous reaction $2B \qquad A$, the equilibrium constant K_p is …… to/than K_c. **(1997 C, 1M)**

37. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium, results in .... in K_p. **(1996, 1M)**

38. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are related by ….. **(1994, 1M)**

True/False

39. The rate of an exothermic reaction increases with increasing temperature. **(1993, 1M)**

40. Catalyst makes a reaction more exothermic. **(1987, 1M)**

41. If equilibrium constant for the reaction, $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $\frac{1}{K}$. **(1984, 1M)**

42. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **(1984, 1M)**

Subjective Questions

43. (a) In the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ when 5 moles of each are taken, the temperature is kept at 298 K the total pressure was found to be 20 bar. Given that

$$G_f(N_2O_4) \quad 100\text{kJ}, \quad G_f(NO_2) \quad 50\text{ kJ}$$

(i) Find G of the reaction.
(ii) The direction of the reaction in which the equilibrium shifts.

(b) A graph is plotted for a real gas which follows van der Waals' equation with pV_m taken on Y-axis and p on X-axis. Find the intercept of the line where V_m is molar volume. **(2004, 4M)**

44. When 3.06 g of solid NH_4SH is introduced into a two litre evacuated flask at 27 C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_c and K_p for the reaction at 27°C.
(ii) What would happen to the equilibrium when more solid NH_4SH is introduced into the flask? **(1999, 7M)**

45. (a) The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atm (relative atomic mass of P 31.0 and Cl 35.5).

(b) Given, $[Ag(NH_3)_2^+] \rightleftharpoons Ag^+ + 2NH_3$,

$K_c \quad 6.2 \quad 10^{8}$ and K_{sp} of AgCl

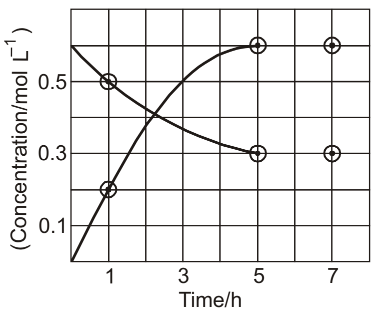
$1.8 \quad 10^{10}$ at 298 K.

If ammonia is added to a water solution containing excess of AgCl(s) only. Calculate the concentration of the complex in 1.0 M aqueous ammonia. **(1998, 3M+5M)**

46. The progress of reaction,

$$A \rightleftharpoons nB$$

with time, is represented in fig. use given below.



Determine :

(i) the value of n
(ii) the equilibrium constant, K and
(iii) the initial rate of conversion of A. **(1994, 3M)**

47. 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed.

Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. **(1993, 5M)**

48. For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

hydrogen gas is introduced into a five litre flask at 327 C, containing 0.2 mole of $CO(g)$ and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constant, K_p and K_c. **(1990, 5M)**

49. The equilibrium constant K_p of the reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. **(1989, 3M)**

50. N_2O_4 is 25% dissociated at 37 C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 37 C. **(1988, 4M)**

51. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction;

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2? **(1987, 5M)**

52. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K? **(1985, 4M)**

53. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 L vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$ **(1984, 6M)**

54. One mole of nitrogen is mixed with three moles of hydrogen in a four litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g), \text{ then}$$

calculate the equilibrium constant, K_c in concentration units. What will be the value of K_c for the following equilibrium?

$$\frac{1}{2}N_2(g) \quad \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$ **(1981, 4M)**

Passage Based Questions

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $_rG$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by . Thus, $_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given, $R \quad 0.083$ L bar K^{1} mol^{1})

55. The equilibrium constant K_p for this reaction at 298 K, in terms of $_{\text{equilibrium}}$ is **(2016 Adv.)**

(a) $\dfrac{8 \; ^2_{\text{equilibrium}}}{2 \quad _{\text{equilibrium}}}$ (b) $\dfrac{8 \; ^2_{\text{equilibrium}}}{4 \quad ^2_{\text{equilibrium}}}$

(c) $\dfrac{4 \; ^2_{\text{equilibrium}}}{2 \quad _{\text{equilibrium}}}$ (d) $\dfrac{4 \; ^2_{\text{equilibrium}}}{4 \quad ^2_{\text{equilibrium}}}$

56. The incorrect statement among the following for this reaction, is **(2016 Adv.)**

(a) Decrease in the total pressure will result in the formation of more moles of gaseous X

(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(c) $_{\text{equilibrium}} \quad 0.7$

(d) $K_C \quad 1$

Topic 2 Ionic Equilibrium

Objective Questions I (Only one correct option)

1. The molar solubility of Cd $(OH)_2$ is 1.84 10^{5}m in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH 12 is **(2019 Main, 12 April II)**

(a) 1.84 10^{9} M (b) $\dfrac{2.49}{1.84}$ 10^{9} M

(c) 6.23 10^{11} M (d) 2.49 10^{10} M

2. What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3$ 2.4 10^{24} **(2019 Main, 12 April II)**

(a) 3 10^{19}

(b) 12 10^{21}

(c) 3 10^{22}

(d) 12 10^{23}

3. The pH of a 0.02 M NH_4Cl solution will be [Given $K_b(NH_4OH)\quad 10^{5}$ and $\log 2\quad 0.301$] **(2019 Main, 10 April II)**

(a) 4.65 (b) 2.65 (c) 5.35 (d) 4.35

4. Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

II. Ionic product of water is temperature dependent.

III. A monobasic acid with $K_a\quad 10^{5}$ has a pH 5. The degree of dissociation of this acid is 50%.

IV. The Le-Chatelier's principle is not applicable to common-ion effect.

The correct statements are **(2019 Main, 10 April I)**

(a) I, II and IV (b) II and III

(c) I and II (d) I, II and III

5. If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct? **(2019 Main, 8 April I)**

(a) $S\quad \frac{K_{sp}}{144}^{1/6}$ (b) $S\quad \frac{K_{sp}}{6912}^{1/7}$

(c) $S\quad \frac{K_{sp}}{929}^{1/9}$ (d) $S\quad \frac{K_{sp}}{216}^{1/7}$

6. If K_{sp} of Ag_2CO_3 is $8\quad 10^{12}$, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is **(2019 Main, 12 Jan II)**

(a) $8\quad 10^{12}$ M (b) $8\quad 10^{13}$ M

(c) $8\quad 10^{10}$ M (d) $8\quad 10^{11}$ M

7. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is [pK_b of $NH_4OH = 4.7$] **(2019 Main, 9 Jan I)**

(a) 9.3 (b) 5.0 (c) 9.0 (d) 5.2

8. An aqueous solution contains an unknown concentration of Ba^{2} . When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is $1\quad 10^{10}$. What is the original concentration of Ba^{2} ? **(2018 Main)**

(a) $5\quad 10^{9}$ M (b) $2\quad 10^{9}$ M

(c) $1.1\quad 10^{9}$ M (d) $1.0\quad 10^{10}$ M

9. Which of the following are Lewis acids? **(2018 Main)**

(a) PH_3 and BCl_3 (b) $AlCl_3$ and $SiCl_4$

(c) PH_3 and $SiCl_4$ (d) BCl_3 and $AlCl_3$

10. Which of the following salts is the most basic in aqueous solution? **(2018 Main)**

(a) $Al(CN)_3$ (b) CH_3COOK

(c) $FeCl_3$ (d) $Pb(CH_3COO)_2$

11. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is **(2017 Main)**

(a) 7.2 (b) 6.9 (c) 7.0 (d) 1.0

12. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(2013 Main)**

(a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L

13. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are $4.0\quad 10^{8}$, $3.2\quad 10^{14}$ and $2.7\quad 10^{15}$, respectively. Solubilities (mol dm^{3}) of the salts at temperature 'T' are in the order **(2008, 3M)**

(a) $MX\quad MX_2\quad M_3X$ (b) $M_3X\quad MX_2\quad MX$

(c) $MX_2\quad M_3X\quad MX$ (d) $MX\quad M_3X\quad MX_2$

14. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1\quad 10^{12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1\quad 10^{14}$ at 25°C) **(2008, 3M)**

(a) $3.7\quad 10^{13}$ M (b) $3.2\quad 10^{7}$ M

(c) $3.2\quad 10^{2}$ M (d) $2.7\quad 10^{2}$ M

15. CH_3NH_2 (0.1 mole, $K_b\quad 5\quad 10^{4}$) is added to 0.08 mole of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is **(2005, 1M)**

(a) $1.6\quad 10^{11}$ (b) $8\quad 10^{11}$

(c) $5\quad 10^{5}$ (d) $8\quad 10^{2}$

16. HX is a weak acid ($K_a\quad 10^{5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is **(2004, 1M)**

(a) 0.01% (b) 0.0001%

(c) 0.1% (d) 0.5%

17. A solution which is 10^{3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{15}, 10^{23}, 10^{20} and 10^{54} respectively, which one will precipitate first? **(2003, 1M)**

(a) FeS (b) MgS (c) HgS (d) ZnS

18. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium. **(2002)**

(a) CuS > ZnS > Na_2S (b) ZnS > Na_2S > CuS

(c) Na_2S > CuS > ZnS (d) Na_2S > ZnS > CuS

19. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is **(2001, 1M)**

(a) $L_s\quad S^{p+q}\quad p^p\quad q^q$ (b) $L_s\quad S^{p+q}\quad p^q\quad q^p$

(c) $L_s\quad S^{pq}\quad p^p\quad q^q$ (d) $L_s\quad S^{pq}\quad (p.q)^{(p\quad q)}$

20. The pH of 0.1 M solution of the following salts increases in the order **(1999, 2M)**

(a) NaCl < NH_4Cl < NaCN < HCl

(b) HCl < NH_4Cl < NaCl < NaCN

(c) NaCN < NH_4Cl < NaCl < HCl

(d) HCl < NaCl < NaCN < NH_4Cl

21. Which of the following solutions will have pH close to 1.0 ? **(1992, 1M)**

(a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
(b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH

22. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25 C) is **(1990, 1M)**

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$

23. Which of the following is the strongest acid? **(1989, 1M)**

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

24. When equal volumes of the following solutions are mixed, precipitation of AgCl (K_{sp} 1.8 10^{10}) will occur only with **(1988, 1M)**

(a) 10^{4} M (Ag^+) and 10^{4} M (Cl)
(b) 10^{5} M (Ag^+) and 10^{5} M (Cl)
(c) 10^{6} M (Ag^+) and 10^{6} M (Cl)
(d) 10^{10} M (Ag^+) and 10^{10} M (Cl)

25. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be **(1988, 1M)**

(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

26. The compound that is not a Lewis acid is **(1985, 1M)**

(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$

27. The conjugate acid of NH_2^- is **(1985, 1M)**

(a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4

28. The best indicator for detection of end point in titration of a weak acid and a strong base is **(1985, 1M)**

(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenolphthalein (8 to 9.6)

29. A certain weak acid has a dissociation constant of 1.0 10^{4}. The equilibrium constant for its reaction with a strong base is **(1984, 1M)**

(a) 1.0 10^{4} (b) 1.0 10^{10}
(c) 1.0 10^{10} (d) 1.0 10^{14}

30. A certain buffer solution contains equal concentration of X and HX. The K_b for X is 10^{10}. The pH of the buffer is **(1984, 1M)**

(a) 4 (b) 7
(c) 10 (d) 14

31. The precipitate of CaF_2, (K_{sp} 1.7 10^{10}) is obtained, when equal volumes of which of the following are mixed? **(1982, 1M)**

(a) 10^{4} M Ca^{2} 10^{4} M F
(b) 10^{2} M Ca^{2} 10^{3} M F
(c) 10^{5} M Ca^{2} 10^{3} M F
(d) 10^{3} M Ca^{2} 10^{5} M F

32. An acidic buffer solution can be prepared by mixing the solution of **(1981, 1M)**

(a) acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

33. Of the given anions, the strongest base is **(1981, 1M)**

(a) ClO (b) ClO_2
(c) ClO_3 (d) ClO_4

34. At 90°C, pure water has [H_3O] as 10^{6} mol L^{1}. What is the value of K_w at 90°C ? **(1981, 1M)**

(a) 10^{6} (b) 10^{12} (c) 10^{14} (d) 10^{8}

35. The pH of 10^{8} M solution of HCl in water is **(1981, 1M)**

(a) 8 (b) 8
(c) between 7 and 8 (d) between 6 and 7

Objective Questions II

(One or more than one correct option)

36. The K_{sp} of Ag_2CrO_4 is 1.1 10^{12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is

(a) 1.1 10^{11} (b) 1.1 10^{10}
(c) 1.1 10^{12} (d) 1.1 10^{9} **(2013 Adv.)**

37. Aqueous solutions of HNO_3 KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) **(2010)**

(a) HNO_3 and CH_3COOH
(b) KOH and CH_3COONa
(c) HNO_3 and CH_3COONa
(d) CH_3COOH and CH_3COONa

38. A buffer solution can be prepared from a mixture of **(1999, 3M)**

(a) sodium acetate and acetic acid in water
(b) sodium acetate and HCl in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

39. Which of the following statement(s) is (are) correct?

(a) The pH of $1.0 \quad 10^{\ 8}$ M solution of HCl is 8 **(1998, 2M)**

(b) The conjugate base of H_2PO_4 is HPO_4^2

(c) Autoprotolysis constant of water increases with temperature

(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point $pH = \frac{1}{2}\ pK_a$

Numerical Value Based Question

40. The solubility of a salt of weak acid (AB) at pH 3 is $Y \quad 10^{\ 3}$ mol $L^{\ 1}$. The value of Y is__ (Given that the value of solubility product of AB (K_{sp}) $\ 2 \quad 10^{\ 10}$ and the value of ionisation constant of HB (K_a) $\ 1 \quad 10^{\ 8}$ **(2018 Adv.)**

Matrix Match Type

41. Dilution processes of different aqueous solutions, with water, are given in List-I. The effects of dilution of the solution on [H] are given in List-II.

Note Degree of dissociation ( ) of weak acid and weak base is 1; degree of hydrolysis of salt 1; [H] represents the concentration of H ions

	List-I		List-II
P.	(10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1.	the value of [H] does not change on dilution
Q.	(20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2.	the value of [H] changes to half of its initial value on dilution
R.	(20 mL of 0.1M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3.	the value of [H] changes to two times of its initial value on dilution.
S.	10 mL saturated solution of $Ni(OH)_2$ in equilibrium with exces solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	4.	the value of [H] changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
		5.	the value of [H] changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in List-I with one or more effect(s) in List-II. The correct option is **(2018 Adv.)**

(a) P 4; Q 2; R 3; S 1

(b) P 4; Q 3; R 2; S 3

(c) P 1; Q 4; R 5; S 3

(d) P 1; Q 5; R 4; S 1

Fill in the Blanks

42. In the reaction, I + I_2 I_3, the Lewis acid is .... **(1997, 1M)**

43. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy. **(1987, 1M)**

44. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be.................. **(1984, 1M)**

45. The conjugate base of HSO_4^- in aqueous solution is …… **(1982, 1M)**

True/False

46. The following species are in increasing order of their acidic property : ZnO, Na_2O_2, P_2O_5, MgO. **(1985, 1/2M)**

47. Solubility of sodium hydroxide increases with increase in temperature. **(1985, 1/2M)**

48. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(1982, 1M)**

Integer Answer Type Questions

49. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\ ^0_X \quad ^0_Y$, the difference in their pK_a values, pK_a (HX) pK_a (HY), is (consider degree of ionisation of both acids to be <<1). **(2015 Adv.)**

50. In 1 L saturated solution of AgCl [K_{sp}(AgCl) $1.6 \quad 10^{\ 10}$], 0.1 mole of CuCl [K_{sp}(CuCl) = $1.0 \quad 10^{\ 6}$] is added. The resultant concentration of Ag in the solution is $1.6 \quad 10^{\ x}$. The value of 'x' is **(2011)**

51. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN	K_2SO_4	$(NH_4)_2C_2O_4$	NaCl
$Zn(NO_3)_2$	$FeCl_3$	K_2CO_3	NH_4NO_3
LiCN			

(2010)

Subjective Questions

52. The dissociation constant of a substituted benzoic acid at 25°C is $1.0 \quad 10^{\ 4}$. The pH of 0.01 M solution of its sodium salt is **(2009)**

53. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given, K_a (HA) = $5 \quad 10^{\ 6}$ and 1. **(2004)**

54. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 250°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH (assuming there is no change in volume on mixing, K_a of acetic acid is $1.75 \quad 10^{5}$ mol/L. **(1984, 1M)**

55. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol/L and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(2000, 5M)**

56. The solubility of $Pb(OH)_2$ in water is $6.7 \quad 10^{6}$ M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH 8. **(1999, 4M)**

57. (a) Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell Ag|Ag^+ (saturated. Ag_2CrO_4 solution.) || Ag^+ (0.1 M) | Ag is 0.164 V at 298 K. **(1998, 6M)**

(b) What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH 12.0)? **(1998, 6M)**

58. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- ions per litre. Calculate the solubility product of AgCl. [K_{sp} (Ag_2CO_3) $8.2 \quad 10^{12}$] **(1997, 5M)**

59. An acid type indicator, HIn differs in colour from its conjugate base (In). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change? ($K_a \quad 1.0 \quad 10^{5}$) **(1997, 2M)**

60. The ionisation constant of NH_4^+ in water is $5.6 \quad 10^{10}$ at 25 C. The rate constant for the reaction of NH_4^+ and OH to form NH_3 and H_2O at 25 C is $3.4 \quad 10^{10}$ L/mol/s. Calculate the rate constant per proton transfer from water to NH_3. **(1996, 3M)**

61. What is the pH of a 0.50 M aqueous NaCN solution?
(pK_b of CN 4.70). **(1996, 2M)**

62. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.
(pK_a of formic acid 3.8 and pK_b of ammonia 4.8) **(1995, 2M)**

63. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ \quad 2CN$

The equilibrium constant, at 25 C, is $4.0 \quad 10^{19}$. Calculate the silver ion concentration in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$. **(1994, 3M)**

64. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? K_{sp} for MS $6.0 \quad 10^{21}$, concentration of saturated H_2S 0.1 M, $K_1 \quad 10^{7}$ and $K_2 \quad 1.3 \quad 10^{13}$, for H_2S. **(1993, 3M)**

65. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.4? (K_a for H_2CO_3 in blood is $7.8 \quad 10^{7}$) **(1993, 2M)**

66. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25 C is $4.42 \quad 10^{5}$. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated? **(1992, 4M)**

67. A 40 mL solution of a weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. **(1991, 6M)**

68. The solubility product of $Ag_2C_2O_4$ at 25 C is $1.29 \quad 10^{11} mol^3L^{3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at 25 C with excess of Ag_2CO_3 till the following equilibrium is reached

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. **(1991, 4M)**

69. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given, $K_a \quad 1.8 \quad 10^{5}$ **(1990, 4M)**

70. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution.

$$K_b[NH_4OH] \quad 1.8 \quad 10^{5}$$
$$K_{sp}[Mg(OH)_2] \quad 8.9 \quad 10^{12}$$
$$K_{sp}[Al(OH)_3] \quad 6 \quad 10^{32}$$

(1989, 3M)

71. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 g formula weight of NaCN?

$K_{HCN} \quad 4.1 \quad 10^{10}$ **(1988, 4M)**

72. What is the pH of the solution when 0.20 mole of HCl is added to one litre of a solution containing
(i) 1 M each of acetic acid and acetate ion,
(ii) 0.1 M each of acetic acid and acetate ion?
Assume the total volume is one litre.
K_a for acetic acid $1.8 \quad 10^{5}$. **(1987, 5M)**

73. The solubility of $Mg(OH)_2$ in pure water is $9.57 \quad 10^{3}$ g/L. Calculate its solubility (in g/L) in 0.02 M $Mg(NO_3)_2$ solution. **(1986, 5M)**

74. The concentration of hydrogen ions in a 0.20 M solution of formic acid is $6.4 \quad 10^{3}$ mol/L. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre.

What will be the pH of this solution? The dissociation constant of formic acid is $2.4 \quad 10^{4}$ and the degree of dissociation of sodium formate is 0.75. **(1985, 3M)**

75. A solution contains a mixture of Ag (0.10 M) and Hg^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated? **(1984, 4M)**
K_{sp} : AgI $8.5 \quad 10^{17}$, HgI_2 $2.5 \quad 10^{26}$

76. The dissociation constant of a weak acid HA is $4.9 \quad 10^{8}$. After making the necessary approximations, calculate
(i) pH
(ii) OH concentration in a decimolar solution of the acid. (Water has a pH of 7). **(1983, 2M)**

77. Give reason for the statement that "the pH of an aqueous solution of sodium acetate is more than seven". **(1982, 1M)**

78. 20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid solution to give 70 mL of the solution. What is the pH of this solution?

Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74.
(Ionisation constant of CH_3COOH $1.8 \quad 10^{5}$). **(1982, 3M)**

79. How many moles of sodium propionate should be added to 1 L of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 moles of HCl are dissolved in the above buffer solution? Compare the last pH value with the pH of 0.010 M HCl solution. Dissociation constant of propionic acid, K_a at 25°C is $1.34 \quad 10^{5}$. **(1981, 4M)**

Answers

Topic 1

1. (d)	**2.** (a)	**3.** (d)	**4.** (a)
5. (d)	**6.** (d)	**7.** (b)	**8.** (b)
9. (b)	**10.** (c)	**11.** (b)	**12.** (b)
13. (b)	**14.** (b)	**15.** (a)	**16.** (b)
17. (a)	**18.** (d)	**19.** (d)	**20.** (d)
21. (d)	**22.** (a)	**23.** (d)	**24.** (b)
25. (d)	**26.** (a)	**27.** (d)	**28.** (a,c)
29. (b)	**30.** (a)	**31.** (b, c, d)	**32.** (c, d, e)
33. (d)	**34.** (c, d)	**35.** (a, b, c, d)	**36.** smaller
37. no change	**38.** $K_p \quad K_c(RT)^{n}$		**39.** T
40. F	**41.** F	**42.** T	**46.** (1.2)
52. (1.86)	**53.** (0.33)	**55.** (b)	**56.** (c)

Topic 2

1. (d)	**2.** (c)	**3.** (c)	**4.** (d)
5. (b)	**6.** (c)	**7.** (a)	**8.** (c)
9. (d)	**10.** (b)	**11.** (b)	**12.** (d)
13. (d)	**14.** (d)	**15.** (b)	**16.** (a)
17. (c)	**18.** (d)	**19.** (a)	**20.** (b)
21. (d)	**22.** (d)	**23.** (a)	**24.** (a)
25. (d)	**26.** (c)	**27.** (a)	**28.** (d)
29. (c)	**30.** (a)	**31.** (b)	**32.** (a)
33. (a)	**34.** (b)	**35.** (d)	**36.** (b)
37. (c, d)	**38.** (a, b, c)	**39.** (b, c)	**40.** (4.47)
41. (d)	**42.** I_2	**43.** hydration	
44. amphoteric	**45.** SO_4^{2}	**46.** F	**47.** F
48. F	**49.** (3)	**50.** ($1.6 \quad 10^{7}$)	**52.** (8)
53. (9)	**55.** (4.86)	**56.** ($1.2 \quad 10^{3}$ M)	
58. ($2 \quad 10^{8}$)	**61.** (11.5)	**62.** (6.50)	**64.** (1)
65. (80)	**67.** ($1.8 \quad 10^{5}$)	**68.** ($9.67 \quad 10^{11}$)	**69.** ($27.78 \quad 10^{3}$)
71. (0.177)	**72.** ($8.7 \quad 10^{4}$ gL ^{1})		**74.** (4.20)
75. (99.83)	**77.** (>7)		

Hints & Solutions

Topic 1 Chemical Equilibrium

1. The incorrect match is $G \quad 0, K \quad 1$.

For an ideal gas $G \quad RT \ln K$.

$$\ln K \quad \frac{G}{RT} \quad \text{and} \quad K \quad e^{\;G\,/\,RT}$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $G \quad 0, - \;G\;/RT$ ve and $e^{\;G\;/\;RT} \quad 1$ and hence, $K \quad 1$. It means that the reaction occur spontaneously in the forward direction or products predominate over reactants.

(ii) If $G \quad 0; \quad G\;/RT$ ve and $e^{\;G\,/\,RT} \quad 1$ and hence, $K \quad 1$. It means that the reaction is non-spontaneous in forward direction (i.e. product side) but spontaneous in reverse direction (i.e. reactants predominate over products or the reaction occurs rarely).

(iii) When $K \quad 1$, then $G \quad 0$. This situation generally occur at equilibrium.

2.

> **Key Idea** The relationship between K_p and K_c is
>
> $$K_p \quad K_c(RT)^{\;n_g}$$
>
> where, $n_g \quad n_{\text{products}} \quad n_{\text{reactants}}$
>
> If $n_g \quad 0$ then $K_p \quad K_c$
>
> If n_g ve then $K_p \quad K_c$
>
> If n_g ve then $K_p \quad K_c$

Consider the following equilibria reactions

(a) $2C(s) \quad O_2(g) \rightleftharpoons 2CO(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad (1) \quad 1$

$n_g \quad 0$ So, $K_p \quad K_c$

(b) $2HI(g) \rightleftharpoons H_2(g) \quad I_2(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

(c) $NO_2(g) \quad SO_2(g) \rightleftharpoons NO(g) \quad SO_3(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

(d) $2NO(g) \rightleftharpoons N_2(g) \quad O_2(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

3. The explanation of given statements are as follows:

(a) For the given equilibrium, H is negative, so the equilibrium constant will decrease with increase in temperature and the equilibrium will shift in the backward direction.

Thus, statement (a) is correct.

(b) When inert gas is added at constant volume and constant temperature, an equilibrium remains undisturbed.

Thus, statement (b) is correct.

(c) For the equilibrium,

$$n_g \quad 2 \quad (2 \quad 1) \quad 1, \text{ i.e. } (\;\text{ve})$$

So, increase in pressure will shift the equilibrium in the forward direction.

Thus, statement (c) is correct.

(d) The reaction takes place in the presence of a catalyst which is $V_2O_5(s)$ in contact process or $NO(g)$ in chamber process.

Thus, statement (d) is incorrect.

4. $S + O_2 \rightleftharpoons SO_2, K_1$

$$SO_2 \rightleftharpoons S + O_2, K_1 \quad \frac{1}{K_1}$$

$$\text{or, } 2SO_2 \rightleftharpoons 2S + 2O_2, K_1 \quad (K_1\;)^2 \quad \frac{1}{K_1^2} \qquad \text{...(i)}$$

$$2S + 3O_2 \rightleftharpoons 2SO_3, K_2 \qquad \text{...(ii)}$$

Now, [(i) (ii)] gives

$$2SO_2 + O_2 \rightleftharpoons 2SO_3, K_3$$

The value of equilibrium constant,

$$K_3 \quad K_2 \quad K_1 \quad K_2 \quad \frac{1}{K_1^2}$$

$$10^{129} \quad \frac{1}{(10^{52})^2} \quad 10^{129 \quad 104} \quad 10^{25}$$

5. For the given chemical reaction,

	A	+	$2B$	$\rightleftharpoons$	$2C$	+	D
At, $t = 0$	a_0		$1.5a_0$		0		0
$t \quad t_{\text{eq}}$	$a_0 \quad x$		$1.5a_0 \quad 2x$		$2x$		x

[x degree of dissociation]

Given, at equilibrium.

$$[A] = [B]$$
$$a_0 \quad x \quad 1.5a_0 \quad 2x$$
$$x \quad 0.5a_0$$

$[A] \quad a_0 \quad x \quad a_0 \quad 0.5a_0 \quad 0.5a_0$

$[B] \quad 1.5a_0 \quad 2x \quad 1.5a_0 \quad 2 \quad 0.5a_0 \quad 0.5a_0$

$[C] \quad 2x \quad 2 \quad 0.5a_0 \quad a_0$

$[D] \quad x \quad 0.5a_0$

Now, $$K \quad \frac{[C]^2[D]}{[A]\,[B]^2}$$

Now, substituting the values in above equation, we get

$$K \quad \frac{(a_0)^2 \quad (0.5a_0)}{(0.5a_0) \quad (0.5a_0)} \quad 4$$

6. The equilibrium reaction for the dissociation of two solids is given as:

$$A(s) \rightleftharpoons \underset{p_1}{B(g)} + \underset{p_1 \;\; p_2}{C(g)}$$

At equilibrium

$$K_{p_1} = x \quad p_B \quad p_C = p_1(p_1 + p_2) \qquad \text{...(i)}$$

Similarly, $D(s) \rightleftharpoons C(g) + E(g)$

At equilibrium $\quad p_1 + p_2 \quad p_2$

$$K_{p_2} = y = p_C \quad p_E = (p_1 + p_2)p_2 \qquad \text{...(ii)}$$

On adding Eq. (i) and (ii), we get.

$$K_{p_1} + K_{p_2} = x \quad y \quad p_1(p_1 + p_2) + p_2(p_1 + p_2)$$
$$(p_1 + p_2)^2$$

or $\sqrt{x \quad y} \quad p_1 \quad p_2$ ...(iii)

Now, total pressure is given as

$$p_T = p_B + p_C + p_E$$
$$= p_1 + (p_1 + p_2) + p_2$$
$$= 2\,(p_1 + p_2) \qquad \text{...(iv)}$$

On substituting the value of $p_1 + p_2$ from Eq. (iii) to Eq. (iv), we get

$$p_T = 2\sqrt{x \quad y}$$

7. $N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium: $p_{N_2} \quad P, \quad p_{H_2} \quad 3P, \qquad p_{NH_3} \quad 2P$

$$p_{(\text{total})} \quad p_{N_2} \quad p_{H_2} \quad p_{NH_3} \sim p_{N_2} \quad p_{H_2}$$
$$[\because P_{(\text{total})} \quad p_{NH_3}]$$
$$p \quad 3p \quad 4p$$

Now, $\quad K_p \quad \dfrac{p^2_{NH_3}}{p_{N_2} \quad p^3_{H_2}} \quad \dfrac{p^2_{NH_3}}{p \quad (3p)^3}$

$$\frac{p^2_{NH_3}}{27 \quad p^4} \quad \frac{p^2_{NH_3}}{27 \quad \frac{P}{4}^{4}} \qquad [\because P \quad 4p]$$

$$K_p \quad \frac{p^2_{NH_3} \quad 4^4}{3^2 \quad 3 \quad P^4}$$

$$p^2_{NH_3} \quad \frac{3^2 \quad 3 \quad P^4 \quad K_p}{4^4}$$

$$p_{NH_3} \quad \frac{3 \quad 3^{1/2} \quad P^2 \quad K_p^{1/2}}{4^2} \quad \frac{3^{3/2} \quad P^2 \quad K_p^{1/2}}{16}$$

8. Molar mass of $NH_4SH \quad 18 \quad 33 \quad 51\,\text{g mol}^{\ 1}$

Number of moles of NH_4SH introduced in the vessel

$$\frac{\text{Weight}}{\text{Molar mass}} \quad \frac{5 \ 1}{51} \quad 0.1\,\text{mol}$$

$$NH_4SH(s) \rightleftharpoons NH_3(g) \quad H_2S(g)$$

	$NH_4SH(s)$	$NH_3(g)$	$H_2S(g)$
Number of moles at t 0	0.1	0	0
At $t \quad t_{eq}$	0.1(1 0.03)	30% of 0.1 0.03	30% of 0.1 0.03
Active mass (mol L ^{1})		$\frac{0.03}{3}$ 0.01	$\frac{0.03}{3}$ 0.01

$$K_C \quad \frac{[NH_3][H_2S]}{[NH_4HS(s)]} \quad \frac{0.01 \quad 0.01}{1} \quad 10^{\ 4}\,(\text{mol L}^{\ 1})^2$$

$$K_p \quad K_C(RT)^{\ n_g}$$

[where, $n_g \quad n_{\text{product}} \quad n_{\text{reactant}}$] 2 0 2

$$K_p \quad K_C(RT)^2$$
$$10^{\ 4} \quad [0.082 \quad (273 \quad 327)]^2\ \text{atm}^2$$
$$0.242\ \text{atm}^2$$

9. We know that, the relationship between K_p and K_C of a chemical equilibrium state (reaction) is

$$K_p \quad K_C(RT)^{\ n_g} \qquad \frac{K_p}{K_C} \quad (RT)^{\ n_g}$$

where, $\quad n_g \quad n_{\text{Products}} \quad n_{\text{Reactants}}$

(i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$(RT)^{2 \ (1 \ 1)} \quad (RT)^0 \quad 1$$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$(RT)^{2 \ 1} \quad RT \quad 24.62\,\text{dm}^3\,\text{atm mol}^{\ 1}$$

(iii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$(RT)^{2 \ (3 \ 1)} \quad (RT)^{\ 2}$$
$$\frac{1}{(24.62\ \text{dm}^3\ \text{atm mol}^{\ 1})^2}$$
$$1.649 \quad 10^{\ 3}\ \text{dm}^{-6}\ \text{atm}^{\ 2}\ \text{mol}^2$$

10. (i) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g); \qquad K_1 \quad \dfrac{[AB]^2}{[A_2][B_2]}$

(ii) $6AB(g) \rightleftharpoons 3A_2(g) \quad 3B_2(g);$

$$K_2 \quad \frac{[A_2]^3[B_2]^3}{[AB]^6} \quad \frac{1}{\left(\dfrac{[AB]^2}{[A_2][B_2]}\right)^3} \quad \frac{1}{K_1^3},$$

$$K_2 \quad K_1^{\ 3}$$

11. Given $[H_2S] \quad 0.10\,\text{M}$

$[HCl] \quad 0.20\,\text{M}$ So, $[H \ ] \quad 0.20\,\text{M}$

$$H_2S \rightleftharpoons H^+ + HS \ , K_1 \quad 1.0 \quad 10^{\ 7}$$
$$HS \ \rightleftharpoons H^+ + S^2 \ , K_2 \quad 1.2 \quad 10^{\ 13}$$

It means for,

$$H_2S \rightleftharpoons 2H^+ + S^2$$
$$K \quad K_1 \quad K_2 \quad 1.0 \quad 10^{\ 7} \quad 1.2 \quad 10^{\ 13}$$
$$1.2 \quad 10^{\ 20}$$

Now $\quad [S^2 \ ] \quad \dfrac{K \quad [H_2S]}{[H \ ]^2}$ [according to the final equation]

$$\frac{1.2 \quad 10^{\ 20} \quad 0.1\ \text{M}}{(0.2\text{M})^2}$$
$$\frac{1.2 \quad 10^{\ 20} \quad 1 \quad 10^{\ 1}\ \text{M}}{4 \quad 10^{\ 2}\text{M}}$$
$$3 \quad 10^{\ 20}\text{M}$$

12. $A \ + \ B \rightleftharpoons C \ + \ D$

	A	B	C	D
Initially at t 0	1	1	1	1
At equilibrium	1 x	1 x	1 x	1 x

$$K_{eq} \quad \frac{[C][D]}{[A][B]} \quad \frac{(1 \quad x)(1 \quad x)}{(1 \quad x)(1 \quad x)} \quad \frac{(1 \quad x)^2}{(1 \quad x)^2}$$

or $\quad 100 \quad \left(\dfrac{1 \quad x}{1 \quad x}\right)^2 \quad$ or $\quad 10 \quad \dfrac{1 \quad x}{1 \quad x}$

or $\quad 10 \quad 10x \quad 1 \quad x$

$$10 \quad 1 \quad x \quad 10x$$
$$9 \quad 11x$$
$$x \quad \frac{9}{11} \quad 0.818$$
$$[D] \quad 1 \quad x \quad 1 \quad 0.818 \quad 1.818$$

13. Given, $G \quad 2494.2\ \text{J}$

$$Q \quad \frac{[B][C]}{[A]^2} \quad \frac{2 \quad \frac{1}{2}}{\frac{1}{2}^{\ 2}} \quad 4$$

We know, $G \quad G \quad RT \ln Q$

$2494.2 \quad 8.314 \quad 300 \ln 4$

28747.27 J (+ ve value)

Also, we have $G \quad RT \ln \frac{Q}{K}$

If G is positive, $Q \quad K$

Therefore, reaction shifts in reverse direction.

14. For the given reaction, $n_g = n_P \quad n_R$

where, n_P number of moles of products

n_R number of moles of reactants

$$K_p = K_c(RT)^{n_g}$$

$$n_g \quad \frac{1}{2}$$

15. When CO_2 is dissolved in water, following equilibria are established:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3$$
$$HCO_3 \rightleftharpoons H^+ + CO_3^2$$

Therefore, in solution, all of the above mentioned species exist.

16. At equilibrium, $G \quad 0$

G(reactants) G(products)

$G(N_2) + 3G(H_2) \quad 2G(NH_3)$

A catalyst does not affect either equilibrium composition or equilibrium constant, it just increases rate of both forward and backward reaction but by the same factor.

17.

$$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+] \qquad K_1 \quad 3.5 \quad 10^{3}$$
$$[Ag(NH_3)^+] + NH_3 \rightleftharpoons [Ag(NH_3)_2^+] \qquad K_2 \quad 1.7 \quad 10^{3}$$

Adding : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$K \quad K_1 \quad K_2 \quad 5.95 \quad 10^{6}$$

18.

$$\underset{1}{N_2O_4(g)} \rightleftharpoons \underset{2}{2NO_2(g)} \qquad \underset{1+}{\text{Total}}$$

$$p_i : \frac{1}{1}p \qquad \frac{2}{1}p \qquad K_p \quad \frac{4^{\ 2}}{1 \quad ^2}p$$

At constant temperature, halving the volume will change both p and but K_p remains constant.

19. $\underset{1 \quad x}{N_2O_4} \rightleftharpoons \underset{2x}{2NO_2}$, $K_p \quad \frac{4x^2 p}{1 \quad x^2}$. K_p is function of temperature only, does not change with either p or x.

20. $A \quad B \rightleftharpoons C \quad D$, $Q \quad \frac{[C][D]}{[A][B]}$

As time passes, amount of products 'C' and 'D' increases, hence Q increases.

21. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad n \quad 2$

$$K_p \quad K_c(RT)^{n}$$

$$K_c \quad \frac{K_p}{(RT)^{n}} \quad \frac{1.44 \quad 10^{5}}{(0.082 \quad 773)^{2}}$$

22. Both temperature and pressure will change the equilibrium amount of $X_3Y(g)$. Temperature changes the value of equilibrium constant.

23. Adding reactant will drive the reaction in forward direction in order to restore equilibrium. Therefore, addition of CO (g) will increase the equilibrium amount of CO_2.

24.

	$N_2O_4 \rightleftharpoons$	$2NO_2$	
At 300 K :	1.0 atm	0	
At 600 K :	2.0 – 0.40	0.80	Total pressure = 2.40 atm

25. In reactions (a), (b) and (c), atleast one of the product is either insoluble precipitate or a gas that drive the reaction continuously to right and do not allow equilibrium to be established. Following is the reversible reaction.

$$KNO_3(aq) + NaCl(aq) \rightleftharpoons KCl(aq) + NaNO_3(aq)$$

26. K_p for a given reversible reaction depends only on temperature.

27. Equilibrium constant of a given reversible reaction depends only on temperature.

28. For the reaction, $A \rightleftharpoons P$

Given, $T_1 < T_2$

$$\frac{\ln K_1}{\ln K_2} \quad \frac{T_2}{T_1} \qquad \ldots\text{(i)}$$

It shows, On increasing the temperature, K decreases so reaction is exothermic i.e., $H^\circ \quad 0$

Besides, graph shows $K > 1$

So $G^\circ < 0$

Now from equation (i)

$$T_1 \ln K_1 > T_2 \ln K_2$$
$$G^\circ_1 > \quad G^\circ_2$$

Likewise ($H^\circ + T_1 \quad S^\circ$) ($H^\circ + T_2 \quad S^\circ$)

or simply $T_1 \quad S^\circ > T_2 \quad S^\circ$

So, $(T_2 \quad T_1) \quad S \quad 0$

$S^\circ < 0$

In other words, increase of G with increase in temperature is possible only when $S \quad 0$. Hence, options (a) and (c) are correct.

29. Since, the reaction is exothermic, there will be less ammonia at equilibrium and higher temperature. However, rate of reaction increases with rise in temperature, NH_3 will be formed at faster rate in the initial stage when the temperature is high.

30. **PLAN** $RCOOR \quad H_2O \xrightarrow{H} RCOOH \quad R\,OH$

Acid hydrolysis of ester is follows first order kinetics.

For same concentration of ester in each case, rate is dependent on [H] from acid.

$$\text{Rate} \quad k[RCOOR\ ]$$

Also for weak acid, $HA \rightleftharpoons H \quad A$

$$K_a \quad \frac{[\mathrm{H}\ \ ][A\ \ ]}{[\mathrm{H}A]}$$

$$(\text{Rate})_{\mathrm{H}A} \quad k[\mathrm{H}\ \ ]_{\mathrm{H}A}$$

$$(\text{Rate})_{\mathrm{H}X} \quad k[\mathrm{H}\ \ ]_{\mathrm{H}X}$$

$$(\text{Rate})_{\mathrm{H}X} \quad 100(\text{Rate})_{\mathrm{H}A}$$

Also in strong acid, $[\mathrm{H}\ \ ] \quad [\mathrm{H}X] \quad 1\,\mathrm{M}$

$$\frac{(\text{Rate})_{\mathrm{H}X}}{(\text{Rate})_{\mathrm{H}A}} \quad 100 \quad \frac{[\mathrm{H}\ \ ]_{\mathrm{H}X}}{[\mathrm{H}\ \ ]_{\mathrm{H}A}} \quad \frac{1}{[\mathrm{H}\ \ ]_{\mathrm{H}A}}$$

$$[\mathrm{H}\ \ ]_{\mathrm{H}A} \quad \frac{1}{100}$$

$$\mathrm{H}A \rightleftharpoons \mathrm{H} \quad A$$

$$1 \qquad 0 \qquad 0$$

$$(1 \quad x) \qquad x \qquad x$$

$$x \quad 0.01$$

$$K_a \quad \frac{[\mathrm{H}\ \ ][A\ \ ]}{[\mathrm{H}A]} \quad \frac{0.01 \quad 0.01}{0.99} \quad 1.01 \quad 10^{\ 4}$$

31. Cl , CN and SCN forms precipitate with Cu (I), remove Cu (I) ion from equilibrium and reaction shifts in backward direction according to Le-Chatelier's principle.

32. If inert gas is introduced at constant pressure, volume of container will have to be increased and this will favour the forward reaction. Also adding $PCl_5(g)$ at constant volume will favour forward reaction because $PCl_5(g)$ is a reactant.

33. $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$,

Adding inert gas at constant volume will not affect partial pressure of reactant or products, hence will not affect equilibrium amount of either reactant or products.

34. $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g), \quad H \quad 0$

$NaNO_3$ and $NaNO_2$ are in solid state, changing their amount has no effect on equilibrium. Increasing temperature will favour forward reaction due to endothermic nature of reaction. Also, increasing pressure will favour backward reaction in which some $O_2(g)$ will combine with $NaNO_2(s)$ forming $NaNO_3$.

35. $C_2H_4 + H_2 \rightleftharpoons C_2H_6, \quad H \quad 32.7$ kcal

The above reaction is exothermic, increasing temperature will favour backward reaction, will increase the amount of C_2H_4. Decreasing pressure will favour reaction in direction containing more molecules (reactant side in the present case). Therefore, decreasing pressure will increase amount of C_2H_4.

Removing H_2, which is a reactant, will favour reaction in backward direction, more C_2H_4 will be formed.

Adding C_2H_6 will favour backward reaction and some of the C_2H_6 will be dehydrogenated to C_2H_4.

36. Smaller : $K_p \quad \frac{K_c}{RT}$

37. changing pressure has no effect on equilibrium constant.

38. $K_p \quad K_c(RT)^{\ n}$, where, $n \quad n$(products) $\quad n$(reactants)

39. Rate of any reaction increases on rising temperature.

40. Catalyst has no effect on thermodynamics of reaction.

41. It is $\frac{1}{\sqrt{K}}$.

42. Evaporation is an endothermic process.

43. (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$G \quad 2 \ G_f\ (NO_2) \quad G_f\ (N_2O_4) = 0$$

Also $\ G \quad RT \ln K \quad 0, \ K \quad 1$

Let the reaction shifts in forward direction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \text{Total}$$

$$5 \quad x \qquad\qquad 5 \quad 2x \qquad 10 \quad x$$

$$p_i: \quad \frac{5 \quad x}{10 \quad x} \ 20 \qquad\qquad \frac{5 \quad 2x}{10 \quad x} \ 20$$

$$K \quad \frac{(5 \quad 2x)^2}{(10 \quad x)^2} \ \frac{10 \quad x}{5 \quad x} \ 20 \quad 1$$

$$81x^2 \quad 405x \quad 450 \quad 0$$

$$x \quad 1.66 \text{ and } -3.33$$

Both values of x indicates that reaction actually proceeds in backward direction.

(b) $$p \quad \frac{a}{Vm^2} \quad (V_m \quad b) \quad RT$$

$$p \quad \frac{ap^2}{(pV)^2} \quad \frac{pV}{p} \quad b \quad RT$$

$$[(pV^2)\,p \quad ap^2][(pV) \quad b] \quad p\,(pV)^2\,RT$$

$$p\ [pV^2 \quad ap](pV \quad bp) \quad p\,(pV^2)\,RT$$

But $p \quad 0$

Intercept $\ RT \qquad (pV)^3 \quad (pV)^2\,RT$

44. (i) Mole of solid NH_4HS taken initially $\ \frac{3.06}{51} \quad 0.06$

At equilibrium $NH_4HS(s) \rightleftharpoons \underset{0.018}{NH_3(g)} + \underset{0.018}{H_2S(g)}$

$$K_c \quad \frac{0.018}{2}^{\ 2} \quad 8.1 \quad 10^{\ 5}$$

$$p\,(NH_3) = \frac{0.018 \quad 0.082 \quad 300}{2} = 0.22 \text{ atm}$$

$$K_p \quad (0.22)^2 \quad 4.84 \quad 10^{\ 2}$$

(ii) Addition of solid NH_4HS will have no effect on equilibrium.

45. (a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ Total moles

$$1 \qquad\qquad\qquad\qquad\qquad 1$$

Average molar mass $\ \frac{208.5}{1.4} \quad 148.9$

$$(\text{density}) \quad \frac{pM}{RT} \quad \frac{1 \quad 148.9}{0.082 \quad 400} \quad 4.54 \text{ g/L}$$

(b) $\underset{x}{AgCl(s)} + \underset{1 \quad 2x}{2NH_3(aq)} \rightleftharpoons \underset{x}{[Ag(NH_3)_2^+]} + \underset{x}{Cl}$

$$K \quad \frac{K_{sp}}{K_c} \quad 2.9 \quad 10^{\ 3} \quad \frac{x}{1 \quad 2x}^{\ 2}$$

$$x \quad 0.049 \text{ M}$$

46. Observing the graph indicates that when 0.20 mole of A is reacted, 0.40 mole of product is formed.

$$\underset{0.20}{A} \rightleftharpoons \underset{0.40}{nB} \qquad n \quad 2$$

At equilibrium, $[A] = 0.30$ M, $[B] = 0.60$ M

$$K_c \quad \frac{[B]^2}{[A]} \quad \frac{0.36}{0.30} \quad 1.2$$

47.
$$CO\,(g) \; + \; 2H_2\,(g) \rightleftharpoons CH_3OH(g)$$
$$0.15 - 0.08 \qquad x \quad 0.16 \qquad\qquad 0.08$$

Total moles at equilibrium $\; x \quad 0.01$

$$x \quad 0.01 \quad \frac{8.5 \quad 2.5}{0.082 \quad 750} \quad 0.34 \qquad x \quad 0.35$$

(i) Partial pressures : CO $\dfrac{0.07}{0.34} \quad 8.5$

$H_2 \quad \dfrac{0.18}{0.34} \quad 8.5$

$CH_3OH \quad \dfrac{0.08}{0.34} \quad 8.5$

$$K_p \quad \frac{0.08}{(0.07)\,(0.18)^2} \quad \frac{0.34}{8.5}^{\;\;2} \quad 0.056$$

(ii) Concentrations : $[CH_3OH] = \dfrac{0.08}{2.5} \quad 0.032$ M

$[H_2] = \dfrac{0.18}{2.5} \quad 0.072$ M

$[CO] \quad \dfrac{0.07}{2.5} \quad 0.028$ M

$$K_c \quad \frac{0.032}{(0.028)\,(0.072)^2} \quad 213.33$$

48.
$$CO\,(g) \; + \; 2H_2\,(g) \rightleftharpoons CH_3OH(g)$$

Mole : $0.2 - 0.10 \qquad x \quad 0.20 \qquad\qquad 0.10 \qquad$ Total moles x

$$x \quad \frac{4.92 \quad 5}{0.082 \quad 600} \quad 0.5$$

moles of H_2 at equilibrium $\; x \quad 0.2 \quad 0.3$

Partial pressures : CO $\dfrac{0.1}{0.5}\,p$, $H_2 \quad \dfrac{0.3}{0.5}\,p$,

$CH_3OH \quad \dfrac{0.1}{0.5}\,p$

$$K_p \quad \frac{\frac{p}{5}}{\frac{p}{5} \quad \frac{3}{5}p^{\;\;2}} \quad \frac{25}{9p^2} \quad \frac{25}{9\,(4.92)^2} \quad 0.11 \text{ atm}^{\;\;2}$$

Concentrations : $[CO] \quad \dfrac{0.1}{5}$ M, $[H_2] \quad \dfrac{0.3}{5}$ M,

$$[CH_3OH] \quad \frac{0.1}{5}\text{ M} \quad K_c \quad \frac{(0.1/5)}{(0.1/5)\,(0.3/5)^2} \quad 277.77 \text{ M}^{\;\;2}.$$

49.
$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons SO_3\,(g)$$

Initial p_i : $\quad 0 \qquad 2 \qquad 1$

Equilibrium p_i : $2p \qquad 2 \quad p \qquad 1 \quad 2p$

$$K_p \quad 900 \quad \frac{(1 \quad 2p)^2}{(2 \quad p)\,(2p)^2} \qquad \text{[Ignoring } p \text{ in comparison to 2]}$$

$$p \quad \frac{1}{87} \text{ atm}$$

Partial pressure of $SO_2 \quad 2p \quad \dfrac{2}{87}$ atm

Partial pressure of $O_2 \quad 2 \quad p \quad 2 \quad \dfrac{1}{87} \quad \dfrac{175}{87}$ atm

Partial pressure of $SO_3 \quad 1 \quad 2p \quad 1 \quad 2 \quad \dfrac{1}{87} \quad \dfrac{85}{87}$ atm

50.
$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \text{Total}$$
$$1 \qquad\qquad 2 \qquad\qquad 1$$

$$p_i : \quad \frac{1}{1}\,p \qquad \frac{2}{1}\,p$$

$$K_p \quad \frac{4^{\;\;2}}{1^{\;\;\;2}}\,p \quad \frac{4\,(0.25)^2}{1 \quad (0.25)^2} \quad 0.26 \text{ atm}$$

When $p \quad 0.10$ atm

$$0.26 \quad \frac{4^{\;\;2}\,(0.1)}{1^{\;\;\;2}} \qquad\qquad 0.62$$

51.
$$SO_2\,(g) + NO_2\,(g) \rightleftharpoons SO_3\,(g) + NO\,(g)$$
$$1 \quad x \qquad 1 \quad x \qquad\qquad x \qquad\quad x$$

$Q_c \quad 1 \quad K_c$, i.e. reaction proceed in forward direction to attain equilibrium.

$$16 \quad \frac{x}{1 \quad x}^{\;2} \qquad x \quad 0.80$$

$[NO] = 0.80$ M, $[NO_2] = 0.20$ M

52. $A_2\,(g) \quad B_2(g) \rightleftharpoons 2AB\,(g) \qquad\qquad n \quad 0$

$$K \quad \frac{[AB]^2}{[A_2][B_2]} \quad \frac{(n_{AB})^2}{n_{A_2} \quad n_{B_2}} \quad \frac{(2x)^2}{(1 \quad x)\,(2 \quad x)}$$

$$50 \quad \frac{4x^2}{x^2 \quad 3x \quad 2} \qquad 23x^2 \quad 75x \quad 50 \quad 0$$

$$x \quad \frac{75 \quad \sqrt{75^2 \quad 4 \quad 23 \quad 50}}{46} \quad 0.93,\ 2.32$$

2.32 is not acceptable because x cannot be greater than 1.

Mole of $AB \quad 2x \quad 2 \quad 0.93 = 1.86$

53. Total moles of gases at equilibrium $\dfrac{pV}{RT} \quad \dfrac{2.05 \quad 100}{0.082 \quad 500} \quad 5.0$

Out of this 5 moles, 1.0 mole is for $N_2\,(g)$ and remaining 4 moles for PCl_5 and its dissociation products.

$$\underset{3 \quad x}{PCl_5} \rightleftharpoons \underset{x}{PCl_3} + \underset{x}{Cl_2}$$
$$3 \quad x \quad 4 \qquad x \quad 1$$

Degree of dissociation $\dfrac{1}{3} \quad 0.33$

54.
$$N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$$

Initial :	1.0	3.0	0
Equilibrium	1 – 0.25 = 0.75	3 – 0.75 = 2.25	0.05

$$[N_2] \quad \frac{0.75}{4},\ [H_2] = \frac{2.25}{4},\ [NH_3] = \frac{0.50}{4}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.50)^2}{(0.75)(2.25)^3} \times 16$$
$$= 0.468\ L^2\ mol^{-2}$$

Also for : $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$

$$K_c' = \sqrt{K_c} = 0.68$$

55. $X_2(g) \rightleftharpoons 2X(g)$

	$X_2(g)$	$2X(g)$	
At $t = 0$	1	0	
At equilibrium	$1 - \frac{x}{2}$	x	(where, $x = \beta_{eq}$)

Total moles $= 1 + \frac{x}{2}$ and Mole fraction, $X_2(g) = \frac{1 - \frac{x}{2}}{1 + \frac{x}{2}}$

$X(g) = \frac{x}{1 + \frac{x}{2}}$ and $p = 2$ bar

Partial pressure, $p_{X_2} = \frac{1 - \frac{x}{2}}{1 + \frac{x}{2}} \cdot p$ and $p_X = \frac{p\,x}{1 + \frac{x}{2}}$

$$K_p = p_X^2 / p_{X_2} = \frac{\left[px \Big/ \left(1 + \frac{x}{2}\right)\right]^2}{p\frac{(1 - x/2)}{1 + \frac{x}{2}}}$$

$$= \frac{4px^2}{(4 - x^2)} = \frac{8\beta_{eq}^2}{(4 - \beta_{eq}^2)}$$

56. (a) $K_p = \frac{4px^2}{(4 - x^2)} \approx px^2 \quad (\because 4 \gg x)$

$$x \propto \sqrt{\frac{1}{p}}$$

If p decreases, x increases. Equilibrium is shifted in the forward side. Thus, statement (a) is correct.

(b) At the start of the reaction, $Q = 0$ where, Q is the reaction quotient $\Delta G = \Delta G^\circ + 2.303RT \log Q$

Since, $\Delta G < 0$, thus ΔG is $-$ve.

Hence, dissociation takes place spontaneously.

Thus, (b) is correct.

(c) If we use $x = 0.7$ and $p = 2$ bar then $K_p = \frac{4 \times 2(0.7)^2}{[4 - (0.7)^2]} = 1.16 \neq 1$

Thus, (c) is incorrect.

(d) At equilibrium, $\Delta G = 0$

$$\Delta G^\circ = -2.303RT \log K_p$$

Since, $\Delta G^\circ = +$ve

Hence, $K_p < 1$

$$K_C = \frac{K_p}{(RT)}$$

Then $K_C < 1$. Thus, (d) is correct.

Topic 2 Ionic Equilibrium

1. **Key Idea** The concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-};\ K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Solubility of $Cd(OH)_2$ $(S) = 1.84 \times 10^{-5}$ M

Given, pH $= 12$ [for $Cd(OH)_2$ in buffer solution]

So, pOH $= 2$ $\quad (\because$ pH $+$ pOH $=$ p$K_w)$

$12 +$ pOH $= 14$

pOH $= 14 - 12 = 2$

$[OH^-] = 10^{-2}$ in buffer solution.

For reaction $Cd(OH)_2 \rightleftharpoons \underset{S}{Cd^{2+}} + \underset{S^2}{2OH^-}$

$$K_{sp} = [Cd^{2+}][OH^-]^2$$
$$K_{sp} = (S)(2S)^2 = 4S^3 = 4(1.84 \times 10^{-5})^3$$
$$K_{sp} = 24.9 \times 10^{-15}$$
$$[Cd^{2+}] = \frac{K_{sp}}{[OH^-]^2}$$
$$[Cd^{2+}] = \frac{24.9 \times 10^{-15}}{(10^{-2})^2} = 24.9 \times 10^{-15} \times 10^{4}$$
$$= 24.9 \times 10^{-11}\ M$$
$$[Cd^{2+}] = 2.49 \times 10^{-10}\ M$$

The expected solubility of $Cd(OH)_2$ in a buffer solution of pH $= 12$ is 2.49×10^{-10} M.

2. **Key Idea** Concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature. For reaction,

$$AB \rightleftharpoons A^+ + B^-$$
$$K_{sp} = [A^+][B^-]$$

	$Al(OH)_3 \rightleftharpoons$	Al^{3+}	$+\ 3OH^-$
Initially	1	0	0
At equilibrium	$1 - S$	S	$3S + 0.2$

$$NaOH \longrightarrow \underset{0.2}{Na^+} + \underset{0.2}{OH^-}$$

K_{sp} of $Al(OH)_3 = 2.4 \times 10^{-24}$ (Given)

$$K_{sp} = [Al^{3+}][OH^-]^3$$
$$2.4 \times 10^{-24} = [S][3S + 0.2]^3 \quad [\because 0.2 \gg S]$$
$$2.4 \times 10^{-24} = [S][0.008]$$
$$[S] = 3 \times 10^{-22}$$

3. **Key Idea** NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). On hydrolysis, NH_4Cl will produce an acidic solution (pH < 7) and the expression of pH of the solution is

$$\text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log C)$$

Given, $K_b\,(NH_4OH) \quad 10^{\;5}$

$$pK_b \quad \log K_b \quad \log(10^{\;5}) \quad 5$$

C concentration of salt solution $\quad 0.02$ M
$2 \quad 10^{\;2}$ M

Now, pH $\quad 7 \quad \frac{1}{2}(pK_b \quad \log C)$

On substituting the given values in above equation, we get

$$7 \quad \frac{1}{2}[5 \quad \log(2 \quad 10^{\;2})]$$

$$7 \quad \frac{1}{2}[5 \quad \log 2 \quad 2]$$

$$7 \quad \frac{1}{2}[5 \quad 0.301 \quad 2] \quad 7 \quad 1.65 \quad 5.35$$

4. The explanation of given statements are as follows:

In statement (I), millimoles of H $\quad 400 \quad 0.1 \quad 2 \quad 80$

Millimoles of OH $\quad 400 \quad 0.1 \quad 40$ (Limiting reagent)

Millimoles of H left $\quad 80 \quad 40 \quad 40$

$$[H \;\;] \quad \frac{40}{400 \quad 400} \quad \frac{40}{800}M \quad \frac{1}{20}M$$

$$pH \quad \log[H \;\;] \quad \log\frac{1}{20}$$

$$\log 1 \quad \log 2 \quad \log 10$$

$$0 \quad 0.301 \quad 1$$

$$1.30$$

Hence, the option (a) is correct.

In statement (II), ionic product of H_2O is temperature dependent.

$$K_w \quad [H \;\;][OH \;\;] \quad 10^{\;14}(\text{mol/L})^2 \text{ at } 25°\text{C}$$

With increase in temperature, dissociation of H_2O units into H and OH ions will also increase. As a result, the value of ionic product, $[H \;\;] \;\; [OH \;\;]$ will be increased. e.g.

Temperature	K_w (mol/L^2)
5ºC	$0.186 \quad 10^{\;14}$
25ºC	$1.008 \quad 10^{\;14}$
45ºC	$4.074 \quad 10^{\;14}$

Hence, the option (b) is correct.

In statement (III), for a weak monobasic acid HA

$$\underset{(1 \quad)C\,M}{HA} \rightleftharpoons \underset{C\,M}{H} \quad \underset{C\,M}{A^{\ominus}}$$

pH of the solution is 5, i.e.

$$[H \;\;] \quad 10^{\;5}\,M \quad C$$

$$K_a \quad \frac{C \quad C}{(1 \quad)C} \quad \frac{10^{\;5}}{1}$$

$$10^{\;5} \quad \frac{10^{\;5}}{1}$$

$$0.5$$

$$\% \quad 50$$

Hence, the option (c) is correct.

In statement (IV), Le-Chatelier's principle is applicable to common ion effect. Because, in presence of common ion (given) by strong electrolyte (say, $Na^+ A$), the product of the concentration terms in RHS increases. For the weaker electrolyte, HA (say) the equilibrium shifts to the LHS, $HA \rightleftharpoons H \quad A^{\ominus}$.

As a result dissociation of HA gets suppressed. Hence, the option (d) is incorrect.

5. **Key Idea** The concentration of a substance in a saturated solution is defined as its solubility(S).
For $A_xB_y \rightleftharpoons xA^{y} \quad yB^{x}\;;\; K_{sp} \quad [A^{y}\;\,]^{x}\,[B^{x}\;\,]^{y}$

For, $Zr_3(PO_4)_4$,

$$Zr_3(PO_4)_4(s) \rightleftharpoons \underset{3SM}{3Zr^{4}}\,(aq) \quad \underset{4SM}{4PO_4^{3}}\,(aq)$$

$$K_{sp} \quad [Zr^{4} \;\,]^3\,[PO_4^{3} \;\,]^4$$

$$K_{sp} \quad (3S)^3(4S)^4 \quad 6912\,S^7 \text{ or } S \quad \frac{K_{sp}}{6912}^{\frac{1}{7}}$$

Thus, the relation between molar solubility(S) and solubility product (K_{sp}) will be

$$S \quad \frac{K_{sp}}{6912}^{1/7}$$

6. Let the solubility of Ag_2CO_3 is S. Now, 0.1 M of $AgNO_3$ is added to this solution after which let the solubility of Ag_2CO_3 becomes S .

$$[Ag \;\;] \quad S \quad 0.1 \text{ and } [CO_3^{2} \;\;] \quad S$$

$$K_{sp} \quad (S \quad 0.1)^2\,(S \;\;) \qquad \text{...(i)}$$

Given, $\quad K_{sp} \quad 8 \quad 10^{\;12}$

$\because$ K_{sp} is very small, we neglect S against S in Eq. (i)

$$K_{sp} \quad (0.1)^2 S$$

or $\quad 8 \quad 10^{\;12} \quad 0.01\,S$

or $\quad S \quad 8 \quad 10^{\;12} \quad 10^2 \quad 8 \quad 10^{\;10}$ M

Thus, molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is $8 \quad 10^{\;10}$ M.

7. The reaction takes place when H_2SO_4 is added to NH_4OH is as follows :

	H_2SO_4	$2NH_4OH$	$(NH_4)_2SO_4 \quad 2H_2O$
	Strong acid	Weak base	Salt of strong acid weak base
Millimoles at $t \quad 0$	$20 \quad 0.1 \quad 2$	$30 \quad 0.2 \quad 6$	0
Millimoles at $t \quad t$	0	2	2

So, the resulting solution is a basic buffer $[NH_4OH \quad (NH_4)_2SO_4]$.

According to the Henderson's equation,

$$pOH \quad pK_b \quad \log\frac{[(NH_4)_2SO_4]}{[NH_4OH]}$$

$$4.7 \quad \log\frac{2}{2} \quad 4.7$$

$$pH \quad 14 \quad pOH \quad 14 \quad 4.7 \quad 9.3$$

8. Its given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^2 solution.

So, we can interpret the volume of unknown Ba^2 solution as 450 mL i.e.

$$\underset{\text{solution}}{\underset{Ba^{2+}}{450\text{mL}}} + \underset{\text{solution}}{\underset{Na_2SO_4}{50\text{mL}}} \quad \underset{\text{solution}}{\underset{BaSO_4}{500\text{mL}}}$$

From this we can calculate the concentration of SO_4^2 ion in the solution *via*

$$M_1V_1 \quad M_2V_2$$

$$1 \quad 50 \quad M_2 \quad 500$$

(as 1M Na_2SO_4 is taken into consideration)

$$M_2 \quad \frac{1}{10} \quad 0.1\text{M}$$

Now for just precipitation,

Ionic product Solubility product (K_{sp})

i.e. $[Ba^{2+}][SO_4^2] \quad K_{sp}$ of $BaSO_4$

Given K_{sp} of $BaSO_4$ 1 10^{10}

So, $[Ba^{2+}][0.1] \quad 1 \quad 10^{10}$

or $[Ba^{2+}] \quad 1 \quad 10^{9}$ M

Remember This is the concentration of Ba^2 ions in final solution. Hence, for calculating the $[Ba^{2+}]$ in original solution we have to use

$$M_1V_1 \quad M_2V_2$$

as $M_1 \quad 450 \quad 10^{9} \quad 500$

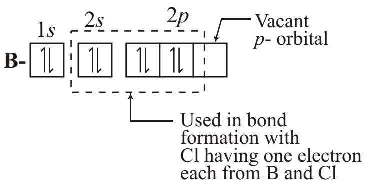
so, $M_1 \quad 1.1 \quad 10^{9}$M

9. **Key Idea** Lewis acids are defined as,
''Electron deficient compounds which have the ability to accept atleast one lone pair.''

The compound given are

PH_3-Octet complete although P has vacant 3*d*-orbital but does not have the tendency to accept lone pair in it. Hence, it cannot be considered as Lewis acid.

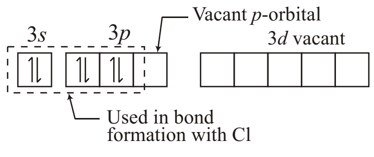
BCl_3-Incomplete octet with following orbital picture.



Hence, vacant *p*-orbital of B can accept one lone pair thus it can be considered as Lewis acid.

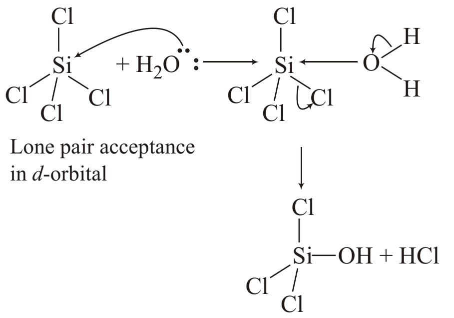
$AlCl_3$-Similar condition is visible in $AlCl_3$ as well i.e.

Al (Valence orbital only)



Hence this compound can also be considered as Lewis acid.

$SiCl_4$ - Although this compound does not have incomplete octet but it shows the tendency to accept lone pair of electrons in its vacant *d*-orbital. This tendency of $SiCl_4$ is visible in following reaction.



Thus, option (b) and (d) both appear as correct but most suitable answer is (d) as the condition of a proper Lewis acid is more well defined in BCl_3 and $AlCl_3$.

10. Among the given salts

$FeCl_3$ is acidic in nature i.e., have acidic solution as it is the salt of weak base and strong acid.

$Al(CN)_3$ and **$Pb(CH_3COO)_2$** are the salts of weak acid and weak base.

CH_3COOK is the salt of strong base and weak acid.

Hence, the solution of CH_3COOK will be most basic because of the following reaction.

$$CH_3COOK + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{(Strong base)}}{KOH}$$

11. For a salt of weak acid and weak base,

$$\text{pH} \quad 7 \quad \frac{1}{2}\text{p}K_a \quad \frac{1}{2}\text{p}K_b$$

Given, pK_a(HA) 3.2, pK_a(BOH) 3.4

$$\text{pH} \quad 7 + \frac{1}{2}(3.2) \quad \frac{1}{2}(3.4)$$

$$7 \quad 1.6 \quad 1.7 \quad 6.9$$

12. pH 1 $[H\ ]$ 10^{1} 0.1 M

pH 2 $[H^+]$ 10^{2} 0.01 M

For dilution of HCl, $M_1V_1 \quad M_2V_2$

$$0.1 \quad 1 \quad 0.01 \quad V_2$$

$$V_2 \quad 10\text{ L}$$

Volume of water to be added 10 1 9 L

13. MX : $K_{sp} \quad S^2 \quad 4 \quad 10^{8}$

$S \quad 2 \quad 10^{4}$

MX_2 : $K_{sp} \quad 4S^3 \quad 3.2 \quad 10^{14}$ $S \quad 2 \quad 10^{5}$

M_3X : $K_{sp} \quad 27S^4 \quad 2.7 \quad 10^{15}$ $S \quad 10^{4}$

Order of solubility is $MX \quad M_3X \quad MX_2$

14. mmol of base = 2.5 $\frac{2}{5}$ 1

mmol of acid required to reach the end point = 1

Volume of acid required to reach the end point $\frac{15}{2}$ mL

Total volume at the end point $\frac{15}{2}$ 2.5 = 10 mL

Molarity of salt at the end point $\frac{1}{10}$ 0.10

$$\begin{array}{ccccccc} B^{+} & + & H_2O & \rightleftharpoons & BOH & + & H^{+} \\ C\ (1 \quad) & & & & C & & C \end{array}$$

$$K_h \quad \frac{K_w}{K_b} \quad 10^{\ \ 2}$$

$$K_h \quad 10^{\ \ 2} \quad \frac{C^{\ \ 2}}{1} \quad \frac{0.1^{\ \ 2}}{1}$$

$$10^{\ \ 2} \qquad 1 \quad 0$$

$$\frac{1 \quad \sqrt{1 \quad 40}}{20} \quad 0.27$$

$$[H^+] \quad C \quad 0.1 \quad 0.27 = 0.027\ M$$

15.

$$\begin{array}{lccccccc} & CH_3NH_2 & + & HCl & & CH_3NH_3^+ & + & Cl \\ \text{Initial :} & 0.10 & & 0.08 & & 0 & & 0 \\ \text{Final :} & 0.02 & & 0 & & 0.08 & & 0.08 \end{array}$$

$$pOH \quad pK_b \quad \log \frac{[CH_3NH_3^+]}{[CH_3NH_2]}$$

$$\log (5 \quad 10^{\ \ 4}) \quad \log \frac{0.08}{0.02} \quad 3.9$$

$$pH = 14 - pOH = 10.1$$

$$[H^+] = 8 \quad 10^{\ \ 11}$$

16. $K_h (X \ ) \quad \frac{K_w}{K_a} \quad \frac{10^{\ \ 14}}{10^{\ \ 5}} \quad 10^{\ \ 9} \qquad \sqrt{\frac{K_h}{C}} \quad \sqrt{\frac{10^{\ \ 9}}{0.10}} \quad 10^{\ \ 4}$

% hydrolysis 100 0.01

17. Minimum S^{2} concentration would be required for precipitation of least soluble HgS.

For HgS, S^{2} required for precipitation is

$$[S^{2} \ ] = \frac{K_{sp}}{[Hg^{2+}]} \quad \frac{10^{\ \ 54}}{10^{\ \ 3}} \quad 10^{\ \ 51}\ M$$

18. Alkali metal salts are usually more soluble than the salts of transition metals. Also, CuS is less soluble than ZnS because of $3d^9$ configuration of Cu^{2+}. Therefore, solubility order is

$$Na_2S > ZnS > CuS$$

19. $$\begin{array}{cccc} A_pB_q & \rightleftharpoons & pA & qB \\ & & pS & qS \end{array}$$

$$K_{sp} \quad (pS)^p\ (qS)^q \quad S^{(p \quad q)} \quad p^p \quad q^q$$

20. NaCN is basic salt, has highest pH while HCl has lowest pH. NaCl is neutral salt has pH = 7 while NH_4Cl is acidic salt, has pH less than 7.

pH : HCl < NH_4Cl < NaCl < NaCN

21. 75 mL $\frac{M}{5}$ HCl 15 mmol HCl

25 mL $\frac{M}{5}$ NaOH 5 mmol NaOH

After neutralisation, 10 mmol HCl will be remaining in 100 mL of solution.

Molarity of HCl in the final solution $\frac{10}{100}$ 0.10

$$pH \quad \log [H^+] \quad \log (0.10) = 1$$

22. In case of hydroxides of Group II A, solubility increases down the group. Therefore, $Be(OH)_2$ is least soluble, has lowest value of K_{sp}.

23. $HClO_4$ is the strongest acid among these.

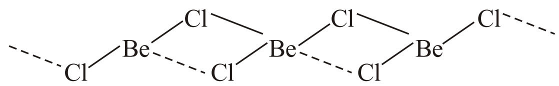
24. For precipitation to occur, $K_{sp} \quad Q_{sp}$.

$$Q_{sp} \quad \frac{10^{\ \ 4}}{2} \quad \frac{10^{\ \ 4}}{2} \quad 2.5 \quad 10^{\ \ 9} \quad K_{sp}$$

Hence, precipitate will be formed in this case. In all other case, $Q_{sp} \quad K_{sp}$ and no precipitation will occur.

25. In stomach, pH is 2-3, i.e. strongly acidic and aspirin will be almost unionised here due to common ion effect. However, pH in small intestine is 8, basic, aspirin will be neutralised here.

26. $BeCl_2$ exist in polymeric forms and has no electron deficiency, not a Lewis acid.



27. $$\begin{array}{ccccccc} NH_2 & + & H_2O & \rightleftharpoons & NH_3 & + & OH \\ \text{Base} & & & & \text{Conjugate acid} & & \end{array}$$

28. When a weak acid (HX) is titrated against a strong base NaOH, basic salt (NaX) is present at the end point which makes end point slightly basic with pH around 8. Hence, phenolphthalein, that changes its colour in this pH range, would be the best choice of indicator to detect the end point.

29. The reaction of HA with strong base is

$$HA \ + \ OH \ \rightleftharpoons \ H_2O \ + \ A$$

$$K \quad \frac{[A \ ]}{[HA][OH \ ]} \quad \frac{[H^+]}{[H^+]} \quad \frac{K_a}{K_w} \quad \frac{10^{\ \ 4}}{10^{\ \ 14}} \quad 10^{10}$$

30. $K_a\ (HX) \quad \frac{K_w}{K_b} \quad 10^{\ \ 4}$

$$pH \quad pK_a \quad \log \frac{[X \ ]}{[HX]}$$

$$pK_a \quad 4 \qquad [\because\ [X \ ] = [HX]]$$

31. For precipitation reaction, $Q_{IP} \quad K_{sp}$.

$$Q_{IP} \quad [Ca^{2+}][F \ ]^2 \quad \frac{10^{\ \ 2}}{2} \quad \frac{10^{\ \ 3}}{2}^{\ 2}$$

$$1.25 \quad 10^{\ \ 9} \quad K_{sp}, \text{precipitate will be formed.}$$

32. Acidic buffer is prepared by mixing weak acid with salt of its conjugate base. Therefore, acetic acid and sodium acetate can be used to prepare acidic buffer.

33. The order of acidic strength of conjugate acids is

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

Reverse is the order of basic strength of their conjugate base, i.e. ClO is the strongest base.

34. $K_w \quad [H_3O^+][OH \;] = 10^{\;6} \quad 10^{\;6} \quad 10^{\;12}$

35. No matter, what is the concentration of HCl, its pH will always be less than 7 at 25°C. In the present case, the solution is very dilute, pH will be between 6 and 7.

36. **PLAN** In presence of common ion (in this case Ag ion) solubility of sparingly soluble salt is decreased.

Let solubility of Ag_2CrO_4 in presence of 0.1 M

$$AgNO_3 \quad x$$

$$Ag_2CrO_4 \rightleftharpoons \underset{2x}{2\,Ag} \quad \underset{x}{CrO_4^2}$$

$$AgNO_3 \rightleftharpoons \underset{0.1}{Ag} \quad \underset{0.1}{NO_3}$$

Total $[Ag \;] \quad (2x \quad 0.1)M \quad 0.1$ M

as $x \quad 0.1$ M

$[CrO_4^2 \;] \quad x$ M

Thus, $\quad [Ag \;]^2 [CrO_4^2 \;] \quad K_{sp}$

$(0.1)^2(x) \quad 1.1 \quad 10^{\;12}$

$\because \qquad x \quad 1.1 \quad 10^{\;10}$ M

37. In HNO_3 and CH_3COONa combination, if HNO_3 is present in limiting amount, it will be neutralised completely, leaving behind some excess of CH_3COONa.

$$CH_3COONa + HNO_3 \qquad CH_3COOH + NaNO_3$$

Buffer combination

38. $CH_3COOH + CH_3COONa$ = Buffer solution

$CH_3COONa + HCl \qquad CH_3COOH + NaCl$

If HCl is taken in limited quantity, final solution will have both CH_3COOH and CH_3COONa needed for buffer solution.

Ammonia and ammonium chloride forms basic buffer.

39. pH of $10^{\;8}$ M solution will be between 6 and 7 but never 8. The conjugate base of an acid is formed by removing a proton (H^+) from acid. Therefore, HPO_4^2 is a conjugate base of H_2PO_4.

$$H_2O \rightleftharpoons H^+ + OH \qquad H \quad 0$$

Increasing temperature will increase equilibrium constant of the above endothermic reaction.

At the mid-point of titration $\quad pH = pK_a$

40. **Key Idea** Solubility of salt of weak acid (AB) in presence of H ions from buffer solution can be calculated with the help of following formula.

$$\text{Solubility} \quad \sqrt{K_{sp}\;\frac{[H^+]}{k_a} \quad 1}$$

Given, pH 3, so $[H^+] \quad 10^{\;3}$

$K_a \quad 1 \;\; 10^{\;8} \qquad K_{sp} \quad 2 \;\; 10^{\;10}$

after putting the values in above formula

$$\text{Solubility} \quad \sqrt{2 \;\; 10^{\;10}\;\; \frac{10^{\;3}}{10^{\;8}} \quad 1} \quad \sqrt{2 \;\; 10^{\;5}} \quad 4.47 \;\; 10^{\;3}M$$

Hence, the value of y 4.47

41. For P, i.e. (10 mL of 0.1 M NaOH 20 mL of 0.1 M acetic acid) is diluted to 60 mL

The correct match is 1, i.e. the value of $[H^+]$ does not change on dilution due to the formation of following buffer.

$$NaOH + CH_3COOH \rightleftharpoons CH_3COO \;\; Na^+ + H_2O$$

Initial millimol	1	2		
Final millimol		1	1	

Final volume – 30 mL (20 10) in which millimoles of CH_3COOH and $CH_3COO \;\; Na^+$ are counted.

For Q, i.e. (20 mL of 0.1 M NaOH 20 mL of 0.1 M CH_3COOH) is diluted to 80 mL

The correct match is 5, i.e. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution.

As per the condition given in Q the resultant solution before dilution contain 2 millimoles of $CH_3COO \;\; Na^+$ in 40 mL solution. Hence, it is the salt of weak acid and strong base. So,

$$[H \;]_{initial} \quad \sqrt{\frac{K_W K_a}{C}}$$

After dilution to 80 mL, the new 'C' becomes $\frac{C}{2}$, So,

$$[H^+]_{new} \quad \sqrt{\frac{K_w K_a}{C/2}} \text{ or } [H^+]_{initial} \quad \sqrt{2}$$

For R, i.e. (20 mL of 0.1 M HCl 20 mL of 0.1 M NH_3) is diluted to 80 mL

The correct match is 4, i.e. the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value of dilution.

As per the condition given in R the resultant solution before dilution contains 2 millimoles of NH_4Cl in 40 mL of solution. Hence, a salt of strong acid and weak base is formed.

For this,

$$[H^+]_{initial} \quad \sqrt{\frac{K_w \quad C}{K_b}}$$

Now on dilution upto 80 mL new conc. becomes $C/2$.

So, $$[H^+]_{new} \quad \sqrt{\frac{K_w \quad \frac{C}{2}}{K_b}}$$

or $$[H^+]_{new} \quad [H \;]_{initial} \quad \frac{1}{\sqrt{2}}$$

For S, i.e. 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL and solid $Ni(OH)_2$ is still present after dilution.

The correct match is 1.

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+} + 2OH$$

as per the condition given it is a sparingly soluble salt. Hence, on dilution the concentration of OH ions remains constant in saturated solution.

So for this solution,

$$[H^+]_{new} = [H^+]_{initial}$$

42. $I_2 : \ I \qquad I_2 = I_3$

43. Hydration energy facilitate solubility.

44. Amphoteric

45. SO_4^{2-} Conjugate base is formed by removing a proton from acid.

46. P_2O_5 is strongest acid and MgO is strongest base.

47. $NaOH + H_2O \qquad NaOH\ (aq); \quad H \quad 0$

48. Lewis acid accept lone pair of electron.

49. Degree of ionisation ($\frac{\wedge m}{\wedge}$

Let $\quad \wedge m\ (HY) \quad x \qquad \wedge m\ (HX) \quad \frac{X}{10}$

$$\frac{\wedge m\ (HX)}{\wedge m\ (XY)} \quad \frac{1}{10} \quad \frac{(HX)}{(HY)} \qquad [\because \wedge \quad (HX) \quad \wedge \quad (HY)]$$

Also : $\quad K_a(HX) \quad (0.01)[\quad HX)]^2 \qquad$ ...(i)

$$K_a(HY) \quad (0.10)[\quad HY)]^2$$

$$0.10\,[10 \quad (HX)]^2 \quad 10[\quad (HX)]^2 \quad \text{... (ii)}$$

$$\frac{K_a(HX)}{K_a(HY)} \quad \frac{0.01}{10} \quad \frac{1}{1000}$$

$$\log K_a(HX) \quad \log K_a(HY) \qquad 3$$

$$\log K_a(HX) \quad [\quad \log K_a(HY)] \quad 3$$

$$pK_a(HX) \quad pK_a(HY) \quad 3$$

50. It is a case of simultaneous solubility of salts with a common ion. Here, solubility product of CuCl is much greater than that of AgCl, it can be assumed that Cl– in solution comes mainly from CuCl.

$$[Cl^-] \quad \sqrt{K_{sp}(CuCl)} \qquad 10^{-3} M$$

Now, for AgCl, $K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$

$$= [Ag^+] \times 10^{-3}$$

$$[Ag^+] = 1.6 \times 10^{-7}$$

51. Basic salts solution will have pH > 7, will change colour of litmus paper red to blue

KCN, K_2CO_3 and LiCN are the only basic salts among these.

52. The hydrolysis reaction is

$$A \quad + H_2O \rightleftharpoons AH + OH$$

$$K_h \quad \frac{K_w}{K_a} \quad 10 \quad ^{10}$$

$$[OH \quad] = \sqrt{K_h C} \quad 10 \quad ^{6}$$

$$pOH = 6 \quad \text{and} \quad pH \quad 8$$

53. At the end-point, $\quad [A \quad] = 0.05$

$$K_b\ (A \quad) \quad K_w / K_a \quad 2 \quad 10 \quad ^{9}$$

$$[OH \quad] = \sqrt{K_b C} \quad \sqrt{2 \quad 10 \quad ^{9} \quad 0.05} \quad 10 \quad ^{5}$$

$$pOH = 5 \quad \text{and} \quad pH = 9$$

54. (i) $CH_3COOH \rightleftharpoons CH_3COO \quad + \quad H^+$

$\quad C\ (1 \quad) \qquad\qquad C \qquad\qquad C$

If no HCl is present,

$$[HCl] \quad \frac{0.2}{2} \quad 0.10\ M$$

$$[CH_3COOH] \quad 0.10\ M$$

The major contributor of H^+ in solution is HCl.

$$K_a \quad \frac{C \quad (0.1)}{C\ (1 \quad)} \quad 1.75 \quad 10 \quad ^{5}$$

$$1.75 \quad 10 \quad ^{4}$$

(ii) mmol of NaOH added $\quad \frac{6}{40} \quad 1000 \quad 150$

$$\text{mmol of HCl} \quad 500 \quad 0.2 = 100$$

$$\text{mmol of } CH_3COOH \quad 500 \quad 0.2 = 100$$

After neutralisation, mmol of CH_3COOH = 50

$$\text{mmol of } CH_3COONa \quad 50$$

$$pH \quad pK_a \quad 4.75$$

55. Partial pressure of SO_2 in air $\quad 10 \quad ^{5}$ atm

$$[SO_2]_{aq} \quad 1.3653 \quad 10 \quad ^{5} mol\ L \quad ^{1}$$

$\because$ $pK_a \quad$ 1.92 and concentration of H_2SO_3 is very low, it is almost completely ionised as

$$H_2SO_3 \rightleftharpoons H^+ \ + \ HSO_3$$

$$[H^+] = 1.3653 \quad 10 \quad ^{5} M$$

$$pH = -\log(1.3653 \quad 10 \quad ^{5}) \quad 4.86$$

56. In water, $\quad K_{sp} \quad 4S^3 \quad 4\ (6.7 \quad 10 \quad ^{6})^3$

$$1.2 \quad 10 \quad ^{15}$$

In buffer of $\ pH = 8, \ pOH = 6, [OH \quad] = 10 \quad ^{6}$

$$K_{sp} \quad S\ [OH \quad]^2$$

$$S \quad \frac{1.2 \quad 10 \quad ^{15}}{10 \quad ^{12}} \quad 1.2 \quad 10 \quad ^{3} M$$

57. (a) $\quad E \quad 0.164 = -0.059 \log \frac{[Ag^+]_{anode}}{0.10}$

$$[Ag^+]_{anode} \quad 1.66 \quad 10 \quad ^{4} M$$

$$[CrO_4^2 \quad] = \frac{[Ag^+]}{2} \quad 8.3 \quad 10 \quad ^{5} M$$

$$K_{sp} \quad [Ag^+]^2 [CrO_4^2 \quad]$$

$$(1.66 \quad 10 \quad ^{4})^2\ (8.3 \quad 10 \quad ^{5})$$

$$2.3 \quad 10 \quad ^{12}$$

(b) pH of HCl 2

$[H\ \ ]\ \ 10^{\ 2}$ M

Moles of H ions in 200 mL of $10^{\ 2}$ M HCl solution

$$\frac{10^{\ 2}}{1000}\quad 200\quad 2\quad 10^{\ 3}$$

Similarly, pH of NaOH 12

$[H\ \ ]\ \ 10^{\ 12}$ M

or $[OH\ \ ]\ \ 10^{\ 2}$ M $[\because [H\ \ ][OH\ \ ]\ \ 10^{\ 14}$ m]

Moles of OH ion in 300 mL of $10^{\ 2}$ M NaOH solution

$$\frac{10^{\ 2}}{1000}\quad 300\quad 3\quad 10^{\ 3}$$

Total volume of solution after mixing 500 mL

Moles of OH ion left in 500 mL of solution

$$(3\quad 10^{\ 3})\quad (2\quad 10^{\ 3})\quad 10^{\ 3}$$

Molar concentration of OH ions in the resulting

solution $\dfrac{10^{\ 3}}{500}\quad 1000\quad 2\quad 10^{\ 3}$ M

pOH log (2 $10^{\ 3}$)

log2 3log10

0.3 ~103 2.699

pH 14 2.699 11.301

58. $2AgCl(s) + CO_3^{2} \rightleftharpoons Ag_2CO_3\ (s)\ +\ 2Cl$

$$K\quad \frac{[Cl\ \ ]^2}{[CO_3^{2}\ \ ]}\quad \frac{[Cl\ \ ]^2}{[CO_3^{2}\ \ ]}\quad \frac{[Ag^+]^2}{[Ag^+]^2}\quad \frac{[K_{sp}\ (AgCl)]^2}{K_{sp}\ (Ag_2CO_3)}$$

$$[Cl\ \ ]\quad \frac{0.0026}{35.5}\ M\quad 7.3\quad 10^{\ 5}\ M$$

The above concentration of Cl indicates that $[CO_3^{2}\ \ ]$ remains almost unchanged.

$$\frac{7.3\quad 10^{\ 5}}{1.5}\quad \frac{[K_{sp}\ (AgCl)]^2}{8.2\quad 10^{\ 12}}$$

$$K_{sp}\,(AgCl)\quad 2\quad 10^{\ 8}$$

59. pH pK_{In} log 10 pK_{In} 1 When $\dfrac{[In\ \ ]}{[HIn]}$ 10

pK_{In} log (0.1) = $pK_{In}\ \ _1$ When $\dfrac{[In\ \ ]}{[HIn]}$ 0.1

pH range is $pK_{In}\ \ _1$ to $pK_{In}\ \ _1$.

60. $K_a\ (NH_4^+)\quad 5.6\quad 10^{\ 10}$

$$K_b\ (NH_3)\quad K_w\,/\,K_a\quad \frac{10^{\ 14}}{5.6\quad 10^{\ 10}}\quad 1.8\quad 10^{\ 5}$$

i.e. $NH_3\quad H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+\quad OH$

$$K\quad \frac{k_1}{k_2}\quad 1.8\quad 10^{\ 5}$$

$$k_1\quad Kk_2\quad 1.8\quad 10^{\ 5}\quad 3.4\quad 10^{10}\quad 6.12\quad 10^5$$

61. $CN\quad +\ H_2O \rightleftharpoons HCN\ +\ OH$

$$K_h\quad 2\quad 10^{\ 5}$$

$$[OH\ \ ] = \sqrt{K_hC}\quad \sqrt{2\quad 10^{\ 5}\quad 0.5}\quad \sqrt{10^{\ 5}}$$

pOH 2.5 and pH = 11.5

62. For salts of weak acid and weak base .

$$pH = 7 + \frac{1}{2}\,(pK_a\quad pK_b)\quad 7\quad \frac{1}{2}\,(3.8\quad 4.8) = 6.50$$

63. $Ag^+ + 2CN \rightleftharpoons Ag(CN)_2$

Initial :	0.03	0.10	0
Equilibrium :	x	0.10 – 0.06	0.03

$$K\quad \frac{1}{4\quad 10^{\ 19}}\quad 2.5\quad 10^{18}$$

$$K\quad 2.5\quad 10^{18}\quad \frac{0.03}{(0.04)^2\ x}$$

$$x\quad 7.50\quad 10^{\ 18}\ M\ Ag^+$$

64. For H_2S, $H_2S \rightleftharpoons 2H^+\ +\ S^2$

$$K\quad K_1\quad K_2\quad 1.3\quad 10^{\ 20}$$

Minimum $[S^2\ \ ]$ required to begin precipitation of

$$MS = \frac{6\quad 10^{\ 21}}{0.05}\quad 1.2\quad 10^{\ 19}$$

$$K\quad 1.3\quad 10^{\ 20}\quad \frac{[H^+]^2\,[S^2\ \ ]}{[H_2S]}\quad [H^+]^2\ \frac{(1.2\quad 10^{\ 19})}{0.10}$$

$[H^+] = 0.10$ M pH = 1

65. Mixing H_2CO_3 with $NaHCO_3$ results in buffer solution.

$$pH = pK_a + \log\frac{[NaHCO_3]}{[H_2CO_3]} = pK_a + \log\frac{n\ (NaHCO_3)}{n\ (H_2CO_3)}$$

$$7.4 = -\log\,(7.8\quad 10^{\ 7})\quad \log\frac{x}{20}$$

x 400 mmol

$NaHCO_3 = 5\quad V$ V 80 mL

66. $K_{sp}\quad 4S^3\quad 4.42\quad 10^{\ 5}$

S 0.022 M

mmol of $Ca(OH)_2$ in 500 mL saturated solution = 11

mmol of NaOH in 500 mL 0.40 M solution = 200

Total mmol of OH = 200 + 2 11 222

$[OH\ \ ] = 0.222$ M

Solubility in presence of NaOH $\dfrac{K_{sp}}{[OH\ \ ]^2}$

$$\frac{4.42\quad 10^{\ 5}}{(0.222)^2}\quad 9\quad 10^{\ 4}\ M$$

mmol of Ca^{2+} remaining in solution = 0.9

mmol of $Ca(OH)_2$ precipitated = 10.1

mg of $Ca(OH)_2$ precipitated = 10.1 7.4 = 747.4 mg

67. Let 40 mL of base contain x mmol of BOH.

$$BOH \;+\; HCl \qquad BCl \;+\; H_2O$$

x 0.5		0.5	When 5 mL acid is added
x 2		2.0	When 20 mL of acid is added

When pH is 10.04, pOH = 3.96 and when pH is 9.14, pOH is 4.86. Therefore,

$$3.96 \quad pK_b \quad \log \frac{0.50}{x \quad 0.5} \qquad \ldots(i)$$

$$3.96 \quad pK_b \quad \log \frac{2.0}{x \quad 2} \qquad \ldots(ii)$$

Subtracting Eq. (i) from Eq. (ii) gives

$$0.90 = \log \frac{2}{x \quad 2} \; \frac{x \quad 0.5}{0.5}$$

$$28 \quad \frac{4\,(x \quad 0.5)}{x \quad 2}$$

x 3.5, substituting in equation (i) gives

$$3.96 \quad pK_b \quad \log \frac{0.5}{3}$$

$$K_b \quad 1.8 \quad 10^{\;5}$$

68. Initial concentration of $K_2C_2O_4 = \frac{0.152}{0.50} \quad 0.304$ M,

Also for the following equilibrium:

$$\underset{0.304 \quad x}{Ag_2CO_3(s) + K_2C_2O_4(aq)} \rightleftharpoons \underset{x}{Ag_2C_2O_4(s) + K_2CO_3}$$

$$K \quad \frac{[CO_3^{2} \;]}{[C_2O_4^{2} \;]} \; \frac{[Ag^+ \;]^2}{[Ag^+ \;]^2} \; \frac{K_{sp}\,(Ag_2CO_3)}{K_{sp}\,(Ag_2C_2O_4)}$$

Given, $0.304 - x \quad 0.0358$

$$x \quad 0.2682$$

$$K \quad \frac{0.2682}{0.0358} \quad 7.5$$

$$K_{sp}\,(Ag_2CO_3) \quad K \quad K_{sp}\,(Ag_2C_2O_4)$$

$$7.5 \quad 1.29 \quad 10^{\;11}$$

$$9.675 \quad 10^{\;11}$$

69. $CH_3COOH \rightleftharpoons CH_3COO \;\; + H^+$

When concentration of CH_3COOH is 1.0 M, ‘ ’ is negligible,

$$[H^+] = \sqrt{K_a C} \quad 4.24 \quad 10^{\;3}\ M$$

$$pH \quad \log (4.24 \quad 10^{\;3}) \quad 2.37$$

Now, let us assume that solution is diluted to a volume where concentration of CH_3COOH (without considering ionisation) is x.

$$\underset{x(1 \quad)}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO} \;+\; \underset{x}{H^+}$$

$$K_a \quad \frac{x \quad ^2}{1}$$

Also, desired pH 2 2.37 = 4.74

$$[H^+] = 1.8 \quad 10^{\;5} \quad x$$

$$K_a \quad 1.8 \quad 10^{\;5} \quad \frac{1.8 \quad 10^{\;5}}{1}$$

$$0.5 \text{ and } x \quad 3.6 \quad 10^{\;5}\ M$$

$$\text{Volume (final)} \quad 1/3.6 \quad 10^{\;5} \quad 27.78 \quad 10^3\ L.$$

70. pOH of buffer solution $\quad pK_b \quad \log \frac{[NH_4^+]}{[NH_4OH]}$

$$\log (1.8 \quad 10^{\;5}) \quad \log \frac{0.25}{0.05} \quad 5.44$$

$$[OH \;] = 3.6 \quad 10^{\;6}\ M$$

$$[Al^{3+}] = \frac{K_{sp}}{[OH \;]^3} \quad \frac{6 \quad 10^{\;32}}{(3.6 \quad 10^{\;6})^3} \quad 1.28 \quad 10^{\;15}\ M$$

$$[Mg^{2+}] = \frac{K_{sp}}{[OH \;]^2} \quad \frac{8.9 \quad 10^{\;12}}{(3.6 \quad 10^{\;6})^2} \quad 0.68\ M$$

71. HCN for buffer will be formed by the reaction

$$NaCN + HCl \qquad NaCl + HCN$$

mmol of NaCN present initially $\quad \frac{0.01}{49} \quad 1000 \quad 0.2$

Let x mmol of HCl is added so that x mmol of NaCN will be neutralised forming x mmol of HCN.

$$pH \quad pK_a \quad \log \frac{[NaCN]}{[HCN]}$$

$$8.5 \quad \log (4.1 \quad 10^{\;10}) \quad \log \frac{0.2 \quad x}{x}$$

$$x \quad 0.177 \text{ mmol}$$

72. (i) 0.20 mole HCl will neutralise 0.20 mole CH_3COONa, producing 0.20 mol CH_3COOH. Therefore, in the solution moles of CH_3COOH = 1.20

Moles of CH_3COONa = 0.80

$$pH \quad pK_a \quad \log \frac{[Salt]}{[Acid]}$$

$$\log (1.8 \quad 10^{\;5}) \quad \log \frac{(0.80)}{(1.20)} = 4.56$$

(ii)

	CH_3COONa	+ HCl	CH_3COOH	+ NaCl
Initial	0.10	0.20	0	0
Final	0	0.10	0.10	0.10

Now, the solution has 0.2 mole acetic acid and 0.1 mole HCl. Due to presence of HCl, ionisation of CH_3COOH can be ignored (common ion effect) and H^+ in solution is mainly due to HCl.

$$[H^+] = 0.10$$

$$pH \quad -\log(0.10) = 1.0$$

73. In pure water, solubility $\quad \frac{9.57}{58} \quad 10^{\;3}\ M$

$$1.65 \quad 10^{\;4}\ M$$

$$K_{sp} \quad 4S^3 \quad 4\,(1.65 \quad 10^{\;4})^3 \quad 1.8 \quad 10^{\;11}$$

In 0.02 M $Mg(NO_3)_2$;

solubility of $Mg(OH)_2$ $\quad \sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}} \quad \dfrac{1}{2}$

$1.5 \quad 10^{\ 5}$ mol $L^{\ 1}$

$1.5 \quad 10^{\ 5} \quad 58$ g $L^{\ 1}$

$8.7 \quad 10^{\ 4}$ g $L^{\ 1}$

74. $HCOOH \rightleftharpoons H^+ + HCOO$

$\underset{1 \quad 0.75}{HCOONa} \rightleftharpoons Na^+ \quad \underset{0.75}{HCOO}$

In the above buffer solution, the significant source of formate ion (HCOO) is HCOONa. Hence,

$$K_a \quad 2.4 \quad 10^{\ 4}$$

$$\frac{[H^+](0.75)}{[HCOOH]}$$

$$[H^+] \quad \frac{2.4 \quad 10^{\ 4} \quad 0.20}{0.75} \quad 6.4 \quad 10^{\ 5}$$

$$pH \quad -\log(6.4 \quad 10^{\ 5}) \quad 4.20$$

76. K_{sp} (AgI) = $8.5 \quad 10^{\ 17} \quad [Ag^+][I\ ]$

[I] required to start precipitation of AgI

$$\frac{8.5 \quad 10^{\ 17}}{0.10} \quad 8.5 \quad 10^{\ 16} \text{ M}$$

$$K_{sp}(HgI_2) \quad 2.5 \quad 10^{\ 26} \quad [Hg^{2+}][I\ ]^2$$

[I] required to start precipitation of HgI_2

$$\sqrt{\frac{2.5 \quad 10^{\ 26}}{0.10}} \quad 5 \quad 10^{\ 13} \text{ M}$$

The above calculation indicates that lower [I] is required for precipitation of AgI. When [I] reaches to $5 \quad 10^{\ 13}$, AgI gets precipitated almost completely.

When HgI_2 starts precipitating,

$$[Ag^+] = \frac{8.5 \quad 10^{\ 17}}{5 \quad 10^{\ 13}} \quad 1.70 \quad 10^{\ 4} \text{ M}$$

$$\% \ Ag^+ \text{ remaining} \quad \frac{1.70 \quad 10^{\ 4} \quad 100}{0.10} \quad 0.17$$

$$\% \ Ag^+ \text{ precipitated} \quad 100 - 0.17 = 99.83$$

76. Molarity (C) $\quad 0.10$

$$[H^+] = \sqrt{K_a \ C} \quad 7 \quad 10^{\ 5} \text{ M } (\quad \text{is negligible})$$

$$pH = 4.15$$

$$[OH\ ] = \frac{K_w}{[H^+]} \quad \frac{10^{\ 14}}{7 \quad 10^{\ 5}}$$

$$1.43 \quad 10^{\ 10} \text{ M}$$

77. Sodium acetate (CH_3COONa) is a basic salt (salt of strong base and weak acid) therefore, its aqueous solution has pH > 7.

78. mmol of NaOH = 20   0.2 = 4

mmol of acetic acid = 50   0.2 = 10

After neutralisation, buffer solution is formed which contain 6 mmol CH_3COOH and 4 mmol CH_3COONa.

$$pH \quad pK_a \quad \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\log(1.8 \quad 10^{\ 5}) \quad \log\frac{4}{6} \quad 4.56$$

Now, let x mmol of NaOH is further added so that pH of the resulting buffer solution is 4.74.

Now, the buffer solution contains (4 x) mmol CH_3COONa and (6 x) mmol of CH_3COOH.

$$4.74 \quad \log(1.8 \quad 10^{\ 5}) \quad \log\frac{4 \quad x}{6 \quad x}$$

$$\frac{4 \quad x}{6 \quad x} \quad 1$$

$$x \quad 1.0 \text{ mmol} \quad 0.2 \quad V$$

$$V \quad 5.0 \text{ mmol NaOH.}$$

79. For acidic buffer, the Henderson's equation is

$$pH = pK_a \quad \log\frac{\text{(mole of salt)}}{\text{(mole of acid)}}$$

$$4.75 = -\log(1.34 \quad 10^{\ 5}) \quad \log\frac{x}{0.02}$$

$x \quad 0.015$ mole of sodium propionate.

Addition of 0.01 mole HCl will increase moles of propionic acid by 0.01 and moles of sodium propionate will decrease by same amount.

New moles of acid = 0.02 + 0.01 = 0.03

New moles of salt = 0.015 – 0.01 = 0.005

$$pH = -\log(1.34 \quad 10^{\ 5}) \quad \log\frac{0.005}{0.030} = 4.09$$

pH of 0.01 HCl = 2, just half of the pH of final buffer solution.

7

Thermodynamics and Thermochemistry

Topic 1 Thermodynamics

Objective Questions I (Only one correct option)

1. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is **(2019 Main, 12 April I)**

(a) 9.0 (b) 10.0 (c) 0.9 (d) 2.0

2. The difference between H and U (H U), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to **(2019 Main, 10 April II)**

(a) 4 RT (b) 3 RT (c) 4 RT (d) 3 RT

3. A process will be spontaneous at all temperature if **(2019 Main, 10 April I)**

(a) H 0 and S 0 (b) H 0 and S 0
(c) H 0 and S 0 (d) H 0 and S 0

4. During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, U (in kJ) is **(2019 Main, 9 April II)**

(a) 8 (b) 12 (c) 12 (d) 8

5. Among the following the set of parameters that represents path functions, is **(2019 Main, 9 April I)**

(A) q W (B) q (C) W (D) H TS

(a) (A) and (D) (b) (A), (B) and (C)
(c) (B), (C) and (D) (d) (B) and (C)

6. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If C_V = 28 JK ^{1} mol ^{1}, calculate U and pV for this process. (R 8.0 JK ^{1}mol ^{1}) **(2019 Main, 8 April II)**

(a) U 2.8 kJ; (pV) 0.8 kJ
(b) U 14 J; (pV) 0.8 J
(c) U 14 kJ; (pV) 4 kJ
(d) U 14 kJ; (pV) 18 kJ

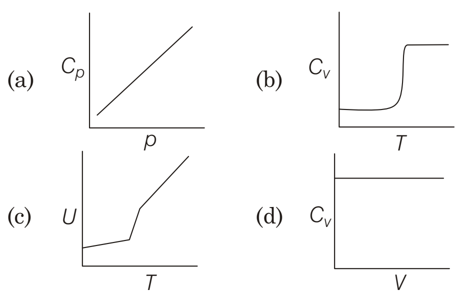
7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero) **(2019 Main, 8 April I)**

(a) Cyclic process : q W
(b) Adiabatic process : U W
(c) Isochoric process : U q
(d) Isothermal process : q W

8. For silver, C_p(J K ^{1}mol ^{1}) 23 0.01 T. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of H will be close to **(2019 Main, 8 April I)**

(a) 62 kJ (b) 16 kJ
(c) 21 kJ (d) 13 kJ

9. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities? **(2019 Main, 12 Jan I)**



10. The standard electrode potential E^{O} and its temperature coefficient $\frac{dE^{O}}{dT}$ for a cell are 2V and 5 10 ^{4} VK ^{1} at 300 K respectively. The cell reaction is

Zn(s) Cu^{2} (aq) Zn^{2} (aq) Cu(s)

The standard reaction enthalpy ($_rH^{O}$) at 300 K in kJ mol ^{1} is, [Use, R 8 JK ^{1} mol ^{1}and F 96,000 C mol ^{1}] **(2019 Main, 12 Jan I)**

(a) 412.8 (b) 384.0
(c) 206.4 (d) 192.0

11. The reaction, $MgO(s)\quad C(s)\quad Mg(s)\quad CO(g)$,
for which $_rH°\quad 491.1$ kJ mol ^{1} and
$_rS°\quad 198.0$ JK ^{1}mol ^{1}, is not feasible at 298 K.
Temperature above which reaction will be feasible is
(a) 2040.5 K (b) 1890.0 K
(c) 2380.5 K (d) 2480.3 K

12. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $_rG°\quad A\quad BT$
Where A and B are non-zero constants.
Which of the following is true about this reaction?
(2019 Main, 11 Jan II)
(a) Endothermic if, $A\quad 0$ and $B\quad 0$
(b) Exothermic if, $B\quad 0$
(c) Exothermic if, $A\quad 0$ and $B\quad 0$
(d) Endothermic if, $A\quad 0$

13. For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$_rG \text{ (in kJ mol}^{-1}) = 120 \quad \frac{3}{8}T$$

The major component of the reaction mixture at T is
(2019 Main, 11 Jan I)
(a) Y if $T\quad 280$ K (b) X if $T\quad 350$ K
(c) X if $T\quad 315$ K (d) Y if $T\quad 300$ K

14. Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, S, for this process is **(2019 Main, 11 Jan I)**
(a) $^2C_p \ln \frac{(T_1\quad T_2)^{1/2}}{T_1T_2}$ (b) $^2C_p \ln \frac{T_1\quad T_2}{4T_1T_2}$
(c) $C_p \ln \frac{(T_1\quad T_2)^2}{4T_1T_2}$ (d) $^2C_p \ln \frac{T_1\quad T_2}{2T_1T_2}$

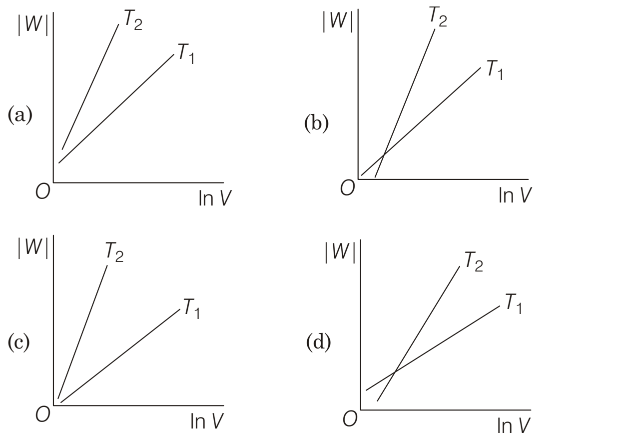
15. The process with negative entropy change is
(2019 Main, 10 Jan II)
(a) synthesis of ammonia from N_2 and H_2
(b) dissociation of $CaSO_4$(s) to CaO(s) and $SO_3(g)$
(c) dissolution of iodine in water
(d) sublimation of dry ice

16. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm ^{2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol ^{1}K ^{1}, the temperature of Al increases by **(2019 Main, 10 Jan II)**
(a) $\frac{3}{2}$ K (b) 1 K (c) 2 K (d) $\frac{2}{3}$ K

17 A process has $H\quad 200$ J mol ^{1} and $S\quad 40$ JK ^{1} mol ^{1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous
(2019 Main, 10 Jan I)
(a) 20 K (b) 4 K (c) 5 K (d) 12 K

18 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is
(Specific heat of water liquid and water vapour are 4.2 kJ K ^{1}kg ^{1} and 2.0 kJK ^{1} kg ^{1}; heat of liquid fusion and vapourisation of water are 334 kJ kg ^{1} and 2491 kJkg ^{1} respectively). (log 273 2.436, log 373 2.572, log 383 2.583) **(2019 Main, 9 Jan II)**
(a) 9.26 kJ kg ^{1} K ^{1} (b) 8.49 kJ kg ^{1}K ^{1}
(c) 7.90 kJ kg ^{1}K ^{1} (d) 2.64 kJ kg ^{1}K ^{1}

19 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 $(T_1\quad T_2)$. The correct graphical depiction of the dependence of work done (W) on the final volume (V) is
(2019 Main, 9 Jan I)



20. The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is 3263.9 kJ mol ^{1} at 25° C; heat of combustion (in kJ mol ^{1}) of benzene at constant pressure will be (R 8.314 JK ^{1}mol ^{1}) **(2018 Main)**
(a) 4152.6 (b) 452.46
(c) 3260 (d) 3267.6

21. U is equal to **(2017 Main)**
(a) isochoric work (b) isobaric work
(c) adiabatic work (d) isothermal work

22. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T 298 K are

$_fG$ [C(graphite)] 0 kJ mol ^{1}

$_fG$ [C(diamond)] 2.9 kJ mol ^{1}

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2 10 ^{6} m^3 mol ^{1}. If C(graphite) is converted to C(diamond) isothermally at T 298K, the pressure at which C(graphite) is in equilibrium with C(diamond), is **(2017 Adv.)**

[Useful information : 1 J $1 \text{kg m}^2\text{s}^{2}$,
1 Pa $1 \text{kg m}^{1} \text{s}^{2}$; 1 bar 10^5 Pa]

(a) 58001 bar (b) 1450 bar
(c) 14501 bar (d) 29001 bar

23. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm.

In this process, the change in entropy of surroundings (S_{surr}) in JK^{1} is (1 L atm   101.3 J) **(2016 Adv.)**

(a) 5.763 (b) 1.013 (c) 1.013 (d) 5.763

24. The following reaction is performed at 298K

$$2NO(g) \quad O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? (K_p 1.6 10^{12}) **(2015 Main)**

(a) $R(298) \ln (1.6 \quad 10^{12}) - 86600$

(b) $86600 \quad R(298) \ln (1.6 \quad 10^{12})$

(c) $86600 - \dfrac{\ln (1.6 \quad 10^{12})}{R(298)}$

(d) $0.5 [2 \quad 86600 - R(298) \ln (1.6 \quad 10^{12})]$

25. For the process, $H_2O(l)$ $H_2O(g)$ at T 100 C and 1 atmosphere pressure, the correct choice is **(2014 Adv.)**

(a) S_{system} 0 and $S_{\text{surrounding}}$ 0
(b) S_{system} 0 and $S_{\text{surrounding}}$ 0
(c) S_{system} 0 and $S_{\text{surrounding}}$ 0
(d) S_{system} 0 and $S_{\text{surrounding}}$ 0

26. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be
(R 8.314 J / mol K, ln 7.5   2.01) **(2013 Main)**

(a) q 208 J, W 208 J
(b) q 208 J, W 208 J
(c) q 208 J, W 208 J
(d) q 208 J, W 208 J

27. For the process $H_2O(l)$ (1 bar, 373 K) $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is **(2007, 3M)**

(a) G 0, S ve (b) G 0, S ve
(c) G ve, S 0 (d) G ve, S ve

28. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is
(Given : ${}_rH_{298\text{K}}$ 54.07 kJ mol^{1},
${}_rS_{298\text{K}}$ 10 JK^{1} mol^{1} and R 8.314 $\text{JK}^{1}\text{mol}^{1}$;
2.303   8.314   298   5705) **(2007, 3M)**

(a) 5 (b) 10 (c) 95 (d) 100

29. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

C D

A B

Given that $S_{(A \quad C)}$ 50 eu
$S_{(C \quad D)}$ 30 eu
$S_{(D \quad B)}$ –20 eu where, eu is entropy unit

Then, $S_{(A \quad B)}$ is **(2006, 3M)**

(a) + 100 eu (b) +60 eu
(c) –100 eu (d) –60 eu

30. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas ? **(2006, 3M)**

(a) $\dfrac{4R}{2}$ (b) $\dfrac{3R}{2}$ (c) $\dfrac{5R}{2}$ (d) 0

31. One mole of monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 L to 2 L. Find out the final temperature (R = 0.0821 L atm K^{1} mol^{1}) **(2005, 1M)**

(a) T (b) $\dfrac{T}{(2)^{5/3 \quad 1}}$

(c) $T \quad \dfrac{2}{3 \quad 0.082}$ (d) $T \quad \dfrac{2}{3 \quad 0.082}$

32. 2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change? **(2004, 1M)**

(a) 4.98 kJ (b) 11.47 kJ (c) –11.47 kJ (d) 0 kJ

33. Spontaneous adsorption of a gas on solid surface is an exothermic process because **(2004, 1M)**

(a) H increases for system (b) S increases for gas
(c) S decreases for gas (d) G increases for gas

34. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K)   (4.0 atm, 5.0 L, 245 K) with a change in internal energy, E 30.0 L-atm. The change in enthalpy (H) of the process in L-atm is **(2002, 3M)**

(a) 40.0 (b) 42.0
(c) 44.0
(d) not defined, because pressure is not constant

35. Which of the following statements is false? **(2001, 1M)**

(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states are specified
(d) Work appears at the boundary of the system

36. In thermodynamics, a process is called reversible when **(2001, 1M)**

(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

37. For an endothermic reaction, where H represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be **(1992, 1M)**

(a) less than H (b) zero
(c) more than H (d) equal to H

38. The difference between heats of reaction at constant pressure and constant volume for the reaction

$2C_6H_6\ (l) + 15O_2 \qquad 12CO_2(g) + 6H_2O(l)$

at 25 C in kJ is **(1991, 1M)**

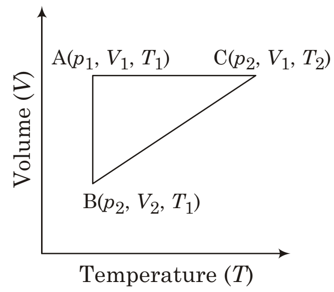
(a) 7.43 (b) + 3.72

(c) 3.72 (d) + 7.43

Objective Questions II

(One or more than one correct option)

39. A reversible cyclic process for an ideal gas is shown below. Here, p, V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively. **(2018 Adv.)**



The correct options is (are)

(a) $q_{AC} \quad U_{BC}$ and $w_{AB} \quad p_2(V_2 \quad V_1)$

(b) $w_{BC} \quad p_2(V_2 \quad V_1)$ and $q_{BC} \quad H_{AC}$

(c) $H_{CA} \quad U_{CA}$ and $q_{AC} \quad U_{BC}$

(d) $q_{BC} \quad H_{AC}$ and $H_{CA} \quad U_{CA}$

40. An ideal gas is expanded form (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) **(2017 Adv.)**

(a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly form V_1 to V_2 under isothermal conditions.

(b) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 \quad T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \quad T_2$

(c) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

(d) The work done on the gas is maximum when it is compressed irrversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1

41. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by **(2017 Adv.)**

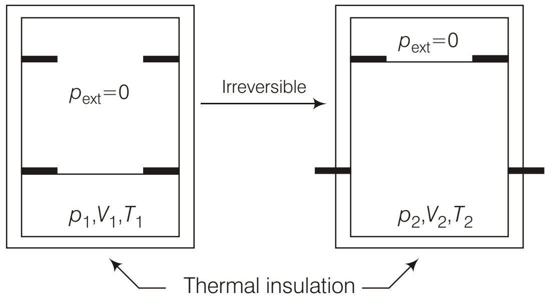
(a) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

(b) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surrounding decreases

(c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

(d) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

42. An ideal gas in thermally insulated vessel at internal pressure p_1, volume V_1 and absolute temperature T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2, respectively. For this expansion



(2014 Adv.)

(a) $q \quad 0$ (b) $T_2 \quad T_1$

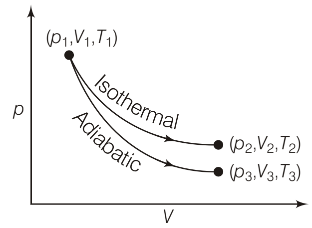
(c) $p_2V_2 \quad p_1V_1$ (d) $p_2V_2 \quad p_1V_1$

43. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are) **(2013 Adv.)**

(a) G is positive (b) S_{system} is positive

(c) $S_{surroundings} \quad 0$ (d) $H \quad 0$

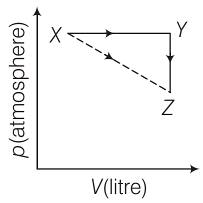
44. The reversible expansion ob an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? **(2012)**



(a) $T_1 \quad T_2$ (b) $T_3 \quad T_1$

(c) $W_{isothermal} \quad W_{adiabatic}$ (d) $U_{isothermal} \quad U_{adiabatic}$

45. For an ideal gas, consider only P-V work in going from initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure.



[Take S as change in entropy and W as work done].

Which of the following choice(s) is (are) correct? **(2012)**

(a) $S_{X \quad Z} \quad S_{X \quad Y} \quad S_{Y \quad Z}$
(b) $W_{X \quad Z} \quad W_{X \quad Y} \quad W_{Y \quad Z}$
(c) $W_{X \quad Y \quad Z} \quad W_{X \quad Y}$
(d) $S_{X \quad Y \quad Z} \quad S_{X \quad Y}$

46. Among the following, extensive property is (properties are) **(2010)**
(a) molar conductivity (b) electromotive force
(c) resistance (d) heat capacity

47. Among the following, the state function(s) is(are)
(a) internal energy **(2009)**
(b) irreversible expansion work
(c) reversible expansion work
(d) molar enthalpy

48. Identify the intensive quantities from the following. **(1993, 1M)**
(a) enthalpy (b) temperature
(c) volume (d) refractive index

Assertion and Reason

Read the following questions and answer as per the direction given below :
(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

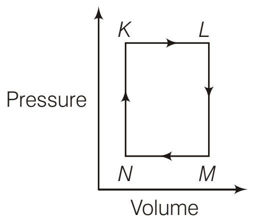
49. **Statement I** There is a natural asymmetry between converting work to heat and converting heat to work.
Statement II No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. **(2008, 3M)**

50. **Statement I** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
Statement II At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **(2008, 3M)**

51. **Statement I** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Statement II The volume occupied by the molecules of an ideal gas is zero. **(2000, S, 1M)**

Passage Based Questions

A fixed mass m of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. **(2013 Adv.)**



52. The pair of isochoric processes among the transformation of states is
(a) K to L and L to M
(b) L to M and N to K
(c) L to M and M to N
(d) M to N and N to K

53. The succeeding operations that enable this transformation of states are
(a) heating, cooling, heating, cooling
(b) cooling, heating, cooling, heating
(c) heating, cooling, cooling, heating
(d) cooling, heating, heating, cooling

Match the Columns

54. Match the thermodynamic processes given under Column I with the expressions given under Column II.

	Column I		Column II
A.	Freezing of water at 273 K and 1 atm	p.	$q \quad 0$
B.	Expansion of 1 mole of an ideal gas into a vacuum under isolated conditions	q.	$W \quad 0$
C.	Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	r.	$S_{sys} \quad 0$
D.	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	s.	$U \quad 0$
		t.	$G \quad 0$

55. Match the transformations in Column I with appropriate options in Column II. **(2011)**

	Column I		Column II
A.	$CO_2(s) \quad CO_2(g)$	p.	Phase transition
B.	$CaCO_3(s) \quad CaO(s) \quad CO_2(g)$	q.	Allotropic change
C.	$2H \quad H_2(g)$	r.	H is positive
D.	$P_{(white,\ solid)} \quad P_{(red,\ solid)}$	s.	S is positive
		t.	S is negative

Fill in the Blanks

56. Enthalpy is an .... property. **(1997, 1M)**

57. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... **(1997)**

58. The heat content of the products is more than that of the reactants in an .... reaction. **(1993, 1M)**

59. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. **(1993, 1M)**

60. C_p C_V for an ideal gas is .... **(1984, 1M)**

61. The total energy of one mole of an ideal monatomic gas at 27 C is ....cal. **(1984, 1M)**

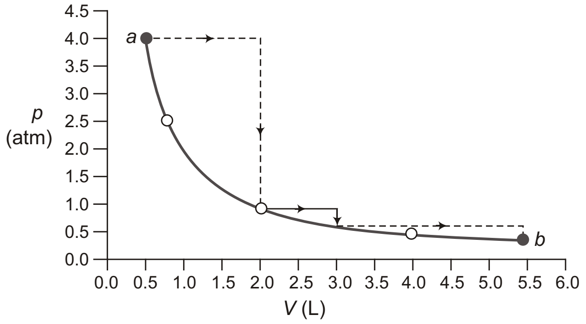
True/False

62. First law of thermodynamics is not adequate in predicting the direction of a process. **(1982, 1M)**

63. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. **(1985, 1/2 M)**

Integer Answer Type Questions

64. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is W_s and that along the dotted line path is W_d, then the integer closest to the ratio W_d / W_s is **(2010)**



Subjective Questions

65. For the reaction, $2CO \quad O_2 \quad 2CO_2$; $H \quad 560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of U at 500 K. (1 L-atm = 0.1 kJ) **(2006, 3M)**

66. 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the H and U. **(2004, 2M)**

67. C_V value of He is always $\frac{3R}{2}$ but C_V value of H_2 is $\frac{3R}{2}$ at low temperature and $\frac{5R}{2}$ at moderate temperature and more than $\frac{5R}{2}$ at higher temperature. Explain in two or three lines. **(2003, 2M)**

68. Two moles of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)

(i) Sketch with labels each of the processes on the same p-V diagram.

(ii) Calculate the total work (W) and the total heat change (Q) involved in the above processes.

(iii) What will be the values of U, H and S for the overall process? **(2002, 5M)**

69. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175 C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175 C. Calculate G for the following equilibria.

$$B \rightleftharpoons A, \qquad G_1 = ?$$
$$B \rightleftharpoons C, \qquad G_2 = ?$$

From the calculated value of G_1 and G_2 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). **(2001, 10M)**

70. Show that the reaction, $CO(g) + \frac{1}{2}O_2(g) \qquad CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is 0.094 kJ mol ^{1} K ^{1}. The standard Gibbs' free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol ^{1}, respectively. **(2000, 3M)**

71. A sample of argon gas at 1 atm pressure and 27 C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process C_{V_m} for argon is 12.49 JK ^{1} mol ^{1}. **(2000, 4M)**

72. A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25 C produces 6.11 L of CO_2. Find out the amount of heat evolved on burning 1 L of the gas mixture. The heat of combustion of ethylene and methane are 1423 and 891 kJ mol ^{1} at 25 C. **(1991, 5M)**

73. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. **(1989, 2M)**

74. Following statement is true only under some specific conditions. Write the conditions for that in not more than two sentences

"The heat energy q, absorbed by a gas is H." **(1984, 1M)**

Topic 2 Thermochemistry

Objective Questions I (Only one correct option)

1. Enthalpy of sublimation of iodine is 24 cal g^{1} at 200°C. If specific heat of $I_2(s)$ and I_2(vap.) are 0.055 and 0.031 cal g^{1} K^{1} respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{1} is **(2019 Main, 12 April I)**

(a) 2.85 (b) 5.7 (c) 22.8 (d) 11.4

2. Given :

(i) C(graphite) $O_2(g)$ $CO_2(g)$; $_rH^{\ominus}$ x kJ mol^{1}

(ii) C(graphite) $\frac{1}{2}O_2(g)$ $CO_2(g)$; $_rH^{\ominus}$ y kJ mol^{1}

(iii) $CO(g)$ $\frac{1}{2}O_2(g)$ $CO_2(g)$; $_rH^{\ominus}$ z kJ mol^{1}

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct? **(2019 Main, 12 Jan II)**

(a) y $2z$ x (b) x y z
(c) z x y (d) x y z

3. Given, $C_{(graphite)}$ $O_2(g)$ $CO_2(g)$; $_rH$ 393.5 kJ mol^{1}

$H_2(g)$ $\frac{1}{2}O_2(g)$ $H_2O(l)$; $_rH$ 285.8 kJ mol^{1}

$CO_2(g)$ 2 $H_2O(l)$ $CH_4(g)+2O_2(g)$; $_rH$ 890.3 kJ mol^{1}

Based on the above thermochemical equations, the value of $_rH$ at 298 K for the reaction, **(2017 Main)**
$C_{(graphite)}$ 2 $H_2(g)$ $CH_4(g)$ will be

(a) 78.8 kJ mol^{1} (b) 144.0 kJ mol^{1}
(c) 74.8 kJ mol^{1} (d) 144.0 kJ mol^{1}

4. The heats of combustion of carbon and carbon monoxide are 393.5 and 283.5 kJ mol^{1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is **(2016 Main)**

(a) 676.5 (b) 676.5
(c) 110.5 (d) 110.5

5. For the complete combustion of ethanol, $C_2H_5OH(l)+3O_2(g)$ $2CO_2(g)+3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{1} at 25°C. Assuming ideality the enthalpy of combustion, $_CH$, for the reaction will be (R = 8.314 J K^{-1}mol^{-1}) **(2014 Main)**

(a) 1366.95 kJ mol^{1} (b) 1361.95 kJ mol^{1}
(c) 1460.50 kJ mol^{1} (d) 1350.50 kJ mol^{1}

6. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are 400 kJ/mol, 300 kJ/mol and 1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is **(2013 Adv.)**

(a) 2900 kJ (b) 2900 kJ
(c) 16.11 kJ (d) 16.11 kJ

7. Using the data provided, calculate the multiple bond energy (kJ mol^{1}) of a C C bond C_2H_2. That energy is (take the bond energy of a C H bond as 350 kJ mol^{1}) **(2012)**

$2C(s)$ $H_2(g)$ $C_2H_2(g)$; H 225 kJ mol^{1}
$2C(s)$ $2C(g)$; H 1410 kJ mol^{1}
$H_2(g)$ $2H(g)$; H 330 kJ mol^{1}

(a) 1165 (b) 837 (c) 865 (d) 815

8. The species which by definition has zero standard molar enthalpy of formation at 298 K is **(2010)**

(a) $Br_2(g)$ (b) $Cl_2(g)$
(c) $H_2O(g)$ (d) $CH_4(g)$

9. The bond energy (in kcal mol^{1}) of C—C single bond is approximately **(2010)**

(a) 1 (b) 10
(c) 100 (d) 1000

10. H_{vap} 30 kJ/mol and S_{vap} 75 Jmol^{-1}K^{-1}. Find the temperature of vapour, at one atmosphere **(2004, 1M)**

(a) 400 K (b) 350 K (c) 298 K (d) 250 K

11. Which of the following reactions defines H_f? **(2003, 1M)**

(a) $C_{(diamond)}+O_2(g)$ $CO_2(g)$
(b) $\frac{1}{2}H_2(g)+\frac{1}{2}F_2(g)$ $HF(g)$
(c) $N_2(g)+3H_2(g)$ $2NH_3(g)$
(d) $CO(g)+\frac{1}{2}O_2(g)$ $CO_2(g)$

12. The H_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are 393.5, 110.5 and 241.8 kJ mol^{1} respectively. The standard enthalpy change (in kJ mol^{1}) for the reaction $CO_2(g)+H_2(g)$ $CO(g)+H_2O(g)$ is **(2000, 1M)**

(a) 524.1 (b) + 41.2
(c) 262.5 (d) 41.2

Objective Question II
(One or more than one correct option)

13. The following is/are endothermic reaction(s) **(1999, 3M)**

(a) Combustion of methane
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethylene
(d) Conversion of graphite to diamond

14. The thermal dissociation of equilibrium of $CaCO_3(s)$ is studied under different conditions. **(2013 Adv.)**

$$CaCO_3(s) \rightleftharpoons CaO(s) \quad CO_2(g)$$

For this equilibrium, the correct statement(s) is/are

(a) H is dependent on T

(b) K is independent of the initial amount of $CaCO_3$

(c) K is dependent on the pressure of CO_2 at a given T

(d) H is independent of the catalyst, if any

Subjective Questions

15. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increases from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{1} is **(2009)**

16. Diborane is a potential rocket fuel which undergoes combustion according to the reaction

$$B_2H_6(g) + 3O_2(g) \qquad B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane. **(2000, 2M)**

$$2B(s) + \frac{3}{2}O_2(g) \qquad B_2O_3(s); \qquad H = \ 1273 \text{ kJ mol}^{1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \qquad H_2O(l); \qquad H = \ 286 \text{ kJ mol}^{-1}$$

$$H_2O(l) \qquad H_2O(g); \qquad H = 44 \text{ kJ mol}^{1}$$

$$2B(s) + 3H_2(g) \qquad B_2H_6(g); \qquad H = 36 \text{ kJ mol}^{1}$$

17. Estimate the average S–F bond energy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are : – 1100, 275 and 80 kJ mol^{-1} respectively. **(1999, 3M)**

18. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propane (g) are –393.5, 285.8 and 20.42 kJ mol^{1} respectively. The enthalpy of isomerisation of cyclopropane to propene is 33.0 kJ mol^{1}. **(1998, 5M)**

19. Compute the heat of formation of liquid methyl alcohol in kJ mol^{1}, using the following data. Heat of vaporisation of liquid methyl alcohol 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H 218 kJ/mol, C 715 kJ/mol, O 249 kJ/mol.
Average bond energies: **(1997, 5M)**
C—H 415 kJ/mol, C—O 356 kJ/mol,
O—H 463 kJ/mol

20. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25 C are 156 and + 49 kJ mol^{1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25 C is 119 kJ mol^{1}. Use these data to estimate the magnitude of the resonance energy of benzene. **(1996, 2M)**

21. The polymerisation of ethylene to linear polyethylene is represented by the reaction,

$$n[CH_2 \quad CH_2] \qquad [CH_2—CH_2]_n$$

where, n has large integral value. Given that the average enthalpies of bond dissociation for C C and C C at 298 K are +590 and +311 kJ/mol respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K. **(1994, 2M)**

22. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10}.
In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc., are the same for both fuels and that the gases behave ideally. Heats of combustions:
CH_4= 809 kJ/mol, C_4H_{10} 2878 kJ/mol **(1993, 3M)**

23. Determine the enthalpy of the reaction,
$C_3H_8(g) + H_2(g) \quad C_2H_6(g) + CH_4(g)$, at 25 C, using the given heat of combustion values under standard conditions.

Compound :	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
H (kJ/mol):	285.8	890.0	1560.0	393.0

The standard heat of formation of $C_3H_8(g)$ is 103 kJ/mol. **(1992, 3M)**

24. Using the data (all values are in kilocalories per mol at 25 C) given below, calculate the bond energy of C C and C H bonds.

$$C(s) \qquad C(g); \qquad H = 172$$

$$H_2(g) \qquad 2H(g); \qquad H = 104$$

$$H_2(g) + \frac{1}{2}O_2(g) \qquad H_2O(l); \qquad H \quad 68.0$$

$$C(s) + O_2(g) \qquad CO_2(g); \qquad H \quad 94.0$$

Heat of combustion of C_2H_6 372.0

Heat of combustion of C_3H_8 530.0 **(1990, 5M)**

25. The standard enthalpy of combustion at 25 C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are 241, 3800 and 3920 kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene. **(1989, 2M)**

26. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows:

$H_f(Al_2O_3)$ 399 kcal/mol

$H_f(Fe_2O_3)$ 199 kcal/mol

Density of Fe_2O_3 5.2 g/cc, Density of Al 2.7 g/cc **(1989, 2M)**

27. The standard molar heat of formation of ethane, carbon dioxide and liquid water are 21.1, 94.1 and 68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. **(1986, 2M)**

28. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. **(1985, 2M)**

29. Given the following standard heats of reactions

(i) heat of formation of water 68.3 kcal

(ii) heat of combustion of acetylene 310.6 kcal

(iii) heat of combustion of ethylene 337.2 kcal

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25 C). **(1984, 4M)**

30. The molar heats of combustion of $C_2H_2(g)$, C (graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $C_2H_2(g)$. **(1983, 2M)**

31. The standard heats of formation of $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ at 298 K are 25.5, 57.8, 94.1 and 22.1 kcal/mol respectively. Calculate H (298 K) for the reaction

$$CCl_4(g) \quad 2H_2O(g) \qquad CO_2(g) \quad 4HCl(g)$$ **(1982, 2M)**

32. The enthalpy for the following reactions (H) at 25°C are given below

(i) $\frac{1}{2}H_2(g) \quad \frac{1}{2}O_2(g) \qquad OH(g) \quad H \qquad 10.06$ kcal

(ii) $H_2(g) \qquad 2H(g) \qquad H \quad 104.18$ kcal

(iii) $O_2(g) \qquad 2O(g) \qquad H \quad 118.32$ kcal

Calculate the O — H bond energy in the hydroxyl radical. **(1981, 2M)**

Passage Based Questions

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (57.0 kJ mol ^{1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \quad 10^{5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

33. Enthalpy of dissociation (in kJ mol ^{1}) of acetic acid obtained from the Expt. 2 is

(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4

34. The pH of the solution after Expt. 2 is

(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

Answers

Topic 1 Thermodynamics

1. (c)	**2.** (a)	**3.** (b)	**4.** (a)
5. (d)	**6.** (c)	**7.** (b)	**8.** (a)
9. (a)	**10.** (a)	**11.** (d)	**12.** (d)
13. (c)	**14.** (c)	**15.** (a)	**16.** (d)
17. (c)	**18.** (a)	**19.** (c)	**20.** (d)
21. (c)	**22.** (c)	**23.** (c)	**24.** (d)
25. (b)	**26.** (a)	**27.** (a)	**28.** (b)
29. (b)	**30.** (a)	**31.** (c)	**32.** (d)
33. (c)	**34.** (c)	**35.** (a)	**36.** (c)
37. (c)	**38.** (a)	**39.** (b,c)	**40.** (a, c, d)
41. (a, b)	**42.** (a,b,c)	**43.** (b,c,d)	**44.** (a,c,d)
45. (a,c)	**46.** (c,d)	**47.** (a,c,d)	**48.** (b, d)
49. (b)	**50.** (d)	**51.** (b)	**52.** (b)
53. (c)			

54. A r, t; B p, q, s; C p, q, s; D p,q, s, t

55. A p, r, s; B r, s; C t; D p, q, t

56. extensive	**57.** zero	**58.** exothermic reaction	
59. isolated	**60.** *R*	**61.** 900	**62.** T
63. T	**64.** (2)	**65.** (563 kJ)	**69.** (12.3 kJ)
70. (285.4 kJ)	**71.** (116.4 J)	**72.** (49.82 kJ)	**73.** (318.96 g)

Topic 2 Thermochemistry

1. (c)	**2.** (d)	**3.** (c)	**4.** (c)
5. (a)	**6.** (c)	**7.** (d)	**8.** (b)
9. (c)	**10.** (a)	**11.** (b)	**12.** (b)
13. (b,c,d)	**14.** (a, b, c, d)	**15.** (9 kJ)	**16.** (2035 kJ)
17. (309.16 kJ)		**18.** (2091.32 kJ)	**19.** (116.4 kJ)
20. (152 kJ/mol)		**21.** (32 kJ/mol)	
22. (5.46 *x*L/h)		**23.** (55 kJ)	
25. (121 kJ/mol)		**27.** (372 kcal/mol)	
28. (22 kcal/mol)		**29.** (41.7 kcal)	
30. (54.2 kcal)		**31.** (41.4 kcal)	
32. (121.31 kcal)		**33.** (1 kJ/mol)	**34.** (4.7)

Hints & Solutions

Topic 1 Thermodynamics

1.

> **Key Idea** Work done during isothermal expansion of an ideal gas is given by the equation.
>
> $W \quad p_{\text{ext}}(V_2 \quad V_1)$

According to the given conditions, the expansion is against constant external pressure. So, the work done is given by following formula;

$W \quad p_{\text{ext}}(V_2 \quad V_1)$

$1\,\text{bar}(10\text{L} \quad 1\text{L}) \quad 9\text{ L bar} \qquad (\because 1\text{L bar} \quad 100\text{J})$

$9 \quad 100\text{ J} \quad 0.9\text{ kJ}$

2.

> **Key Idea** The relation between H and U is
>
> $H \quad U \quad n_g RT$
>
> where, $n_g \quad n_p \quad n_R$
>
> number of moles of gaseous products number of moles of gaseous reactants.

The general combustion reaction of a hydrocarbon is as follows :

$$C_xH_y \quad x \quad \frac{y}{4}O_2 \qquad xCO_2 \quad \frac{y}{2}H_2O$$

For heptane, $x \quad 7$, $y \quad 16$

$$C_7H_{16}(l) + 11O_2(g) \qquad 7CO_2(g) + 8H_2O(l)$$

$$n_g \quad 7 \quad 11 \quad 4$$

Now, from the principle of thermochemistry,

$$H \quad U \quad n_g RT$$

$$H \quad U \quad n_g RT \quad 4RT$$

3. A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. $G \quad 0$.

Spontaneity of a process is decided by the value of G, which can be predicted from the Gibb's equation, $G \quad H \quad T \; S$ for positive/negative signs of H and S at any/higher/lower temperature as:

H	***S***	**Comment on temperature (T)**	***G***	**Comment on the process**
0	0	at any temp.	0	spontaneous
0	0	at any temp.	0	non-spontaneous
0	0	at lower temp.	0	spontaneous
0	0	at higher temp.	0	spontaneous

4. In the given system, during the compression of a spring the workdone is 10 kJ and 2 kJ of heat is escaped to the surroundings. So, $q \quad 2\text{ kJ}$ and $W \quad 10\text{ kJ}$

According to the first law of thermodynamics,

$$U \quad q \quad W \quad 2\text{ kJ} \quad 10\text{kJ}$$

$$U \quad 8\text{ kJ}$$

The change in internal energy, U (in kJ) is 8 kJ.

5. q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. $q \quad W$ and option (d), i.e. $H–TS$ are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

6. Given,

$n \quad 5\text{ mol},\ T_2 \quad 200\text{ K},\ T_1 \quad 100\text{ K}$

$C_V \quad 28\text{ JK}^{\;1}\text{mol}^{\;1}$

$U \quad nC_V \; T$

$nC_V(T_2 \quad T_1)$

$5\text{ mol} \quad 28\text{ JK}^{\;1}\text{mol}^{\;1} \quad (200 \quad 100)\text{ K}$

$14{,}000\text{ J} \quad 14\text{ kJ}$

$pV \quad nR \; T$

$nR(T_2 \quad T_1)$

$5\text{ mol} \quad 8\text{JK}^{\;1}\text{mol}^{\;1} \quad (200 \quad 100)\text{ K}$

$4000\text{ J} \quad 4\text{ kJ}$

7. From the 1st law of thermodynamics,

$$U \quad q \quad W$$

where, U change in internal energy

q heat

W work done

The above equation can be represented for the given processes involving ideal gas as follows:

(a) **Cyclic process** For cyclic process, $U \quad 0$

$$q \quad W$$

Thus, option (a) is correct.

(b) **Adiabatic process** For adiabatic process,

$$q \quad 0$$

$$U \quad W$$

Thus, option (b) is incorrect.

(c) **Isochoric process** For isochoric process, $V \quad 0$.

Thus, $W \quad 0 \qquad (\because W \quad p \; V)$.

$$V \quad q$$

Thus, option (c) is correct.

(d) **Isothermal process** For isothermal process, $U \quad 0$

$$q \quad W$$

Thus, option (d) is correct.

8. According to Kirchoff's relation,

$$H \quad n \; {}_{T_1}^{T_2} C_p dT \qquad \ldots\text{(i)}$$

where, H Change in enthalpy.

C_p Heat capacity at constant pressure.

Given, n 3 moles, T_1 300 K, T_2 1000 K, C_p 23 0.01 T

On substituting the given values in Eq. (i), we get

$$H \quad 3 \;{}_{300}^{1000}(23 \quad 0.01\,T)dT \quad 3 \;{}_{300}^{1000} 23dT \quad 0.01T\; dT$$

$$3 \;\; 23T \quad \frac{0.01\,T^2}{2}\Big|_{300}^{1000}$$

$$3 \;\; 23\,(1000 \quad 300) \quad \frac{0.01}{2}(1000^2 \quad 300^2)$$

$$3\,[16100 \quad 4550] \quad 61950\text{ J} \quad 62\text{ kJ}$$

9. For diatomic ideal gases,

$$C_V \quad \frac{f}{2}R \text{ and } C_p \quad \frac{f}{2} \quad 1 \;\; R$$

where, f degree of freedom

f translational degree of freedom rotational degree of freedom

3 2 5 [at normal temperature]

The explanation of various plots are as follows.

(a) We know that, C_p is heat capacity at constant pressure. Thus, it does not vary with the variation in pressure. Hence, plot given in option (a) is incorrect.

(b) In this plot, C_V first increases slightly with increase in temperature and then increases sharply with temperature. The sharp increase is due to increase in degree of freedom.

Thus, plot given in option (b) is correct.

(c) For ideal gases,

Internal energy (U) T

Thus, as temperature increases internal energy also increases. As temperature increases further degree of freedom also increases thus, there is slight variation in the graph. First translational degree of freedom is present followed by rotational and vibrational degree of freedom. Hence, plot given in option (c) is also correct.

(d) C_V is heat capacity at constant volume. Thus, it does not vary with variation in volume. Hence, plot given in option (d) is correct.

10. Given,

$$E \quad 2\text{V}, \quad \frac{dE}{dT} \quad 5 \quad 10^{\;4}\,\text{VK}^{\;1}$$

$$T \quad 300\text{K}, \; R \quad 8\,\text{JK}^{\;1}\text{mol}^{\;1},$$

$$F \quad 96000\,\text{Cmol}^{\;1}$$

According to Gibbs-Helmholtz equation,

$$G \quad H \quad T\; S \qquad \ldots\text{(i)}$$

Also, $$G \quad nFE_{\text{cell}} \qquad \ldots\text{(ii)}$$

On substituting the given values in equation (ii), we get

$$G \quad 2 \quad 96000\text{ C mol}^{\;1} \quad 2\text{V}$$

[$\because n$ 2 for the given reaction]

$$4 \quad 96000\text{J mol}^{\;1}$$

$$384000\text{J mol}^{\;1}$$

Now, $$S \quad nF\,\frac{dE}{dT}$$

or $$S \quad 2 \quad 96000\,\text{C mol}^{\;1} \quad (\;5 \quad 10^{\;4}\text{VK}^{\;1})$$

$$96\,\text{JK}^{\;1}\,\text{mol}^{\;1}$$

Thus, on substituting the values of G and S in Eq. (i), we get

$$384000\,\text{J mol}^{\;1}$$

$$H \quad 300\text{ K} \quad (\;96\text{ JK}^{\;1}\text{mol}^{\;1})$$

$$H \quad 384000 \quad 28800\,\text{J mol}^{\;1}$$

$$412800\text{J mol}^{\;1}$$

$$412.800\text{ kJ mol}^{\;1}$$

11. According to Gibbs-Helmholtz equation,

$${}_rG \quad {}_rH \quad T\;{}_rS$$

For a reaction to be feasible (spontaneous)

$${}_rG \quad 0$$

$${}_rH \quad T\;{}_rS \;<0$$

Given, ${}_rH$ 491.1 kJ mol$^{\;1}$,

${}_rS$ 198 JK$^{\;1}$mol$^{\;1}$

$$491.1 \quad 10^3 \quad T \quad 198 \quad 0$$

$$T \quad \frac{491.1 \quad 10^3}{198} \quad 2480.3\text{ K}$$

Above 2480.3 K reaction will become spontaneous.

12. According to Gibb's Helmholtz equation,

$${}_rG \quad {}_rH \quad T\;{}_rS$$

Given, $${}_rG \quad A \quad BT$$

On comparing above two equations, we get,

$$A \quad H \text{ and } S \quad B$$

We know that, if H is negative, reaction is exothermic and when it is positive, reaction is endothermic.

If A 0, i.e. positive, reaction is endothermic.

13. For a given value of T,

(i) If ${}_rG$ becomes < 0, the forward direction will be spontaneous and then the major and minor components will be Y and X respectively.

(ii) If ${}_rG$ becomes > 0, the forward direction will be non-spontaneous and then the major and minor components will be X and Y respectively.

(a) ${}_rG \quad 120 \quad \frac{3}{8} \quad 280 \quad 15$

i.e. ${}_rG$ O 0, major component X;

(b) ${}_rG \quad 120 \quad \frac{3}{8} \quad 350 \quad 11.25$

i.e. ${}_rG$ 0, major component Y

(c) ${}_rG \quad 120 \quad \frac{3}{8} \quad 315 \quad 1.875$

i.e. ${}_rG$ 0, major component X

(d) ${}_rG \quad 120 \quad \frac{3}{8} \quad 300 \quad 7.5$

i.e. ${}_rG$ 0, major component X

14. At the thermal equilibrium,

final temperature $T_f \quad \dfrac{T_1 \quad T_2}{2}$

for the 1st block, $S_{\mathrm{I}} \quad C_p \ln \frac{T_f}{T_1}$

for the 2nd block, $S_{\mathrm{II}} \quad C_p \ln \frac{T_f}{T_2}$

When brought in contact with each other,

$$S \quad S_{\mathrm{I}} \quad S_{\mathrm{II}} \quad C_p \ln \frac{T_f}{T_1} \quad C_p \ln \frac{T_f}{T_2}$$

$$C_p \ln \frac{T_f}{T_1} \frac{T_f}{T_2} \quad C_p \ln \frac{T_f^2}{T_1 T_2}$$

$$C_p \ln \frac{\left(\frac{T_1 \quad T_2}{2}\right)^2}{T_1 T_2} \quad C_p \ln \frac{(T_1 \quad T_2)^2}{4T_1 T_2}$$

15. The explanation of all the options are as follows :

(a) $N_2(g) \quad 3H_2(g) \qquad 2NH_3(g)$,

$n_g \quad 2 \quad (1 \quad 3) \qquad 2$

So, S is also negative (entropy decreases)

(b) $CaSO_4(s) \qquad CaO(s) \quad SO_3(g)$,

$n_g \quad (1 \quad 0) \quad 0 \qquad 1$

So, S ve

(c) In dissolution, S ve because molecules/ions of the solid solute (here, iodine) become free to move in solvated/dissolved state of the solution,

$$I_2(s) \xrightarrow[\text{(KI)}]{\text{Water}} I_2(aq)$$

(d) In sublimation process, molecules of solid becomes quite free when they become gas,

$$\underset{\text{Dry ice}}{CO_2(s)} \qquad CO_2(g)$$

So, S will be positive.

16. It is an irreversible isothermal compression of an ideal gas.

(i) $dE \quad dq \quad p(V_f \quad V_i)$

where, dE Internal energy change

dq amount of heat released

$0 \quad dq \quad p(V_f \quad V_i)$

[$\because dE \quad 0$ for an isothermal process]

$dq \qquad 4\,(1 \quad 5) \quad 16\text{ J}$

(ii) $dq \quad n \quad C \qquad T$ (for Al)

$16\text{ J} \quad 1\text{ mol} \quad 24\text{ J mol}^{1}\text{ K}^{1} \qquad T$

$$T \quad \frac{16}{24}\text{K} \quad \frac{2}{3}\text{K}$$

17. $G \quad H \quad T\,S$

The process will be spontaneous, when

G ve, i.e. $|T \; S| \quad | \; H|$

Given : $H \quad 200\text{ J mol}^{1}$ and $S \quad 40\text{ JK}^{1}\text{mol}^{1}$

$$T \quad \frac{|\;H|}{|\;S|} \quad \frac{200}{40} \quad 5\text{ K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

18. The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:

$$\underset{273\text{K}}{H_2O(s)} \xrightarrow{S_1} \underset{273\text{K}}{H_2O(l)} \xrightarrow{S_2} \underset{373\text{K}}{H_2O(l)}$$

$$\downarrow S_3$$

$$\underset{383\text{K}}{H_2O(g)} \xleftarrow[S_4]{} \underset{373\text{K}}{H_2O(g)}$$

$$S_1 \quad \frac{H_{\text{Fusion}}}{T_{\text{Fusion}}} \quad \frac{334\text{ kJ kg}^{1}}{273\text{ K}} \quad 1.22\text{ kJ kg}^{1}\text{K}^{1}$$

$$S_2 \quad C \ln \frac{T_2}{T_1} \quad 4.2\text{ kJ K}^{1}\text{kg}^{1} \ln \frac{373\text{ K}}{273\text{ K}}$$

$4.2 \quad 2.303\,(\log 373 \quad \log 273)\text{ kJ K}^{1}\text{kg}^{1}$

$4.2 \quad 2.303\,(2.572 \quad 2.436) \quad 1.31\text{ kJ K}^{1}\text{kg}^{1}$

$$S_3 \quad \frac{H_{\text{vap.}}}{T_{\text{vap.}}} \quad \frac{2491\text{ kJ kg}^{1}}{373\text{ K}}$$

$6.67\text{ kJ kg}^{1}\text{K}^{1}$

$$S_4 \quad C \ln \frac{T_2}{T_1} \quad 2\text{ kJ K}^{1}\text{kg}^{1} \ln \frac{383\text{ K}}{373\text{ K}}$$

$2 \quad 2.303\,(\log 383 \quad \log 373)\text{ kJ K}^{1}\text{kg}^{1}$

$2 \quad 2.303\,(2.583 \quad 2.572)\text{ kJ K}^{1}\text{kg}^{1}$

$0.05\text{ kJ K}^{1}\text{kg}^{1}$

$S_{\text{Total}} \quad S_1 \quad S_2 \quad S_3 \quad S_4$

$1.22 \quad 1.31 \quad 6.67 \quad 0.05$

$9.26\text{ kJ kg}^{1}\text{K}^{1}$

19. For isothermal reversible expansion,

$$|W| \quad nRT \ln \frac{V_f}{V_i} \quad nRT \ln \frac{V}{V_i}$$

where, V final volume, V_i initial final.

or $|W| \quad nRT \ln V \quad nRT \ln V_i$

On comparing with equation of straight line, $y \quad mx \quad c$, we get

slope $m \quad nRT$

intercept $nRT \ln V_i$

Thus, plot of $|W|$ with $\ln V$ will give straight line in which slope of $2(T_2)$ is greater than slope of $1(T_1)$ which is given in all options.

Now, if $V_i \quad 1$ then y intercept ($nRT \; V_i$) becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y-intercept goes above and other y-intercept goes below. Thus, option (b) and (d) are incorrect.

If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y-intercept. But they cannot give same y-intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then y-intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

20. **Key idea** Calculate the heat of combustion with the help of following formula

$$H_p \quad U \quad n_g RT$$

where, H_p Heat of combustion at constant pressure
U Heat at constant volume (It is also called E)
n_g Change in number of moles (In gaseous state).
R Gas constant; T Temperature.

From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g) \quad 6CO_2(g) + 3H_2O(l)$$

Change in the number of gaseous moles i.e.

$$n_g \quad 6 \quad \frac{15}{2} \quad \frac{3}{2} \text{or} \quad 1.5$$

Now we have n_g and other values given in the question are

$$U \quad 3263.9 \text{ kJ/mol}$$
$$T \quad 25 \; C \quad 273 \quad 25 \quad 298 \text{ K}$$
$$R \quad 8.314 \text{ JK}^{\;1} \text{mol}^{\;1}$$

So, $H_p \quad (\; 3263.9) \quad (\; 1.5) \quad 8.314 \quad 10^{\;3} \quad 298$

$$3267.6 \text{ kJ mol}^{\;1}$$

21. According to first law of thermodynamics,

$$U \quad q \quad W \quad q \quad p \; V$$

In isochoric process (V 0), U q
In isobaric process (p 0), U q
In adiabatic process (q 0), U W
In isothermal process (T 0) and U 0
U is equal to adiabatic work.

22. $G \quad H \quad TS \quad U \quad pV \quad TS$

$$dG \quad dU \quad pdV \quad Vdp \quad TdS \quad SdT \quad Vdp \quad SdT$$
$$[\because dU \quad pdV \quad dq \quad TdS]$$
$$dG \quad Vdp \text{ if isothermal process } (dT \quad 0)$$
$$G \quad V \; p$$

Now taking initial state as standard state

$$G_{gr} \quad G_{gr} \quad V_{gr} \; p \qquad \ldots\text{(i)}$$
$$G_d \quad G_d \quad V_d \; p \qquad \ldots\text{(ii)}$$

Now (ii)-(i) gives,

$$(V_d \quad V_{gr}) \; p \quad G_d \quad G_{gr} \quad (G_{gr} \quad G_d$$

At equilibrium, $G_d \quad G_{gr}$

$$(V_{gr} \quad V_d) \; p \quad G_d \quad G_{gr} \quad 2.9 \quad 10^3 \text{ J}$$
$$p \quad \frac{2.9 \quad 10^3}{2 \quad 10^{\;6}} \text{Pa} \quad \frac{29}{2} \quad 10^8 \text{ Pa} \quad \frac{29000}{2} \text{ bar}$$
$$p \quad p_0 \quad \frac{29000}{2} \quad 1 \quad \frac{29000}{2} \quad 14501 \text{ bar}$$

23. By first law, $E \quad Q \quad W$

For isothermal expansion, $E \quad 0$

$$Q \quad W$$
$$Q_{\text{irrev}} \quad W_{\text{irrev}} \quad p \; V \quad 3(2 \quad 1) \quad 3 \text{ L atm}$$

Also, $S_{\text{surr}} \quad \dfrac{Q_{\text{irrev}}}{T} \quad \dfrac{(\;\;3 \quad 101.3) \text{ J}}{300 \text{ K}} \quad \dfrac{303.9}{300} \quad 1.013 \text{ JK}^{\;1}$

24. For the given reaction,

$$2NO(g) \quad O_2(g) \rightleftharpoons 2NO_2(g)$$

Given, $G_f(\text{NO}) \quad 86.6 \text{ kJ/mol}$

$$G_f(\text{NO}_2) \quad ?$$
$$K_p \quad 1.6 \quad 10^{12}$$

Now, we have,

$$G_f \quad 2 \; G_{f(\text{NO}_2)} \quad [2 \; G_{f(\text{NO})} \quad G_{f(\text{O}_2)}]$$
$$RT \; \ln K_p \quad 2 \; G_{f(\text{NO}_2)} \quad [2 \quad 86{,}600 \quad 0]$$
$$G_{f(\text{NO}_2)} \quad \frac{1}{2}[2 \quad 86600 \quad R \quad 298 \ln (1.6 \quad 10^{12})]$$
$$G_{f(\text{NO}_2)} \quad 0.5\,[2 \quad 86{,}600 \quad R \quad (298) \ln (1.6 \quad 10^{12})]$$

25. **PLAN** This problem is based on assumption that total entropy change of universe is zero.

At 100°C and 1 atmosphere pressure,

$$H_2O\,(l) \rightleftharpoons H_2O(g) \text{ is at equilibrium.}$$

For equilibrium, $S_{\text{total}} \quad 0$
and $S_{\text{system}} \quad S_{\text{surrounding}} \quad 0$

As we know during conversion of liquid to gas entropy of system increases, in a similar manner entropy of surrounding decreases.

$$S_{\text{system}} \quad 0 \text{ and } S_{\text{surrounding}} \quad 0$$

26. The process is isothermal expansion, hence

$$q \quad W$$
$$E \quad 0$$
$$W \quad -2.303 \; nRT \; \log \frac{V_2}{V_1}$$
$$2.303 \quad 0.04 \quad 8.314 \quad 310 \quad \log \frac{335}{50}$$
$$208 \text{ J}$$
$$q \quad 208 \text{ J}$$
$$W \quad 208 \text{ J} \quad \text{(expansion work)}$$

27. At transition point (373 K, 1.0 bar), liquid remains in equilibrium with vapour phase, therefore $G \quad 0$. As vaporisation occur, degree of randomness increases, hence $S \quad 0$.

28. $G \quad H \quad T \; S = -54.07 \quad 10^3 \text{ J} - 298 \times 10 \text{ J}$

$$-57.05 \times 10^3 \text{ J}$$

Also, $G \quad 2.303 \; RT \log K$

$$\log K \quad \frac{G}{2.303 \; RT}$$
$$\frac{57.05 \quad 10^3}{5705} \quad 10$$

29. Entropy is a state function hence,

$$S_{A \quad B} \quad S_{A \quad C} \quad S_{C \quad D} \quad S_{D \quad B}$$
$$50 \text{ eu} + 30 \text{ eu} + (-20 \text{ eu})$$
$$60 \text{ eu}$$

30. Given, $\frac{p}{V} \quad 1 \qquad p \quad V$ ...(i)

Also from first law : $dq \quad C_V dT \quad pdV$

For one mole of an ideal gas : $pV \quad RT$

$$pdV \quad Vdp \quad RdT \qquad ...(ii)$$

From (i) $\qquad pdV \quad Vdp$

Substituting in Eq. (ii) gives

$$2pdV \quad RdT \qquad pdV \quad \frac{R}{2}dT$$

$$dq \quad C_V dT \quad \frac{R}{2}dT$$

$$\frac{dq}{dT} \quad C_V \quad \frac{R}{2} \quad \frac{3}{2}R \quad \frac{R}{2} \quad 2R$$

31. For an irreversible, adiabatic process;

$$0 \quad C_V (T_2 \quad T_1) \quad p_e (V_2 \quad V_1)$$

Substituting the values

$$C_V (T \quad T_2) \quad 1(2 \quad 1) \text{atm L}$$

$$T \quad T_2 \quad \frac{1}{C_V} \quad \frac{2}{3R} \qquad T_2 \quad T \quad \frac{2}{3 \quad 0.082}$$

32. In case of reversible thermodynamic process,

$$H \quad nC_p \quad T$$

Process is isothermal, $T \quad 0 \qquad H \quad 0$

33. For a spontaneous process $G \quad 0$

Also; $G \quad H \quad T \ S$

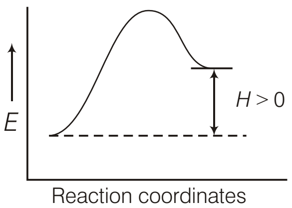
For adsorption of gas on solid surface, $S \quad 0$. Therefore, in order to be $G \quad 0$, H must be negative.

34. $H \quad U \quad (pV) \quad 30 \quad 2(5 \quad 3) \quad 5(4-2) = 44$ L atm.

35. Work is not a state-function, it depends on path followed.

36. In a reversible thermodynamic process, system always remains in equilibrium with surroundings.

37.



Minimum value of activation energy must be greater than H.

38. $H \quad E \quad n_g RT \qquad H \quad E \quad n_g RT \quad 3RT$

$$3 \quad 8.314 \quad 298 \quad 7433 \text{ J} = -7.43 \text{ kJ}$$

39. In the given curve AC represents **isochoric process** as volume at both the points is same i.e., V_1

Similarly, AB represents **isothermal process** (as both the points are at T_1 temperature) and BC represents **isobaric process** as both the points are at p_2 pressure.

Now (i) for option (a)

$$q_{AC} \quad U_{BC} \quad nC_V (T_2 \quad T_1)$$

where, n number of moles

C_v specific heat capacity at constant volume

However, $W_{AB} \quad p_2(V_2 \quad V_1)$ instead

$$W_{AB} \quad nRT_1 \ln \frac{V_2}{V_1}$$

So, this option is incorrect.

(ii) For option (b)

$$q_{BC} \quad H_{AC} \quad nC_p (T_2 \quad T_1)$$

where, C_p specific heat capacity at constant pressure

Likewise,

$$W_{BC} \quad p_2(V_1 \quad V_2)$$

Hence, this option is correct.

(iii) For option (c)

as $\qquad nC_p (T_2 \quad T_1) \quad nC_V (T_2 \quad T_1)$

so $\qquad H_{CA} \quad U_{CA}$

and $\qquad q_{AC} \quad U_{BC}$

Hence, this option is also correct.

(iv) For option (d)

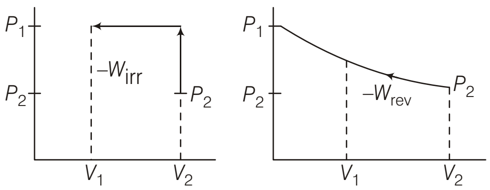
Although $q_{BC} \quad H_{AC}$

but $H_{CA} \quad U_{CA}$

Hence, this option is incorrect.

40.

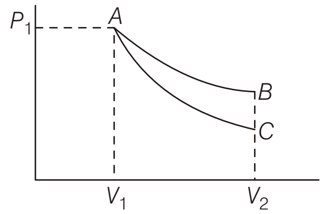
(a)



Irreversible compression $\qquad$ Reversible compression

Maximum work is done on the system when compression occur irreversibly and minimum work is done is reversible compression.

(b)



AB is isothermal and AC is adiabatic path. Work done is area under the curve. Hence, less work is obtained in adiabatic process than in isothermal

(c) It is incorrect. In adiabatic expansion cooling is observed, hence $U \quad nC_v \quad T \quad 0$.

(d) $q \quad 0$ (adiabatic), $W \quad 0$ (Free expansion)

Hence, $U \quad 0, \quad T \quad 0$ (Isothermal)

41. $S_{\text{surr}} \quad \frac{H}{T_{\text{surr}}}$

For endothermic reaction, if T_{surr} increases, S_{surr} will increase.
For exothermic reaction, if T_{surr} increases, S_{surr} will decrease.

42. **PLAN** This problem includes concept of isothermal adiabatic irreversible expansion.

Process is adiabatic because of the use of thermal insolution therefore, $q \quad 0$

$\because \quad p_{ext} \quad 0$

$w \quad p_{ext} \quad V \quad 0 \quad V \quad 0$

Internal energy can be written as

$$U \quad q \quad W \quad 0$$

The change in internal energy of an ideal gas depends only on temperature and change in internal energy (U) 0 therefore, T 0 hence, process is isothermal and

$$T_2 \quad T_1$$

and $$p_2V_2 \quad p_1V_1$$

(d) $p_2V_2 \quad p_1V_1$ is incorrect, it is valid for adiabatic reversible process.

Hence, only (a), (b) and (c) are correct choices.

43. **PLAN** When an ideal solution is formed process is spontaneous thus

According to Raoult's law, for an ideal solution

$$H \quad 0, \quad V_{min} \quad 0$$

From the relation

$$G \quad H \quad T\,S$$

Since, $$H \quad 0$$

$$G \quad ve$$

i.e. less than zero. and $S_{surroundings} \quad 0$

Therefore, $S_{sys} \quad ve$

i.e. more than zero.

44. (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 \quad T_2$.

(b) Since, change of state (p_1, V_1, T_1) to (p_3, V_3, T_3) is an adiabatic expansion it brings about cooling of gas, therefore, $T_3 \quad T_1$.

(c) Work done is the area under the curve of p-V diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than the same under adiabatic curve, hence $W_{isothermal} \quad W_{adiabatic}$

(d) $U \quad nC_v \quad T$

In isothermal process, $U \quad 0$ as $T \quad 0$

In adiabatic process, $U \quad nC_v(T_3 \quad T_1) \quad 0$ as $T_3 \quad T_1$.

$$U_{isothermal} \quad U_{adiabatic}$$

NOTE Here only magnitudes of work is being considered otherwise both works have negative sign.

45. (a) Entropy is a state function, change in entropy in a cyclic process is zero.

Therefore, $S_{X \quad Y} \quad S_{Y \quad Z} \quad S_{Z \quad X} \quad 0$

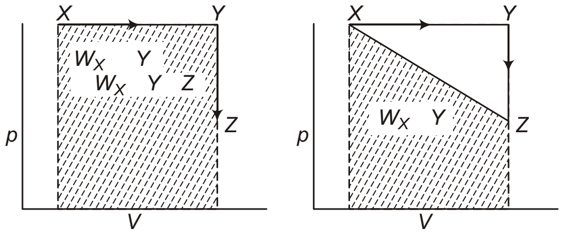
$$S_{Z \quad X} \quad S_{X \quad Y} \quad S_{Y \quad Z}$$

$$S_{X \quad Z}$$

Analysis of options (b) and (c)

Work is a non-stable function, it does depends on the path followed. $W_{Y \quad Z} \quad 0$ as $V \quad 0$.

Therefore, $W_{X \quad Y \quad Z} \quad W_{X \quad Y}$. Also, work is the area under the curve on p-V diagram.



As shown above $W_{X \quad Y} \quad W_{Y \quad Z} \quad W_{X \quad Y} \quad W_{X \quad Y \quad Z}$ but not equal to $W_{X \quad Z}$.

46. Resistance and heat capacity are mass dependent properties, hence they are extensive.

47. Internal energy, molar enthalpy are state function. Also, reversible expansion work is a state function because between given initial and final states, there can be only one reversible path.

48. Intensive properties are those property which do not depends on amount of sample. Both temperature and refractive index are intensive properties while enthalpy and volumes are extensive properties as they depends on amount of sample.

49. Statement I is true, it is statement of first law of thermodynamics.

Statement II is true, it is statement of second law of thermodynamics. However, Statement II is not the correct explanation of statement I.

50. Statement I is false. At equilibrium

$$G \quad 0, G \quad 0.$$

Statement II is true, spontaneous direction of reaction is towards lower Gibbs free energy.

51. Statement I is true.

$$dq \quad dE \quad p_{ext}\,dV \quad 0$$
$$T \quad 0$$
$$dE \quad 0\,; \quad p_{ext} \quad 0$$
$$p_{ext}\,dV \quad 0$$

Statement II is true. According to kinetic theory of gases, volume occupied by molecules of ideal gas is zero.

However, Statement II is not the correct explanation of Statement I.

52. $L \quad M$ At constant V — isochoric,

$N \quad K$

53. **PLAN** By Boyle's law at constant temperature, $p \quad \frac{1}{V}$

By Charles' law at constant pressure, $V \quad T$

Process taking place at

Constant temperature — isothermal

Constant pressure — isobaric

Constant volume — isochoric

Constant heat — adiabatic

K	L	At constant p, volume increases	thus, heating
L	M	At constant V, pressure decreases	thus, cooling
M	N	At constant p, volume decreases	thus, cooling
N	K	At constant V, pressure increases	thus, heating

54. (A) r, t ; (B) p, q, s ; (C) p, q, s ; (D) q, s, t

(A) $H_2O(l) \underset{1\,atm}{\overset{0\,C}{\rightleftharpoons}} H_2O(s)$

$q \quad 0, W \quad 0$ (expansion)

$S_{sys} \quad 0$ (solid state is more ordered than liquid state)

$U < 0; \quad G = 0$ (At equilibrium)

(B) $q = 0$ (isolated), $W = 0$ ($p_{ext} = 0$)

$S_{sys} \quad 0 \because V_2 \quad V_1$

$U \quad 0 \because q \quad W \quad 0$

$G \quad 0 \because p_2 \quad p_1$

(C) $q \quad 0$ (isothermal mixing of ideal gases at constant p)

$W \quad 0 \because \quad U \quad 0; q \quad 0, \quad S_{sys} \quad 0$

$\because \; V_2 \quad V_1, \quad U \quad 0$

$\because \quad T \quad 0$

$G \quad 0 \because$ mixing is spontaneous.

(D) $q \quad 0$ (returning to same state and by same path)

$W \quad 0$

$S_{sys} \quad 0$ (same initial and final states)

$U \quad 0$

$\because T_i \quad T_f, \quad G \quad 0$

55. (A) $CO_2(s) \qquad CO_2(g)$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence S is positive.

(B) $CaCO_3(s) \qquad CaO(s) + CO_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, $S > 0$.

(C) $2H \qquad H_2(g)$

A new H—H covalent bond is being formed, hence, $H \quad 0$.

Also, product is less disordered than reactant, $S < 0$.

(D) Allotropes are considered as different phase, hence $P_{(white,\ solid)} \qquad P_{(red,\ solid)}$ is a phase transition as well as allotropic change.

Also, red phosphorus is more ordered than white phosphorus, $S \quad 0$.

56. Extensive : Enthalpy is an extensive property while molar enthalpy is an intensive property.

57. Zero : $W \quad p \; V \quad 0 \because \quad V \quad 0$

58. Exothermic reaction.

59. **Isolated** This system neither exchange matter nor energy with surroundings.

60. R : For an ideal gas, $C_p \quad C_V \quad R$

61. 900 cal : $E \quad \frac{3}{2}RT \quad \frac{3}{2} \quad 2 \quad 300$ cal

62. **True** First law deals with conservation of energy while second law deals with direction of spontaneous change.

63. **True** Diatomic gases have more degree of freedom than a monatomic gas.

64. Work done along dashed path $| \; W| \quad p \; V$

$$4 \quad 1.5 \quad 1 \quad 1 \quad \frac{2}{3} \quad 2.5 \quad 8.65 \text{ L atm}$$

Work done along solid path $W \quad nRT \ln \frac{V_2}{V_1} \quad p_1V_1 \ln \frac{V_2}{V_1}$

$$2 \quad 2.3 \log \frac{5.5}{0.5} \quad 2 \quad 2.3 \log 11 \quad 4.79$$

$$\frac{W_d}{W_s} \quad \frac{8.65}{4.79} \quad 1.80 \quad 2$$

65. $H \quad U \quad (pV) \quad U \quad V \; p$

$U \quad H \quad V \; p$

$-560 - 1 \quad 30 \quad 0.1 = -563$ kJ

66. $U \quad q \quad W$

For adiabatic process, $q \quad 0$, hence $U \quad W$

$W \quad p(\;V) \quad p(V_2 \quad V_1)$

$U \quad 100\,(99 \quad 100) \quad 100$ bar mL

$H \quad U \quad (pV)$

where, $pV \quad p_2V_2 \quad p_1V_1$

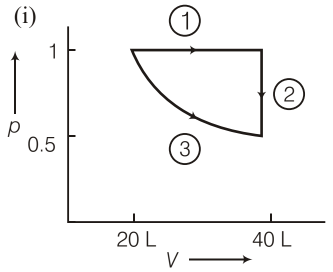
67. He is monatomic, so it has only three degree of freedom (translational only) at all temperature hence, C_V value is always $\frac{3}{2}R$.

Hydrogen molecule is diatomic, has three translational, two rotational and one vibrational degree of freedom. The energy spacing between adjacent levels are in the order of :

translational < rotational < vibrational

At lower temperature only translational degree of freedom contribute to heat capacity while at higher temperature rotational and vibrational degree of freedom starts contributing to heat capacity.

68. (i)



(ii) $W_1 \quad p \; V \quad 20$ L atm

$W_2 \quad 0 \quad \because \quad V \quad 0$

$W_3 \quad nRT \ln \frac{40}{20} \quad 20 \ln 2$

Total work done $W_1 \quad W_2 \quad W_3$

$20 \text{ L atm} \quad 0 \quad 20 \ln 2$

-6.14 atm

From first law : $q \quad E \quad (\;W) \quad W$

$(\because \quad E \quad 0$ for cyclic process)

$q \quad 6.14 \text{ L atm} = 622.53 \text{ J}$

(iii) All the states function, U, H and S are zero for cyclic process.

69. At equilibrium : $\underset{95.2\%}{B} \rightleftharpoons \underset{1.3\%}{A}$

$$K_1 \quad \frac{13}{952}$$

$$\underset{95.2\%}{B} \rightleftharpoons \underset{3.5\%}{C}$$

$$K_2 \quad \frac{35}{952}$$

$$G_1 \quad RT \ln K_1$$

$$-8.314 \quad 448 \quad 2.303 \log \frac{13}{952} = 16 \text{ kJ}$$

$$G_2 \quad RT \ln K_2$$

$$-8.314 \quad 448 \quad 2.303 \log \frac{35}{952}$$

$$12.3 \text{ kJ}$$

70. $_rG \quad _fG$ (products) – $_fG$ (reactants)

$-394.4 - (-137.2) = -257.2 \text{ kJ} < 0$

The above negative value of G indicates that the process is spontaneous.

Also, $G \quad H \quad T\,S$

$H \quad G \quad T\,S$

$-257.2 + 300\,(-0.094)$

$-285.4 \text{ kJ} < 0$

71. Given : $C_V \quad 12.49 \qquad C_p \quad 20.8$

$$\frac{C_p}{C_V} \quad 1.66$$

In case of reversible adiabatic expansion :

$$TV^{\;\;1} \text{ constant}$$

$$\frac{T_2}{T_1} \quad \frac{V_1}{V_2}^{\;\;1} \quad \frac{V_1}{V_2}^{0.66}$$

$$T_2 \quad T_1 \quad \frac{V_1}{V_2}^{0.66}$$

$$300 \quad \frac{1}{2}^{0.66} \quad 189.86 \text{ K}$$

$$H \quad nC_p \quad T$$

$$\frac{1 \quad 1.25}{0.082 \quad 300} \quad 20.8 \quad (189.86 \quad 300) \text{ J}$$

$$-116.4 \text{ J}$$

72. Let the mixture contain x litre of CH_4 and $3.67 \quad x$ litre of ethylene.

$$\underset{x}{CH_4} + O_2 \qquad \underset{x}{CO_2}$$

$$\underset{3.67 \quad x}{C_2H_4} + O_2 \qquad \underset{2\,(3.67 \quad x)}{2CO_2}$$

Given : $x \quad 2\,(3.67 \quad x) \quad 6.11 \text{ L}$

$x \quad 1.23 \text{ L}$

Volume of ethylene 2.44 L

Total moles of gases in l litre $\frac{pV}{RT} \quad \frac{1 \quad 1}{0.082 \quad 298} \quad 0.04$

Also, CH_4 and ethylene are in 1 : 2 volume (or mole) ratio, moles of CH_4 $\frac{0.04}{3}$ and moles of ethylene $\frac{2 \quad 0.04}{3}$

Heat evolved due to methane $\frac{0.04}{3} \quad 891 \quad 11.88 \text{ kJ}$

Heat evolved due to ethylene $\frac{2 \quad 0.04}{3} \quad 1423 \quad 37.94 \text{ kJ}$

Total heat evolved on combustion of 1.0L gaseous mixture at 25°C is $11.88 + 37.94 = 49.82$ kJ

73. Moles of H_2O needs to perspire $\frac{1560}{2 \quad 44} \quad 17.72$

Weight of water needs to perspire $17.72 \quad 18 \quad 318.96$ g

74. At constant pressure, $q \quad H$.

Topic 2 Thermochemistry

1.

> **Key Idea** When q is the amount of heat involved in a system then at constant pressure
> $q \quad q_p$ and $C_p \quad T \quad H$

Given reaction :

$$I_2(s) \qquad I_2(g)$$

Specific heat of $I_2(s)$ $0.055 \text{ cal g}^{\;1} \text{ K}^{\;1}$.

Specific heat of I_2(vap) $0.031 \text{ cal g}^{-1}\text{K}^{-1}$.

Enthalpy (H_1) of sublimation of iodine 24 cal g^{-1}

If q is the amount of heat involved in a system then at constant pressure $q \quad q_p$ and

$$H \quad C_p \quad T$$

$$H_2 \quad H_1 \quad C_p(T_2 \quad T_1)$$

$$H_2 \quad H_1 \quad C_p(T_2 \quad T_1)$$

$$H_2 \quad 24 \quad (0.031 \quad 0.055)\,(250 \quad 200)$$

$$H_2 \quad 24 \quad (\;0.024)\,(50) \quad 24 \quad 1.2 \quad 22.8 \text{ cal/g}$$

Thus, the enthalpy of sublimation of iodine at 250°C is 22.8 cal/g.

2. Second equation given in this question is wrong. Hence, No answer in correct.

If corrected second equation is given,

i.e. $\quad C(\text{graphite}) \quad \frac{1}{2} O_2(g) \qquad CO\,(g)$

and if we take the above reaction in consideration then $x \quad y \quad z$ will be the answer as:

(ii) $C(\text{graphite}) \quad \frac{1}{2}O_2(g) \qquad CO(g), \quad _rH \quad y\,\text{kJ/mol}$

(iii) $CO(g) \quad \frac{1}{2}O_2(g) \qquad CO_2(g), \qquad _rH \quad z\,\text{kJ/mol}$

Summing up both the equation you will get equation (i):

$$C(\text{graphite}) \quad O_2(g) \qquad CO_2(g), \qquad _rH \quad x\,\text{kJ/mol}$$

Hence, x, y and z are related as:

$$x \quad y \quad z$$

3. Based on given $_rH$

$_fH \quad H_{CO_2} \quad 393.5\,\text{kJ mol}^{\ 1}$ ...(i)

$_fH \quad H_{H_2O} \quad 285.8\,\text{kJ mol}^{\ 1}$ ...(ii)

$_fH \quad H_{O_2} \quad 0.00$ (elements) ...(iii)

Required thermal reaction is for $_fH$ of CH_4

Thus, from III

$890.3 \quad [\ _fH \ (CH_4) + 2\ _fH \ (O_2)]$

$[\ _fH \ (CO_2) \quad 2\ _fH \ (H_2O)]$

$_fH \ (CH_4) + 0] \quad [\ 393.5 \quad 2 \quad 285.5]$

$_fH \ (CH_4) = \ 74.8\ \text{kJ / mol}$

4. $C(s) + O_2(g) \qquad CO_2(g); \quad H \qquad 393.5\ \text{kJ mol}^{\ 1}$ ...(i)

$CO + \frac{1}{2}O_2 \qquad CO_2(g); \ H \qquad 283.5\,\text{kJ mol}^{\ 1}$ ...(ii)

On subtracting Eq. (ii) from Eq. (i), we get

$C\ (s) + \frac{1}{2}O_2(g) \qquad CO(g);$

$H \quad (\ 393.5 \quad 283.5)\text{kJ mol}^{\ 1}$

$110\ \text{kJ mol}^{\ 1}$ (approx.)

5. $C_2H_5OH\ (l) + 3O_2(g) \qquad 2CO_2(g) + 3H_2O(l)$

$U \quad 1364.47\,\text{kJ/mol}$

$H \quad U \quad n_gRT$

$n_g \quad 1$

$$H = \ 1364.47 + \frac{1 \quad 8.314 \quad 298}{1000}$$

[Here, value of R in unit of J must be converted into kJ]

$1364.47 \quad 2.4776 \qquad 1366.9476\ \text{kJ/mol}$

or $\quad 1366.95\ \text{kJ/mol}$

6. **PLAN** $_cH$ (Standard heat of combustion) is the standard enthalpy change when one mole of the substance is completely oxidised.

Also standard heat of formation ($_fH$) can be taken as the standard of that substance.

$H_{CO_2} \quad _fH \ (CO_2) \quad 400\ \text{kJ mol}^{\ 1}$

$H_{H_2O} \quad _fH \ (H_2O) \quad 300\ \text{kJ mol}^{\ 1}$

$H_{\text{glucose}} \quad _fH \ (\text{glucose}) \quad 1300\ \text{kJ mol}^{\ 1}$

$H_{O_2} \quad _fH \ (O_2) \quad 0.00$

$C_6H_{12}O_6(s) \quad 6\ O_2(g) \qquad 6CO_2(g) \quad 6H_2O(l)$

$_cH$ (glucose) $\quad 6[\ _fH \ (CO_2) \quad _fH \ (H_2O)]$

$[\ _fH \ (C_6H_{12}O_6) \quad 6\ _fH \ (O_2)]$

$6[\ 400 \quad 300] \quad [\ 1300 \quad 6 \quad 0]$

$2900\ \text{kJ mol}^{\ 1}$

Molar mass of $C_6H_{12}O_6 \quad 180\ \text{g mol}^{\ 1}$

Thus, standard heat of combustion of glucose per gram

$$\frac{2900}{180} \quad 16.11\ \text{kJ g}^{\ 1}$$

To solve such problem, students are advised to keep much importance in unit conversion. As here, value of R ($8.314\ \text{J K}^{\ 1}\ \text{mol}^{\ 1}$) in $\text{JK}^{\ 1}\ \text{mol}^{\ 1}$ must be converted into kJ by dividing the unit by 1000.

7. For calculation of C C bond energy, we must first calculate dissociation energy of C_2H_2 as

$C_2H_2(g) \qquad 2C(g) + 2H(g)$ ...(i)

Using the given bond energies and enthalpies :

$C_2H_2(g) \qquad 2C(g) + 2H(g); \quad H \quad 225\ \text{kJ}$ ...(ii)

$2C(s) \qquad 2C(g); \quad H \quad 1410\ \text{kJ}$ ...(iii)

$H_2(g) \qquad 2H(g); \quad H \quad 330\ \text{kJ}$ ...(iv)

Adding Eqs. (ii), (iii) and (iv) gives Eq. (i).

$C_2H_2(g) \qquad 2C(g) + 2H(g); \quad H \quad 1515\ \text{kJ}$

$1515\ \text{kJ} \quad 2 \quad (C \quad H)\ \text{BE} \quad (C \quad C)\ \text{BE}$

$2 \quad 350 \quad (C \quad C)\ \text{BE}$

$(C \quad C)\ \text{BE} \quad 1515 \quad 700 \quad 815\ \text{kJ / mol}$

8. Elements in its standard state have zero enthalpy of formation. Cl_2 is gas at room temperature, therefore H_f of $Cl_2(g)$ is zero.

9. C—C bond energy is approximately 100 kcal.

10. $T \quad \dfrac{H_{\text{vap}}}{S_{\text{vap}}} \quad \dfrac{30{,}000}{75} \quad 400\ \text{K}$

11. $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \qquad HF(g)$

Here H Standard molar enthalpy of formation of HF(g).

12. $CO_2(g) + H_2(g) \qquad CO(g) + H_2O(g)$

$H \quad _fH$ (products) $\quad _fH$ (reactants)

$-110.5 - 241.8 - (-393.5) = +41.20\ \text{kJ}$

13. $H_2O \qquad H_2 + \frac{1}{2}O_2, \quad H \quad 0$

It is reverse of combustion of $H_2(g)$, hence endothermic.

$C_2H_6 \qquad C_2H_4 \quad H_2; \qquad H \quad 0$

Here, more stable (saturated) hydrocarbon is being transformed to less stable (unsaturated) hydrocarbon, hence endothermic.

$C_{(gr)} \qquad C_{(d)}, \qquad H \quad 0$

More stable allotrope is being converted to less stable allotrope.

14. **PLAN** Heat of reaction is dependent on temperature (Kirchhoff's equation) in heterogeneous system, equilibrium constant is independent on the molar concentration of solid species.

Heat of reaction is not affected by catalyst. It lowers activation energy.

$$CaCO_3(s) \rightleftharpoons CaO(s) \quad CO_2(g)$$

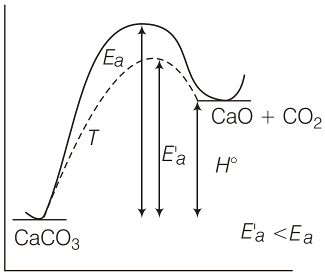
By Kirchhoff's equation,

H_2 (at T_2) H_1 (at T_1) $C_p(T_2 \quad T_1)$

H varies with temperature. Thus, (a) is correct.

$K \quad p_{CO_2}$

K is dependent on pressure of CO_2 but independent of molar concentration of $CaCO_3$. Thus, (b) and (c) are correct. At a given temperature, addition of catalysis lowers activation energy, H remaining constant. Thus, (d) is also correct.



E_a Activation energy in absence of catalyst

E_a Activation energy in presence of catalyst

15. Temperature rise $T_2 \quad T_1$ 298.45 – 298 = 0.45 K

q heat capacity T = 2.5 0.45 = 1.125 kJ

Heat produced per mole $\dfrac{1.125}{3.5}$ 28 9 kJ

16. $H_r \quad H_f\ (B_2O_3) + 3\ H_f\ (H_2O) - H_f\ (B_2H_6)$

$H_f\ (H_2O)(g) \quad H_f\ (H_2O)(l) + 44 \quad -242$ kJ

$H_r \quad -1273 - 3 \quad 242 - 36$

-2035 kJ

17. $SF_6\ (g) \quad S\ (g) + 6F\ (g)$

$H \quad H_f$ (products) H_f (reactants)

275 + 6 80 + 1100 = 1855 kJ

Average S—F bond energy $\dfrac{1855}{6}$ = 309.16 kJ/mol

18. Given : Cyclopropane Propene (C_3H_6); H 33 kJ

Propene (C_3H_6) $\dfrac{9}{2}O_2 \quad 3CO_2(g) + 3H_2O(l)$;

H – 3 (393.5 + 285.8) – 20.42 = – 2058.32 kJ

Adding :

Cyclopropane $\dfrac{9}{2}O_2\ (g) \quad 3CO_2(g) + 3H_2(g)$;

$H \quad H_1 \quad H_2$

33 (2058.32) kJ

H 2091.32 kJ

19. Given : $CH_3OH\ (g) \quad CH_3OH\ (l)$; H 38 kJ

$C\ (g) + 4H\ (g) + O\ (g) \quad CH_3OH\ (g)$;

H (3 415 356 463)

∵ $H \quad H_1 \quad H_2$ 2064 kJ

$C(g) \quad C(g)$; H 715 kJ

$2H_2\ (g) \quad 4H\ (g)$;

H 2 2 218 872 kJ

$\dfrac{1}{2}O_2\ (g) \quad O\ (g)$; H 249 kJ

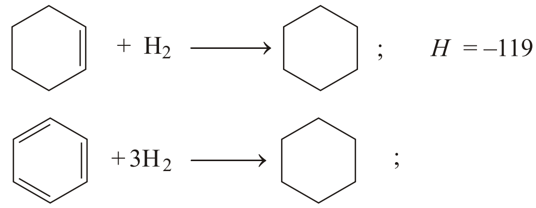
Adding : $C\ (gr) + 2H_2\ (g) + \dfrac{1}{2}O_2\ (g) \quad CH_3OH(l)$

H 266 kJ/mol

$\dfrac{1 \quad 1.25}{0.082 \quad 300}$ 20.8 (189.86 300) J

116.4 J

20.



H = –119 × 3 = – 357 kJ (Theoretical)

– 357 kJ = H_f (cyclohexane) H_f (C_6H_6)

$H_f\ (C_6H_6)_{Theoretical}$ = – 156 + 357 = 201 kJ

Resonance energy H_f (exp.) H_f (Theoretical)

49 – 201 – 152 kJ/mol

21. Per mole of ethylene polymerized, one C C bond is broken and two C—C bonds are formed.

H (Polym.) 590 2 311

– 32 kJ/mol

22. At same temperature and pressure, equal volumes contain equal moles of gases.

Let 1.0 L of CH_4 contain 'n' mol

x L of CH_4 contain nx mol

Heat evolved in combustion by x L CH_4 = 809 nx kJ

Now, 2878 kJ energy is evolved from 1 mole $\dfrac{1}{n}$ L C_4H_{10}.

809 nx kJ energy will be evolved from $\dfrac{809\ nx}{2878\ n}$ L of C_4H_{10}

0.28 x L of C_4H_{10}

Also, the combustion reaction of butane is

$C_4H_{10} + \dfrac{13}{2}O_2 \quad 4CO_2 + 5H_2O$

Rate of supply of oxygen $\dfrac{13}{2}$ 0.28 x 3

= 5.46 x L/h

23. First we need to determine heat of combustion of C_3H_8.

$3C(gr) + 4H_2(g) \quad C_3H_8\ (g) \quad H_f$ 103 kJ

– 103 kJ = – 3 393 – 4 285.80 – H_{comb} (C_3H_8)

$H_{\text{comb}}(C_3H_8) = -2219.20$ kJ

$H_r \quad H_{\text{comb}}$ (reactants) $\quad H_{\text{comb}}$ (products)

$-2219.20 - 285.80 + 1560 + 890$

$= -55$ kJ

24. Let x kcal be the C—C bond energy and y kcal be the C—H bond energy per mole.

$2C(gr) + 3H_2(g) \quad C_2H_6(g);$

$H \quad -2 \quad 94 - 3 \quad 68 + 372$

-20 kcal

$-\ 20$ kcal $\quad 2 \quad 172 \quad 3 \quad 104 \quad$ BE (C_2H_6)

BE (C_2H_6) $\quad 676$ kcal

Similarly, $3C(gr) + 4H_2(g) \quad C_3H_8(g);$

$H \quad -3 \quad 94 - 4 \quad 68 + 530$

$= -24$ kcal

-24 kcal $\quad 3 \quad 172 \quad 4 \quad 104 \quad$ BE (C_3H_8)

BE (C_3H_8) $\quad 956$ kcal

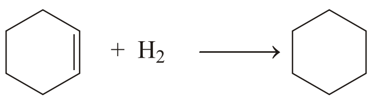
Also, $\quad$ BE (C_2H_6) $\quad 676$ kcal $\quad x \quad 6y$ $\quad$ …(i)

BE (C_3H_8) $\quad 956$ kcal $\quad 2x \quad 8y$ $\quad$ …(ii)

Solving Eqs. (i) and (ii) gives

$y \quad 99$ kcal (C—H) BE

$x \quad 82$ kcal (C—C) BE

25. 

$H \quad H_{\text{comb}}$ (reactants) $\quad H_{\text{comb}}$ (products)

$= -3800 - 241 - (-3920)$

$= -121$ kJ/mol

26. $Fe_2O_3(s) + 2Al(s) \quad Al_2O_3(s) + 2Fe(s)$

$H_r \quad H_f$ (products) $\quad H_f$ (reactants)

$= -399 - (-199)$

$= -200$ kcal

Mass of reactants $\quad 56 \quad 2 \quad 16 \quad 3 \quad 27 \quad 2 \quad 214$ g

Fuel value/gram $\quad \frac{200}{214} \quad 0.93$ kcal/g

Volume of reactants $\quad \frac{160}{5.2}$ cc $+ \frac{54}{2.7}$ cc $= 50.77$ cc

Fuel value/cc $\quad \frac{200}{50.77} \quad 3.94$ kcal/cc

27. $H \quad H_f$ (products) $\quad H_f$ (reactants)

$-2 \quad 94.1 - 3 \quad 68.3 - (-21.1)$

-372 kcal/mol

28. $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \quad HCl(g); \quad H_f$

$H_f \quad$ BE (reactants) $\quad$ BE (products)

$\frac{1}{2}(104 \quad 58) \quad 103 = -22$ kcal/mol

29. $C_2H_2 + H_2 \quad C_2H_4$

$H \quad H_{\text{comb}}$ (reactants) $\quad H_{\text{comb}}$ (products)

$-310.6 - 68.3 - (-337.2)$

-41.7 kcal

30. The standard state formation reaction of $C_2H_2(g)$ is :

$2C(g) + H_2(g) \quad C_2H_2(g); \quad H_f$

$H_r \quad H_{\text{comb}}$ (reactants) $\quad H_{\text{comb}}$ (products)

$-2 \quad 94.05 - 68.32 - (-310.62)$

54.2 kcal $= \ H_f(C_2H_2)$

31. $H_r \quad {}_fH$ (products) $\quad {}_fH$ (reactants)

$-94.1 + 4(-22.1) - (-25.5 - 2 \quad 57.8)$

$= -41.4$ kcal

32. $H \quad$ BE (reactants) $\quad$ BE (products)

$10.06 \quad \frac{1}{2}(104.18) \quad \frac{1}{2}(118.32) \quad$ BE (O $\quad$ H)

BE (O—H) = 121.31 kcal

33. Let C JK ^{1} be the heat capacity of calorimeter.

Mass of solution $\quad 200$ mL $\quad 1$ g mL ^{1} $\quad 200$ g

Heat evolved in Expt.1

$57 \quad 1000 \quad 0.1$(mol) $\quad 5700$ J

5700 J $\quad (200 \quad 4.2 \quad C) \quad 5.7$

$1000 \quad 200 \quad 4.2 \quad C$ $\quad$ …(i)

Let x kJ/mol is heat evolved in neutralisation of acetic acid.

$x \quad 1000 \quad 0.10 \quad (200 \quad 4.2 \quad C) \quad 5.6$

$\frac{x \quad 100}{5.6} \quad 200 \quad 4.2 \quad C$ $\quad$ …(ii)

From (i) and (ii) : $x \quad 56$ kJ/mol

Enthalpy of ionisation of acetic acid

$56 \quad (\quad 57) \quad 1$ kJ/mol

34. $CH_3COOH + NaOH \quad CH_3COONa + H_2O$

200 mmol	100 mol	0	0
100 mmol	0	100 mmol	

A buffer is now formed.

$$K_a \quad \frac{[H^+][CH_3COO\ \ ]}{[CH_3COOH]} \quad [H\ \ ]$$

$[\because [CH_3COOH] \quad [CH_3COO\ \ ]]$

$pH \quad pK_a \quad \log(2 \quad 10^{\ 5}) \quad 5 \quad \log 2 \quad 4.7$

Download Chapter Test
http://tinyurl.com/y6ylao38 *or*

8

Solid State

Objective Questions I (Only one correct option)

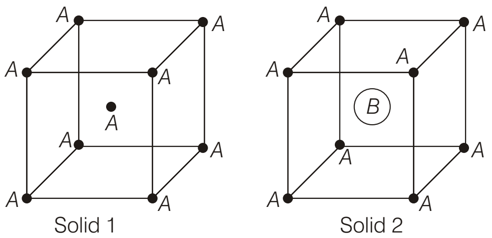
1. The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are, respectively. **(2019 Main, 12 April II)**

(a) 8 : 1 : 6 (b) 1 : 2 : 4
(c) 4 : 2 : 1 (d) 4 : 2 : 3

2. An element has a face-centred cubic (fcc) structure with a cell edge of a. The distance between the centres of two nearest tetrahedral voids in the lattice is **(2019 Main, 12 April I)**

(a) $\sqrt{2}a$ (b) a (c) $\dfrac{a}{2}$ (d) $\dfrac{3}{2}a$

3. Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more is solid 2 than in 1. What is the approximate packing efficiency in solid 2? **(2019 Main, 8 April II)**



(a) 65% (b) 90%
(c) 75% (d) 45%

4. The statement that is incorrect about the interstitial compounds is **(2019 Main, 8 April II)**

(a) they are very hard
(b) they have metallic conductivity
(c) they have high melting points
(d) they are chemically reactive

5. Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is **(2019 Main, 8 April I)**

(a) A_2BO_4 (b) AB_2O_4
(c) A_2B_2O (d) A_4B_2O

6. The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is (Edge length is represented by 'a') **(2019 Main, 11 Jan II)**

(a) 0.134 a (b) 0.027 a (c) 0.047 a (d) 0.067 a

7. A solid having density of $9 \quad 10^3 \text{ kg m}^{\ 3}$ forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid?
[Avogadro constant $6 \quad 10^{23} \text{ mol}^{\ 1}$, $\quad 3$] **(2019 Main, 11 Jan I)**

(a) 0.03050 kg mol ^{1} (b) 0.4320 kg mol ^{1}
(c) 0.0432 kg mol ^{1} (d) 0.0216 kg mol ^{1}

8. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms ? **(2019 Main, 10 Jan II)**

(a) hcp lattice- A, $\dfrac{2}{3}$ tetrahedral voids-B
(b) hcp lattice-A, $\dfrac{1}{3}$ tetrahedral voids-B
(c) hcp lattice-B, $\dfrac{1}{3}$ tetrahedral voids-A
(d) hcp lattice-B, $\dfrac{2}{3}$ tetrahedral voids-A

9. Which primitive unit cell has unequal edge lengths ($a \quad b \quad c$) and all axial angles different from 90°? **(2019 Main, 10 Jan I)**

(a) Hexagonal (b) Monoclinic
(c) Tetragonal (d) Triclinic

10. At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm ^{3}) at this temperature?
[Atomic mass of Cu $\quad$ 63.55 u] **(2019 Main, 9 Jan II)**

(a) $\dfrac{211}{x^3}$ (b) $\dfrac{205}{x^3}$
(c) $\dfrac{105}{x^3}$ (d) $\dfrac{422}{x^3}$

11. The one that is extensively used as a piezoelectric material is **(2019 Main, 9 Jan I)**

(a) quartz (b) tridymite
(c) amorphous silica (d) mica

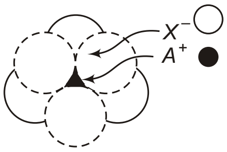
12. Which type of 'defect' has the presence of cations in the interstitial sites? **(2018 Main)**
(a) Schottky defect (b) Vacancy defect
(c) Frenkel defect (d) Metal deficiency defect

13. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be **(2017 Main)**
(a) $2a$ (b) $2\sqrt{2}\,a$
(c) $\sqrt{2}\,a$ (d) $\frac{a}{\sqrt{2}}$

14. Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately **(2015 Main)**
(a) 1.86Å (b) 3.22Å
(c) 5.72Å (d) 0.93Å

15. CsCl crystallises in body centred cubic lattice. If 'a' its edge length, then which of the following expressions is correct? **(2014 Main)**
(a) $r_{Cs} \quad r_{Cl} \quad 3a$ (b) $r_{Cs} \quad r_{Cl} \quad \frac{3a}{2}$
(c) $r_{Cs} \quad r_{Cl} \quad \frac{\sqrt{3}}{2}a$ (d) $r_{Cs} \quad r_{Cl} \quad \sqrt{3}a$

16. The arrangement of X ions around A ion in solid AX is given in the figure (not drawn to scale). If the radius of X is 250 pm, the radius of A is **(2013 Adv.)**

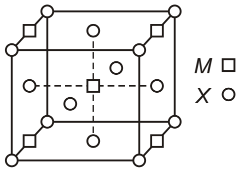


(a) 104 pm (b) 125 pm
(c) 183 pm (d) 57 pm

17. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3} would be
(a) 7.01% (b) 4.08% **(2013 Main)**
(c) 6.05% (d) 5.08%

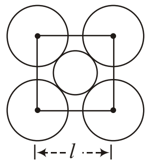
18. Which of the following exists as covalent crystals in the solid state? **(2013 Main)**
(a) Iodine (b) Silicon
(c) Sulphur (d) Phosphorus

19. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound, is **(2012)**



(a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}

20. The packing efficiency of the two-dimensional square unit cell shown below is **(2010)**



(a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

21. Which of the following fcc structure contains cations in alternate tetrahedral voids? **(2005, 1M)**
(a) NaCl (b) ZnS (c) Na_2O (d) CaF_2

22. A substance A_xB_y crystallises in a face centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y **(2002, 1M)**
(a) AB_3
(b) A_4B_3
(c) A_3B
(d) composition cannot be specified

23. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is **(2001, S, 1M)**
(a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4

24. The coordination number of a metal crystallising in a hexagonal close-packed structure is **(1999, 2M)**
(a) 12 (b) 4 (c) 8 (d) 6

Objective Questions II
(One or more than one correct option)

25. The correct statement(s) for cubic close packed (ccp) three dimensional structure is (are) **(2016 Adv.)**
(a) The number of the nearest neighbours of an atom present in the topmost layer is 12
(b) The packing efficiency of atom is 74%
(c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
(d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

26. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n respectively, are **(2015 Adv.)**
(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

27. The correct statement(s) regarding defects in solids is/are
(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion **(1999)**
(b) Frenkel defect is a dislocation defect
(c) Trapping of an electron in the lattice leads to the formation of F-centre
(d) Schottky defects have no effect on the physical properties of solids

28. Which of the following statement(s) is/are correct?

(a) The coordination number of each type of ion in CsCl crystal is 8 **(1998, 2M)**

(b) A metal that crystallises in bcc structure has a coordination number of 12

(c) A unit cell of an ionic crystal shares some of its ions with other unit cells

(d) The length of the unit cell in NaCl is 552 pm.

(r_{Na} 95 pm; r_{Cl} 181 pm)

Numerical Value

29. Consider an ionic solid *MX* with NaCl structure. Construct a new structure (*Z*) whose unit cell is constructed from the unit cell of *MX* following the sequential instruction given below. Neglect the charge balance. **(2018 Adv.)**

(a) Remove all the anions (X) except the central one

(b) Replace all the face centered cations (M) by anions (X)

(c) Remove all the corner cations (M)

(d) Replace the central anion (X) with cation (M)

The value of $\dfrac{\text{Number of anions}}{\text{Number of cations}}$ in Z is ___

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct Statement II is correct Statement II is the correct explanation of Statement I

(b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I

(c) Statement I is correct Statement II is incorrect

(d) Statement I is incorrect Statement II is correct

30. **Statement I** In any ionic soid (*MX*) with Schottky defects, the number of positive and negative ions are same.

Statement II Equal numbers of cation and anion vacancies are present. **(2001, 1M)**

Passage Based Questions

Passage

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (hcp), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer.

Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

31. The number of atoms in one of this hcp unit cell is **(2008, 3 4M = 12M)**

(a) 4 (b) 6 (c) 12 (d) 17

32. The volume of this hcp unit cell is

(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$ (c) $12\sqrt{2}r^3$ (d) $\dfrac{64r^3}{3\sqrt{3}}$

33. The empty space in this hcp unit cell is

(a) 74 % (b) 47.6 % (c) 32 % (d) 26 %

Match the Columns

34. Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. **(2007, 6M)**

	Column I		Column II
A.	Simple cubic and face centred cubic	p.	have these cell parameters a b c and 90
B.	Cubic and rhombohedral	q.	are two crystal systems
C.	Cubic and tetragonal	r.	have only two crystallographic angles of 90°
D.	Hexagonal and monoclinic	s.	belong to same crystal system

Integer Answer Type Questions

35. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm ^{3}, then the number of atoms present in 256 g of the crystal is N 10^{24}. The value of N is **(2017 Adv.)**

36. The number of hexagonal faces that are present in a truncated octahedron is **(2011)**

37. Silver (atomic weight 108 g mol ^{1}) has a density of 10.5 g cm ^{3}. The number of silver atoms on a surface of area 10 ^{12} m^2 can be expressed in scientific notation as y 10^x. The value of x is **(2010)**

Subjective Questions

38. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. (N_A 6 10^{23}). Give the answer in pm. **(2006, 3M)**

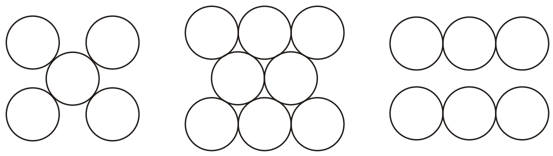
39. An element crystallises in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure. **(2005, 2M)**

40. The crystal *AB* (rock salt structure) has molecular weight 6.023y u. Where, y is an arbitrary number in u. If the minimum distance betweeen cation and anion is $y^{1/3}$ nm and the observed density is 20 kg/m^3. Find the (i) density in kg/m^3 and (ii) type of defect. **(2004, 2M)**

41. (i) Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centres are within this area.

(ii) Find the maximum number of marbles per unit area and deduce an expression for calculating it. **(2003, 4M)**

42. The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structures and identify these planes in your diagram. **(2000)**



43. A metal crystallises into two cubic phases, face centred cubic (fcc) and body centred cubic (bcc), whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of fcc and bcc. **(1999, 3M)**

44. Chromium metal crystallises with a body centred cubic lattice. The length of the unit edge is found to be 287 pm. Calculate the atomic radius . What would be the density of chromium in g/cm^3? **(1997, 3M)**

45. A metallic element crystallises into a lattice containing a sequence of layers of *ABABAB*...... Any packing of layers leaves out voids in the lattice. What percentage of this lattice is empty space? **(1996, 3M)**

46. Sodium crystallises in a bcc cubic lattice with the cell edge, a 4.29 Å. What is the radius of sodium atom? **(1994, 2M)**

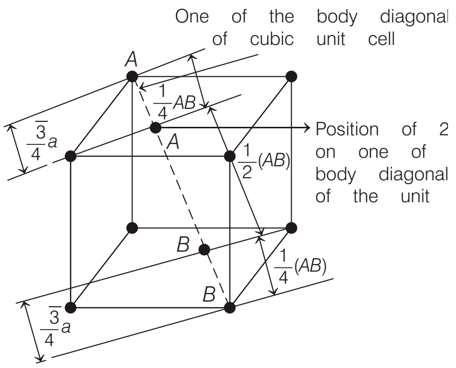
Answers

1. (b)	**2.** (c)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (d)	**7.** (a)	**8.** (c)	**9.** (d)
10. (d)	**11.** (a)	**12.** (c)	**13.** (d)	**14.** (a)	**15.** (c)	**16.** (a)	**17.** (b)	**18.** (b)
19. (b)	**20.** (d)	**21.** (b)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (b,c,d)	**26.** (a)	**27.** (b,c)
28. (a,c,d)	**29.** (3)	**30.** (a)	**31.** (b)	**32.** (a)	**33.** (d)	**34.** A p, s; B q; C q; D q, r		
35. (2)	**36.** (8)	**37.** (7)	**38.** (217 pm)	**39.** (117 pm)	**43.** (1.26)	**44.** (7.3 g/cm^3)		
45. (0.74)	**46.** (1.86 Å)							

Hints & Solutions

1. The ratio of number of atoms present in simple cubic, body centred cubic and face centered cubic structure are 1 : 2 : 4 respectively.

2. In fcc unit cell, two tetrahedral voids are formed on each of the four non-parallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.



The angle between body diagonal and an edge is $\cos^{-1}(1/\sqrt{3})$. So, the projection of the line on an edge is $a/4$. Similarly, other tetrahedral void also will be $a/4$ away. So, the distance between these two is $a \quad \frac{a}{4} \quad \frac{a}{4} \quad \frac{a}{2}$.

3. **Key Idea** Packing efficiency

$$\frac{\text{Volume occupied by sphere}}{\text{Volume of cube}} \quad 100$$

Given,

$$r_B \quad 2r_A$$

$$a_2 \quad a_1 \quad \frac{50}{100} a_1 \quad 1.5\, a_1$$

For bcc lattice

$$4r_A \quad \sqrt{3}\, a_1$$

$$r_A \quad \frac{\sqrt{3}\, a_1}{4}$$

$$a_1 \quad \frac{4r_A}{\sqrt{3}}$$

$$a_2 \quad 1.5 \quad \frac{4r_A}{\sqrt{3}}$$

$$\frac{3}{2} \quad \frac{4r_A}{\sqrt{3}}$$

$$a_2 \quad 2\sqrt{3}\, r_A$$

Packing efficiency $\dfrac{\dfrac{4}{3}\, r_A^3 \quad z_A \quad \dfrac{4}{3}\, r_B^3 \quad z_B}{a_2^3}$

[As the atoms A are present at the edges only $z_A \quad \dfrac{1}{8} \quad 8 \quad 1$, atom B is present only at the body centre $z_B \quad 1$]

$$\text{PE}_2 \quad \frac{\dfrac{4}{3}\, r_A^3 \quad 1 \qquad \dfrac{4}{3}\, r_B^3 \quad 1}{a_2^3}$$

$$\frac{\dfrac{4}{3}\, r_A^3 \quad \dfrac{4}{3} \quad (2r_A)^3}{(2\sqrt{3}\, r_A)^3} \qquad \frac{\dfrac{4}{3}\, r_A^3 \quad 9}{8 \quad 3\sqrt{3}\, r_A^3} \qquad \overline{2\sqrt{3}}$$

$$90.72\% \quad 90\%$$

4. Interstitial compounds are formed when a neutral atom with a small radius occupies in an interstitial hole (tetrahedral or octahedral voids) in a transition metal's hcp or ccp lattices (host lattice). Examples of small atoms (guest atom) are H, B, C and N.

Interstitial compounds are non-stoichiometric (Birtholide) in composition. They are very hard with very high melting points. The electrical conductivity of interstitial compounds are comparable to that of the pure metal. These are chemically unreactive in nature.

5. The number of element 'B' in the crystal structure = 4 N

Number of tetrahedral voids = 2N

Number of octahedral voids = N

Number of 'A' in the crystal $\dfrac{N}{2} \quad \dfrac{4}{2} \quad 2$

Number of oxygen (O) atoms $\quad 2N \quad 2 \quad 4 \quad 8$

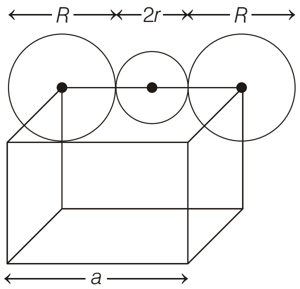
The structure of bimetallic oxide $\quad A_2\, B_4\, O_8 \quad AB_2\, O_4$

6. For body centred cubic bcc structure,

radius (R) $\dfrac{\sqrt{3}}{4}a$ ...(i)

Where, a edge length

According to question, the structure of cubic unit cell can be shown as follows:



$$a \quad 2(R \quad r) \qquad \text{...(ii)}$$

On substituting the value of R from Eq. (i) to Eq. (ii), we get

$$\frac{a}{2} \quad \frac{\sqrt{3}}{4}a \quad r$$

$$r \quad \frac{a}{2} \quad \frac{\sqrt{3}}{4}\, a \quad \frac{2a \quad \sqrt{3}a}{4}$$

$$r \quad \frac{a(2 \quad \sqrt{3})}{4}$$

$$r \quad 0.067a$$

7. Density of a crystal

$$d \quad \frac{M \quad Z}{N_A \quad a^3} \qquad M \quad \frac{d \quad N_A \quad a^3}{Z}$$

Given, $d \quad 9 \quad 10^3$ kg m ^{3}

M Molar mass of the solid

Z 4 (for fcc crystal)

N_A Avogadro's constant $6 \quad 10^{23}$ mol ^{1}

a Edge length of the unit cell

$200\sqrt{2}$ pm $\quad 200\sqrt{2} \quad 10^{\ 12}$ m

On substituting all the given values, we get

$$\frac{(9 \quad 10^3)\ \text{kg m}^{\ 3} \quad (6 \quad 10^{23})\ \text{mol}^{\ 1} \quad (200\sqrt{2} \quad 10^{\ 12})^3 \text{m}^3}{4}$$

$$0.0305 \text{ kg mol}^{\ 1}$$

8. Total effective number of atoms in hcp unit lattice Number of octahedral voids in hcp 6

Number of tetrahedral voids (TV) in hcp

2 Number of atoms in hcp lattice

2 6 12

As, formula of the lattice is A_2B_3.

Suppose,	A	B
	$\dfrac{1}{3}$ TV	(hcp)
	$\dfrac{1}{3}$ 12	6
	$\dfrac{2}{3}$	1
	2	3

So, $A \quad \dfrac{1}{3}$ tetrahedral voids, B hcp lattice

9. Triclinic primitive unit cell has dimensions as, $a \quad b \quad c$ and 90 .

Among the seven basic or primitive crystalline systems, the triclinic system is most unsymmetrical. In other cases, edge length and axial angles are given as follows :

Hexagonal : $a \quad b \quad c$ and $\quad 90 , \quad 120$

Monoclinic : $a \quad b \quad c$ and $\quad 90 , \quad 90$

Tetragonal : $a \quad b \quad c$ and $\quad 90$

10. For fcc, rank of the unit cell (Z) 4

Mass of one Cu-atom, M 63.55 u

Avogadro's number, N_A $6.023 \quad 10^{23}$ atom

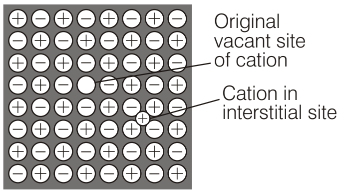
Edge length, $a \quad x$ Å $\quad x \quad 10^{\ 8}$ cm

density (d) $\dfrac{Z \quad M}{N_A \quad a^3}$

$$\frac{4 \quad 63.55}{6.023 \quad 10^{23} \quad (x \quad 10^{\ 8})^3} \quad \frac{422.048}{x^3}\ \mathrm{g\,cm}^{\ 3}$$

11. Piezoelectric materials are those materials that produce an electric current when they are placed under mechanical stress. Crystalline solids can be used as piezoelectric material hence, quartz is a correct answer.

12. It is the ''Frenkel defect'' in which cations leave their original site and occupy interstitial site as shown below.



13. For fcc arrangement, $4r \quad \sqrt{2}a$

where, r radius and a edge length

Closest distance $\quad 2r \quad \frac{\sqrt{2}\,a}{2} \quad \frac{a}{\sqrt{2}}$

14. For bcc unit cell, $\sqrt{3}\,a \quad 4a$

$$r \quad \frac{\sqrt{3}}{4}a$$

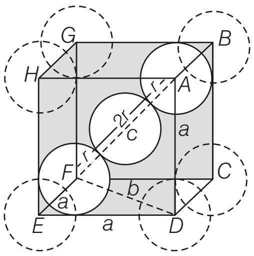
$$\frac{\sqrt{3}}{4} \quad 4.29\text{Å} \quad 1.85\text{Å}$$

$$r \quad 1.85\text{Å} \quad 1.86\text{Å}$$

15. In CsCl, Cl lies at corners of simple cube and Cs at the body centre. Hence, along the body diagonal, Cs and Cl touch each other so $r_{\mathrm{Cs}} \quad r_{\mathrm{Cl}} \quad 2r$

Calculation of *r*

In EDF,



Body centred cubic unit cell

$$FD \quad b \quad \sqrt{a^2 \quad a^2} \quad \sqrt{2}\,a$$

In AFD,

$$c^2 \quad a^2 \quad b^2 \quad a^2 \quad (\sqrt{2}\,a)^2 \quad a^2 \quad 2a^2$$

$$c^2 \quad 3a^2 \qquad c \quad \sqrt{3}\,a$$

As AFD is an equilateral triangle.

$$\sqrt{3}\,a \quad 4r \qquad\qquad [\because C \quad 3r \quad r \quad r]$$

$$r \quad \frac{\sqrt{3}\,a}{4}$$

Hence, $r_{\mathrm{Cs}} \quad r_{\mathrm{Cl}} \quad 2r \quad 2 \quad \frac{\sqrt{3}}{4}a \quad \frac{\sqrt{3}}{2}a$

16. PLAN Given arrangement represents octahedral void and for this

$$\frac{r\ \ (\text{cation})}{r\ \ (\text{anion})} \quad 0.414$$

$$\frac{r(A\ \ )}{r(X\ \ )} \quad 0.414$$

$$r(A\ \ ) \quad 0.414 \quad r(X\ \ ) \quad 0.414 \quad 250\text{pm}$$

$$103.5\text{ pm} \quad 104\text{ pm}$$

17. From the valency of M^{2} and M^{3}, it is clear that three M^{2} ions will be replaced by M^{3} causing a loss of one M^{3} ion. Total loss of them from one molecule of $MO \quad 1 \quad 0.98 \quad 0.02$

Total M^{3} present in one molecule of

$$MO \quad 2 \quad 0.02 \quad 0.04$$

That M^{2} and $M^{3} \quad 0.98$

Thus, % of $M^{3} \quad \frac{0.04 \quad 100}{0.98} \quad 4.08\%$

18. Silicon exists as covalent crystal in solid state. (Network like structure, as seen in diamond).

19. Contribution of atom from the edge centre is 1/4. Therefore, number of

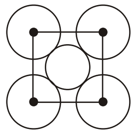
$$M \quad \frac{1}{4} \quad 4\text{ (from edge centre)} \quad 1\text{ (from body centre)} \quad 2$$

$$\text{Number of } X \quad \frac{1}{8} \quad 8\text{ (from corners)} \quad \frac{1}{2} \quad 6$$

(from face centre) $\quad 4$

Empirical formula $\quad M_2X_4 \quad MX_2$

20. Contribution of circle from corner of square $\frac{1}{4}$



Effective number of circle per square

$$\frac{1}{4} \quad 4 \quad 1\text{(at centre)} \quad 2$$

Area occupied by circle $\quad 2 \quad r^2, r \quad$ radius.

Also, diagonal of square $4r \quad \sqrt{2}\,L$, where L side of square.

$$\text{Packing fraction} \quad \frac{\text{Area occupied by circles}}{\text{Area of square}}$$

$$\frac{2 \quad r^2}{L^2} \quad \frac{2 \quad r^2}{8r^2} \quad \frac{}{4} \quad 0.785$$

% packing efficiency $\quad 78.5\%$.

21. In ZnS, S^{2} (sulphide ions) are present at fcc positions giving four sulphide ions per unit cell. To comply with 1 : 1 stoichiometry, four Zn^{2} ions must be present in four alternate tetrahedral voids out of eight tetrahedral voids present.

In NaCl, Na^+ ions are present in octahedral voids while in Na_2O, Na^+ ions are present in all its tetrahedral voids giving the desired 2 : 1 stoichiometry. In CaF_2, Ca^{2+} ions occupies fcc positions and all the tetrahedral voids are occupied by fluoride ions.

22. In cubic system, a corner contribute $\frac{1}{8}$th part of atom to one unit cell and a face centre contribute $\frac{1}{2}$ part of atom to one unit cell.

Therefore,

Number of A per unit cell $\quad \frac{1}{8} \quad 8 \quad 1$

Number of B per unit cell $\frac{1}{2}$ 6 3

Formula AB_3

23. In NaCl, Na^+ occupies body centre and edge centres while Cl occupies corners and face centres, giving four Na and four Cl per unit cell. In the present case A represent Cl and B represents Na^+. Two face centres lies on one axis.

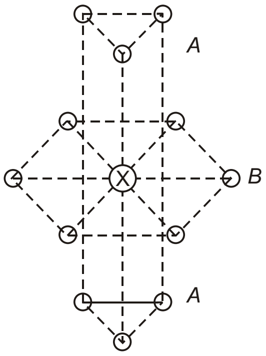
Number of A removed 2 $\frac{1}{2}$ 1

Number of B is removed because it is not present on face centres.

A remaining 4 1 3, B remaining 4,

Formula A_3B_4

24. Three consecutive layers of atoms in hexagonal close packed lattice is shown below:



Atom X is in contact of 12 like atoms, 6 from layer B and 3 from top and bottom layers A each.

25. (a) Nearest neighbour in the topmost layer of ccp structure is 9 thus, incorrect.

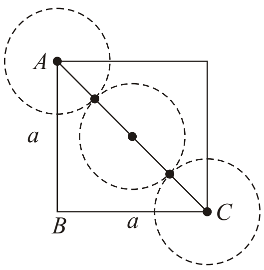
(b) Packing efficiency is 74% thus, correct.

(c) Tetrahedral voids 2

Octahedral voids = 1 per atom thus, correct.

(d) Edge length, a $\frac{4}{\sqrt{2}}r$ $2\sqrt{2}r$

thus, correct



Explanation Edge length a

Radius r

AC^2 AB^2 BC^2

$(4r)^2$ a^2 a^2 $2a^2$

$4r$ $\sqrt{2}a$

r $\frac{\sqrt{2}}{4}a$ $\frac{a}{2\sqrt{2}}$ a $2\sqrt{2}\,r$

In ccp structure, number of spheres is 4.

Hence, volume of 4 spheres $4\ \frac{4}{3}\ r^3$

Total volume of unit cell a^3 $(2\sqrt{2}r)^3$

% of packing efficiency

$$\frac{\text{Volume of 4 spheres}}{\text{Volume of unit cell}} \quad \frac{4\ \frac{4}{3}\ r^3}{[2(\sqrt{2}r)]^3} \quad 100$$

74.05% ~ 74%

26. Oxide ions are at ccp positions, hence $4O^{2-}$ ions. Also, there are four octahedral voids and eight tetrahedral voids. Since 'm' fraction of octahedral voids contain Al^{3+} and 'n' fraction of tetrahedral voids contain Mg^{2+} ions, to maintain etectroneutrality $2(2Al^{3+} = +6$ charge) and ($Mg^{2+} = +2$ charge), will make unit cell neutral

Hence: m $\frac{2}{4}$ $\frac{1}{2}$, n $\frac{1}{8}$

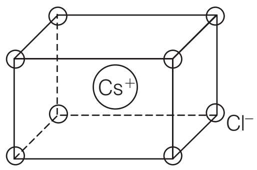
27. (a) Wrong statement. A small difference in sizes of cation and anion favour Schottky defect while Frenkel defect is favoured by large difference in sizes of cation and anion.

(b) Correct statement. In Frenkel defect the smaller atom or ion gets dislocated from its normal lattice positions and occupies the interstitial space.

(c) **Correct Statement** In F-centre defect, some anions leave the lattice and the vacant sites hold the electrons trapped in it maintaining the overall electroneutrality of solid.

(d) Wrong statement : In Schottky defect, some of the atoms or ions remaining absent from their normal lattice points without distorting the original unit cell dimension. This lowers the density of solid.

28. (a) The unit cell of CsCl has bcc arrangement of ions in which each ion has eight oppositely charged ions around it in the nearest neighbours as shown below :



Unit cell of CsCl

(b) In bcc, coordination number of atom is 8.

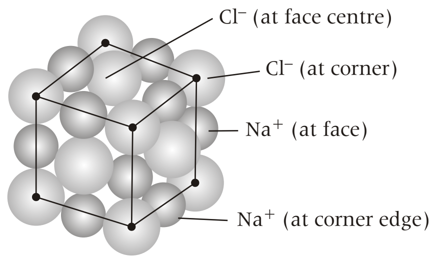
(c) In an unit cell, a corner is shared in eight unit cells and a face centre is shared between two adjacent unit cells.

(d) In NaCl unit cell; $2(r_{Na^+}$ r_{Cl} $)$ a

a $2\,(95$ $181)$ 552 pm

Hence, a, c, d are correct.

29. The unit cell of initial structure of ionic solid MX looks like



In NaCl type of solids cations (Na) occupy the octahedral voids while anions (Cl) occupy the face centre positions.

However, as per the demand of problem the position of cations and anions are swapped.

We also know that (for 1 unit cell)

(A) Total number of atoms at FCC = 4

(B) Total number of octahedral voids = 4

(as no. of atoms at FCC = No. of octahedral voids)

Now taking the conditions one by one

(i) If we remove all the anions except the central one than number of left anions.

$$4 \quad 3 \quad 1$$

(ii) If we replace all the face centred cations by anions than effective number of cations will be $4 \quad 3 \quad 1$

Likewise effective number of anions will be $1 \quad 3 \quad 4$

(iii) If we remove all the corner cations then effective number of cations will be $1 \quad 1 \quad 0$

(iv) If we replace central anion with cation then effective number of cations will be $0 \quad 1 \quad 1$

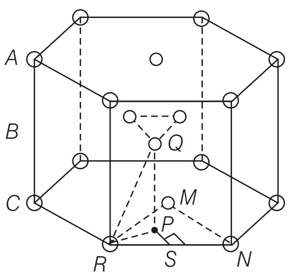
Likewise effective number of anions will be $4 \quad 1 \quad 3$

Thus, as the final outcome, total number of cations present in Z after fulfilling all the four sequential instructions $\quad 1$

Likewise, total number of anions $\quad 3$

Hence, the value of $\dfrac{\text{Number of anions}}{\text{Number of cations}} \quad \dfrac{3}{1} \quad 3$

30. In ionic solid MX (1 : 1 solid) same number of M^{n} and X^{n} ions are lost in Schottky defect to maintain electroneutrality of solid.

31. 

A hcp unit cell

Contribution of atoms from corner $\quad 1/6$

Contribution from face centre $\quad 1/2$

Total number of atoms per unit cell $\quad 12 \quad \dfrac{1}{6} \quad 2 \quad \dfrac{1}{2} \quad 3 \quad 6$

32. In close packed arrangement, side of the base $\quad 2r$

$$RS \quad r$$

Also MNR is equilateral triangle, $\quad PRS \quad 30$

In triangle PRS, $\cos 30 \quad \dfrac{RS}{PR} \quad \dfrac{\sqrt{3}}{2}$

$$PR \quad \frac{2}{\sqrt{3}} RS \quad \frac{2}{\sqrt{3}} r$$

In right angle triangle $PQR : PQ \quad \sqrt{QR^2 \quad PR^2} \quad 2\sqrt{\dfrac{2}{3}}\, r$

Height of hexagon $\quad 2PQ \quad 4\sqrt{\dfrac{2}{3}}\, r$

Volume = Area of base $\quad$ height $\quad 6\dfrac{\sqrt{3}}{4}(2r)^2 \quad 4\sqrt{\dfrac{2}{3}}\, r$

$$24\sqrt{2}\, r^3$$

33. Packing fraction $\quad \dfrac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$

$$6 \quad \frac{4}{3} \quad r^3 \quad \frac{1}{24\sqrt{2}\, r^3} \quad 0.74$$

Fraction of empty space $\quad 1 \quad 0.74 = 0.26 \quad 26\%$

34. A. Simple cubic and face centred cubic both have cell parameters $a \quad b \quad c$ and $\quad 90$. Also both of them belongs to same, cubic, crystal system.

B. The cubic and rhombohedral crystal system belongs to different crystal system.

C. Cubic and tetragonal are two different types of crystal systems having different cell parameters.

D. Hexagonal and monoclinic are two different crystal system and both have two of their crystallographic angles of 90°.

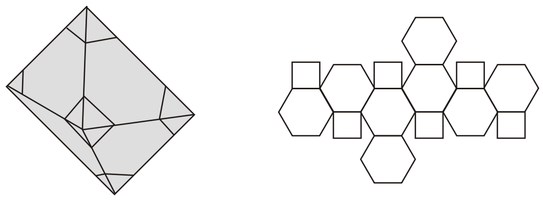
35. Density ( ) $\quad 8 \quad \dfrac{4 \quad M}{N_A(4 \quad 10^{\;8}\,\text{cm})^3}$

$$M \quad 128 \quad 10^{\;24} N_A \qquad \text{No of atoms} \quad \frac{256}{M} \quad N_A$$

$$\frac{256}{128 \quad 10^{\;24} N_A} \quad N_A \quad 2 \quad 10^{24}$$

36. The truncated octahedron is the 14-faced Archimedean solid, with 14 total faces : 6 squares and 8 regular hexagons.

The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron as :



Truncated octahedron

Truncated octahedron unfolded in two-dimension

37. Ag crystallises in fcc unit cell with 4 atoms per unit cell.

$$\frac{4 \quad 108}{6.023 \quad 10^{23} \quad a^3} \quad 10.5 \text{ g cm}^{\;3}.$$

a^3 (Volume of unit cell) $\quad 6.83 \quad 10^{\;23}$ cm^3

$a \quad 4 \quad 10^{\;8}$ cm $\quad 4 \quad 10^{\;10}$ m

Surface area of unit cell $\quad a^2 \quad 1.6 \quad 10^{\;19}$ m^2

Number of unit cells on $10^{\;12}$ m^2 surface

$$\frac{10^{\;12}}{1.6 \quad 10^{\;19}} \quad 6.25 \quad 10^6$$

∵ There are two atoms (effectively) on one face of unit cell Number of atoms on $10^{\;12}$ m^2 surface $\quad 2 \quad$ number of unit cell

$1.25 \quad 10^7$. $\qquad$ [∵ $\; y \quad 10^x$]

$$x \quad 7 \qquad y \quad 1.25$$

38. From the given information, the number of atoms per unit cell and therefore, type of unit cell can be known as

$$\frac{NM}{N_A a^3}$$

$$N \quad \frac{N_A a^3}{M} \quad \frac{2 \quad 6 \quad 10^{23} \quad (5 \quad 10^{\ 8}\ \text{cm})^3}{75} \quad 2\ (\text{bcc})$$

In bcc, $4r \quad \sqrt{3}a$

$$r \quad \frac{\sqrt{3}}{4}a \quad \frac{\sqrt{3}}{4} \quad 5 \quad 10^{\ 10}\text{m}$$

$$2.17 \quad 10^{\ 10}\ \text{m} \quad 217\ \text{pm}$$

39. In a cubic crystal system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom creating these voids then

$$\frac{r_1}{r_2}_{\text{octa}} \quad 0.414 \quad \text{and} \quad \frac{r_1}{r_2}_{\text{tetra}} \quad 0.225$$

The above radius ratio values indicate that octahedral void has larger radius, hence for maximum diameter of atom to be present in interstitial space :

$$r_1 \quad 0.414\ r_2$$

Also in fcc, $\quad 4r_2 \quad \sqrt{2}a$

$$\text{Diameter required } (2r_1) \quad (2r_2) \quad 0.414$$

$$\frac{a}{\sqrt{2}} \quad 0.414$$

$$\frac{400 \quad 0.414}{\sqrt{2}} \quad 117\ \text{pm}$$

40. (i) In rock salt like crystal AB, there are four AB units per unit cell. Therefore, density (d) is

$$d \quad \frac{4 \quad 6.023\,y}{6.023 \quad 10^{23} \quad 8y \quad 10^{\ 27}}$$

$$[\because a \quad 2y^{1/3}\,\text{nm} \quad 2y^{1/3} \quad 10^{\ 9}\,\text{m}]$$

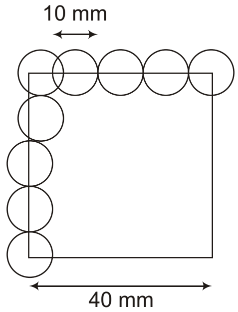
$$5 \quad 10^3\ \text{g/m}^3 \quad 5\ \text{kg/m}^3$$

(ii) Since, observed density is greater than expected, theoretical density, there must be some excess metal occupying interstitial spaces. This type of defect is known as **metal excess defect**.

41. (i) Side of square = 40 mm

Diameter of marble = 10 mm

Number of marble spheres along an edge of square with their centres within the square = 5 (shown in diagram)

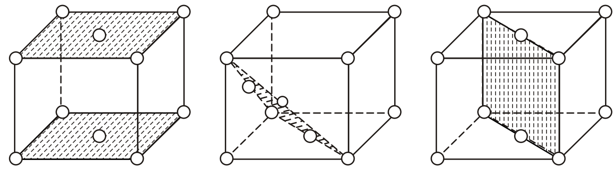


Maximum number of marbles per unit area $\quad 5 \quad 5 \quad 25$

(ii) If x mm is the side of square and d is diameter of marble then maximum number of marbles on square area with centres within square area can be known by the following general formula :

$$N \quad \frac{x}{d} \quad 1^{\ 2}$$

42.



43. Density $\quad \dfrac{N}{a^3}$

$$\frac{d_1}{d_2} \quad \frac{N_1}{N_2} \quad \frac{a_2}{a_1}^{3} \quad \frac{4}{2} \quad \frac{3}{3.5}^{3} = 1.26$$

44. In bcc unit cell, $4r \quad \sqrt{3}a$

$$r\,(\text{Cr}) \quad \frac{\sqrt{3}a}{4} \quad \frac{\sqrt{3}}{4} \quad 287\ \text{pm} \quad 124.3\ \text{pm}$$

Density of solid $\quad \dfrac{NM}{N_A\ a^3}$

$N \quad$ Number of atoms per unit cell, $\quad M \quad$ Molar mass

$a^3 \quad$ Volume of cubic unit cell, $\quad N_A \quad$ Avogadro's number

$$\frac{2 \quad 52\ \text{g}}{6.023 \quad 10^{23}} \quad \frac{1}{2.87 \quad 10^{\ 8}\ \text{cm}}^{3} \quad 7.3\ \text{g / cm}^3$$

45. The given arrangement : $ABABAB$...... represents hexagonal close-packed unit cell in which there are six atoms per unit cell. Also, volume of unit cell $\quad 24\sqrt{2}r^3$.

$$\text{Packing fraction} \quad \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$6 \quad \frac{4}{3} \quad r^3 \quad \frac{1}{24\sqrt{2}\,r^3} \quad 0.74$$

Percent empty space $\quad 100\ (1 \quad 0.74) \quad 26\%$

46. In bcc arrangement of atoms : $4r \quad \sqrt{3}a$, atoms on body diagonal remain in contact

$$r \quad \frac{\sqrt{3}\,a}{4} \quad \frac{\sqrt{3} \quad 4.29}{4} \quad 1.86\ \text{Å}$$

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http://tinyurl.com/y6yuk3b2 *or*

9

Solution and Colligative Properties

Topic 1 Solution and Vapour Pressure of Liquid Solutions

Objective Questions I (Only one correct option)

1. The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg ^{1}) of the aqueous solution is **(2019 Main, 12 April I)**

(a) $13.88 \quad 10^{2}$ (b) $13.88 \quad 10^{1}$
(c) 13.88 (d) $13.88 \quad 10^{3}$

2. What would be the molality of 20% (mass/mass) aqueous solution of KI? (Molar mass of KI = 166 g mol ^{1}) **(2019 Main, 9 April I)**

(a) 1.48 (b) 1.51
(c) 1.35 (d) 1.08

3. Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is **(2019 Main, 9 April I)**

x_M mole fraction of M in solution;
x_N mole fraction of N in solution;
y_M mole fraction of M in vapour phase;
y_N mole fraction of N in vapour phase

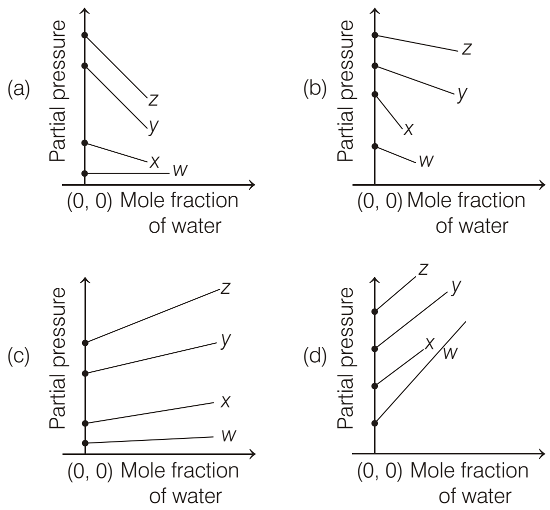
(a) $\frac{x_M}{x_N} \quad \frac{y_M}{y_N}$

(b) $\frac{x_M}{x_N} \quad \frac{y_M}{y_N}$

(c) $\frac{x_M}{x_N} \quad \frac{y_M}{y_N}$

(d) $(x_M \quad y_M) \quad (x_N \quad y_N)$

4. For the solution of the gases w, x, y and z in water at 298 K, the Henry's law constants (K_H) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is **(2019 Main, 8 April II)**



5. The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are **(2019 Main, 8 April I)**

(a) 450 mmHg, 0.4, 0.6 (b) 500 mmHg, 0.5, 0.5
(c) 450 mmHg, 0.5,0.5 (d) 500 mmHg, 0.4,0.6

6. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are $7 \quad 10^3$ Pa and $12 \quad 10^3$ Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is **(2019 Main, 10 Jan I)**

(a) $x_A \quad 0.76; x_B \quad 0.24$ (b) $x_A \quad 0.28; x_B \quad 0.72$
(c) $x_A \quad 0.4; x_B \quad 0.6$ (d) $x_A \quad 0.37; x_B \quad 0.63$

7. Which one of the following statements regarding Henry's law is not correct? **(2019 Main, 8 Jan I)**

(a) Different gases have different K_H (Henry's law constant) values at the same temperature
(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids
(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas
(d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution

8. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is **(2016 Main)**

(a) 76.0 (b) 752.4 (c) 759.0 (d) 7.6

9. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 Torr. The molar mass of the substance is **(2015, 1M)**

(a) 32 (b) 64 (a) 128 (b) 488

10. The Henry's law constant for the solubility of N_2 gas in water at 298 K is $1.0 \quad 10^5$ atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is **(2009)**

(a) $4.0 \quad 10^{4}$ (b) $4.0 \quad 10^{5}$
(c) $5.0 \quad 10^{4}$ (d) $4.0 \quad 10^{6}$

11. A molal solution is one that contains one mole of a solute in **(1986, 1M)**

(a) 1000 g of the solvent (b) 1 L of the solvent
(c) 1 L of the solution (d) 22.4 L of the solution

12. For a dilute solution, Raoult's law states that **(1985, 1M)**

(a) the lowering of vapour pressure is equal to the mole fraction of solute
(b) the relative lowering of vapour pressure is equal to the mole fraction of solute
(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution
(d) the vapour pressure of the solution is equal to the mole fraction of solvent

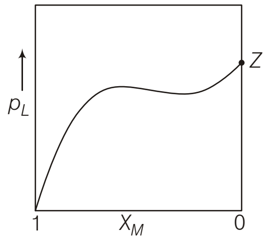
13. An azeotropic solution of two liquids has boiling point lower than either of them when it **(1981, 1M)**

(a) shows negative deviation from Raoult's law
(b) shows no deviation from Raoult's law
(c) shows positive deviation from Raoult's law
(d) is saturated

Objective Questions II

(One or more than one correct option)

14. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is (are) **(2017 Adv.)**



(a) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from x_L 0 to x_L 1
(b) Attractive intermolecular interactions between L - L in pure liquid L and M - M in pure liquid M are stronger than those between L - M when mixed in solution
(c) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when x_L 0
(d) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when x_L 1

15. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are) **(2016 Adv.)**

(a) carbon tetrachloride + methanol
(b) carbon disulphide + acetone
(c) benzene + toluene
(d) phenol + aniline

Numerical Value Based Question

16. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 torr. The value of x_A / x_B in the new solution is ____.

(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T) **(2018 Adv. Paper-1)**

True/False

17. Following statement is true only under some specific conditions. Write the condition for it.
"Two volatile and miscible liquids can be separated by fractional distillation into pure components." **(1994)**

Subjective Questions

18. The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 min, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **(2001, 4M)**

19. The molar volume of liquid benzene (density 0.877 g/mL) increases by a factor of 2750 as it vaporises at 20 C and that of liquid toluene (density 0.867 g mL ^{1}) increases by a factor of 7720 at 20 C. A solution of benzene and toluene at 20 C has a vapour pressure of 45.0 torr. Find the mole fraction of benzene in the vapour above the solution. **(1996, 3M)**

20. What weight of the non-volatile solute urea (NH_2— CO—NH_2) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? **(1993, 3M)**

21. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100 C is 70%. If the vapour-pressure of water at 100 C is 760mm, calculate the vapour pressure of the solution. **(1991, 4M)**

22. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance? **(1990, 3M)**

23. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solute. **(1989, 3M)**

24. The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **(1986, 4M)**

25. An organic compound ($C_xH_{2y}O_y$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 L. The water collected during cooling weight 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. **(1983, 5M)**

26. Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states. **(1982, 4M)**

27. The vapour pressure of pure benzene is 639.70 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of Hg. Calculate the molality of the solution. **(1981, 3M)**

28. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL ? To what volume should 100 mL of this solution be diluted in order to prepare a 1.5 N solution ? **(1978, 2M)**

Topic 2 Colligative Properties

Objective Questions I (Only one correct option)

1. A solution is prepared by dissolving 0.6 g of urea (molar mass 60 g mol ^{1}) and 1.8 g of glucose (molar mass 180 g mol ^{1}) in 100 mL of water at 27°C. The osmotic pressure of the solution is (R 0.08206 L atm K ^{1} mol ^{1}) **(2019 Main, 12 April II)**

(a) 8.2 atm (b) 2.46 atm (c) 4.92 atm (d) 1.64 atm

2. 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\frac{T_b(A)}{T_b(B)}$, is **(2019 Main, 10 April II)**

(a) 5 : 1 (b) 10 : 1
(c) 1 : 5 (d) 1 : 0.2

3. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be
(Molar mass of urea 60 g mol ^{1}) **(2019 Main, 10 April I)**

(a) 0.027 mmHg
(b) 0.031 mmHg
(c) 0.017 mmHg
(d) 0.028 mmHg

4. Molal depression constant for a solvent is 4.0 K kg mol ^{1}. The depression in the freezing point of the solvent for 0.03 mol kg ^{1} solution of K_2SO_4 is
(Assume complete dissociation of the electrolyte) **(2019 Main, 9 April II)**

(a) 0.18 K (b) 0.36 K
(c) 0.12 K (d) 0.24 K

5. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L ^{1}) in solution is **(2019 Main, 9 April I)**

(a) 4 10 ^{2} (b) 16 10 ^{4}
(c) 4 10 ^{4} (d) 6 10 ^{2}

6. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is

(Given that K_f 5 K kg mol ^{1}, molar mass of benzoic acid 122 g mol ^{1}) **(2019 Main, 12 Jan II)**

(a) 1.8 g (b) 1.0 g (c) 2.4 g (d) 1.5 g

7. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is **(2019 Main, 12 Jan I)**

(a) 4A (b) 2A (c) 3A (d) A

8. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is **(2019 Main, 11 Jan II)**

(a) 1.6 (b) 1.8 (c) 2.2 (d) 2.0

9. The freezing point of a diluted milk sample is found to be 0.2 C, while it should have been 0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample? **(2019 Main, 11 Jan I)**

(a) 2 cups of water to 3 cups of pure milk
(b) 1 cup of water to 3 cups of pure milk
(c) 3 cups of water to 2 cups of pure milk
(d) 1 cup of water to 2 cups of pure milk

10. Elevation in the boiling point for 1 molal solution of glucose is 2 K . The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is **(2019 Main, 10 Jan II)**

(a) K_b 1.5 K_f (b) K_b 0.5 K_f
(c) K_b K_f (d) K_b 2K_f

11. A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto –10° C. If K_f for water is 1.86 K kg mol ^{1}, then amount of water (in g) separated as ice is **(2019 Main, 9 Jan II)**

(a) 32 (b) 48 (c) 64 (d) 16

12. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point? **(2018 Main)**

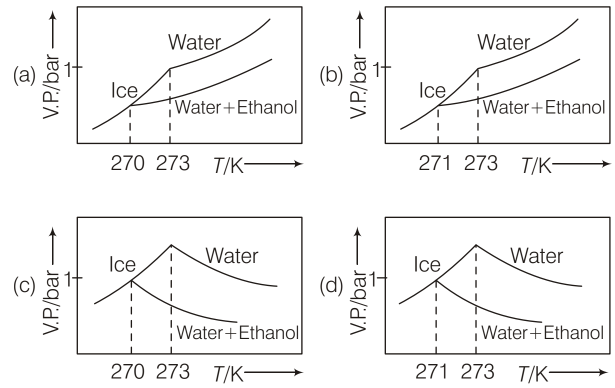
(a) $[Co(H_2O)_6]Cl_3$ (b) $[Co(H_2O)_5Cl]Cl_2$ H_2O
(c) $[Co(H_2O)_4Cl_2]Cl$ $2H_2O$ (d) $[Co(H_2O)_3Cl_3]$ $3H_2O$

13. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be
(K_f for benzene 5.12 K kg mol ^{1}) **(2017 Main)**

(a) 64.6 % (b) 80.4 % (c) 74.6 % (d) 94.6 %

14. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol ^{1}. The figures shown below represent plots of vapour pressure (V.P.) *versus* temperature (T). [Molecular weight of ethanol is 46 g mol ^{1}] **(2017 Adv.)**

Among the following, the option representing change in the freezing point is



15. Consider separate solution of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2(aq)$, 0.250 M $KBr(aq)$ and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is true about these solution, assuming all salts to be strong electrolytes?

(a) They all have the same osmotic pressure **(2014 Main)**
(b) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure
(c) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure
(d) 0.500 M $C_2H_5OH(aq)$ has the highest osmotic pressure

16. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K_b 0.76 K kg mol ^{1}). **(2012)**

(a) 724 (b) 740
(c) 736 (d) 718

17. The freezing point (in C) of solution containing 0.1 g of $K_3[Fe(CN)_6]$ (mol. wt. 329) in 100 g of water (K_f 1.86 K kg mol ^{1}) is **(2011)**

(a) 2.3 10 ^{2} (b) 5.7 10 ^{2}
(c) 5.7 10 ^{3} (d) 1.2 10 ^{2}

18. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f 1.72 K kg mol ^{1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is **(2007, 3M)**

(a) 0.5 (b) 1
(c) 2 (d) 3

19. The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is. [Some useful data, K_b 0.52 K kg mol ^{1}, molecular weight of $CuCl_2$ 134.4 g]. **(2005, 1M)**

(a) 0.05 (b) 0.1
(c) 0.16 (d) 0.21

20. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. Degree of dissociation of Na_2SO_4 is **(2004, S, 1M)**

(a) 75% (b) 50%
(c) 25% (d) 85%

21. During depression of freezing point in a solution the following are in equilibrium **(2003)**

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

22. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to **(1996, 1M)**

(a) ionisation of benzoic acid
(b) dimerisation of benzoic acid
(c) trimerisation of benzoic acid
(d) solvation of benzoic acid

23. The freezing point of equimolal aqueous solutions will be highest for **(1990, 1M)**

(a) $C_6H_5NH_3Cl$ (aniline hydrochloride)
(b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$
(d) $C_6H_{12}O_6$ (glucose)

24. Which of the following 0.1 M aqueous solution will have the lowest freezing point? **(1989, 1M)**

(a) Potassium sulphate (b) Sodium chloride
(c) Urea (d) Glucose

25. When mercuric iodide is added to the aqueous solution of potassium iodide **(1987, 2M)**

(a) freezing point is raised
(b) freezing point is lowered
(c) freezing point does not change
(d) boiling point does not change

Objective Questions II

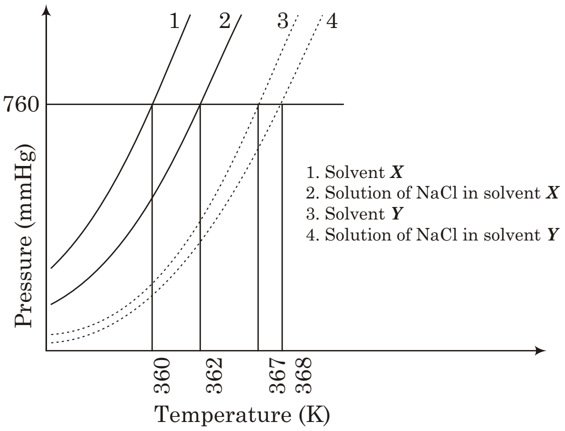
(One or more than one correct option)

26. In the depression of freezing point experiment, it is found that the **(1999, 3M)**

(a) vapour pressure of the solution is less than that of pure solvent
(b) vapour pressure of the solution is more than that of pure solvent
(c) only solute molecules solidify at the freezing point
(d) only solvent molecules solidify at the freezing point

Numerical Value Based Question

27. The plot given below shows p T curves (where p is the pressure and T is the temperature) for two solvents X and Y and isomolal solution of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerisation in these solvents. If the degree of dimerisation is 0.7 in solvent Y, the degree of dimerisation in solvent X is ____. **(2018 Adv.)**

Subjective Questions

28. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of K_f 14. If the depression in freezing point is 7 K, then find the percentage of phenol that dimerises. **(2006, 2M)**

29. 1.22 g C_6H_5COOH is added into two solvents and data of T_b and K_b are given as :

(i) In 100 g CH_3COCH_3 T_b 0.17, K_b 1.7 K kg/mol
(ii) In 100 g benzene, T_b 0.13 and K_b 2.6 K kg/mol

Find out the molecular weight of C_6H_5COOH in both the cases and interpret the result. **(2004, 2M)**

30. Consider the three solvents of identical molar masses. Match their boiling point with their K_b values

Solvents	Boiling point	K_b values
X	100°C	0.92
Y	27°C	0.63
Z	283°C	0.53

(2003)

31. To 500 cm^3 of water, 3.0 10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{3}, respectively. **(2000, 3M)**

32. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67% and oxygen : 38.07%,

(i) Calculate the empirical formula of the minor product.
(ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher

than that of pure benzene. Calculate the molar mass of the minor product then determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol ^{1}). **(1999)**

33. A solution of a non-volatile solute in water freezes at 0.30 C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 K kg mol ^{1}. Calculate the vapour pressure of this solution at 298 K. **(1998, 4M)**

34. Addition of 0.643 g of a compound to 50 mL of benzene (density : 0.879 g/mL) lowers the freezing point from 5.51 C to 5.03 C. If K_f for benzene is 5.12, calculate the molecular weight of the compound. **(1992, 2M)**

Passage Based Questions

Passage 1

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life.

One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given, freezing point depression constant of water

$$(K_f^{\text{water}}) \quad 1.86 \text{ K kg mol }^{1}$$

Freezing point depression constant of ethanol

$$(K_f^{\text{ethanol}}) \quad 2.0 \text{ K kg mol }^{1}$$

Boiling point elevation constant of water

$$(K_b^{\text{water}}) \quad 0.52 \text{ K kg mol }^{1}$$

Boiling point elevation constant of ethanol

$$(K_b^{\text{ethanol}}) \quad 1.2 \text{ K kg mol }^{1}$$

Standard freezing point of water 273 K

Standard freezing point of ethanol 155.7 K

Standard boiling point of water 373 K

Standard boiling point of ethanol 351.5 K

Vapour pressure of pure water 32.8 mm Hg

Vapour pressure of pure ethanol 40 mm Hg

Molecular weight of water 18 g mol ^{1}

Molecular weight of ethanol 46 g mol ^{1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(2008, 3 4M 12M)**

35. The freezing point of the solution M is

(a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K

36. The vapour pressure of the solution M is

(a) 39.3 mm Hg (b) 36.0 mm Hg
(c) 29.5 mm Hg (d) 28.8 mm Hg

37. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K

Fill in the Blank

38. Given that T_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\lim_{m \quad 0} (T_f / m)$ is equal to ...... **(1994, 1M)**

Integer Answer Type Question

39. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is 0.0558°C, the number of chloride(s) in the coordination sphere of the complex is

$[K_f$ of water $= 1.86$ K kg mol $^{1}]$ **(2015 Adv.)**

40. MX_2 dissociates into M^{2} and X ions in an aqueous solution, with a degree of dissociation ( ) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is **(2014 Adv.)**

Answers

Topic 1

1. (c)	**2.** (b)	**3.** (a)	**4.** (a)
5. (d)	**6.** (b)	**7.** (b)	**8.** (b)
9. (b)	**10.** (a)	**11.** (b)	**12.** (b)
13. (c)	**14.** (b, d)	**15.** (a, b)	**16.** (19)
17. T	**19.** (0.72)	**20.** (18.5)	**21.** (746.32 mm)
22. (65.25)	**23.** (0.75)	**24.** (0.657)	**27.** (0.158)
28. (180.40 mL)			

Topic 2

1. (c)	**2.** (c)	**3.** (c)	**4.** (b)
5. (d)	**6.** (c)	**7.** (c)	**8.** (b)
9. (c)	**10.** (d)	**11.** (c)	**12.** (d)
13. (d)	**14.** (b)	**15.** (a)	**16.** (a)
17. (a)	**18.** (a)	**19.** (c)	**20.** (a)
21. (a)	**22.** (b)	**23.** (d)	**24.** (a)
25. (a)	**26.** (a, d)	**27.** (0.05)	**28.** (75%)
30. (0.23°C)	**33.** (23.44 mm)	**34.** (156 g/mol)	**35.** (d)
36. (a)	**37.** (b)	**38.** (K_f)	**40.** (2)

Hints & Solutions

Topic 1 Solution and Vapour Pressure of Liquid Solutions

1. **Key Idea** Molality (m) $\dfrac{\text{Mass of solute } (w_2) \quad 1000}{\text{Molar mass of solute } (M_2) \\ \text{mass of solvent } (w_1)}$

$$m \quad \frac{w_2}{M_2} \quad \frac{1000}{w_1}$$

and also, $m \quad n_2 \quad \dfrac{1000}{n_1 \quad M_1}$

X_{solvent} 0.8 (Given) It means that $n_{\text{solvent}}(n_1)$ 0.8 and $n_{\text{solute}}(n_2)$ 0.2

Using formula $m \quad n_2 \quad \dfrac{1000}{n_1 \quad M_1} \quad 0.2 \quad \dfrac{1000}{0.8 \quad 18} \quad 13.88 \text{ mol kg}^{1}$

2. **Key Idea** Molality is defined as number of moles of solute per kg of solvent.

$$m \quad \frac{w_2}{Mw_2} \quad \frac{1000}{w_1}$$

w_2 mass of solute, Mw_2 molecular mass of solute
w_1 mass of solvent.

The molality of 20% (mass/mass) aqueous solution of KI can be calculated by following formula.

$$m \quad \frac{w_2 \quad 1000}{Mw_2 \quad w_1}$$

20% aqueous solution of KI means that 20 gm of KI is present in 80 gm solvent.

$$m \quad \frac{20}{166} \quad \frac{1000}{80} \quad 1.506 \quad 1.51 \text{ mol/kg}$$

3. **Key Idea** For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law.

Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$$p^{\circ}_N \quad p^{\circ}_M$$

So, by using Raoult's law

$$y_N \quad x_N \qquad \ldots\text{(i)}$$

and $\quad x_M \quad y_M \qquad \ldots\text{(ii)}$

Multiplying (i) and (ii) we get

$$y_N\, x_M \quad y_M\, x_N$$

$$\frac{x_M}{x_N} \quad \frac{y_M}{y_N}$$

Thus, correct relation is (a).

4. According to Henry's law (at constant temperature)

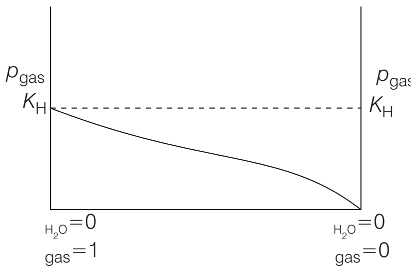
$p_{\text{gas}} \quad K_{\text{H}} \quad {}_{\text{gas (solute)}} \quad K_{\text{H}} \quad [1 \quad {}_{\text{H}_2\text{O (solvent)}}]$

$p_{\text{gas}} \quad K_{\text{H}} \quad K_{\text{H}} \quad {}_{\text{H}_2\text{O}}$

p_{gas} partial pressure of the gas above its solution with a liquid (solvent) say water.

${}_{\text{gas}}$ mole fraction of the gas (solute) in the solution.

${}_{\text{H}_2\text{O}}$ mole fraction of water (solvent).



[i.e. $p_{\text{gas}} \quad K_{\text{H}}$] Higher the value of K_{H}, higher will be the partial pressure of the gas (p_{gas}), at a given temperature. The plot of p_{gas} *vs* ${}_{\text{H}_2\text{O}}$ gives a (ve) slope.

$$p_{\text{gas}} \quad K_{\text{H}} \quad K_{\text{H}} \quad {}_{\text{H}_2\text{O}}$$

Comparing the above equation with the equation of straight line $y \quad mx \quad c$

Slope $\quad K_{\text{H}}$, intercept $\quad K_{\text{H}}$

So, (i) Higher the value of K_{H}, more (ve) will be the slope and it is for z (K_{H} 40 Kbar)

(ii) Higher the value of K_{H}, higher with the value of intercept, i.e. partial pressure and it is also for z.

5. *(d)* According to Dalton's law of partial pressure

$$p_{\text{total}} \quad p_A \quad p_B$$

$$p_A \quad {}_A \quad p_B \quad {}_B \qquad \ldots\text{(i)}$$

Given, p°_A 400 mm Hg, p°_B 600 mm Hg

$${}_B \quad 0.5, \quad {}_A \quad {}_B \quad 1$$

$${}_A \quad 0.5$$

On substituting the given values in Eq. (i). We get,

p_{total} 400 0.5 600 0.5 500 mm Hg

Mole fraction of A in vapour phase,

$$Y_A \quad \frac{p_A}{p_{\text{total}}} \quad \frac{p^{\circ}_A \quad {}_A}{p_{\text{total}}} \quad \frac{0.5 \quad 400}{500} \quad 0.4$$

Mole of B in vapour phase,

$$Y_A \quad Y_B \quad 1$$

$$Y_B \quad 1 \quad 0.4 \quad 0.6$$

6. For ideal solution,

$$p \quad x_A p_A \quad x_B p_B$$

$\because \quad x_A$ 0.4, x_B 0.6

p_A 7 10^3 Pa, p_B 12 10^3 Pa

On substituting the given values in Eq. (i), we get

$$p \quad 0.4 \quad 7 \quad 10^3 \quad 0.6 \quad 12 \quad 10^3$$

$$10 \quad 10^3 \text{ Pa} \quad 1 \quad 10^4 \text{ Pa}$$

In vapour phase,

$$x_A \quad \frac{p_A}{p} \quad \frac{x_A p_A}{p} \quad \frac{0.4 \quad 7 \quad 10^3}{1 \quad 10^4} \quad 0.28$$

$$x_B \quad 1 \quad 0.28 \quad 0.72 \qquad\qquad [\because x_A \quad x_B \quad 1]$$

7. At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant (K_H)

$$K_H \quad \frac{\text{Pressure}}{\text{Solubility of a gas in a liquid}} \quad \frac{P}{S}$$

Thus, higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

8. **Key Idea** Vapour pressure of water (p) 760 torr

$$\text{Number of moles of glucose} \quad \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{\ 1})}$$

$$\frac{18\text{ g}}{180\text{ gmol}^{\ 1}} \quad 0.1\text{ mol}$$

Molar mass of water 18 g/mol

Mass of water (given) 178.2g

Number of moles of water

$$\frac{\text{Mass of water}}{\text{Molar mass of water}}$$

$$\frac{178.2\text{g}}{18\text{ g/mol}} \quad 9.9\text{ mol}$$

Total number of moles (0.1 9.9) moles 10 moles

Now, mole fraction of glucose in solution Change in pressure with respect to initial pressure

$$\text{i.e.} \quad \frac{p}{p} \quad \frac{0.1}{10}$$

or p 0.01p 0.01 760 7.6 torr

Vapour pressure of solution (760 7.6) torr 752.4 torr

9. Given, p 185 Torr at 20°C

p_s 183 Torr at 20°C

Mass of non-volatile substance, m 1.2 g

Mass of acetone taken 100 g

M ?

$$\text{As, we have} \quad \frac{p \quad p_s}{p_s} \quad \frac{n}{N}$$

Putting the values, we get,

$$\frac{185 \quad 183}{183} \quad \frac{\frac{1.2}{M}}{\frac{100}{58}} \qquad \frac{2}{183} \quad \frac{1.2 \quad 58}{100 \quad M}$$

$$M \quad \frac{183 \quad 1.2 \quad 58}{2 \quad 100}$$

$$M \quad 63.684 \quad 64\text{ g/mol}$$

10. Give, K_H 1 10^5 atm, $_{N_2}$ 0.8

n_{H_2O} 10 moles, p_{total} 5 atm

p_{N_2} p_{total} $_{N_2}$ 5 0.8 4 atm

According to Henry's law,

$$p_{N_2} \quad K_H \quad _{N_2}$$

$$4 \quad 10^5 \quad _{N_2}$$

$$_{N_2} \quad 4 \quad 10^{\ 5}$$

$$\frac{n_{N_2}}{n_{N_2} \quad n_{H_2O}} \quad 4 \quad 10^{\ 5}$$

$$\frac{n_{N_2}}{n_{N_2} \quad 10} \quad 4 \quad 10^{\ 5}$$

$$n_{N_2} \quad 4 \quad 10^{\ 4}$$

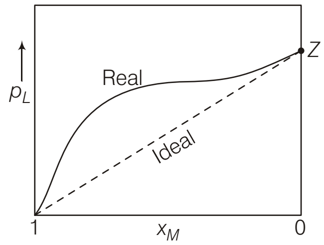
11. Molality = moles of solute present in 1.0 kg of solvent.

12. The relative lowering of vapour pressure :

$$\frac{p}{p} \quad _2 \qquad \text{(mole fraction of solute)}$$

13. In case of positive deviation from Raoult's law, the observed vapour pressure is greater than the ideal vapour pressure and boiling point of azeotrope becomes lower than either of pure liquid.

14. The graph shown indicates that there is positive deviation because the observed vapour pressure of L is greater than the ideal pressure



Since, deviation is positive, the intermolecular force between L and M is smaller than the same in pure L and pure M.

Also as x_L 1, x_M 0, the real curve approaching ideal curve where Raoult's law will be obeyed.

15. When intermolecular attraction between two components A and B in the mixture is same as between A and A or B and B, hence it is a case of ideal solution.

When intermolecular attraction between A and B in a mixture is smaller than that between A and A or B and B, then mixture is more vaporised, bp is lowered. It is a case of positive deviation from Raoult's law.

When intermolecular attraction between A and B is higher than that between A and A or B and B, then mixture is less vaporised, bp is increased. It is a case of negative deviation.

(a) Methanol molecules (CH_3OH) are hydrogen bonded. In a mixture of CCl_4 and CH_3OH, extent of H-bonding is decreased. Mixture is more vaporised thus, positive deviation from Raoult's law.

(b) Acetone molecules have higher intermolecular attraction due to dipole-dipole interaction. With CS_2, this interaction is decreased thus, positive deviation.

(c) Mixture of benzene and toluene forms ideal solution.

(d) Phenol and aniline have higher interaction due to intermolecular H-bonding. Hence, negative deviation.

16. **Key Idea** Use the formula

$$p_{\text{Total}} \quad p_A \quad _A \quad p_B \quad _B$$

and for equimolar solutions $_A \quad _B \quad \frac{1}{2}$

Given, p_{Total} 45 torr for equimolar solution

p_A 20 torr

So, $\quad 45 \quad p_A \frac{1}{2} \quad p_B \frac{1}{2} \quad \frac{1}{2}(p_A \quad p_B)$

or $\quad p_A \quad p_B \quad 90\,\text{torr}$ …(i)

But we know p_A 20 torr

so, $\quad p_B \quad 90 \quad 20 \quad 70\,\text{torr}$ (From Eq. (i))

Now, for the new solution from the same formula

Given, $\quad p_{\text{Total}} \quad 22.5\,\text{torr}$

So, $\quad 22.5 \quad 20 \quad _A \quad 70(1 \quad _A)$ (As $_A \quad _B \quad 1$)

or $\quad 22.5 \quad 70 \quad 50 \quad _A$

So, $\quad _A \quad \frac{70 \quad 22.5}{50} \quad 0.95$

Thus $\quad _B \quad 1 \quad 0.95 \quad 0.05$ (as $_A \quad _B \quad 1$)

Hence, the ratio

$$\frac{_A}{_B} \quad \frac{0.95}{0.05} \quad 19$$

17. It will be true only if boiling points of two liquids are significantly different.

18. Let after 100 min, x moles of A are remaining unpolymerised moles of B 12

Moles of non-volatile solute = 0.525

$$\text{Mole fraction of } A \quad \frac{}{12 \quad 0.525}$$

$$\text{Mole fraction of } B \quad \frac{12}{12 \quad 0.525}$$

$$400 \quad \frac{}{12.525} \quad 300 \quad \frac{12}{12.525} \quad 500$$

9.9

Moles of A polymerised in 100 min = 10 – 9.9 = 0.10

$$k \quad \frac{1}{t}\ln\frac{10}{9.9} \quad \frac{1}{100}\ln\frac{10}{9.9}\ \text{min}^{\ 1}$$

$$1.005 \quad 10^{\ 4}\ \text{min}^{\ 1}$$

19. Volume of 1.0 mole liquid benzene = $\frac{78}{0.877}$ mL = 88.94 mL

Molar volume of benzene vapour at 20°C

$$\frac{88.94 \quad 2750}{1000}\,\text{L} \quad 244.58\ \text{L}$$

$$\text{VP of pure benzene at 20°C} \quad \frac{0.082 \quad 293}{244.58} \quad 760\,\text{mm}$$

$$74.65\ \text{mm}$$

Similarly; molar volume of toluene vapour

$$= \frac{92}{0.867} \quad \frac{7720}{1000}\,\text{L} = 819.2\text{L}$$

$$\text{VP of pure toluene} \quad \frac{0.082 \quad 293}{819.2} \quad 760\,\text{mm} = 22.3\text{mm}$$

Now, let mole fraction of benzene in the liquid phase

$$4.65 \quad + 22.3\,(1 - \quad) \quad 45$$

$$0.43$$

Mole fraction of benzene in vapour phase

$$\frac{\text{Partial vapour pressure of benzene}}{\text{Total vapour pressure}}$$

$$\frac{74.65 \quad 0.43}{45} \quad 0.72$$

20. Vapour pressure of solution = 0.75 VP of water

$$75 \quad 100 \quad _1 : \quad _1 \quad \text{mole fraction of solute}$$

$$_1 \quad \frac{3}{4} \text{ and } \quad _2 \quad 1 \quad _1 \quad \frac{1}{4}$$

$$\frac{_2}{_1} \quad \frac{n_2}{n_1} \quad \frac{1}{3}$$

$$n_2 \quad \frac{n_1}{3} \quad \frac{100}{18 \quad 3} = 1.85$$

Weight of urea $\quad 1.85 \quad 60 = 111$ g

$$\text{Molality} \quad \frac{n_2}{n_1} \quad \frac{1000}{M_1}$$

$$\frac{1}{3} \quad \frac{1000}{18} = 18.5$$

21. $Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3$

$\quad 1 \qquad\qquad\qquad 2$

$$i \quad 1 \quad 2 \quad \text{where,} \quad 0.7$$

$$i \quad 1 \quad 2 \quad 0.7 = 2.4$$

$$\text{Mole fraction of solvent} \quad \frac{n_1}{n_1 \quad in_2}$$

$$\frac{\frac{100}{18}}{\frac{100}{18} \quad 2.4 \quad \frac{7}{164}} = 0.982$$

$$p \quad p_0 \quad _1 \quad 760 \quad 0.982$$

(VP of H_2O at 100°C = 760 mm of Hg)

746.32 mm

22. According to Raoult's law :

$$p \quad p_0 \quad _1$$

$$600 \quad 640 \quad \frac{n_1}{n_1 \quad n_2}$$

$$\frac{n_2}{n_1} \quad \frac{64}{60} \quad 1 \quad \frac{1}{15}$$

$$n_2 \quad \frac{39}{78} \quad \frac{1}{15} \quad 0.033$$

$$\frac{2.175}{M} \quad 0.033$$

$$M = 65.25$$

23. At 373 K (bp) of H_2O, Vapour pressure = 760 mm

VP of solution at 373 K 750 mm

$$p \quad p_0 \quad _1$$

or $\quad 750 \quad 760 \quad _1$

$_1 \quad \frac{75}{76}$ mole fraction of H_2O

$_2 \quad 1 \quad \frac{75}{76} \quad \frac{1}{76}$ mole fraction of solute

Now $\quad \frac{n_2}{n_1 \quad n_2} \quad \frac{1}{76}$

$\frac{n_1}{n_2} \quad 75$

Molality $\frac{n_2}{n_1 M_1} \quad 1000 \quad \frac{1000}{75 \quad 18} \quad 0.74$ molal

24. Moles of ethanol $\frac{60}{46} = 1.3$

Moles of methanol $= \frac{40}{32} = 1.25$

Mole fraction of ethanol $= \frac{1.3}{1.3 \quad 1.25} = 0.51$

Vapour pressure of solution $\quad p_{\text{ethanol}} \quad p_{\text{methanol}}$

$0.51 \quad 44.5 + 0.49 \quad 88.7$

66.16 mm

Mole fraction of methanol in vapour phase

$\frac{p_{\text{methanol}}}{\text{Total vapour pressure}}$

$\frac{43.463}{66.16} \quad 0.657$

25. From lowering of vapour pressure information :

$\frac{0.104}{17.5} \quad _2 \quad \frac{n_2}{n_1 \quad n_2}$

$\frac{n_1}{n_2} \quad 1 \quad 168.27$

$\frac{n_1}{n_2} = 167.27$

$\frac{1000}{18} \quad \frac{M}{50} \quad 167.27$

$M \quad 150$ g/mol

Also, the combustion reaction is :

$C_xH_{2y}O_y \quad xO_2 \qquad xCO_2 \quad yH_2O$

$\because$ 18 y g of H_2O is produced from 1.0 mole of compound.

0.9 g of H_2O will be produced from $\frac{0.9}{18y} = \frac{1}{20y}$ mol

At the end, moles of O_2 left $\quad \frac{x}{20y}$

moles of CO_2 formed $\quad \frac{x}{20y}$

Total moles of gases at STP $\quad \frac{2x}{20y} \quad \frac{2.24}{22.4}$

$x \quad y$

Molar mass; $150 \quad 12x \quad 2x \quad 16x \quad 30x$

$x \quad \frac{150}{30} \quad 5$

Formula $\quad C_5H_{10}O_5$

26. When 1.0 mole of A is mixed with 3 moles of B.

$550 \quad 0.25\, p_A + 0.75\, p_B$ ...(i)

When 1.0 mole of A is mixed with 4 moles of B.

$560 \quad 0.20\, p_A + 0.80\, p_B$ ...(ii)

Now, solving (i) and (ii) $p_A \quad 400$ mm

$p_B \quad 600$ mm.

27. According to Raoult's law :

$p \quad p_0 \;_1 \quad 631.9 = 639.7 \quad _1$

$_1 \quad 0.9878 \qquad _2 = 0.0122$

Molality $= \frac{0.0122}{0.9878 \quad 78} \quad 1000 \quad 0.158$

28. Let us consider 1.0 L of solution.

Weight of solution = 1000 $\quad$ 1.02 = 1020 g

Weight of $H_2SO_4 \quad 1020 \quad \frac{13}{100} = 132.60$ g

Weight of H_2O = 1020 – 132.60 = 887.40 g

Molarity $\frac{132.60}{98} \quad 1.353$ M

Molality $\frac{132.60}{98} \quad \frac{1000}{887.40} \quad 1.525$ m

Normality $\quad 2 \quad M = 2.706$

$2.706 \quad 100 \quad 1.5\, V$

$V \quad 180.40$ mL

Topic 2 Colligative Properties

1. **Key Idea** Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).

Thus, $\quad C, \quad CRT$ (for dilute solution)

$\frac{n}{V} RT$

For the relation, $\quad CRT \quad \frac{n}{V} RT$

Given, mass of urea $\quad 0.6$ g

Molar mass of urea $\quad 60$ g mol ^{1}

Mass of glucose $\quad 1.8$ g

Molar mass of glucose $\quad 180$ g mol ^{1}

$\frac{[n_2 \text{ (urea)} \quad n_2\text{(glucose)}]}{V} RT$

$\frac{\frac{0.6}{60} \quad \frac{1.8}{180}}{100} \quad 1000 \quad 0.0821 \quad 300$

$(0.01 \quad 0.01) \quad 10 \quad 0.0821 \quad 300$

4.92 atm

2. The expression of elevation of boiling point,

$T_b \quad K_b \quad m \quad i$

$k_b \quad \frac{w_2 \quad 1000}{M_2 \quad w_1} \quad i$

where, m molality

i van't Hoff factor 1 (for non-electrolyte/non-associable)

w_2 mass of solute in g 1 g (present in both of the solutions)

M_2 molar mass of solute in g mol ^{1} (same solute in both of the solutions)

w_1 mass of solvent in g 100 g (for both of the solvents A and B)

K_b ebullioscopic constant

So, the expression becomes,

$$T_b \quad K_b$$

$$\frac{T_b(A)}{T_b(B)} \quad \frac{K_b(A)}{K_b(B)} \quad \frac{1}{5} \qquad \text{Given } \frac{K_b(A)}{K_b(B)} \quad \frac{1}{5}$$

3. **Key Idea** For dilute solution, lowering of vapour pressure (p) p^0 p and relative lowering of vapour pressure $\frac{p}{p^0}$ which is a colligative property of solutions.

$$\frac{p}{p^0} \quad _B \; i \qquad p \quad _B \; i \; p^0$$

where, p^0 vapour pressure of pure solvent

i van't Hoff factor

$_B$ mole fraction of solute

Given,

p vapour pressure of pure water of 25° C 35 mm Hg

$_B$ mole fraction of solute (urea)

$$\frac{n_B}{n_A \quad n_B} \quad \frac{\frac{0.60}{60}}{\frac{360}{18} \quad \frac{0.60}{60}} \quad \frac{0.01}{20 \quad 0.01}$$

$$\frac{0.01}{20.01} \quad 0.0005$$

i van't Hoff factor = 1 (for urea)

Now, according to Raoult's law

$$p \quad _B \; i \; p^o$$

On substituting the above given values, we get

p 0.0005 1 35 0.0175 mm Hg

4. **Key Idea** Depression in freezing point (T_f) is given by

T_f iK_fm

i vant Hoff factor

K_f molal depression constant

m molality

K_f 4.0 K kg mol ^{1} (Given)

m 0.03 mol kg ^{1} (Given)

T_f ?

For K_2SO_4, i 3

It can be verified by the following equation :

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^2$$

Using formula

$$T_f \quad iK_f \quad m$$

$$T_f \quad 3 \quad 4 \quad 0.03 \quad 0.36\,\text{K}$$

5. **Key Idea** Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature, CRT

Concentration of $BaCl_2$ 0.01M (Given)

$_{XY}$ 4 $_{BaCl_2}$ (Given)

i CRT 4 i CRT ...(i)

For the calculation of i,

XY X Y (Here, i 2)

$BaCl_2$ Ba^2 2Cl (Here, i 3)

Putting the values of i in (i)

$$2 \quad [XY] \quad 4 \quad 3 \quad [BaCl_2]$$

$$2 \quad [XY] \quad 12 \quad 0.01$$

$$[XY] \quad \frac{12 \quad 0.01}{2}$$

So, the concentration of XY 0.06 mol L ^{1}

6 10 ^{2} mol L ^{1}

6. Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Now, we know that depression in freezing point (T_f) is given by following equation:

$$T_f \quad i \; K_f \quad m \quad \frac{i \quad K_f \quad w_{solute} \quad 1000}{Mw_{solute} \quad w_{solvent}} \qquad \text{...(i)}$$

Given, w_{solute} (benzoic acid) w g

$w_{solvent}$ (benzene) 30 g

Mw_{Solute} (benzoic acid) 122 g mol ^{1}, T_f 2 K

K_f 5 Kkg mol ^{1}, % 80 or 0.8

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Initial	1	0
Final	1	/ 2
	1 0.8 0.2	0.8 / 2 0.4

Total number of moles at equilibrium 0.2 0.4 0.6

$$i \quad \frac{\text{Number of moles at equilibrium}}{\text{Number of moles present initially}}$$

$$i \quad \frac{0.6}{1} \quad 0.6$$

On substituting all the given values in Eq. (i), we get

$$2 \quad \frac{0.6 \quad 5 \quad w \quad 1000}{122 \quad 30}, \quad w \quad 2.44\text{ g}$$

Thus, weight of acid (w) is 2.4 g.

7. Given, Freezing point of 4% aqueous solution of X.

Freezing point of 12% aqueous solution of Y

or $(T_f)_X \quad (T_f)_Y$ [$\because$ T_f T_f T_f]

K_f m_X $K_f m_Y$

where, m_X and m_Y are molality of X and Y, respectively.

or m_X m_Y

Now, molality $\frac{\text{Number of moles of solute } (n)}{\text{Mass of solvent (in kg)}}$

$n \quad \frac{\text{Weight}}{\text{Molecular mass}}$

$\frac{w_X}{M_X \quad (w_{\text{solvent}})_1} \quad \frac{w_Y}{M_Y \quad (w_{\text{solvent}})_2}$

Given, $w_X \quad 4$ and $w_{(\text{solvent})_1} = 96$

$w_Y \quad 12$ and $w_{(\text{solvent})_2} = 88$

$M_X \quad A$

$\frac{4 \quad 1000}{M_X \quad 96} \quad \frac{12 \quad 1000}{M_Y \quad 88}$

Thus, $M_Y \quad \frac{12 \quad 1000 \quad M_X \quad 96}{4 \quad 1000 \quad 88}$

$\frac{96 \quad 12}{4 \quad 88} \quad A \quad 3.27A \quad 3A$

8. The ionisation of K_2HgI_4 in aqueous solution is as follows:

$$K_2[HgI_4] \rightleftharpoons 2K \quad [HgI_4]^2$$

van't Hoff factor (i) for ionisation reaction is given as, $i \quad 1 \quad\quad n \quad 1)$

where,

n number of ions,

degree of ionisation or dissociation

From above equation, it is clear that $n \quad 3$

$i \quad 1 \quad 0.4 \ (3 \quad 1)$

[Given, % 40% or 0.4]

1.8

9. We know that,

Depression in freezing points (T_f)

$T_f \quad T_f \quad K_f \quad m \quad i$

where, K_f molal depression constant

m molality $\frac{w_{\text{solute}} \quad 1000}{M_{\text{solute}} \quad w_{\text{solvent (in g)}}}$

i van't Hoff factor

For diluted milk

$T_{f_1} \quad K_f \quad m_1 \quad i$

$0 \quad (0.2) \quad 0.2 \quad K_f \quad \frac{w_{\text{milk}} \quad 1000}{M_{\text{milk}} \quad w_1(H_2O)} \quad 1$

For pure milk

$T_{f_2} \quad K_f \quad m_2 \quad i$

$0 \quad (\ 0.5) \quad 0.5 \quad K_f \quad \frac{w_{\text{milk}} \quad 1000}{M_{\text{milk}} \quad w_2(H_2O)} \quad 1$

So, $\frac{0.2}{0.5} \quad \frac{K_f}{K_f} \quad \frac{w_{\text{milk}} \quad 1000}{M_{\text{milk}} \quad w_1(H_2O)} \quad \frac{M_{\text{milk}} \quad w_2(H_2O)}{w_{\text{milk}} \quad 1000} \quad \frac{w_2(H_2O)}{w_1(H_2O)}$

$\frac{w_2(H_2O) \text{ (in pure milk)}}{w_1(H_2O) \text{ (in diluted milk)}} \quad \frac{2}{5}$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

10. Elevation in boiling point (T_b) $K_b \quad m \quad i$

Depression is freezing point (T_f) $K_f \quad m \quad i$

where, m molality

For the glucose solution (van't Hoff factor, i 1),

$T_b^{1m} \quad T_f^{2m} \quad 2K$

So, $K_b \quad 1 \quad 1 \quad K_f \quad 2 \quad 1 \quad\quad K_b \quad 2K_f$

11. Considering the expression of the depression in freezing point of a solution,

$T_f \quad K_f \quad m \quad i$

$T_f \quad T_f \quad K_f \quad \frac{w_B \quad 1000}{M_B \quad w_A(\text{in g})} \quad i$ …(i)

Here, T_f 0 C, T_f 10 C

w_B mass of ethylene glycol 62 g

M_B molar mass of ethylene glycol

$CH_2 — CH_2$

OH OH

62 g mol 1

w_A mass of water in g as liquid solvent,

i van't-Hoff factor 1 (for ethylene glycol in water)

K_f 1.86 K kg mol 1

On substituting in Eq. (i), we get

$0 \quad (\quad 10) \quad 1.86 \quad \frac{62 \quad 1000}{62 \quad w_A} \quad 1$

$w_A \quad \frac{1.86 \quad 62 \quad 1000}{10 \quad 62} \quad 186 \text{ g}$

So, amount of water separated as ice (solid solvent)

$250 \quad w_A \quad (250 \quad 186) \text{g} \quad 64 \text{ g}$

12. **Key idea** ''Addition of solute particles to a pure solvent results to depression in its freezing point.''
All the compounds given in question are ionic in nature so, consider their van't Hoff factor (i) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

Number of solute particles van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which solute with minimum van't Hoff factor is present

Now, for $Co(H_2O)_6]Cl_3 \rightleftharpoons [Co(H_2O)_6]^{3+} + 3Cl$

van't Hoff factor (i) is 4. Similarly for,

$[Co(H_2O)_5Cl]Cl_2 \ H_2O \rightleftharpoons [Co(H_2O)_5Cl]^{2+} + 2Cl$ 'i' is 3

$[Co(H_2O)_4Cl_2]Cl \ 2H_2O \rightleftharpoons [Co(H_2O)_4Cl_2]^+ + Cl$ 'i' is 2

and for $[Co(H_2O)_3Cl_3] \ 3H_2O$, 'i' is 1 as it does not show ionisation. Hence, $[Co(H_2O)_3Cl_3] \ 3H_2O$ have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

13. Let the degree of association of acetic acid (CH_3COOH) in benzene is , then

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Initial moles	1	0
Moles at equilibrium	1	$\frac{}{2}$

Total moles $1 \quad \frac{}{2} \quad 1 \quad \frac{}{2}$ or $i \quad 1 \quad \frac{}{2}$

Now, depression in freezing point (T_f) is given as

$$T_f \quad i K_f m \qquad \ldots(i)$$

where, K_f molal depression constant or cryoscopic constant.

m molality

$$\text{Molality} \quad \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} \quad \frac{0.2}{60} \quad \frac{1000}{20}$$

Putting the values in Eq. (i)

$$0.45 \quad 1 \quad \frac{}{2} \quad (5.12) \quad \frac{0.2}{60} \quad \frac{1000}{20}$$

$$1 \quad \frac{}{2} \quad \frac{0.45 \quad 60 \quad 20}{5.12 \quad 0.2 \quad 1000}$$

$$1 \quad \frac{}{2} \quad 0.527 \qquad \frac{}{2} \quad 1 \quad 0.527$$

$$0.946$$

Thus, percentage of association 94.6%

14. $T_f \quad i k_f m_2$

$$1 \quad 2 \quad \frac{34.5}{46 \quad 500} \quad 1000 \quad 3$$

Vapour pressure curves shown in (*b*) is in agreement with the calculated value of T_f. (*a*) is wrong, vapour pressure decreases on cooling.

15. **PLAN** This problem includes concept of colligative properties (osmotic pressure here) and van't Hoff factor. Calculate the effective molarity of each solution.

i.e. effective molarity van't Hoff factor molarity

0.5 M C_2H_5OH (*aq*) $\quad i \quad 1$

Effective molarity 0.5

0.25 M KBr (*aq*) $\quad i \quad 2$

Effective molarity 0.5 M

0.1 M $Mg_3(PO_4)_2$(*aq*) $\quad i \quad 5$

Effective molarity 0.5 M

0.125 M Na_3PO_4 (*aq*) $\quad i \quad 4$

Effective molarity 0.5 M

Molarity is same hence, all colligative properties are also same.

NOTE This question is solved by assuming that the examiner has taken $Mg_3(PO_4)_2$ to be completely soluble. However, in real it is insoluble (sparingly soluble).

16. The elevation in boiling point is

$$T_b \quad K_b \ m: m \quad \text{molality} \quad \frac{n_2}{w_1} \quad 1000$$

[n_2 Number of moles of solute, w_1 Weight of solvent in gram]

$$2 \quad 0.76 \quad \frac{n_2}{100} \quad 1000$$

$$n_2 \quad \frac{5}{19}$$

Also, from Raoult's law of lowering of vapour pressure :

$$\frac{p}{p} \quad x_2 \quad \frac{n_2}{n_1 \quad n_2} \quad \frac{n_2}{n_1} \qquad [\because n_1 \quad n_2]$$

$$p \quad 760 \quad \frac{5}{19} \quad \frac{18}{100} \quad 36 \text{ mm of Hg}$$

$$p \quad 760 \quad 36 \quad 724 \text{ mm of Hg}$$

17. van't Hoff factor (i) = 4 $\{3K^+ + [Fe(CN)_6]^{3-}$

$$\text{Molality} \quad \frac{0.1}{329} \quad \frac{1000}{100} \quad \frac{1}{329}$$

$$- \ T_f \quad iK_f \cdot m$$

$$4 \quad 1.86 \quad \frac{1}{329} \quad 2.3 \quad 10^{-2}$$

$$T_f \quad -2.3 \quad 10^{-2} \text{ C}$$

(As % freezing point of water is 0ºC)

18. $$\text{Molality} \quad \frac{20}{172} \quad \frac{1000}{50} \quad 2.325 \text{ m}$$

$$T_f \quad 2 \quad iK_f \ m$$

$$i \quad \frac{2}{1.72 \quad 2.325} = 0.5$$

19. $$\text{Molality} \quad \frac{13.44}{134.1} = 0.1$$

$$i \quad 3$$

$$T_b \quad iK_b \ m \quad 3 \quad 0.52 \quad 0.1 = 0.156$$

20. For isotonic solutions, they must have same concentrations of ions, Therefore,

$$0.004 \ i \ (Na_2SO_4) \quad 0.01$$

$$i \quad \frac{0.01}{0.004} = 2.5$$

Also $\underset{1}{Na_2SO_4} \rightleftharpoons \underset{2}{2Na^+} \quad SO_4^2 \qquad \underset{1 \quad 2}{i}$

$$i \quad 1 \quad 2 \quad 2.5$$

$$0.75 \quad 75\%$$

21. During freezing, liquid solvent solidify and solid solvent remains in equilibrium with liquid solvent.

22. In benzene, benzoic acid dimerises as :

$$C_6H_5COOH \rightleftharpoons \frac{1}{2}(C_6H_5COOH)_2$$

23. $C_6H_5NH_3Cl$: $i = 2$;

$Ca(NO_3)_2$: $i = 3$

$La(NO_3)_3$: $i = 4$;

$C_6H_{12}O_6$: $i = 1$

Lower the value of i, smaller will be the depression in freezing point, higher will be the freezing temperature, if molalities are equal. Hence, glucose solution will have highest freezing temperature.

24. K_2SO_4 : $i \quad 3$

NaCl : $i = 2$

Urea : $i = 1$

Glucose : $i = 1$

Greater the value of *i*, greater the lowering in freezing point, lower will be the freezing temperature, if molarity in all cases are same. Therefore, K_2SO_4 solution has the lowest freezing point.

25. Addition of HgI_2 to KI solution establishes the following equilibrium :

$$HgI_2 + 2KI \rightleftharpoons K_2[HgI_4]$$

The above equilibrium decreases the number of ions (4 ions on left side of reactions becomes three ions on right side), hence rises the freezing point.

26. In depression of freezing point experiment, vapour pressure of solution is less than that of pure solvent as well as only solvent molecules solidify at freezing point.

27. From the graph we can note

T_b for solution X i.e.,

$$T_{b(X)} \quad 362 \quad 360 \quad 2$$

Likewise, T_b for solution Y i.e., $T_{b(Y)} \quad 368 \quad 367 \quad 1$

Now by using the formula

$$T_b \quad i \quad \text{molality of solution} \times \; K_b$$

For solution X

$$2 \quad i \quad m_{\text{NaCl}} \quad K_{b(X)} \qquad \ldots\text{(i)}$$

Similarly for solution y

$$1 \quad i \quad m_{\text{NaCl}} \quad K_{b(Y)} \qquad \ldots\ldots\text{(ii)}$$

from Eq. (i) and (ii) above

$$\frac{K_{b(X)}}{K_{b(Y)}} \quad \frac{2}{1} \text{or } 2 \quad \text{or} \quad K_{b(X)} \quad 2K_{b(Y)}$$

For solute S

	$2S$	S_2	(given due to dimerisation)
Initial		0	
Final	(1)	$\frac{}{2}$	

So, here $\quad i \quad 1 \quad \frac{}{2}$

$$T_{b[X](s)} \quad 1 \quad \frac{1}{2} \quad K_{b(X)}$$

$$T_{b[Y](s)} \quad 1 \quad \frac{2}{2} \quad K_{b(Y)}$$

Given, $\quad T_{b(X)(s)} \quad 3 \quad T_{b(Y)(s)}$

$$1 \quad \frac{}{2} \quad K_{b(X)} \quad 3 \quad 1 \quad \frac{2}{2} \quad K_{b(Y)}$$

or $\quad 2 \quad 1 \quad \frac{1}{2} \quad 3 \quad 1 \quad \frac{2}{2} \qquad [\because K_{b(X)} \quad 2K_{b(Y)}]$

or $\quad 2 \quad 1 \quad \frac{1}{2} \quad 3 \quad 1 \quad \frac{0.7}{2} \qquad$ (as given, $_2$ 0.7)

or $\quad 4 \quad 2 \;_1 \quad 6 \quad 2.1 \quad$ or $\quad 2 \;_1 \quad 0.1$

so, $\quad _1 \quad 0.05$

28. Molar mass of solute (M_B) $\dfrac{1000 \quad K_f \quad W_B}{W_A \quad T_f}$

$$M_B \quad \frac{1000 \quad 14 \quad 75.2}{1000 \quad 7}$$

$$M_B \quad 150.4 \text{ g per mol}$$

Actual molar mass of phenol 94 g/mol

Now, van't Hoff factor, i $\dfrac{\text{Calculated molar mass}}{\text{Observed molar mass}}$

$$i \quad \frac{94}{150.4} \quad 0.625$$

Dimerisation of phenol can be shown as :

	$2C_6H_5OH$	$\rightleftharpoons$	$(C_6 \; H_5OH)_2$
Initial	1		0
At equilibrium	1 –		$\frac{}{2}$

Total number of moles at equilibrium, $i \quad 1 \quad \frac{}{2}$

$$i \quad 1 \quad \frac{}{2}$$

But i 0.625, thus, $\quad 0.625 \quad 1 \quad \frac{}{2}$

$$\frac{}{2} \quad 1 \quad 0.625$$

$$0.75$$

Thus, the percentage of phenol that dimerises is 75%.

29. (i) $T_b \quad K_b \quad m_2$

$$0.17 \quad 1.7 \quad \frac{1.22}{M} \quad \frac{1000}{100} \qquad M \quad 122$$

(ii) $0.13 \quad 2.6 \quad \dfrac{1.22}{M} \quad \dfrac{1000}{100} \qquad M \quad 244$

The above molar masses suggests thapt benzoic acid is monomeric in acetone while dimeric in benzene.

30. Higher the value of K_b of a solvent suggest that there is larger polarity of solvent molecules, which in turn implies higher boiling point due to dipole-dipole interaction.

Therefore, the correct order of K_b values of the three given solvents is

Solvents	Boiling point	K_b
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

31. Mass of water $\quad 500 \quad 0.997 \text{ g} = 498.5 \text{ g}$

Also $\quad \underset{1}{CH_3COOH} \rightleftharpoons CH_3COO \quad + \quad H^+$

$$i \quad 1 \qquad 1.23$$

$$T_f \quad iK_f \quad m \quad 1.23 \quad 1.86 \quad \frac{3}{60} \quad \frac{1000}{498.5} \quad 0.23°\text{C}$$

32. (i) **Empirical formula determination**

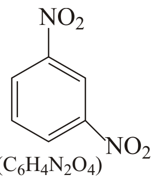
Elements	C	H	N	O
Weight %	42.86	2.40	16.67	38.07
Moles	3.57	2.40	1.19	2.38
Simplest ratio	3	2	1	2

Empirical formula = $C_3H_2NO_2$

(ii) $\quad T_b \quad 1.84 = 2.53 \quad \dfrac{5.5}{M} \quad \dfrac{1000}{45}$

$$M \quad 168$$

∵ Empirical formula weight (84) is half of molar mass, molecular formula is $C_6H_4N_2O_4$ a dinitrobenzene :



$(C_6H_4N_2O_4)$

33. $T_f \quad K_f \; m_2$

$$m_2 \quad \frac{0.3}{1.86} \quad 0.1613$$

Also, $$m_2 \quad \frac{n_2}{n_1} \quad \frac{1000}{M_1} = 0.1613$$

$$\frac{n_2}{n_1} \quad \frac{0.1613 \quad 18}{1000} = 2.9 \quad 10^{\ 3}$$

$$\frac{n_2}{n_1} \quad 1 \quad \frac{n_2 \quad n_1}{n_1} \quad 2.9 \quad 10^{\ 3} \quad 1$$

$$\frac{n_1}{n_1 \quad n_2} \quad _1 \quad \frac{1}{1 \quad 2.9 \quad 10^{\ 3}} = 0.997$$

$$p \quad p_{0\ \ 1} = 23.51 \quad 0.997 \quad 23.44 \text{ mm}$$

34. $T_f \quad 5.51 \quad 5.03 \quad 0.48$

$$T_f \quad 0.48 \quad K_f \; m$$

$$0.48 = 5.12 \quad \frac{0.643}{M} \quad \frac{1000}{50 \quad 0.879}$$

$$M = 156 \text{ g/mol}$$

35. In the given solution 'M', H_2O is solute.

Therefore, molality of H_2O $\frac{0.1}{0.9 \quad 46} \quad 1000 = 2.4$

$$T_f \quad K_f^{\text{ethanol}} \quad 2.4 \quad 2 \quad 2.4 \quad 4.8$$

$$T_f \quad 155.7 - 4.8 = 150.9 \text{ K}$$

36. Vapour pressure $p\,(H_2O) \quad p(\text{ethanol})$

$$32.8 \quad 0.1 \quad 40 \quad 0.9$$

$$3.28 + 36$$

$$= 39.28 \text{ mm}$$

37. Now ethanol is solute.

Molality of solute $\frac{0.1}{0.9 \quad 18} \quad 1000 = 6.17$

$$T_b \quad 6.17 \quad 0.52 = 3.20$$

$$T_b \quad 373 + 3.2$$

$$= 376.2 \text{ K}$$

38. $\lim_{m \quad 0} \frac{T_f}{m} \quad K_f$ (Cryoscopic constant)

39. $1 \quad T_f \quad iK_f m$

$$T_f \quad 0 - (-0.0558 \ \ C)$$

$$0.0558 \ \ C$$

i (vant Hoff's factor) $\frac{0.0558}{1.86 \quad 0.01} \quad 3$

This indicates that complex upon ionisation produces three ions as:

$[Co(NH_3)_5Cl]Cl_2 \quad [Co(NH_3)_5Cl]^{2+}(aq) \quad 2Cl \ \ (aq)$

Thus, only one Cl is inside the coordination sphere.

40. $MX_2 \qquad M^2 \qquad 2X$

van't Hoff factor for any salt can be calculated by using equation $i \quad 1 \quad (n \quad 1)$

where, n number of constituent ions

$$i(MX_2) \quad 1 \quad (3 \quad 1) \quad 1 \quad 2$$

$$\frac{(\ T_f)_{\text{observed}}}{(\ T_f)_{\text{theoretical}}} \quad i \quad 1 \quad 2$$

$$i \quad 1 \quad 2 \quad 0.5 \qquad i \quad 2$$

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10

Electrochemistry

Topic 1 Electrochemical Cells

Objective Questions I (Only one correct option)

1. Given,

Co^{3} e Co^{2} ; E 1.81 V

Pb^{4} $2e$ Pb^{2} ; E 1.67 V

Ce^{4} e Ce^{3} ; E 1.61 V

Bi^{3} $3e$ Bi; E 0.20 V

Oxidising power of the species will increase in the order **(2019 Main, 12 April I)**

(a) Ce^{4} Pb^{4} Bi^{3+} Co^{3}
(b) Bi^{3} Ce^{4} Pb^{4} Co^{3}
(c) Co^{3} Ce^{4} Bi^{3} Pb^{4}
(d) Co^{3} Pb^{4} Ce^{4} Bi^{3}

2. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode? **(2019 Main, 9 April II)**

(a) 0.20 (b) 0.10 (c) 0.15 (d) 0.05

3. Calculate the standard cell potential (in V) of the cell in which following reaction takes place

$$Fe^{2+}(aq) + Ag^{+}(aq) \quad Fe^{3+}(aq) + Ag(s)$$

Given that,

$$E_{Ag^{+}/Ag} \quad x\text{ V}$$
$$E_{Fe^{2+}/Fe} \quad y\text{ V}$$
$$E_{Fe^{3+}/Fe} \quad z\text{ V}$$

(2019 Main, 8 April II)

(a) x $2y$ $3z$ (b) x y
(c) x y z (d) x z

4. Given, that $E^{\ominus}_{O_2/H_2O} = +1.23\text{V}$;

$E^{\ominus}_{S_2O_8^{2}/SO_4^{2}} = 2.05\text{V}$;

$E^{\ominus}_{Br_2/Br^{\ominus}} = +1.09\text{V}$,

$E^{\ominus}_{Au^{3+}/Au} = +1.4\text{V}$

The strongest oxidising agent is **(2019 Main, 8 April I)**

(a) Au^{3} (b) O_2 (c) $S_2O_8^{2}$ (d) Br_2

5. Consider the following reduction processes:

Zn^{2} $2e$ $Zn(s)$; E 0.76 V

Ca^{2} $2e$ $Ca(s)$; E 2.87 V

Mg^{2} $2e$ $Mg(s)$; E 2.36 V

Ni^{2} $2e$ $Ni(s)$; E 0.25 V

The reducing power of the metals increases in the order **(2019 Main, 10 Jan I)**

(a) Zn < Mg < Ni < Ca (b) Ni < Zn < Mg < Ca
(c) Ca < Zn < Mg < Ni (d) Ca < Mg < Zn < Ni

6. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process is (Molar mass of $PbSO_4$ 303 g mol^{1}) **(2019 Main, 9 Jan I)**

(a) 11.4 (b) 7.6 (c) 15.2 (d) 22.8

7. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane? (Atomic weight of B 10.8) **(2018 Main)**

(a) 6.4 hours (b) 0.8 hours (c) 3.2 hours (d) 1.6 hours

8. Given, $E_{Cl_2/Cl}$ 1.36 V, $E_{Cr^{3+}/Cr}$ 0.74 V

$E_{Cr_2O_7^{2}/Cr^{3}}$ 1.33 V, $E_{MnO_4/Mn^{2+}}$ 1.51 V

Among the following, the strongest reducing agent is **(2017 Main)**

(a) Cr (b) Mn^{2+}
(c) Cr^{3+} (d) Cl

9. For the following electrochemical cell at 298 K,

$$Pt(s) \mid H_2(g, 1\text{bar}) \mid H \ (aq, 1\text{ M}) \parallel M^{4} \ (aq), M^{2} \ (aq) \mid Pt(s)$$

$$E_{cell} \quad 0.092\text{ V when } \frac{[M^{2} \ (aq)]}{[M^{4} \ (aq)]} \quad 10^{x}$$

$$\text{Given : } E_{M^{4+}/M^{2+}} \quad 0.151\text{ V}; 2.303\frac{RT}{F} \quad 0.059\text{ V}$$

The value of x is **(2016 Adv.)**

(a) 2 (b) 1
(c) 1 (d) 2

10. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu 63.5 u) **(2015 Main)**

(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

11. Given, $E_{Cr^{3+}/Cr}$ 0.74 V; $E_{MnO_4/Mn^{2+}}$ 1.51 V

$E_{Cr_2O_7^2/Cr^{3+}}$ 1.33 V; $E_{Cl/Cl}$ 1.36 V

Based on the data given above strongest oxidising agent will be **(2013 Main)**

(a) Cl (b) Cr^3 (c) Mn^2 (d) MnO_4

12. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is (1 F 96500 C mol ^{1})

(a) 9.65 10^4 s (b) 19.3 10^4 s **(2008, 3M)**

(c) 28.95 10^4 s (d) 38.6 10^4 s

13. In the electrolytic cell, flow of electrons is from **(2003, 1M)**

(a) cathode to anode in solution

(b) cathode to anode through external supply

(c) cathode to anode through internal supply

(d) anode to cathode through internal supply

14. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below :

$MnO_4(aq) + 8H^+(aq) + 5e \quad Mn^{2+}(aq) + 4H_2O(l),$ E 1.51 V

$Cr_2O_7^2(aq) + 14H^+(aq) + 6e \quad 2Cr^{3+}(aq) + 7H_2O(l),$ E 1.38 V

$Fe^{3+}(aq) + e \quad Fe^{2+}(aq) \quad E$ 0.77 V

$Cl_2(g) + 2e \quad 2Cl(aq) \quad E$ 1.40 V

Identify the incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$ **(2002, 3M)**

(a) MnO_4 can be used in aqueous HCl

(b) $Cr_2O_7^2$ can be used in aqueous HCl

(c) MnO_4 can be used in aqueous H_2SO_4

(d) $Cr_2O_7^2$ can be used in aqueous H_2SO_4

15. Saturated solution of KNO_3 is used to make 'salt-bridge' because **(2001, 1M)**

(a) velocity of K^+ is greater than that of NO_3^-

(b) velocity of NO_3 is greater than that of K^+

(c) velocities of both K^+ and NO_3 are nearly the same

(d) KNO_3 is highly soluble in water

16. The gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25 C. If the order of reduction potential is $Z \quad Y \quad X$, then **(1999, 2M)**

(a) Y will oxidise X and not Z

(b) Y will oxidise Z and not X

(c) Y will oxidise both X and Z

(d) Y will reduce both X and Z

17. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, 3.03 and 1.18 V respectively. The order of reducing power of the corresponding metals is

(a) $Y > Z > X$ (b) $X > Y > Z$ **(1998, 2M)**

(c) $Z > Y > X$ (d) $Z > X > Y$

18. The standard reduction potentials $E°$, for the half reactions are as

$Zn \quad Zn^{2+} + 2e$, E + 0.76 V

$Fe = Fe^{2+} + 2e$, E 0.41 V

The emf for the cell reaction,

$Fe^{2+} + Zn \quad Zn^{2+} \quad Fe$ is **(1989, 1M)**

(a) – 0.35 V (b) + 0.35 V (c) + 1.17 V (d) 1.17 V

19. When a lead storage battery is discharged **(1986, 1M)**

(a) SO_2 is evolved

(b) lead is formed

(c) lead sulphate is consumed

(d) sulphuric acid is consumed

20. The reaction,

$$\frac{1}{2}H_2(g) \quad AgCl(s) \rightleftharpoons H^+(aq) + Cl(aq) + Ag(s)$$

occurs in the galvanic cell **(1985, 1M)**

(a) Ag|AgCl (s)|KCl(soln) | $AgNO_3$|Ag

(b) Pt|$H_2(g)$|HCl(soln) | $AgNO_3$ (soln)|Ag

(c) Pt|$H_2(g)$HCl(soln) | AgCl(s)|Ag

(d) Pt | $H_2(g)$ | KCl(soln) | AgCl(s)|Ag

21. The electric charge for electrode deposition of one gram equivalent of a substance is **(1984, 1M)**

(a) one ampere per second

(b) 96,500 coulombs per second

(c) one ampere for one hour

(d) charge on one mole of electrons

22. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potential) are

Ag^+/Ag + 0.80, $Hg_2^{2+}/2Hg$ 0.79

Cu^{2+}/Cu + 0.34, Mg^{2+}/Mg 2.37

With increasing voltage, the sequence of deposition of metals on the cathode will be **(1984, 1M)**

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu (d) Cu, Hg, Ag

23. Faraday's laws of electrolysis are related to the **(1983, 1M)**

(a) atomic number of the cation

(b) atomic number of the anion

(c) equivalent weight of the electrolyte

(d) speed of the cation

24. The standard reduction potentials at 298K for the following half cells are given :

$Zn^2 (aq) \quad 2e \rightleftharpoons Zn(s); \; E° = \; 0.762$ V

$Cr^3 (aq) \quad 3e \rightleftharpoons Cr(s); \; E° = \; 0.740$ V

$2H\ (aq)\quad 2e \rightleftharpoons H_2(g)$; $E° = 0.000\ V$

$Fe^3\ (aq)\quad e \rightleftharpoons Fe^2\ (aq)$; $E° =\ 0.770\ V$

Which is the strongest reducing agent? **(1981, 1M)**

(a) $Zn(s)$ (b) $Cr(s)$ (c) $H_2(g)$ (d) $Fe^2\ (aq)$

Objective Questions II

(One or more than one correct option)

25. In a galvanic cell, the salt-bridge **(2014 Adv.)**

(a) does not participate chemically in the cell reaction

(b) stops the diffusion of ions from one electrode to another

(c) is necessary for the occurrence of the cell reaction

(d) ensures mixing of the two electrolytic solutions

26. For the reduction of NO_3^- ion in an aqueous solution E is 0.96 V. Values of E for some metal ions are given below

$V^2\ (aq)\quad 2e^-\quad V;\quad E\quad 1.19\ V$

$Fe^{3+}(aq)\quad 3e^-\quad Fe;\quad E\quad 0.04 V$

$Au^3\ (aq)\quad 3e^-\quad Au;\quad E\quad 1.40\ V$

$Hg^2\ (aq)\quad 2e^-\quad Hg;\quad E\quad 0.86 V$

The pair(s) of metals that is/are oxidised by NO_3^- in aqueous solution is (are) **(2009)**

(a) V and Hg (b) Hg and Fe (c) Fe and Au (d) Fe and V

Numerical Value Based Question

27. For the electrochemical cell,

$Mg(s)|Mg^2\ (aq,\ 1\ M)\ ||\ Cu^2\ (aq,\ 1\ M)\ |\ Cu(s)$

The standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^2 is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is _____.

(Given, $\frac{F}{R}\quad 11500\ K\ V^{\ 1}$, where F is the Faraday constant and R is the gas contant, In (10) 2.30) **(2018 Adv.)**

28. Consider an electrochemical cell : $A(s)\,|\,A^n\ (aq, 2M)||B^{2n}\ (aq, 1M)\,|\,B(s)$. The value of $H^{\ominus}$ for the cell reaction is twice of $G^{\ominus}$ at 300 K. If the emf of the cell is zero, the $S^{\ominus}$ (in J K ^{1} mol ^{1}) of the cell reaction per mole of B formed at 300 K is …… .

(Given : ln(2) 0.7, R (universal gas constant) 8.3 J K ^{1} mol ^{1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) **(2018 Adv.)**

Passage Based Questions

Passage

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately $6.023\quad 10^{23}$) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes

(atomic mass : Na 23, Hg 200, 1 F 96500 C).

(2007, 3 4M = 12M)

29. The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0

(c) 2.0 (d) 3.0

30. If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed from this solution is

(a) 200 (b) 225

(c) 400 (d) 446

31. The total charge (coulombs) required for complete electrolysis is

(a) 24125 (b) 48250

(c) 96500 (d) 193000

Subjective Questions

32. The following electrochemical cell has been set-up :

$Pt(1)\,|\,Fe^{3+}, Fe^{2+}\ (a\quad 1)\,|\,Ce^{4+}, Ce^{3+}(a\quad 1)\,|\,Pt(2)$

$E\ (Fe^{3+}, Fe^{2+})\quad 0.77\ V$

and $E\ (Ce^{4+}, Ce^{3+})\quad 1.61\ V$

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current, will the current increases or decreases with time? **(2000, 2M)**

33. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 min. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **(2000, 3M)**

34. A cell, $Ag\,|\,Ag^+||Cu^{2+}\,|\,Cu$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. **(1999, 6M)**

35. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 h at a current of 8.46 A? What is the area of the tray, if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.

(1997, 3M)

36. The Edison storage cell is represented as:

$Fe\ (s)\,/\,FeO(s)\,/\,KOH(aq)\,/Ni_2O_3(s)\,/\,Ni(s)$

The half-cell reactions are :

$Ni_2O_3(s) + H_2O\ (l) + 2e \rightleftharpoons 2NiO(s) + 2OH\ ,$

$E\quad + 0.40\ V$

$FeO\ (s)\quad H_2O(l)\quad 2e \rightleftharpoons Fe(s) + 2OH\ ,$

$E\quad 0.87\ V$

(i) What is the cell reaction?

(ii) What is the cell emf ? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3? **(1994, 4M)**

37. The standard reduction-potential for the half-cell

$NO_3\,(aq) + 2H^+ + e \qquad NO_2\;(g) + H_2O$ is 0.78 V

(i) Calculate the reduction-potential in $8\,M\;H^+$.

(ii) What will be the reduction-potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration. **(1993, 2M)**

38. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.

$$CrO_3\,(aq) + 6H^+\,(aq) + 6e \qquad Cr\;(s) + 3H_2O$$

Calculate (i) How many grams of chromium will be plated out by 24,000 C and (ii) How long will it take to plate out 1.5 g of chromium by using 12.5 A current? **(1993, 2M)**

39. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to the reaction.

$$2Cl^-\;(aq) + 2H_2O \rightleftharpoons 2OH\;\;(aq) + H_2(g) + Cl_2(g)$$

A direct current of 25 A with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation) **(1992, 3M)**

40. For the galvanic cell,

Ag | AgCl(s), KCl (0.2 M) || KBr (0.001 M), AgBr (s) | Ag

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25 C.

$[K_{sp}$ (AgCl) 2.8 10 ^{10}, K_{sp} (AgBr) 3.3 10 $^{13}]$ **(1992, 4M)**

41. A current of 1.70 A is passed through 300.0 mL of 0.160M solution of a $ZnSO_4$ for 230 s with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition Zn. Assume the volume of the solution to remain constant during the electrolysis. **(1991, 4M)**

42. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 V, how much energy will be consumed? **(1990, 3M)**

43. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 A. Calculate the volume of gases evolved at NTP during the entire electrolysis. **(1989, 5M)**

44. In a fuel cell hydrogen and oxygen react to produces electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 L of H_2 at STP react in 15 min, what is the average current produced? If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited?

Anode reaction : $H_2 + 2OH \qquad 2H_2O + 2e$

Cathode reaction : $O_2 + 2H_2O + 2e \qquad 4OH$ **(1988, 4M)**

45. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10 ^{6} M hydrogen ions. The emf of the cell is 0.118 V at 25 C. Calculate the concentration of hydrogen ions at the positive electrode. **(1988, 2M)**

46. A 100 watt, 110 V incandecent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 h? **(1987, 5M)**

47. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 g/mL is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge.

Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are

$Pb + SO_4^{2} \qquad PbSO_4 + 2e$ (charging)

$PbO_2 + 4H^+ + SO_4^{2} + 2e$

$PbSO_4 + 2H_2O$ (discharging) **(1986, 5M)**

48. How long a current of 3 A has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer?

Density of silver is 10.5 g/cm^3. **(1985, 3M)**

49. In an electrolysis experiment current was passed for 5 h through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in ampere.

(Atomic weight of Au 197 and atomic weight of Cu 63.5) **(1983, 3M)**

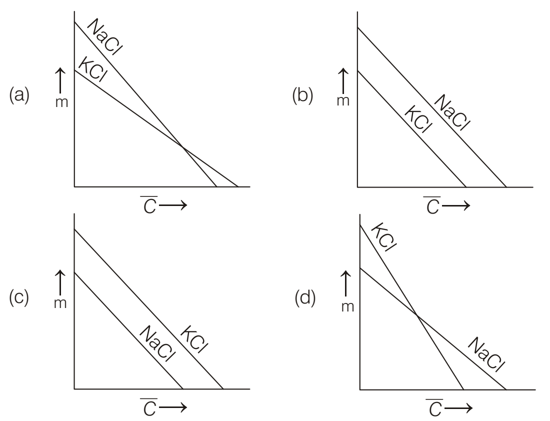
50. A current of 3.7 A is passed for 6 h between nickel electrodes in 0.5 L of a 2.0 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis? **(1978, 2M)**

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

Objective Questions I (Only one correct option)

1. The decreasing order of electrical conductivity of the following aqueous solution is
0.1 M formic acid (A),
0.1 M acetic acid (B),
0.1 M benzoic acid (C). **(2019 Main, 12 April II)**
(a) $A > C > B$ (b) $C > B > A$
(c) $A > B > C$ (d) $C > A > B$

2. Which one of the following graphs between molar conductivity $_{m}$) *versus* $\sqrt{C}$ is correct? **(2019 Main, 10 April II)**



3. Consider the statements S_1 and S_2 :
$\mathbf{S_1}$: Conductivity always increases with decrease in the concentration of electrolyte.
$\mathbf{S_2}$: Molar conductivity always increases with decrease in the concentration of electrolyte.
The correct option among the following is **(2019 Main, 10 April I)**
(a) S_1 is correct and S_2 is wrong
(b) S_1 is wrong and S_2 is correct
(c) Both S_1 and S_2 are wrong
(d) Both S_1 and S_2 are correct

4. The standard Gibbs energy for the given cell reaction in kJ mol ^{1} at 298 K is
$Zn(s) \quad Cu^{2} \ (aq) \qquad Zn^{2} \ (aq) \quad Cu(s),$
$E \quad$ 2V at 298 K
(Faraday's constant, F = 96000 C mol ^{1}) **(2019 Main, 9 April I)**
(a) 384 (b) 192 (c) 384 (d) 192

5. $_{m}$ for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2 mol ^{1}, respectively. If the conductivity of 0.001 M HA is 5 10 ^{5} S cm ^{1}, degree of dissociation of HA is **(2019 Main, 12 Jan II)**
(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.125

6. Given the equilibrium constant (K_C) of the reaction :
$$Cu(s) \quad 2Ag^{+}(aq) \qquad Cu^{2} \ (aq) \quad 2Ag(s)$$
is 10 10^{15}, calculate the E_{cell} of this reaction at 298 K.
$$2.303\frac{RT}{F} \text{ at 298 K} \quad 0.059 \text{ V}$$
(2019 Main, 11 Jan II)
(a) 0.4736 V (b) 0.04736 mV
(c) 0.4736 mV (d) 0.04736 V

7. For the cell, $Zn(s)\,|Zn^{2+}(aq)\,||\,M^{x+}(aq)\,|M(s)$, different half cells and their standard electrode potentials are given below.

M^x (aq)/M(s)	Au^3 (aq)/ Au(s)	Ag (aq)/ Ag(s)	Fe^3 (aq)/ Fe^2 (aq)	Fe^2 (aq)/ Fe(s)
$E_{M^x\ /M}$/V	1.40	0.80	0.77	0.44

If $E_{Zn^2\ /Zn}$ 0.76 V, which cathode will give a maximum value of E_{cell} per electron transferred? **(2019 Main, 11 Jan I)**
(a) $\frac{Ag^+}{Ag}$ (b) $\frac{Fe^{2+}}{Fe}$ (c) $\frac{Au^3}{Au}$ (d) $\frac{Fe^{3+}}{Fe^{2+}}$

8. In the cell,
$Pt(s)\,|H_2\,(g, 1\text{ bar})|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$ the cell potential is 0.92 V when a 10 ^{6} molal HCl solution is used. The standard electrode potential of (AgCl/ Ag,Cl) electrode is Given, $\frac{2.303RT}{F}$ 0.06 V at 298 K
(a) 0.40 V (b) 0.20 V (c) 0.94 V (d) 0.76 V

9. If the standard electrode potential for a cell is 2V at 300 K, the equilibrium constant (K) for the reaction,
$$Zn(s) \quad Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) \quad Cu(s)$$
at 300 K is approximately
(R 8 JK ^{1}mol ^{1}, F = 96000 C mol ^{1}) **(2019 Main, 9 Jan II)**
(a) $e^{\ 160}$ (b) e^{160} (c) $e^{\ 80}$ (d) e^{320}

10. For the following cell,
$Zn(s)|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$
when the concentration of Zn^2 is 10 times the concentration of Cu^2 , the expression for G (in J mol ^{1}) is
[F is Faraday constant; R is gas constant; T is temperature; E (cell) 1.1 V] **(2017 Adv.)**
(a) 2.303 RT 1.1 F (b) 1.1 F
(c) 2.303 RT 2.2 F (d) 2.2 F

11. Galvanisation is applying a coating of **(2016 Main)**
(a) Cr (b) Cu
(c) Zn (d) Pb

12. Given below are the half-cell reactions **(2014 Main)**

$Mn^{2} \quad 2e \quad\quad Mn\,;\ E \quad 1.18\ eV$

$2\,(Mn \quad e \quad\quad Mn^{2}\ );\ E \quad 1.51\,eV$

The E for $3Mn^{2} \quad Mn + 2Mn^{3+}$ will be

(a) 2.69 V; the reaction will not occur
(b) 2.69 V; the reaction will occur
(c) 0.33 V; the reaction will not occur
(d) 0.33 V; the reaction will occur

13. The equivalent conductance of NaCl at concentration C and at infinite dilution are $_{C}$ and , respectively. The correct relationship between $_{C}$ and is given as (where, the constant B is positive) **(2014 Main)**

(a) $_{C} \quad (B)\,C$ (b) $_{C} \quad (B)\,C$
(c) $_{C} \quad (B)\sqrt{C}$ (d) $_{C} \quad (B)\sqrt{C}$

14. Resistance of 0.2 M solution of an electrolyte is 50 The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 S m ^{1} and resistance of same solution of the same electrolyte is 280 . The molar conductivity of 0.5 M solution of the electrolyte in Sm^2mol^{1} is **(2014 Main)**

(a) 5 10^{4} (b) 5 10^{3}
(c) 5 10^{3} (d) 5 10^{2}

15. The standard reduction potential data at 25°C is given below.

$E\ (Fe^{3}\ /\ Fe^{2}\ ) \quad 0.77\ V;\ E\ (Fe^{2}\ /\ Fe) \quad 0.44\ V;$

$E\ (Cu^{2}\ /\ Cu) \quad 0.34\ V;\ E\ (Cu\ /\ Cu) \quad 0.52\ V;$

$E\ (O_2(g) \quad 4H \quad 4e\ ) \quad 2H_2O) \quad 1.23\ V;$

$E\ (O_2(g) \quad 2H_2O \quad 4e\ ) \quad 4OH) \quad 0.40\ V$

$E\ (Cr^{3}\ /\ Cr) \quad 0.74\ V;\ E\ (Cr^{2}\ /\ Cr) \quad 0.91\ V$

Match E of the rebox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists. **(2013 Adv.)**

	Column I		Column II
P.	$E\ (Fe^{3}\ /\ Fe)$	1.	0.18 V
Q.	$E\ (4H_2O \rightleftharpoons 4H \quad 4OH\ )$	2.	– 0.4 V
R.	$E\ (Cu^{2} \quad Cu \quad 2\,Cu\ )$	3.	– 0.04 V
S.	$E\ (Cr^{3}\ ,\ Cr^{2}\ )$	4.	– 0.83 V

Codes

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

16. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in Column I. The variation in conductivity of these reactions is given in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns. **(2013 Adv.)**

	Column I		Column II
P.	$(C_2H_5)_3N$ CH_3COOH X Y	1.	Conductivity decreases and then increases
Q.	KI(0.1 M) $AgNO_3$(0.01 M) X Y	2.	Conductivity decreases and then does not change much
R.	CH_3COOH KOH X Y	3.	Conductivity increases and then does not change much
S.	NaOH HI X Y	4.	Conductivity does not change much and then increases

Codes

	P	Q	R	S		P	Q	R	S
(a)	3	4	2	1	(b)	4	3	2	1
(c)	2	3	4	1	(d)	1	4	3	2

17. Consider the following cell reaction,

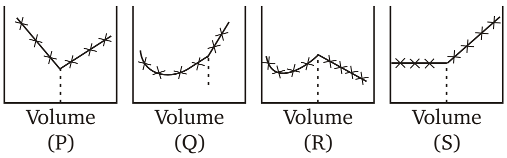
$$2Fe(s) + O_2(g) + 4H^+(aq) \quad 2Fe^{2+}(aq) + 2H_2O(l),$$

$$E \quad 1.67\ V$$

At $[Fe^{2+}]$ 10^{3} M, P(O_2) 0.1 atm and pH 3, the cell potential at 25 C is **(2011)**

(a) 1.47 V (b) 1.77 V
(c) 1.87 V (d) 1.57 V

18. $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ( ) *versus* the volume of $AgNO_3$ is



(2011)

(a) (P) (b) (Q) (c) (R) (d) (S)

19. The half cell reactions for rusting of iron are :

$$2H^+ \quad 2e \quad \frac{1}{2}O_2 \quad H_2O(l); \quad E \quad 1.23\,V$$

$$Fe^{2} \quad 2e \quad Fe(s); \quad E \quad 0.44\ V$$

G (in kJ) for the reaction is **(2005, 1M)**

(a) – 76 (b) – 322
(c) – 122 (d) – 176

20. $Zn\,|\,Zn^{2+}\ (a \quad 0.1M)\,||\,Fe^{2+}\ (a \quad 0.01M)\,|\,Fe.$

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is **(2004, 1M)**

(a) $10^{0.32/0.059}$ (b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

21. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is **(2001, 1M)**

(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

22. For the electrochemical cell, $(M|M \quad)||(X \quad |X)$, $E \;(M \quad /M) \quad 0.44$ V and $E \;(X/X \quad) \quad 0.33$ V.

From this data one can deduce that **(2000, 1M)**

(a) $M + X \qquad M^{+} + X$ is the spontaneous reaction

(b) $M^{+} + X^{-} \qquad M + X$ is the spontaneous reaction

(c) $E_{cell} \quad 0.77$ V

(d) $E_{cell} \qquad 0.77$ V

23. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half-cell is **(1997, 1M)**

(a) 0.184 V (b) 0.827 V (c) 0. 521 V (d) 0.490 V

Numerical Value Based Question

24. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below

$$2Cu(g) + H_2O(g) \qquad Cu_2O(s) + H_2(g)$$

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is …… .

(Given : total pressure 1 bar, R (universal gas constant) 8 J K ^{1} mol ^{1}, ln(10) 2.30 Cu(s) and $Cu_2O(s)$ are mutually immiscible.)

At 1250 K : $2Cu(s) + 1/2\,O_2(g) \qquad Cu_2O(s)$;

$$G^{\ominus} \qquad 78{,}000 \text{ J mol}^{\;1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \qquad H_2O(g);$$

$G^{\ominus} \qquad 1{,}78{,}000$ J mol ^{1}; G is the Gibbs energy **(2018 Adv.)**

Passage Based Questions

Passage I

The electrochemical cell shown below is a concentration cell. $M|M^{2}$ (saturated solution of a sparingly soluble salt, MX_2)$||M^{2}$ (0.001 mol dm ^{3})$|M$. The emf of the cell depends on the difference in concetration of M^{2} ions at the two electrodes. The emf of the cell at 298K is 0.059 V. **(2012)**

25. The solubility product (K_{sp} : mol^{3}dm ^{9}) of MX_2 at 298 based on the information available the given concentration cell is (take 2.303 R 298/F 0.059 V)

(a) 1 10 ^{15} (b) 4 10 ^{15}

(c) 1 10 ^{12} (d) 4 10 ^{12}

26. The value of G (kJ mol ^{1}) for the given cell is (take 1 F 96500 C mol ^{1})

(a) 5.7 (b) 5.7 (c) 11.4 (d) –11.4

Passage II

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

$$M(s)\,|\,M \quad (aq;\, 0.05 \text{ molar})\,||\,M \quad (aq;\, 1 \text{ molar})\,|\,M(s)$$

For the above electrolytic cell the magnitude of the cell potential $|E_{cell}|$ 70 mV. **(2010)**

27. For the above cell

(a) E_{cell} 0; G 0 (b) E_{cell} 0; G 0

(c) E_{cell} 0; G 0 (d) E_{cell} 0; G 0

28. If the 0.05 molar solution of M is replaced by a 0.0025 molar M solution, then the magnitude of the cell potential would be

(a) 35 mV (b) 70 mV

(c) 140 mV (d) 700 mV

Passage III

Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential (E) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 17–19. **(2007, 4 3M = 12M)**

$I_2 + 2e$	2I	E	0.54
$Cl_2 \quad 2e$	2Cl	E	1.36
$Mn^{3} \quad e$	Mn^{2}	E	1.50
$Fe^{3} \quad e$	Fe^{2}	E	0.77
$O_2 + 4H^{+} + 4e$	$2H_2O$	E	1.23

29. Among the following, identify the correct statement.

(a) Chloride ion is oxidised by O_2

(b) Fe^{2} is oxidised by iodine

(c) Iodide ion is oxidised by chlorine

(d) Mn^{2} is oxidised by chlorine

30. While Fe^{3} is stable, Mn^{3} is not stable in acid solution because

(a) O_2 oxidises Mn^{2} to Mn^{3}

(b) O_2 oxidises both Mn^{2} to Mn^{3} and Fe^{2} to Fe^{3}

(c) Fe^{3} oxidises H_2O to O_2

(d) Mn^{3} oxidises H_2O to O_2

31. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in the presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$

(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

Passage IV

Tollen's reagent is used for the detection of aldehydes. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.

$$Ag \quad e \qquad Ag; \quad E_{red} \quad 0.80\text{ V}$$

$$C_6H_{12}O_6 \quad H_2O \qquad \underset{\text{Gluconic acid}}{C_6H_{12}O_7} \quad 2H \quad 2e\ ; \qquad E_{oxi} \quad 0.05\text{ V}$$

$$Ag(NH_3)_2 \quad e \qquad Ag\,(s) \quad 2NH_3; \qquad E_{red} = 0.337\text{ V}$$

[Use $2.303 \dfrac{RT}{F} \quad 0.0592$ and $\dfrac{F}{RT} \quad 38.92$ at 298 K]

(2006, 3 4M 12M)

32. $2Ag \quad C_6H_{12}O_6 \quad H_2O \qquad 2Ag\,(s) \quad C_6H_{12}O_7 \quad 2H$

Find ln K of this reaction.

(a) 66.13 (b) 58.38 (c) 28.30 (d) 46.29

33. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

(a) E_{oxi} will increase by a factor of 0.65 from E_{oxi}

(b) E_{oxi} will decrease by a factor of 0.65 from E_{oxi}

(c) E_{red} will increase by a factor of 0.65 from E_{red}

(d) E_{red} will decrease by a factor of 0.65 from E_{red}

34. Ammonia is always added in this reaction. Which of the following must be incorrect?

(a) NH_3 combines with Ag to form a complex

(b) $Ag(NH_3)_2$ is a stronger oxidising reagent than Ag

(c) In the absence of NH_3 silver salt of gluconic acid is formed

(d) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode

Subjective Questions

35. We have taken a saturated solution of AgBr, K_{sp} is $12 \quad 10 \ ^{14}$. If $10 \ ^{7}$ M of $AgNO_3$ are added to 1 L of this solution, find conductivity (specific conductance) of this solution in terms of $10 \ ^{7}$ Sm ^{1} units. **(2006, 6M)**

Given, $_{(Ag\ )} \quad 6 \quad 10 \ ^{3}$ Sm^2 mol ^{1},

$_{(Br\ )} \quad 8 \quad 10 \ ^{3}$ Sm^2 mol ^{1},

$_{(NO_3^-)} \quad 7 \quad 10 \ ^{3}$ Sm^2 mol ^{1}.

36. Calculate G_r of the following reaction:

(a) Ag (aq) Cl (aq) AgCl(s)

Given

G_f (AgCl)	109 kJ/mol
G_f (Cl)	129 kJ/mol
G_f (Ag^+)	77 kJ/mol

Represent the above reaction in form of a cell. Calculate $E°$ of the cell. Find $\log_{10} K_{sp}$ of AgCl. **(2005, 6M)**

(b) $6.539 \quad 10 \ ^{2}$ g of metallic Zn (u 65.39) was added to 100 mL of saturated solution of AgCl. Calculate $\log_{10} \dfrac{[Zn^{2}\ ]}{[Ag\ ]^2}$. Given that

$$Ag \quad e \qquad Ag; \qquad E \quad 0.80\text{V}$$

$$Zn^{2} \quad 2e \qquad Zn; \qquad E \quad 76\text{V}$$

Also find how many moles of Ag will be formed?

37. Find the equilibrium constant for the reaction

$$Cu^{2+} \quad In^{2} \rightleftharpoons Cu \quad In^{3+}$$

Given that $E_{Cu^{2+}/Cu^+} \quad 0.15\text{V},$

$E_{In^{2+}/In^+} \quad 0.4\text{V},$

$E_{In^{3+}/In^+} \quad 0.42\text{ V}$ **(2004, 4M)**

38. (a) Will pH value of water be same at temperature 25°C and 4°C? Justify in not more than 2 or 3 sentences.

(b) Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ in the other cell. Given : $2.303\,RT/F \quad 0.06\text{V}$. **(2003, 2M)**

39. The standard potential of the following cell is 0.23 V at 15 C and 0.21 V at 35 C.

$$Pt\,|\,H_2(g)\,|\,HCl(aq)\ |\,AgCl(s)\,|\,Ag\,(s)$$

(i) Write the cell reaction.

(ii) Calculate H and S for the cell reaction by assuming that these quantities remain unchanged in the range 15 C to 35 C.

(iii) Calculate the solubility of AgCl in water at 25 C.

Given, the standard reduction potential of the (Ag^+ (aq)/Ag (s) is 0.80 V at 25 C. **(2001, 10M)**

40. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the emf of the cell Ag | Ag^+ (Saturated Ag_2CrO_4 solution.) ||Ag (0.1 M) | Ag is 0.164 V at 298 K. **(1998, 6M)**

41. Calculate the equilibrium constant for the reaction, $2Fe^{3+} \quad 3I \rightleftharpoons 2Fe^{2+} + I_3$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for Fe^{3+}/Fe^{2} and $I_3\,/\,I$ couples. **(1998, 3M)**

42. Calculate the equilibrium constant for the reaction

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

Given, E $(Ce^{4+}/Ce^{3}\ )$ 1.44 V, E $(Fe^{3+}/Fe^{2}\ )$=0.68 V **(1997, 2M)**

43. The standard reduction potential for Cu^{2+}/Cu is +0.34 V. Calculate the reduction potential at pH 14 for the above couple. K_{sp} of Cu $(OH)_2$ is $1.0 \quad 10 \ ^{19}$. **(1996, 3M)**

44. An excess of liquid mercury is added to an acidified solution of $1.0 \quad 10 \ ^{3}$M Fe^{3+}. It is found that 5 % of Fe^{3+} remains at equilibrium at 25 C. Calculate E (Hg^{2+}/Hg) assuming that the only reaction that occurs is

$$2Hg + 2Fe^{3+} \qquad Hg_2^{2+} + 2Fe^{2+}$$

Given, E (Fe^{3+}/Fe^{2+}) 0.77 V **(1995, 4M)**

45. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, K_{sp} 8.7 10 ^{17}, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the I / AgI/Ag electrode. **(1994, 3M)**

46. Zinc granules are added in excess to a 500 mL of 1.0 M nickel nitrate solution at 25 C until the equilibrium is reached. If the standard reduction potential of Zn^{2+} / Zn and Ni^{2+}/ Ni are – 0.75 V and – 0.24 V respectively. Find out the concentration of Ni^{2+} in solution at equilibrium. **(1991, 2M)**

47. The standard reduction potential of Cu^{2+}/ Cu and Ag^+/ Ag electrodes are 0.337 and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell, at 25 C, be zero if the concentration of Cu^{2+} is 0.01 M? **(1990, 3M)**

48. The standard reduction potential at 25 C of the reaction, $2H_2O + 2e \rightleftharpoons H_2 + 2OH$, is 0.8277 V. Calculate the equilibrium constant for the reaction,

$$2H_2O \rightleftharpoons H_3O^+ + OH \quad \text{at } 25 \text{ C.}$$ **(1989, 3M)**

49. The emf of a cell corresponding to the reaction.

$$Zn(s) + 2H^+(aq) \qquad Zn^{2+}(0.1M) + H_2, (g, 1\,atm)$$

is 0.28 V at 25 C.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$$E\ (Zn^{2+}/Zn) \quad 0.76\ V\ E_{H^+/H_2} \quad 0$$ **(1986, 4M)**

50. Give reasons in one or two sentences.

"Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor." **(1985, 1M)**

51. Consider the cell,

$$Zn\ |\ Zn^2\ (aq)\ (1.0\ M)\ ||\ Cu^2\ (aq)\ (1.0\ M)\ |\ Cu$$

The standard reduction potentials are 0.350 V for

$$Cu^2\ (aq) \quad 2e \qquad Cu$$

and 0.763 V for $Zn^2\ (aq) \quad 2e \qquad Zn$

(i) Write down the cell reaction.
(ii) Calculate the emf of the cell.
(iii) Is the cell reaction spontaneous or not? **(1982, 2M)**

Integer Type Questions

52. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinised Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm ^{2}. The conductance of this solution was found to be 5 10 ^{7} S. The pH of the solution is 4. The value of limiting molar conductivity ($_m$) of this weak monobasic acid in aqueous solution is Z 10^2 S cm ^{1} mol ^{1}. The value of Z is **(2017 Adv.)**

53. All the energy released from the reaction X Y, $_rG$ = 193 kJ mol ^{1} is used for oxidising M as M M^3 $2e$, E 0.25 V.

Under standard conditions, the number of moles of M oxidised when one mole of X is converted to Y is [F 96500 C mol] **(2015 Adv.)**

Answers

Topic 1

1. (b)	**2.** (d)	**3.** (a)	**4.** (c)
5. (b)	**6.** (b)	**7.** (c)	**8.** (a)
9. (d)	**10.** (b)	**11.** (d)	**12.** (b)
13. (c)	**14.** (a)	**15.** (c)	**16.** (a)
17. (a)	**18.** (b)	**19.** (d)	**20.** (c)
21. (d)	**22.** (c)	**23.** (c)	**24.** (a)
25. (a, b)	**26.** (a,b,d)	**27.** (10)	
28. (−11.62 JK mol ^{1})		**29.** (b)	**30.** (d)
31. (d)	**33.** (8 10 ^{5} M)	**34.** (0001 V)	**35.** (300 cm^2)
36. (245.11 kJ)	**39.** (1.4085 M)	**40.** (0.037 V)	**41.** (0.154 M)
42. (347.40 kJ)	**44.** (190.50 g)	**45.** (10 ^{4} M)	**46.** (19.1 g)
47. (265 Ah)	**48.** (125 s)	**49.** (0.80 A)	**50.** (1.172 M)

Topic 2

1. (a)	**2.** (c)	**3.** (b)	**4.** (c)
5. (d)	**6.** (a)	**7.** (a)	**8.** (b)
9. (b)	**10.** (c)	**11.** (c)	**12.** (a)
13. (c)	**14.** (a)	**15.** (d)	**16.** (a)
17. (d)	**18.** (d)	**19.** (b)	**20.** (b)
21. (b)	**22.** (b)	**23.** (c)	**24.** (−14.16)
25. (b)	**26.** (d)	**27.** (b)	**28.** (c)
29. (c)	**30.** (d)	**31.** (a)	**32.** (b)
33. (c)	**34.** (d)	**35.** (55)	**37.** (10^{10})
38. (0.05 M)	**40.** (2.45 10 ^{12})		**41.** (5.89 10^7)
42. (6.88 10^{12})	**43.** (0.222 V)	**44.** (0.7926 V)	**46.** (1.7 10^{17})
47. (1.57 10 ^{9})	**48.** (1.04 10 ^{14})		**49.** (8.6)
52. (6 10^2 S cm ^{1} mol ^{1})		**53.** (4 mol)	

Hints & Solutions

Topic 1 Electrochemical Cells

1. **Key Idea** Negative E means that redox couple is weaker oxidising agent than H /H_2 couple. Positive $E°$ means that redox couple is a stronger oxidising agent than H / H_2 couple

Given, $Co^3 \quad e \quad Co^2$; E 1.81 V

$Pb^4 \quad 2e \quad Pb^2$; E 1.67 V

$Ce^4 \quad e \quad Ce^3$; E 1.61 V

$Bi^3 \quad 3e \quad Bi$; E 0.20 V

Oxidising power of the species increases in the order of $Bi^{3+} \quad Ce^4 \quad Pb^4 \quad Co^3$.

Higher the emf value, stronger the oxidising power. The maximum value of emf is possessed by Co^3 . Hence, it has maximum oxidising power. Whereas Bi^3 possess the lowest emf value. Hence, it has minimum oxidising power.

2. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. It means that 0.1 equivalent of Ni^2 will be discharged.

Electrolysis of $Ni(NO_3)_2$ gives

$$Ni^{2+} + 2e \quad Ni \quad \text{(Atomic mass of Ni } 58.7)$$

Number of equivalents Number of moles number of electrons.

0.1 Number of moles 2

Number of moles of Ni $\frac{0.1}{2}$ 0.05

3. $Fe^{2+}(aq) + Ag^+(aq) \quad Fe^{3+}(aq) + Ag(s)$

$$E^\circ_{cell} \quad E^\circ_{Ag^+/Ag} \quad E^\circ_{Fe^{3+}/Fe^2} \quad xV \quad E^\circ_{Fe^{3+}/Fe^2} \qquad \ldots \text{(i)}$$

Now, for two half-cells

(i) $Fe^{2+} + 2e \quad Fe$; $E^\circ_{Fe^{2+}/Fe} \quad E^\circ_1 \quad y\text{V} \quad G^\circ_2 \quad 2FE^\circ_1$

(ii) $Fe^{3+} + 3e \quad Fe$; $E^\circ_{Fe^{3+}/Fe} \quad E^\circ_2 \quad z\text{V} \quad G^\circ_2 \quad 3FE^\circ_2$

So, $Fe^{3+} + e^- \quad Fe^{2+}$; $E^\circ_{Fe^{3+}/Fe^2} \quad E^\circ_3$?

; $G^\circ_3 \quad 1 \quad FE^\circ_3$

Again, $G^\circ_3 \quad G^\circ_2 \quad G^\circ_1$

$FE^\circ_3 \quad 3FE^\circ_2 \quad (\quad 2FE^\circ_1)$

$E^\circ_3 \quad 2E^\circ_1 \quad 3E^\circ_2 \quad E^\circ_3 \quad 3E^\circ_2 \quad 2E^\circ_1$

$E^\circ_{Fe^{3+}/Fe^2} \quad (3z \quad 2y)\text{V}$

So, from equation (i)

$E^\circ_{cell} \quad xV \quad (3z \quad 2y)\text{ V} \quad (x \quad 3z \quad 2y)\text{ V}$

4. Higher the standard reduction potential ($E°_{M^n \ /M}$), better is oxidising agent. Among the given, $E_{S_2O_8^2 \ /SO_4^2}$ is highest, hence $S_2O_8^2$ is the strongest oxidising agent.

The decreasing order of oxidising agent among the given option is as follows:

$$S_2O_8^2 \quad Au^3 \quad O_2 \quad Br_2$$

5. Reducing power of an element $\frac{1}{\text{Standard reduction potential}}$

Here, $E_{M^2 \ /M}$ values of the given metals are as,

Metals	Ni	Zn	Mg	Ca
***E* (V)**	0.25	0.76	2.36	2.87

Reducing power

Thus, the correct order of increasing reducing power of the given metal is,

Ni < Zn < Mg < Ca.

6. **Key Idea** This question is based upon Faraday's first law which states that "Mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

During charging:

$$Pb \quad SO_4^2 \quad PbSO_4 \quad 2e$$

1 F 1 g-equiv. of $PbSO_4$

$\frac{1}{2}$mol of $PbSO_4$ $\frac{303}{2}$g $PbSO_4$

0.05 F $\frac{303}{2}$ 0.05 g of $PbSO_4$

7.575 g of $PbSO_4$

7. Given that, i 100 amp. also, 27.66 g of diborane (B_2H_6)

Molecular mass of B_2H_6 10.8 2 6 27.6

Number of moles of B_2H_6 in 27.66 g $\frac{\text{Given mass}}{\text{Molar mass}} \quad \frac{27.66}{27.6}$ 1

Now consider the equation

$$B_2H_6 \quad 3O_2 \quad B_2O_3 + 3H_2O$$

From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water i.e.

$$H_2O \rightleftharpoons 2H \quad O$$

$$2H \xrightarrow[\text{Cathode}]{2e} 2H \quad H_2$$

$$O \xrightarrow[2e]{\text{Anode}} O \xrightarrow[\text{atoms}]{\text{2 such}} O_2$$

From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 12(3 4) moles of electrons will be needed.

So, the total amount of charge required to produce 3 moles of oxygen will be 12 F or 12 96500

We know $Q \quad it$

So, 12 96500 100 t in seconds

or $\frac{12 \quad 96500}{100 \quad 3600}$ t in hours 3.2 hours

8. The substances which have lower reduction potentials are stronger reducing agents. Therefore, Cr ($E_{Cr^{3+}/Cr}$ 0.74 V) is the strongest reducing agent among all the other given options.

9. Oxidation at anode

$H_2(g) \quad 2H^+(aq) + 2e\ ; \ E_{SHE} \quad 0.00\ V$

Reduction at cathode

$M^{4+}(aq) \quad 2e \quad M^{2+}(aq); \ E_{M^{4+}/M^{2+}} \quad 0.151\ V$

Net: $M^4 \ (aq) \quad H_2(g) \quad M^2 \ (aq) \quad 2H^+(aq)$;

$$K \quad \frac{[M^{2+}][H^+]^2}{[M^{4+}]\,p_{H_2}} (E_{cell} \quad 0.151\ V) \quad \frac{[M^{2+}]}{[M^{4+}]}$$

$$E_{cell} \quad E_{cell} \quad \frac{0.059}{2}\log K$$

$$0.092 \quad 0.151 \quad \frac{0.059}{2}\log\frac{[M^2\ ]}{[M^4\ ]}$$

$$0.059 \quad \frac{0.059}{2}\log 10^x$$

$$\log 10^x \quad 2$$

$$x \quad 2$$

10. Given, $Q \quad 2F$

Atomic mass of Cu 63.5u

Valency of the metal Z 2

We have, $CuSO_4 \quad Cu^2 \quad SO_4^2$

$$\underset{1mol}{Cu^2} \quad \underset{\substack{2mol \\ 2F}}{2\,e} \quad \underset{1mol = 63.5g}{Cu}$$

Alternatively.

$$W \quad ZQ \quad \frac{E}{F} \quad 2F \quad 2E \quad \frac{2 \quad 63.5}{2} \quad 63.5$$

11. Higher the standard reduction potential, better is oxidising agent. Among the given $E_{MnO_4/Mn^{2+}}$ is highest, hence MnO_4 is the strongest oxidising agent.

12. 0.01 mol of H_2 0.02 g equivalent

Coulombs required 0.02 96500 1930 C

$$Q \quad It \quad 1930\ C$$

$$t \quad \frac{1930}{10 \quad 10^{\ 3}} \quad 19.3 \quad 10^4\ s$$

13. In electrolytic cell electrolysis occur at the cost of electricity :

At cathode : $M^{n+} \quad ne \quad M$

(electron gone in solution)

At anode : $X^n \quad X \quad ne$

(electron supplied to anode)

Therefore, electron is moving from cathode to anode *via* internal circuit.

14. MnO_4 cannot be used for oxidation of Fe^{2+} in HCl medium because the following reaction is spontaneous :

$MnO_4 \quad Cl \quad Mn^{2+} \quad Cl_2; \quad E \quad 1.51 \quad 1.40 = 0.11\ V$

In all other cases, the redox process between oxidising agent and medium (HCl or H_2SO_4) are non-spontaneous, would not interfere oxidation of Fe^{2+}.

15. One of the requirement for electrolyte used in salt-bridge is, both cation and anion must have comparable size so that they migrate towards electrodes of opposite polarity at comparable speeds.

16. Higher the value of reduction potential, stronger the oxidising agent.

$\because \quad E \ : Z \quad Y \quad X$

Y will oxidise X but not Z.

17. Lower the value of E, stronger the reducing agent.

Reducing power:

Y (E 3.03 V) Z(E 1.18 V) X (E 0.52 V).

18.

$Fe^{2+} \quad 2e \quad Fe\ ; \quad E \quad 0.41V$

$Zn \quad Zn^{2+} + 2e\ ; E \quad 0.76V$

$Fe^{2+} \quad Zn \quad Zn^{2+} + Fe\ ; \quad E \quad 0.35V$

19. In a lead storage battery, sulphuric acid is consumed as :

$$Pb + PbO_2 + 2H_2SO_4 \quad 2PbSO_4 + 2H_2O$$

20. In a galvanic cell, oxidation occur in the left hand electrode chamber and reduction in right hand electrode chamber. In the following cell.

$$Pt \mid H_2(g) \mid HCl\ (l) \| AgCl\ (s) \mid Ag(s)$$

The cell reactions are :

$\frac{1}{2}H_2(g)$	H^+	e		At anode
$AgCl(s) + e$	Ag	Cl		At cathode
Net : $\frac{1}{2}H_2(g)$ $AgCl(s)$	H	Ag(s)	Cl	

21. One gram equivalent of an electrolyte required 1.0 mole of electronic charge for discharging.

22. In aqueous solution, only those ions who are less electropositive than hydrogen (E > 0) would be deposited.

Therefore, in the present case, only Ag, Hg and Cu would be deposited on passing electricity through aqueous solution of these ions, Mg will not be deposited.

Also, higher the value of E, easier will be their reduction, therefore, the sequence in which ions will be deposited on increasing voltage across the electrodes is :

Ag, Hg, Cu.

23. Faraday's law of electrolysis is related to equivalent weight of electrolytes as "the number of Faraday's passed is equal to the number of gram equivalent of electrolytes discharged."

24. Lower the value of E, stronger the reducing agent.

25. **PLAN** This problem is based on characteristics of salt-bridge.

Functions of salt-bridge are

(i) It connects the two half-cells and completes the cell circuit.

(ii) It keeps the solutions of two half-cells and complete the cell circuit but does not participate chemically in the cell reaction.

(iii) It maintains the diffusion of ions from one electrode to another electrode.

(iv) A cell reaction may also occur in the absence of salt-bridge. Sometimes, both the electrodes dip in the same electrolyte

solution and in such cases we do not require a salt-bridge."
So, option (c) is incorrect.

(v) This prevent mixing of two electrolytic solutions hence, option (d) is incorrect choice.

Hence, correct choices are (a), (b).

26. Metals with $E°$ value less than 0.96 V will be able to reduce NO_3 in aqueous solution.Therefore, metals V (E 1.19 V), Fe ($E°$ = – 0.04 V), Hg ($E°$ = 0.86 V) will all reduce NO_3 but Au ($E°$ = 1.40 V) cannot reduce NO_3 in aqueous solution.

27. (10) Equation of cell reaction according to the cell notation given, is

Reduction

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

Oxidation

Given, E_{cell} 2.70 V, T 300 K

with $[Mg^{2+}(aq)]$ 1 M and $[Cu^{2+}(aq)]$ 1 M

and n 2

Further, E_{cell} 2.67 V

with $[Cu^{2+}(aq)]$ 1M

and $[Mg^{2+}(aq)]$ xM

and $\frac{F}{R}$ 11500 KV ^{1}

where F Faraday constant, R gas constant

From the formula,

$$E_{cell} \quad E_{cell} \quad \frac{RT}{nF}\ln\frac{[Mg^{2}\ (aq)]}{[Cu^{2+}(aq)]}$$

After putting the given values

$$2.67 \quad 2.70 \quad \frac{RT}{2F}\ln\frac{x}{1}$$

or $$2.67 \quad 2.70 \quad \frac{R \quad 300}{2F} \quad \ln x$$

$$0.03 \quad \frac{R \quad 300}{2F} \quad \ln x$$

or $$\ln x \quad \frac{0.03 \quad 2}{300} \quad \frac{F}{R}$$

$$\frac{0.03 \quad 2 \quad 11500}{300} \quad 2.30$$

So, $\ln x$ 2.30

or x 10 (as given ln (10) 2.30)

28. Given,

$$A(s)|A^{n} \ (aq, 2\text{ M}) \ || \ B^{2n} \ (aq, 1\text{ M}) \ | \ B(s)$$

So, reactions at respective electrode will be

Anode $A(s) \quad A^{n} \quad ne \quad 2$

Cathode $B^{2n} \quad 2ne \quad B(s)$

Overall reaction

$$2A(s) \quad B^{2n}\ (aq) \quad 2A^{n}\ (aq) \quad B(s)$$

Further,

H 2 G and E_{cell} 0 is also given

Now by using the Nernst equation

$$E_{cell} \quad E_{cell} \quad \frac{RT}{nF}\ln\frac{[\text{Product}]}{[\text{Reactant}]}$$

After putting the values

$$0 \quad E_{cell} \quad \frac{RT}{2nF}\ln\frac{[A^{n}\ ]^{2}}{[B^{2n}\ ]}$$

or $$E \quad \frac{RT}{2nF}\ln\frac{[2]^{2}}{[1]} \quad \frac{RT}{2nF}\ln 4 \qquad \ldots\text{(i)}$$

Further from the formula,

$$G \quad nFE \qquad G \quad 2nFE$$

Now putting the value of E from eq. (i)

$$G \quad 2nF \quad \frac{RT}{2nF}\ln 4 \qquad \ldots\text{(ii)}$$

$$G \quad RT\ln 4$$

Finally, using the formula

$$G \quad H \quad T\ S$$

$$G \quad 2\ G \quad T\ S \qquad \text{(as } H \quad 2\ G\text{, given)}$$

$$G \quad T\ S$$

or $$S \quad \frac{G}{T} \quad \frac{RT\ln 4}{T}$$

(from eq. (ii), G $RT\ln 4$)

$$R\ln 4 \quad 8.3 \quad 2 \quad 0.7$$

(as all values given)

$$11.62\text{ J/K-mol}$$

29. Moles of NaCl electrolysed 4 $\frac{500}{1000}$ 2.0

moles of Cl_2 produced = 1.0

$$2Cl \qquad Cl_2 \quad 2e$$

30. **At cathode** $Na^{+} + e \xrightarrow{Hg} \underset{\text{Amalgam}}{Na(Hg)}$

Two moles of Na formed during electrolysis would produce two moles of Na(Hg) amalgam.

mass of amalgam 2 (23 200) 446 g

31. Two Faraday of electric charge would be required for electrolysis of 2.0 moles of NaCl.

total coulombs 2 96500 = 193000 C

32. Since, activities of all the ions are unity, E_{cell} E_{cell}. Also, left hand electrode is at lower reduction potential, it act as anode and

$$E \quad E\ (Ce^{4+}, Ce^{3+}) \quad E\ (Fe^{3+}, Fe^{2+}) = 0.84$$

i.e. electrons will flow from left to right hand electrode and current from right hand electrode [Pt (2)] to left hand electrode [Pt(1)].

Also, $$E \quad E \quad 0.0592 \log\frac{[Fe^{3+}][Ce^{3+}]}{[Fe^{2+}][Ce^{4+}]}$$

As electrolysis proceeds, E will decrease and therefore, current.

33. The number of Faraday's passed $\frac{2 \quad 10^{\ 3} \quad 16 \quad 60}{96500}$

$$1.99 \quad 10^{\ 5}$$

number of gram equivalent of Cu^{2+} deposited

$$1.99 \quad 10^{\ 5}$$

number of moles of Cu^{2+} deposited $\frac{1.99}{2}\ 10^{5}\ \ 10^{5}$

Absorbance is directly proportional to $[Cu^{2+}]$. Therefore, if 'C' be the initial molarity, 0.5 C will be the final molarity.

$0.5\,C\ \ 0.25\ \ 10^{5}\qquad C\ \ 8\ \ 10^{5}$ M

34. The number of Faraday's passed $\frac{9.65\ \ 60\ \ 60}{96500} = 0.36$ F

After electrolysis : $[Ag^+] = 1.36$ M

$$[Cu^{2+}] = 1 - \frac{0.36}{2}\ \ 0.82\text{ M}$$

E_1 (before electrolysis) E

E_2 (after electrolysis) $E\ \ \frac{0.0592}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$

$$E_1\ \ E_2\ \ \frac{0.0592}{2}\log\frac{(1.36)^2}{0.82} = 0.01\text{ V (decreased)}$$

35. Coulombs passed = 8.46 8 60 60 = 243648 C

Number of Faraday's passed $\frac{243648}{96500}$ 2.52

Weight of Cu plated 2.52 $\frac{63.5}{2}$ g 80.01 g

Volume of Cu plated $\frac{80.01}{10.5}$ 7.62 cm^3

Area plated out $\frac{7.62}{0.00254}$ 3000 cm^2

36. Given, $FeO\,(s)/Fe\,(s)$ $\qquad E° = -0.87$ V

and $\quad Ni_2O_3/NiO\,(s)$ $\qquad E° = +0.40$ V

Electrode at lower reduction potential act as anode and that at higher reduction potential act as cathode.

(i) Electrodes reaction :

$$Fe(s) + 2OH \qquad FeO\,(s) + H_2O\,(l) \qquad E° = +0.87\text{ V}$$

$$Ni_2O_3\,(s) + H_2O\,(l) + 2e \qquad 2NiO\,(s) + 2OH \qquad E° = 0.40\text{ V}$$

Net : $Fe\,(s) + Ni_2O_3\,(s) \qquad 2NiO\,(s) + FeO\,(s)$

$$E° = 1.27\text{ V}$$

(ii) Emf is independent of concentration of KOH.

(iii) Maximum amount of energy that can be obtained G

$G\quad nE\ F = -2\ \ 1.27\ \ 96500$ J = – 245.11 kJ

i.e. 245.11 kJ is the maximum amount of obtainable energy.

37. (i) $E\ \ 0.78 - 0.0592\log\frac{1}{8^2} = 0.887$ V

(ii) $E\ \ 0.78 - 0.0592\log\frac{1}{(10^{7})^2} = -0.0488$ V

38. Molar mass of Cr = 52 g

Equivalent mass of Cr $\frac{52}{6}$ g

(i) Mass of Cr deposited on passing 24000 Coulombs

$$\frac{24000}{96500}\ \ \frac{52}{6}\text{ g}\ \ 2.15\text{ g}$$

(ii) Number of gram equivalent of Cr $\frac{1.5}{52}\ \ 6\ \ \frac{9}{52}$

Coulombs required for 1.5 g Cr $\frac{9}{52}$ 96500 It

$$t\ \ \frac{9\ \ 96500}{52\ \ 12.5}\text{ s}\ \ 22.27\text{ min}$$

39. At anode $\qquad 2Cl \qquad Cl_2\ \ 2e$

At cathode $\quad 2H_2O + 2e \qquad H_2 + 2OH$

1 kg Cl_2 $\frac{1000}{35.5}$ equivalent of Cl_2 28.17 equivalent

Theoretical electricity requirement = 28.17 F

∵ Efficiency is only 62%

Electricity requirement (experimental)

$\frac{28.17\ \ 100}{62}$ F = 45.44 F

45.44 96500 = 25 t (in second)

t = 48.72 h

Also, gram equivalent of HO produced = 28.17

Molarity of HO $\frac{28.17}{20}$ 1.4085 M

40. $[Ag^+]$ in left hand electrode chamber $\frac{2.8\ \ 10^{10}}{0.2}$

$1.4\ \ 10^{9}$ M

$[Ag^+]$ in right hand electrode chamber $\frac{3.3\ \ 10^{13}}{0.001}$

$3.3\ \ 10^{10}$ M

$$\text{emf} = 0 - 0.0592\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$= -0.0592\log\frac{1.4\ \ 10^{9}}{3.3\ \ 10^{10}} = -0.037\text{ V}$$

Therefore, the cell as written is non-spontaneous and its reverse will be spontaneous with emf = 0.037 V.

41. Faraday's passed $\frac{1.7\ \ 230}{96500}$ 4.052 10^{3} F

Faradays used for reduction of Zn^{2+} 4.052 10^{3} 0.9

= 3.65 10^{3}

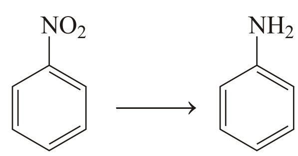
Meq. of Zn^{2+} reduced = 3.65

Initial meq. of Zn^{2+} 300 0.16 2 96

Meq. of Zn^{2+} remaining 96 3.65 92.35

Molarity of Zn^{2+} $\frac{92.35}{2}\ \ \frac{1}{300}$ 0.154 M

42.



Change in oxidation number at nitrogen 4 (2) 6

Equivalent weight of nitrobenzene $\frac{123}{6}$ g gram equivalent of nitrobenzene $\frac{12.3 \quad 6}{123} = 0.60$

Theoretical requirement 0.60 96500 C = 57900 C

Actual requirement of electricity 2 57900 115800 C

∵ $V \quad C \quad J$

Energy consumed 115800 3 J 347.40 kJ

43. If the salt is $CuSO_4$

During deposition of Cu at cathode, $O_2(g)$ will evolve at anode

gram-equivalent of Cu deposited $\frac{0.4 \quad 2}{63.5}$ 0.0126

Volume of O_2 liberated at NTP at anode

= 0.0126 5600 mL = 70.56 mL

In the next 7 min, H_2 at cathode and O_2 at anode would be produced.

Faraday's passed $\frac{1.2 \quad 7 \quad 60}{96500}$ 5.22 $10^{\ 3}$

Volume of H_2 (at NTP) 5.22 $10^{\ 3}$ 11200 mL

= 58.46 mL

Volume of O_2 (at NTP) 5.22 $10^{\ 3}$ 5600 mL = 29.23 mL

Therefore, $O_2(g)$ at NTP 70.56 + 29.23 99.79 mL

$H_2(g)$ at NTP 58.46 mL

44. Total number of gram equivalent of H_2 used $\frac{67.2}{11.2}$ 6

6 96500 15 60 I I 643.33 A

Mass of Cu deposited 6 $\frac{63.5}{2}$ g 190.50 g

45. ∵ Emf = 0.118 V > 0, it is galvanic cell and anode is negative electrode :

At anode : $H_2(g) \quad 2H^+(10^{\ 6}\,M) \quad 2e$

At cathode : $2H^+\ (x) + 2e \quad H_2$

Cell reaction : $H^+(x) \quad H^+\ (10^{\ 6}\,M)$

Emf = 0.118 V = 0 – 0.0592 log $\frac{10^{\ 6}}{x}$ $\quad x \quad 10^{\ 4}$ M

46. 100 W lamp will produce 100 Js $^{\ 1}$.

100 J 110 C $\quad C$ $\frac{10}{11}$ Coulombs

Therefore, total Coulomb passed in 10 h

$\frac{10}{11}$ 10 60 60 = 32727.27 C

Number of gram equivalent of Cd^{2+} deposited

$\frac{32727.27}{96500} = 0.34$

Weight of Cd deposited = 0.34 $\frac{112.4}{2}$ g 19.1 g

47. For 1.0 L H_2SO_4 :

Initial mass of H_2SO_4 = 1294 $\frac{39}{100}$ 504.66 g

Final mass of H_2SO_4 = 1139 $\frac{20}{100}$ 227.80 g

H_2SO_4 consumed/litre 504.66 – 227.80 = 276.86 g

Total H_2SO_4 used up 276.86 3.5 = 969.01 g

$\frac{969.01}{98}$ mol = 9.888 mol

∵ 1 mole of H_2SO_4 is associated with transfer of 1.0 mole of electrons, total of 9.888 moles of electron transfer has occurred.

Coulomb produced = 9.888 96500

Ampere-hour $\frac{9.888 \quad 96500}{3600}$ 265 Ah

48. Volume of Ag coating 80 cm^2 $\frac{0.005}{10}$ cm 0.04 cm^3

mass of Ag coating 0.04 10.5 g = 0.42 g

gram equivalent of Ag $\frac{0.42}{108}$ number of Faraday's

$\frac{0.42}{108}$ 96500 C = 3 t $\quad t$ 125 s

49. Moles of Au deposited $\frac{9.85}{197}$ 0.05

gram equivalent of Au deposited 0.05 3 = 0.15

Now, according to Faraday's law of electrolysis, if same quantity of electricity is passed through different cells connected in series, same number of gram equivalents of electrolytes are discharged at respective electrodes.

gram equivalent of Cu deposited = 0.15

amount of Cu deposited 0.15 $\frac{63.5}{2}$ 4.7625 g

Also, Coulombs passed 0.15 96500 I 5 60 60

I $\frac{0.15 \quad 96500}{5 \quad 3600}$ 0.80 A

50. During electrolysis, Ni^{2+} will be reduced at cathode and H_2O will be oxidised at anode.

Number of Faraday's passed $\frac{3.7 \quad 6 \quad 60 \quad 60}{96500} = 0.828$

0.828 g equivalent of Ni^{2+} will be deposited at cathode.

Initial moles of Ni^{2+} ion 2 0.5 = 1.0

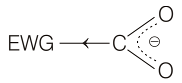
Moles of Ni^{2+} ion remaining after electrolysis = 1.0 – $\frac{0.828}{2}$

= 0.586

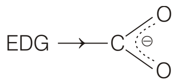
Molarity of Ni^{2+} in final solution $\frac{0.586}{0.50}$ 1.172 M

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

1. Electrical conductivity of the given aqueous solutions depends on the degree of ionisation. Degree of ionisation is directly proportional to the acidic strength. Electron withdrawing groups (EWGs) increases the stability of the carboxylate ion by dispersing the negative charge through resonance effect on the conjugate while electron donating groups (EDGs) decreases the stability of the carboxylate ion by intensifying the negative charge.



Acidity of carboxylic acids increases due to the presence of electron withdrawing groups (EWGs)



Acidity of carboxylic acids decreases due to the presence of electron donating groups

The correct order of acidic strength and electrical conductivity is as follows:

$$\underset{A}{\text{HCOOH}} \quad \underset{C}{\text{PhCOOH}} \quad \underset{B}{\text{CH}_3\text{COOH}}$$

2. NaCl and KCl are strong electrolytes. So, the study of their molar conductances ($_m$) can be experimentally verified by Debye-Huckel Onsagar equation,

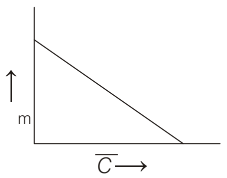
$${}^{c}_{\text{m}} \quad {}^{0}_{\text{m}} \quad B\sqrt{C}$$

${}^{c}_{\text{m}}$ molar conductance at concentration.

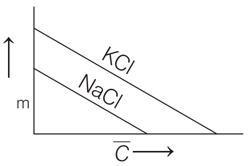
${}^{0}_{\text{m}}$ molar conductance at infinite dilution. i.e. C 0

B Debye-Huckel Onsagar constant.

For (both NaCl and KCl) a strong binary electrolyte like AB, the nature of the plot of $_{\text{m}}$ vs $\sqrt{C}$ will be



Size of Na is being smaller than K and Na will remain in more hydrated state, i.e. larger sized in aqueous solution. As a result, ionic mobility as well as ionic conductance of Na (or NaCl as $Cl^{\ominus}$ is common to NaCl and KCl) will be lower than K (or KCl). Thus, the plot of $_{\text{m}}$ vs $\sqrt{C}$ for NaCl and KCl is as follows :



3. The explanation of statements (S_1 and S_2) are as follows :

In conductivity cell, conductivity ( ) is equal to the sum of ionic conductances (c), of an electrolytic solution present is unit volume of the solution enclosed by two electrodes of unit area (a 1) separated by a unit length (l 1).

$$c \ \frac{l}{a} \qquad c \text{when } l \ 1, a \ 1$$

So, with decrease in the concentration of electrolyte, number of ions in the given unit volume also decreases, i.e. [conductivity] also decreases.

Thus, statement S_1 is wrong. S_2 : Molar conductivity ($_m$) is defined as the conducting power of all the ions present in a solution containing 1 mole of an electrolyte.

$$_m \qquad V_{\text{mL}} \qquad \frac{1000}{M}$$

where, V_{mL} volume in mL containing 1 mole of electrolyte

m molar concentration (mol/L)

So, in a conductivity cell

$$_m \quad \frac{1}{M}$$

i.e. molar conductivity increases with decrease in the concentration (M) of electrolyte.

Thus, statement S_2 is correct.

4. **Key Idea** Gibbs energy of the reaction is related to E $_{\text{cell}}$ by the following formula

G^o nFE $_{\text{cell}}$

G^o Gibbs energy of cell

nF amount of charge passed

E EMF of a cell

Given reaction is,

$$\text{Zn} \quad \text{Cu}^2 \qquad \text{Zn}^2 \quad \text{Cu}$$

E^o_{cell} 2.0 V

F 96000 C

n 2

To find the value of G^o (kJ mol), we use the formula

$$G^o \quad nFE^o_{\text{cell}}$$

$$G^o \quad 2 \quad 96000 \quad 2 \qquad 384000 \text{ J/mol}$$

In terms of kJ/mol, $G^o \ \dfrac{384000}{1000} \quad 384$ kJ/mol

5. According to Kohlrausch's law, the molar conductivity of HA at infinite dilution is given as,

$$_{\text{m}}(\text{H}A) \quad [\ _{\text{m}}(\text{H} \ ) \quad _{\text{m}}(\text{Cl} \ )] \quad [\ _{m}(\text{Na} \ ) \quad _{m}(A \ )]$$
$$[\ _{\text{m}}(\text{Na} \ ) \quad _{\text{m}}(\text{Cl} \ )]$$

$$425.9 \quad 100.5 \quad 126.4 \quad 400 \text{ S cm}^2 \text{ mol} \ ^1$$

Also, molar conductivity at given concentration is given as,

$$_{\text{m}} \quad \frac{1000}{M}$$

Given, conductivity 5 10 ^{5} S cm ^{1}

M Molarity 0.001 M

$$_{\text{m}} \quad \frac{1000 \quad 5 \quad 10 \ ^5\text{S cm} \ ^1}{10 \ ^3 \text{ M}} \quad 50 \text{ S cm}^2 \text{ mol} \ ^1$$

Therefore, degree of dissociation (, of HA is,

$$\frac{_{\text{m}}}{_{\text{m}}} \quad \frac{50\text{S cm}^2\text{mol} \ ^1}{400 \text{ S cm}^2\text{mol} \ ^1} \quad 0.125$$

6. According to Nernst equation,

$$E_{\text{cell}} \quad E \ _{\text{cell}} \quad \frac{2.303 \ RT}{nF}\log Q$$

Given, $\dfrac{2.303 \ RT}{F}$ 0.059 V

$$E_{\text{cell}} \quad E \ _{\text{cell}} \quad \frac{0.059}{n} \log Q$$

At equilibrium, E_{cell} 0

$$E \ _{\text{cell}} \quad \frac{0.059}{n} \log K_C$$

For the given reaction, n 2

Also, K_C 10 10^{15} [given]

$$E \ _{\text{cell}} \quad \frac{0.059}{2} \log (10 \quad 10^{15}) \quad 0.472\text{V} \quad 0.473\text{V}$$

7.

Cell Anode (A) Cathode (C)	E_{cell} (SRP) E_C E_A	E_{cell} free $\bar{e}$ transfer
1. Zn Ag $[Zn + 2Ag^{+}$ Zn^{2+} $2Ag]$	0.80 (0.76) 1.56 V for 2e	$\frac{1.56}{2}$ 0.78 V
2. Zn Fe $[Zn$ Fe^{2} Zn^{2+} $Fe]$	0.44 (0.76) 0.32 V for 2e	$\frac{0.32}{2}$ 0.16 V
3. Zn Au $[3Zn$ $2Au^{3}$ $3Zn^{2}$ $2Au]$	1.40 (0.76) 2.4 V for 6e	$\frac{2.16}{6}$ 0.36 V
4. Zn Fe $[3Zn$ $2Fe^{3}$ Zn^{2} $2Fe^{2+}]$	0.77 (0.76) 1.53 V for 2e	$\frac{1.53}{2}$ 0.765 V

8. It is an electrochemical cell. The overall cell reaction can be written, as

$$\underset{(1\text{ bar})}{H_2(g)} \quad 2AgCl(s) \qquad \underset{(10\ ^{6}\text{ M})}{2HCl(aq)} \quad 2Ag(s)$$

(i) According to Nernst equation,

$$E_{\text{cell}} \quad (E_{\text{cathode}} \quad E_{\text{anode}}) \quad \frac{2.303 \quad RT}{n \quad F} \log \frac{[HCl]^2[Ag]^2}{p_{H_2}[AgCl]^2}$$

Here, (i) E_c $E_{AgCl/Ag,\ Cl}$ E_{cathode}

(ii) E_{anode} $E_{2H\ /H_2}$ 0.00 V

(Standard hydrogen electrode)

$$0.92 \quad (E_c \quad 0) \quad 0.06 \quad \log \frac{(10\ ^{6})^2 \quad 1^2}{1 \quad 1^2}$$

$$E_c \quad 0.06 \quad 6 \quad 2$$

$$E_c \quad 0.92 \quad 0.72 \quad 0.20\text{ V}$$

Note 10 ^{6} molal HCl is a very dilute solution.
So, 10 ^{6} m ~ 10 ^{6} M

9. The relationship between standard electrode potential (E) and equilibrium constant (K) of the cell reaction,

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

can be expressed as,

$$E \quad \frac{RT}{nF}\ln K \qquad K \quad e^{nFE\ /\ RT}$$

Given, n 2, F 96000 C mol ^{1}

E 2 V, R 8 JK ^{1}mol ^{1}

T 300 K

$$K \quad e^{\frac{2\ \ 96000\ \ 2}{8\ \ 300}} \qquad e^{160}$$

10. The redox reaction is : $Zn(s) + Cu^{2+}$ $Zn^{2+} + Cu$

The Nernst equation is E E $\frac{2.303RT}{2F}$ log10

$$1.1 \quad \frac{2.303RT}{2F}$$

Also, G nEF $2F$ 1.1 $\frac{2.303RT}{2F}$

$$2.2F \quad 2.303RT$$

$$2.303RT \quad 2.2F$$

11. Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

12. Standard electrode potential of reaction [E] can be calculated as

$$E^{\circ}_{\text{cell}} \quad E_R \quad E_P$$

where, E_R SRP of reactant , E_P = SRP of product

If E°_{cell} +ve, then reaction is spontaneous otherwise non-spontaneous.

$$Mn^{3} \xrightarrow{E_1\ =\ 1.51\text{ V}} Mn^{2}$$

$$Mn^{2} \xrightarrow{E_2\ =\ \ 1.18\text{ V}} Mn$$

For Mn^{2} disproportionation,

$$E \quad 1.51\text{ V} \quad 1.18\text{ V} \quad 2.69\text{ V} \quad 0$$

Thus, all reaction will not occur.

13. According to Debye Huckel Onsager equation,

$$_C \qquad B\sqrt{C}$$

where, $_C$ limiting equivalent conductivity at concentration C
limiting equivalent conductivity at infinite dilution
C concentration

14. In order to solve the problem, calculate the value of cell constant of the first solution and then use this value of cell constant to calculate the value of k of second solution. Afterwards, finally calculate molar conductivity using value of k and m.

For first solution,

$$k \quad 1.4\text{ Sm}^{1}, \ R \quad 50 \quad , \ M \quad 0.2$$

Specific conductance ( ) $\frac{1}{R}$ $\frac{l}{A}$

$$1.4\text{ Sm}^{1} \quad \frac{1}{50} \quad \frac{l}{A}$$

$$\frac{l}{A} \quad 50 \quad 1.4\text{ m}^{1}$$

For second solution, $R \quad 280, \frac{l}{A} \quad 50 \quad 1.4 \text{ m}^{1}$

$$\frac{1}{280} \quad 1.4 \quad 50 \quad \frac{1}{4}$$

Now, molar conductivity

$$_{m} \quad \frac{}{1000 \quad m} \quad \frac{1/4}{1000 \quad 0.5} \quad \frac{1}{2000}$$

$$5 \quad 10^{4} \text{ S m}^{2} \text{ mol}^{1}$$

15. **PLAN** When different number of electrons are involved in a redox reaction

$$G_{\text{net}} \quad G_{1} \quad G_{2}$$

$$n_3FE_{3} \quad n_1FE_{1} \quad n_2FE_{2}$$

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3}$$

(P) E_3 Fe^{3} /Fe

Net reaction Fe^{3} Fe

is obtained from

	n	E
Fe^{3} e Fe^{2}	n_1 1	E_1^{d} 0.77 V
Fe^{2} $2e$ Fe	n_2 2	E_2 0.44 V
∵ Fe^{3} $3e$ Fe	n_3 3	E_3 ?

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3} \quad \frac{0.77 \quad 2(\ 0.44)}{3} \quad \frac{0.11}{3} \quad 0.04 \text{ V}$$

Thus, P — (3)

Net reaction

$$4H_2O \rightleftharpoons 4H \quad 4OH$$

is obtained from

	n	E
$2H_2O$ O_2 4H $4e$	n_1 4	1.23 V
$2H_2O$ O_2 $4e$ 4OH	n_2 4	0.40 V
$4H_2O$ 4H $4e$	n_3 4	?

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3} \quad E_{1} \quad E_{2}$$

$$1.23 \quad 0.40 \quad 0.83 \text{ V}$$

Thus, Q — (4)

(R) Cu^{2} Cu 2Cu

For thus E of Cu^{2} Cu

is also required.

	n	E
Cu^{2} $2e$ Cu	2	0.34 V
Cu Cu e	1	0.52 V
Cu^{2} e Cu	E_{3}	?

$$E_3 \quad \frac{n_1E_1 \quad n_2E_2}{n_3} \quad \frac{2 \quad 0.34 \quad 1 \quad (\ 0.52)}{1} \quad 0.16 \text{ V}$$

Also,

	n	E
Cu Cu e	n_1 1,	0.52 V
Cu^{2} e Cu	n_2 1	0.10 V
Cu^{2} Cu 2Cu		

$$E \quad 0.52 \quad 0.16 \quad 0.36 \text{ V}$$

Thus, (R) — (1)

(S) Cr^{3} Cr^{2}

is obtained from

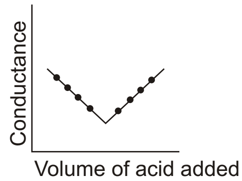
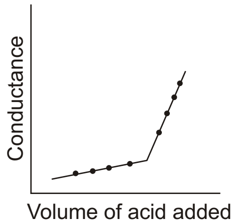
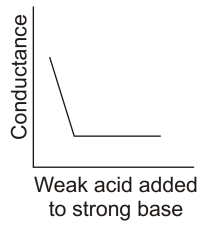
	n	E
Cr^{3} $3e$ Cr	3	0.74 V
Cr Cr^{2} $2e$	2	0.91 V
Cr^{3} e Cr^{2}	1	?

$$E_3 \quad \frac{0.74 \quad 3 \quad 2 \quad 0.91}{1} \quad 0.4 \text{ V}$$

Thus, S (2)

P — (3), Q — (4), R — (1), S — (2)

16. The variation is conductivities in general can be seen as :

	In burette acid	In flask base	Curve
I.	Strong (HI)	Strong (NaOH)	Conductance first decreases due to formation of H_2O and then increases due to addition of strong electrolyte. 
II.	Strong (CH_3COOH)	Weak (KOH)	Conductance increases slightly as NH_4 (salt) is hydrolysed forming HCl. After neutral point, it acid increases rapidly due to addition of strong 
III.	Weak (CH_3COOH)	Strong (KOH)	Conductivity decreases due to neutralisation of conducting strong base and then remains constant due to addition of weak acid. 

	In burette acid	In flask base	Curve
IV.	Weak $[(C_2H_5)_3N]$	Weak (CH_3COOH)	Conductivity increases due to formation of ions and then remains constant due to addition of weak base.
V.	KX	$AgNO_3$	Insoluble salt AgX is formed, hence conductance remains constant. It increases due to addition of KX.

17. The half reactions are $Fe(s) \quad Fe^{2+}(aq) + 2e^- \quad 2$

$$O_2(g) + 4H^+ + 4e^- \quad 2H_2O$$

$$2Fe(s) + O_2(g) + 4H^+ \quad 2Fe^{2+}(aq) + 2H_2O(l);$$

$$E = E^o - \frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4(0.1)} \quad 1.57V$$

18. As $AgNO_3$ is added to solution, KCl will be displaced according to following reaction.

$$AgNO_3(aq) + KCl(aq) \quad AgCl(s) + KNO_3(aq)$$

For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added $AgNO_3$ remain in solution increasing ionic concentration, hence conductivity increases.

19. The net reaction is

$$2H^+ + \frac{1}{2}O_2 + Fe \quad H_2O + Fe^{2+}; E \quad 1.67\ V$$

$$G \quad nE\ F \quad \frac{2\ \ 1.67\ \ 96500}{1000}\ kJ \quad -322.31\ kJ$$

20. The cell reaction is :

$$Zn + Fe^{2+} \rightleftharpoons Zn^{2+} \quad Fe;\ E_{cell} \quad 0.2905\ V$$

$$E \quad E \quad \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$E \quad 0.2905 + \frac{0.059}{2}\log\frac{0.1}{0.01} \quad 0.32\ V$$

Also $\quad E \quad \frac{0.059}{n}\log K$

$$\log K \quad \frac{2E}{0.059} \quad \frac{0.32}{0.0295}$$

$$K \quad (10)^{0.32/0.0295}$$

21. In LiCl, NaCl and KCl, anions are same.

Cations have same charge but different size. Smaller cations are more heavily hydrated in aqueous solution giving larger hydrated radius and thus smaller ionic speeds and equivalent conductance.

Equivalent conductance : KCl > NaCl > LiCl

22. The spontaneous cell reaction is

$$X \quad M \quad M \quad X; E \quad 0.11V$$

23. E is an intensive property :

		E	G	$nE\ F$
(i) Cu^{2+} $2e$	Cu		0.337 V	– 0.674 F
(ii) Cu^{2+} e	Cu^+		0.153 V	– 0.153 F

Subtracting (ii) from (i) gives :

$$Cu^+ \quad e \quad Cu \quad G \quad 0.521\ F = \quad nE\ F$$

$$E \quad 0.521\ V$$

$\because \quad n \quad 1$

24. Given

(i) $2Cu(s) + \frac{1}{2}O_2(g) \quad Cu_2O(s); \quad G^o = \quad 78000\ J\ mol^{\ 1}$

$= 78\ kJ\ mol^{\ 1}$

(ii) $H_2(g) \quad \frac{1}{2}O_2(g) \quad H_2O(g); \quad G^o = \quad 178000\ J\ mol^{\ 1}$

$= 178\ kJ\ mol^{\ 1}$

So, net reaction is (By (i)-(ii))

$$2Cu(s) + H_2O(g) \quad Cu_2O(s) + H_2(g);$$

$G = 100000$ J/mol or 10^5 J/mol = 100 kJ mol ^{1}

Now , for the above reaction

$$G \quad G^o + RT\ \ln\ \frac{p_{H_2}}{p_{H_2O}}$$

and to prevent above reaction,

$$G \quad 0$$

So,

$$G^o \quad RT\ln\frac{p_{H_2}}{p_{H_2O}} \quad 0$$

After putting the values,

$$10^5 \quad 8 \quad 1250\ \ln\ \frac{p_{H_2}}{p_{H_2O}} \quad 0$$

or $\quad 10^5 \quad 10^4\ \ln\ \frac{p_{H_2}}{p_{H_2O}} \quad 0$

or $\quad 10^4(\ln p_{H_2} \quad \ln p_{H_2O}) \quad 10^5$

or $\quad \ln\ p_{H_2} \quad 10 \quad \ln p_{H_2O}$

or $\quad \ln p_{H_2} \quad 10 \quad 2.3\log(0.01)$ (as p_{H_2O} 1%)

$\quad 10 \quad 4.6$

so $\quad \ln p_{H_2} \quad 14.6$

25. For the given concentration cell, the cell reaction are

$M \quad M^2$ at left hand electrode.

$M^2 \quad M$ at right hand electrode

M^2 (RHS electrode) $\quad M^2$ (LHS electrode)

$E \quad 0$

Applying Nernst equation

$$E_{cell} \quad 0.059 \quad 0 \quad \frac{0.059}{2}\log\frac{[M^2\ \ ]\text{ at LHS electrode}}{0.001}$$

$$\log\frac{[M^2\ \ ]\text{ at LHS electrode}}{0.001} \quad 2$$

$$[M^2\ \ ]\text{ at LHS electrode} \quad 10^{\ 2} \quad 0.001 \quad 10^{\ 5}\ M$$

The solubility equilibrium for MX_2 is

$$MX_2(s) \rightleftharpoons M^2 \ (aq) \quad 2X \ (aq)$$

Solubility product, K_{sp} $\quad][M^2 \ ][X \ ]^2$

$$10^{\ 5} \quad (2 \quad 10^{\ 5})^2 \quad 4 \quad 10^{\ 15}$$

[$\because$ In saturated solution of $MX_2, [X \ ] \quad 2[M^2 \ ]$]

26. $G \qquad nEF \qquad \dfrac{2 \quad 0.059 \quad 96500}{1000}$ kJ $\quad$ 11.4 kJ

27. $M(s) \quad M \ (aq, 1\,\text{M}) \qquad M \ (aq, 0.05\,\text{M}) \quad M(s)$

$$E_{cell} \quad 0 \quad \frac{2.303\ RT}{F} \log \frac{0.05}{1} \quad 0$$

Hence, $|E_{cell}| \quad E_{cell}$ $\quad$ 0.70 V and $\quad G \quad$ 0 for spontaneity of reaction.

28. $E_{cell} \quad E \quad \dfrac{0.0538}{1} \log 0.0025 \quad 0.139$ V $\quad$ 140 mV

29. For spontaneous redox reaction : $\quad E_{cell} \quad 0$

For $\qquad 2I \ + Cl_2 \qquad 2Cl \ + I_2$

$\qquad E \quad 1.36 - 0.54 = 0.82 \text{ V} > 0$

i.e. Cl_2 will spontaneously oxidise I .

In other cases $E_{cell} \quad$ 0, they are non-spontaneous.

30. For the reaction :

(i) $4Fe^{3+} + 2H_2O \qquad 4Fe^{2+} + 4H^+ + O_2; E \qquad 0.46$ V

(ii) $4Mn^{3+} + 2H_2O \qquad 4Mn^{2+} + 4H^+ + O_2; E \qquad 0.27$ V

As evidenced above, reaction (i) is non-spontaneous, therefore, Fe^{3+} is stable in acid solution. However, reaction (ii) is spontaneous Mn^{3+} oxidises H_2O to O_2 and itself reduced to Mn^{2+} in acidic medium.

31. Sodium fusion extract from aniline produces NaCN which reacts with Fe^{2+} to form $[Fe(CN)_6]^4$. The complex ion then reacts with Fe^{3+} to give blue precipitate of prussian blue.

$$Fe^{3+} + [Fe(CN)_6]^4 \rightleftharpoons \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3}$$

32. $E°$ for $2Ag^+ + C_6H_{12}O_6 + H_2O \rightleftharpoons 2Ag(s)$

$\qquad + C_6H_{12}O_7 + 2H^+$ is 0.75 V

Also $\quad E \quad \dfrac{0.0592}{2} \log K \qquad \log K \quad \dfrac{2E}{0.0592} \quad 25.33$

$\ln K \quad 2.303 \log K \quad 58.35$

33. On increasing concentration of NH_3, the concentration of H^+ ion decreases, therefore,

$$E_{red} \quad E_{red} \quad \frac{0.0592}{2} \log [H \ ]^2 \quad 0 \quad \frac{0.0592}{2} \quad 2 \log 10^{\ 11}$$

0.65 V

i.e. E_{red} increases by 0.65 V.

34. NH_3 has no effect on the $E°$ of glucose/gluconic acid electrode.

35. The solubility of AgBr in $10^{\ 7}$ M $AgNO_3$ solution is determined as

$$\underset{}{AgBr} \rightleftharpoons \underset{S + 10^{\ 7}}{Ag^+} + \underset{S}{Br}$$

$$AgNO_3 \qquad \underset{S + 10^{\ 7}}{Ag^+} + \underset{10^{\ 7}}{NO_3}$$

$$K_{sp} \quad 14 \quad 10^{\ 14} \quad S\,(S \quad 10^{\ 7})$$

Solving for S gives : $\quad S \quad 3 \quad 10^{\ 7}$ M

$[Br \ ] \quad 3 \quad 10^{\ 7}$ M,

$[Ag^+] = 4 \quad 10^{\ 7}$ M,

$[NO_3] \quad 10^{\ 7}$ M

(sp. conductance)

$$[8 \quad 10^{\ 3} \quad 3 \quad \overset{Br}{10^{\ 7}} \quad \overset{Ag}{6} \quad 10^{\ 3} \quad \overset{NO_3}{4} \quad 10^{\ 7}$$

$$7 \quad 10^{\ 3} \quad 10^{\ 7}]1000$$

$24 \quad 10^{\ 7} \quad 24 \quad 10^{\ 7} \quad 7 \quad 10^{\ 7}$

$55 \quad 10^{\ 7}$ S m ^{1}

55 (in terms of $10^{\ 7}$ S m ^{1})

36. (a) $\quad G \qquad G_f$ (products) $\qquad G_f$ (reactants)

$\qquad = -109 - (-129 + 77)$ kJ $= -57$ kJ

Cell : $\qquad$ Ag | AgCl, Cl || Ag^+ | Ag

For K_{sp}; reaction is AgCl $(s) \rightleftharpoons Ag^+ + Cl$

$G \quad$ 57 kJ

$G \quad RT \ln K_{sp}$

$$\log K_{sp} \quad \frac{G}{2.3\ RT} \qquad \frac{57 \quad 1000}{2.3 \quad 8.314 \quad 298} \qquad 10$$

Now, $\qquad E°$ of $Ag^+ + Cl \rightleftharpoons$ AgCl

$$E \quad \frac{G}{nF} \quad \frac{57000}{96500} \quad 0.59 \text{ V}$$

(b) The cell reaction is :

$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag; E° = 1.56$ V

$$0 \quad E \quad \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\log \frac{[Zn^{2+}]}{[Ag^+]^2} \quad \frac{2E}{0.059} \quad \frac{2 \quad 1.56}{0.059} \quad 52.88$$

Moles of Zn added $\quad \dfrac{6.539 \quad 10^{\ 2}}{65.39} \quad 10^{\ 3}$

Moles of Ag formed $\quad 2 \quad 10^{\ 3}$.

37. Given,

$In^{2+} + e \qquad In^+ \quad E° = -0.40 \qquad$ ...(i)

$G \quad$ 0.40 F

$In^{3+} + 2e \qquad In^+ \quad E° = -0.42 \qquad$ ...(ii)

$G \quad$ 0.84 F

Subtracting (i) from (ii)

$In^{3+} + e \qquad In^{2+}; \qquad G \quad 0.44\text{ F} = -E\ F$

$E \quad 0.44$ V

Now, for : $\quad Cu^{2+} + In^{2+} \qquad Cu^+ + In^{3+}$

$$E \quad E\ (Cu^{2+}/Cu^+) \quad E\ (In^{3+}/In^{2+})$$

$0.15 - (-0.44) = 0.59$ V

Also $\qquad E° \quad 0.0590 \log K$

$$\log K \quad \frac{E}{0.059} \quad 10 \qquad K \quad 10^{10}$$

38. (a) $\text{pH} = -\log [H^+]$

In pure water, $[H^+]$ depends on value of K_w which is

$$K_w \quad [H^+][OH \quad]$$

$\because$ K_w is a function of temperature, $[H^+]$ will change with temperature.

(b) Let the emf of first cell be X volt.

emf of 2nd cell $\quad (X \quad 0.03)$ volt

$[Cu^{2+}]$ in 2nd cell = 0.50 M

$[Cu^{2+}]$ in 1st cell = ?

$$E_1 \quad E_1 \quad \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_2 \quad E_1 \quad \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_2}$$

$$E_2 \quad E_1 \quad \frac{2.303\,RT}{2F} \quad \log \frac{[Cu^{2+}]_2}{[Cu^{2+}]_1}$$

$$0.03 = 0.03 \log \frac{0.50}{[Cu^{2+}]_1}$$

$$\frac{0.50}{[Cu^{2+}]_1} \quad 10 \qquad [Cu^{2+}]_1 \quad 0.05 \text{ M}$$

39. **At anode** $\quad \frac{1}{2} H_2 \qquad H^+ \quad e \;; E° = 0$

At cathode $\quad AgCl\,(s) + e \qquad Ag + Cl \;; E° = ?$

(i) Cell reaction : $\frac{1}{2} H_2 \quad AgCl\,(s) \qquad Ag + H^+ + Cl$

(ii) $\quad G \quad nE\;F \quad H \quad T\;\; S$

At 15°C : $-0.23 \quad 96500 \quad H \quad 288 \quad S$ …(i)

At 35°C : $-0.21 \quad 96500 \quad H \quad 308 \quad S$ …(ii)

$96500\,(0.23 \quad 0.21) \quad 20 \quad S$

$$S \quad \frac{96500 \quad 0.02}{20} \quad 96.5 \text{ J}$$

Substituting value of S in (i)

$H \quad 288 \quad (\;96.5) \quad 0.23 \quad 96500 \quad -49.987$ kJ

(iii) At 25°C

$$E \quad 96500 \quad 49987 \quad 298\,(\;96.5)$$

$$E \quad 0.22 \text{ V}$$

$AgCl\,(s) + e \qquad Ag + Cl \;; E° = 0.22$ V

$Ag \qquad Ag^+ + e\;; \quad E° = -0.80$ V

Adding : $AgCl\,(s) \qquad Ag^+ + Cl \;; \quad E° = -0.58$ V

$$E \quad 0.0592 \log K_{sp}$$

$$\log K_{sp} \quad \frac{0.58}{0.0592} \quad 9.79$$

$$K_{sp} \quad 1.6 \quad 10^{\;\;10}$$

40. $E \quad 0 \quad \frac{0.0592}{1} \log \frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$

$$0.164 \quad 0.0592 \log \frac{[Ag^+]_{anode}}{0.10}$$

$[Ag^+]_{anode} \quad 1.7 \quad 10^{\;\;4}$ M

In saturated Ag_2CrO_4 solution present in anode chamber :

$$Ag_2CrO_4\,(s) \rightleftharpoons 2Ag \quad + \quad CrO_4^2$$

$$1.7 \quad 10^{\;\;4} \text{ M} \quad \frac{1.7}{2} \quad 10^{\;\;4} \text{M}$$

$$K_{sp} \quad [Ag^+]^2 [CrO_4^2 \;]$$

$$(1.7 \quad 10^{\;\;4})^2 \quad \frac{1.7}{2} \quad 10^{\;\;4}$$

$$2.45 \quad 10^{\;\;12}$$

41. For $\quad 2\,Fe^{3+} \quad 3I \rightleftharpoons 2Fe^{2+} \quad I_3$

$$E \quad E\;(Fe^{3+}/Fe^{2+}) \quad E\;(I_3/I\;)$$

$$0.77 - 0.54 = 0.23 \text{ V}$$

$\because \quad E \quad \frac{0.0592}{2} \log K \qquad (n \quad 2)$

$$\log K \quad \frac{2E}{0.0592} \quad \frac{2 \quad 0.23}{0.0592} = 7.77$$

$$K \quad 5.89 \quad 10^7$$

42. $\quad Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$

$$E° \quad E°\,(Ce^{4+}/Ce^{3+}) - E\;\;(Fe^{3+}/Fe^{2+})$$

$$1.44 - 0.68 = 0.76 \text{ V}$$

$\because \quad E° \quad 0.0592 \log K$

$$\log K \quad \frac{E}{0.0592} \quad \frac{0.76}{0.0592} \quad 12.83$$

$$K \quad 6.88 \quad 10^{12}$$

43. pH = 14

pOH = 0

$[OH \;\;] = 1.0$ M

$$K_{sp} \quad 10^{\;\;19} \quad [Cu^{2+}][OH \;\;]^2$$

$$[Cu^{2+}] \quad \frac{10^{\;\;19}}{[OH \;\;]^2} \quad 10^{\;\;19}$$

For reaction : $Cu^{2+} + 2e \qquad Cu;\;\; E° = 0.34$ V

$$E \quad E \quad \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]}$$

$$0.34 - \frac{0.0592}{2} \log 10^{19} \quad -0.222 \text{ V}$$

44. For reaction,

$$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$$

Initial :	$10^{\;\;3}$ M	0	0
Equilibrium :	$5 \quad 10^{\;\;5}$	$4.75 \quad 10^{\;\;4}$	$9.5 \quad 10^{\;\;4}$

$$K \quad \frac{[Fe^{2+}]^2 [Hg_2^{2+}]}{[Fe^{3+}]^2}$$

$$\frac{(9.5 \quad 10^{\;\;4})^2\,(4.75 \quad 10^{\;\;4})}{(5 \quad 10^{\;\;5})^2} = 0.17$$

$\because \quad E \quad \frac{0.0592}{2} \log K \quad 0.0226$ V

$$E\;\;(Fe^3 \;/Fe^2\;) \quad E\;\;(Hg_2^2 \;/Hg)$$

$$E\;\;(Hg_2^{2+}/Hg) = 0.77 + 0.0226 \quad 0.7926 \text{ V}$$

45. In a saturated AgI solution;

$[Ag^+] \quad \sqrt{8.7 \quad 10^{\;17}}$ M

$9.32 \quad 10^{\;9}$ M

$E_{Ag^+/Ag} \quad E \quad 0.0592 \log \frac{1}{[Ag^+]}$

$0.799 - 0.0592 \log \frac{1}{9.32 \quad 10^{\;9}}$

0.324 V

Also, for $AgI \rightleftharpoons Ag^+ + I$; $E° = 0.0592 \log K_{sp}$

$= -0.95$ V

Ag $\quad Ag^+ \quad e$; $E° = -0.799$ V

$AgI + e \quad Ag + I \qquad E° = x$

Adding : $\quad AgI \quad Ag^+ + I$; $E° = -0.95$ V

$= x - 0.799$

$x \quad 0.151$ V

46. The redox reaction is

$Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni \quad E° = +0.51$ V

$E \quad \frac{0.0592}{2} \log K$

$\log K \quad \frac{0.51 \quad 2}{0.0592} \quad 17.23$

$K \quad 1.7 \quad 10^{17}$

Such a high value of equilibrium constant indicates that the reaction is almost complete. Therefore, concentration of Zn^{2+} in solution will be equal to initial concentration of Ni^{2+} ion, i.e. 1.0 M.

47. The galvanic cell is : $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

Cell reaction : $Cu + 2Ag^+ \rightleftharpoons Cu^{2+} + 2Ag$; $E° = 0.462$ V

$E \quad 0 \quad 0.462 \quad \frac{0.0592}{2} \log \frac{(0.01)}{[Ag^+]^2}$

$[Ag^+] = 1.57 \quad 10^{\;9}$ M

48. $H_2O + e \rightleftharpoons \frac{1}{2} H_2 + HO$; $E° = -0.8277$ V

$\frac{1}{2} H_2 + H_2O \rightleftharpoons H_3O^+ + e$; $\quad E° = 0$ V

$2H_2O \rightleftharpoons H_3O^+ + HO \qquad E° = -0.8277$ V

$E° \quad 0.0592 \log K$

$\log K \quad \frac{0.8277}{0.0592} \quad 13.98$

$K \quad 1.04 \quad 10^{\;14}$.

49. **At anode** $\quad Zn \quad Zn^{2+} \quad 2e \quad E \quad 0.76$ V

At cathode $2H^+ \quad 2e \quad H_2(g) \quad E° \quad 0.00$ V

For $\quad Zn + 2H^+ \quad Zn^{2+} + H_2(g) \; E° \quad 0.76$ V

$E \quad E \quad \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$

$\frac{2\,(E \quad E\,)}{0.0592} \quad \log [Zn^{2+}] \quad 2 \log \frac{1}{[H^+]}$

$16.2 = -\log (0.1) - 2$ pH

pH $\quad \frac{1 \quad 16.2}{2} \quad 8.6$

50. For conductivity, the charge carriers are required. In anhydrous state, HCl is not ionised and no charge carrier ions are available, hence bad conductor. However, in aqueous solution, HCl is fully ionised producing H and Cl and conducts electricity.

51. (i) The cell reaction is

$Zn \quad Cu^{2+} \qquad Zn^{2+} + Cu$

(ii) $E_{cell} \quad E_{cathode} \quad E_{anode} = 0.350 - (-0.763) = 1.113$ V

$\because$ Both Zn^{2+} and Cu^{2+} are at unit concentrations,

$E \quad E \quad 1.113$ V

(iii) $\because \quad E_{cell} \quad 1.113 \text{ V} > 0$

$G \quad nEF \quad 0$

Therefore, the cell reaction is spontaneous.

52. pH $\quad C \quad 10^{\;4}$

$\frac{10^{\;4}}{0.0015}$

Also, conductance $(G) \quad \frac{A}{l}$

$G \quad \frac{l}{A} \quad 5 \quad 10^{\;7} \quad \frac{120}{1} \quad 6 \quad 10^{\;5}$

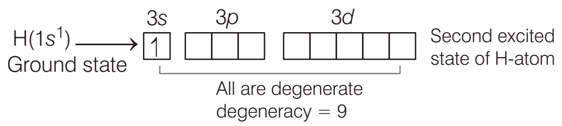
$_c \quad \frac{1000}{C}$

$\frac{6 \quad 10^{\;5} \quad 1000}{0.0015}$

$\frac{_c}{\;} \quad \frac{6 \quad 10^{\;5} \quad 1000}{0.0015} \quad \frac{0.0015}{10^{\;4}}$

$600 \quad 6 \quad 10^2 \text{ S cm}^{\;1}\text{mol}^{\;1}$

53. Energy obtained as one mole X is converted into Y is 193 kJ.



Energy consumed in converting one mole of M to M^3

$nE \quad F \quad 2 \quad 96500 \quad 0.25 \text{ J} \quad \frac{96500}{2}$ J

$193 \quad 10^3 \quad n \quad \frac{96500}{2} \qquad n \quad 4$ mol

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http://tinyurl.com/y6pveqhz *or*

11

Chemical Kinetics

Objective Questions I (Only one correct option)

1. NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation,

$$2N_2O_5(g) \quad 4NO_2(g) + O_2(g)$$

The initial concentration of N_2O_5 is 3.00 mol $L^{\ 1}$ and it is 2.75 mol $L^{\ 1}$ after 30 minutes. The rate of formation of NO_2 is **(2019 Main, 12 April II)**

(a) 4.167 $\ 10^{\ 3}$ mol $L^{\ 1}$ $min^{\ 1}$ (b) 1.667 $\ 10^{\ 2}$ mol $L^{\ 1}$ $min^{\ 1}$
(c) 8.333 $\ 10^{\ 3}$ mol $L^{\ 1}$ $min^{\ 1}$ (d) 2.083 $\ 10^{\ 3}$ mol $L^{\ 1}$ $min^{\ 1}$

2. In the following reaction; $xA \quad yB$

$$\log_{10}\frac{d[A]}{dt} \quad \log_{10}\frac{d[B]}{dt} \quad 0.3010$$

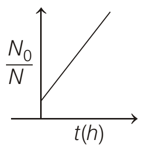
A and B respectively can be **(2019 Main, 12 April I)**

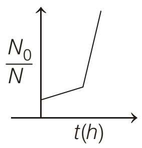
(a) *n*-butane and *iso*-butane (b) C_2H_2 and C_6H_6
(c) C_2H_4 and C_4H_8 (d) N_2O_4 and NO_2

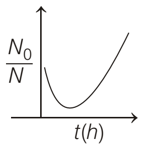
3. For the reaction of H_2 with I_2, the rate constant is 2.5 $\ 10^{\ 4}$ $dm^3 mol^{\ 1} s^{\ 1}$ at 327ºC and 1.0 dm^3 $mol^{\ 1}$ $s^{\ 1}$ at 527ºC. The activation energy for the reaction, in kJ $mol^{\ 1}$ is ($R \quad$ 8.314 $JK^{\ 1}$ $mol^{\ 1}$) **(2019 Main, 10 April II)**

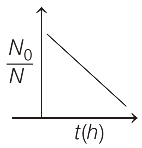
(a) 59 (b) 72 (c) 150 (d) 166

4. A bacterial infection in an internal wound grows as $N(t) \quad N_0 \exp(t)$, where the time t is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} \quad 5N^2$. What will be the plot of $\frac{N_0}{N}$ *vs t* after 1 hour? **(2019 Main, 10 April I)**

(a)


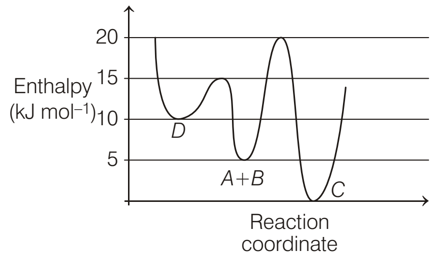
(b)


(c)


(d)


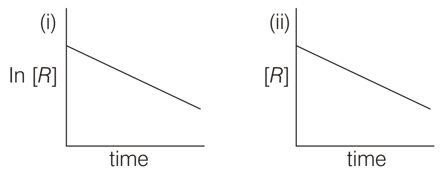
5. Consider the given plot of enthalpy of the following reaction between A and B. $A \quad B \quad C+D$

Identify the incorrect statement. **(2019 Main, 9 April II)**



(a) D is kinetically stable product.
(b) Formation of A and B from C has highest enthalpy of activation.
(c) C is the thermodynamically stable product.
(d) Activation enthalpy to form C is 5 kJ $mol^{\ 1}$ less than that to form D.

6. The given plots represent the variation of the concentration of a reaction R with time for two different reactions (i) and (ii). The respective orders of the reactions are **(2019 Main, 9 April I)**



(a) 1, 1 (b) 0, 2
(c) 0, 1 (d) 1, 0

7. For a reaction scheme, $A \overset{k_1}{\quad} B \overset{k_2}{\quad} C$, if the rate of formation of B is set to be zero then the concentration of B is given by **(2019 Main, 8 April II)**

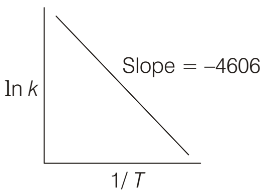
(a) $k_1k_2[A]$ (b) $\frac{k_1}{k_2}[A]$
(c) $(k_1 \quad k_2)[A]$ (d) $(k_1 \quad k_2)[A]$

8. For the reaction, $2A + B \quad C$, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is **(2019 Main, 8 April I)**

$[A]$(mol L^{-1})	$[B]$(mol L^{-1})	**Initial rate** (mol $L^{-1}s^{-1}$)
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

(a) rate $= k[A][B]^2$ (b) rate $= k[A]^2[B]^2$
(c) rate $= k[A][B]$ (d) rate $= k[A]^2[B]$

9. For a reaction, consider the plot of ln k *versus* $1/T$ given in the figure. If the rate constant of this reaction at 400 K is $10^{-5}\ s^{-1}$, then the rate constant at 500 K is **(2019 Main, 12 Jan II)**



(a) $4 \times 10^{-4}\ s^{-1}$ (b) $10^{-6}\ s^{-1}$
(c) $10^{-4}\ s^{-1}$ (d) $2 \times 10^{-4}\ s^{-1}$

10 Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg? **(2019 Main, 12 Jan I)**
(a) 20 (b) 25 (c) 40 (d) 50

11. The reaction, $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be **(2019 Main, 11 Jan II)**
(a) 7.2 h (b) 18.0 h (c) 12.0 h (d) 9.0 h

12. If a reaction follows the Arrhenius equation, the plot ln$k$ *vs* $1/(RT)$ gives straight line with a gradient ($-y$) unit. The energy required to activate the reactant is **(2019 Main, 11 Jan I)**

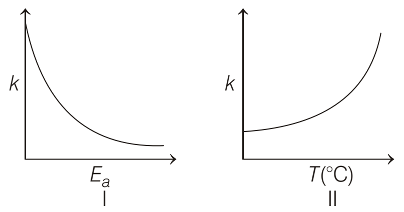
(a) $\frac{y}{R}$ unit (b) $-y$ unit (c) yR unit (d) $-y$ unit

13. For an elementary chemical reaction,

$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is **(2019 Main, 10 Shift II)**

(a) $2k_1[A_2] - k_{-1}[A]^2$ (b) $k_1[A_2] + k_{-1}[A]^2$
(c) $2k_1[A_2] - 2k_{-1}[A]^2$ (d) $k_1[A_2] - k_{-1}[A]^2$

14. Consider the given plots for a reaction obeying Arrhenius equation ($0°C < T < 300°C$) : (k and E_a are rate constant and activation energy, respectively) **(2019 Main, 10 Jan I)**



Choose the correct option.
(a) Both I and II are wrong
(b) Both I and II are correct
(c) I is wrong but II is right
(d) I is right but II is wrong

15 For the reaction, $2A + B \rightarrow$ products

When concentration of both (A and B) becomes double, then rate of reaction increases from 0.3 mol $L^{-1}\ s^{-1}$ to 2.4 mol $L^{-1}\ s^{-1}$.

When concentration of only A is doubled, the rate of reaction increases from 0.3 mol $L^{-1}\ s^{-1}$ to 0.6 mol $L^{-1}\ s^{-1}$.
Which of the following is true? **(2019 Main, 9 Jan II)**
(a) The whole reaction is of 4th order
(b) The order of reaction w.r.t. B is one
(c) The order of reaction w.r.t. B is 2
(d) The order of reaction w.r.t. A is 2

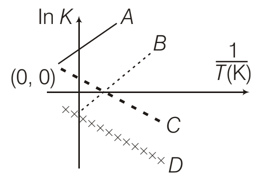
16 The following results were obtained during kinetic studies of the reaction; **(2019 Main, 9 Jan I)**

$$2A + B \rightarrow \text{Products}$$

Experiment	$[A]$ (in mol L^{-1})	$[B]$ (in mol L^{-1})	**Initial rate of reaction** (in mol $L^{-1}\ min^{-1}$)
I.	0.10	0.20	6.93×10^{-3}
II.	0.10	0.25	6.93×10^{-3}
III.	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is
(a) 5 (b) 10
(c) 100 (d) 1

17. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction? **(2018 Main)**



(a) A and B (b) B and C
(c) C and D (d) A and D

18. At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is : **(2018 Main)**
(a) 2 (b) 3
(c) 1 (d) 0

19. Two reactions R_1 and R_2 have identical pre- exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2, respectively at 300 K, then ln $\frac{k_2}{k_1}$ is equal to ($R = 8.314$ J $mol^{-1}K^{-1}$) **(2017 Main)**
(a) 8 (b) 12 (c) 6 (d) 4

20. Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be **(2016 Main)**

(a) $6.93\ \ 10^{4}$ mol min ^{1} (b) 2.66 L min ^{1} at STP
(c) $1.34\ \ 10^{2}$ mol min ^{1} (d) $6.93\ \ 10^{2}$ mol min ^{1}

21. Higher order (>3) reactions are rare due to **(2015 Main)**

(a) low probability of simultaneous collision of all the reacting species
(b) increase in entropy and activation energy as more molecules are involved
(c) shifting of equilibrium towards reactants due to elastic collisions
(d) loss of active species on collision

22. For the elementary reaction, $M \quad N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is **(2014 Adv.)**

(a) 4 (b) 3
(c) 2 (d) 1

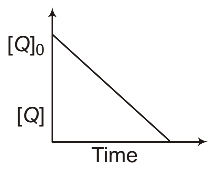
23. For the non-stoichiometric reaction, $2A + B \quad C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. **(2014 Main)**

	Initial concentration $[A]$	Initial concentration $[B]$	Initial rate of formation of C (mol L ^{1}s ^{1})
(i)	0.1 M	0.1 M	$1.2\ \ 10^{3}$
(ii)	0.1 M	0.2 M	$1.2\ \ 10^{3}$
(iii)	0.2 M	0.1 M	$2.4\ \ 10^{3}$

The rate law for the formation of C is

(a) $\dfrac{dC}{dt} = k[A][B]$ (b) $\dfrac{dC}{dt} = k[A]^2[B]$
(c) $\dfrac{dC}{dt} = k[A][B]^2$ (d) $\dfrac{dC}{dt} = k[A]$

24. In the reaction, $P \quad Q \qquad R \quad S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is **(2013 Adv.)**

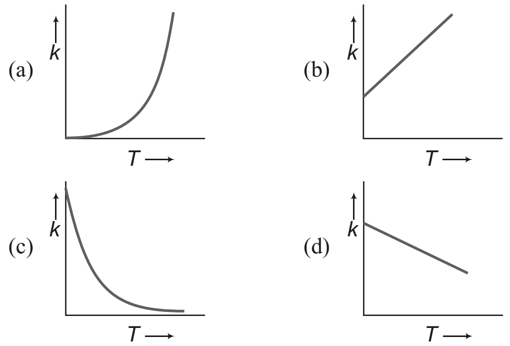


(a) 2 (b) 3 (c) 0 (d) 1

25. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R \quad 8.314$ JK ^{1} mol ^{1} and log 2 $\quad 0.301$) **(2013 Main)**

(a) 53.6 kJ mol ^{1} (b) 48.6 kJ mol ^{1}
(c) 58.5 kJ mol ^{1} (d) 60.5 kJ mol ^{1}

26. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **(2010)**



27. For a first order reaction, $A \quad P$, the temperature (T) dependent rate constant (k) was found to follow the equation :

$$\log k \quad \frac{2000}{T} \quad 6.0$$

the pre-exponential factor A and the activation energy E_a, respectively, are **(2009)**

(a) $1.0\ \ 10^6$ s ^{1} and 9.2 kJ mol ^{1}
(b) 6.0 s ^{1} and 16.6 kJ mol ^{1}
(c) $1.0\ \ 10^6$ s ^{1} and 16.6 kJ mol ^{1}
(d) $1.0\ \ 10^6$ s ^{1} and 38.3 kJ mol ^{1}

28. Under the same reaction conditions, initial concentration of 1.386 mol dm ^{3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\dfrac{k_1}{k_0}$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is **(2008, 3M)**

(a) 0.5 mol ^{1} dm^3 (b) 1.0 mol dm ^{3}
(c) 1.5 mol dm ^{3} (d) 2.0 mol ^{1} dm^3

29. Consider a reaction, $aG \quad bH \qquad$ products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is **(2007, 3M)**

(a) 0 (b) 1
(c) 2 (d) 3

30. Which one of the following statement(s) is incorrect about order of reaction? **(2005, 1M)**

(a) Order of reaction is determined experimentally
(b) Order of reaction is equal to sum of the power of concentration terms in differential rate law
(c) It is not affected with stoichiometric coefficient of the reactants
(d) Order cannot be fractional

31. (A) follows first order reaction, (A) product. Concentration of A, changes from 0.1 M to 0.025 M in 40 min. Find the rate of reaction of A when concentration of A is 0.01 M. **(2004, 1M)**

(a) 3.47 10^{-4} M min^{-1} (b) 3.47 $10^{\ 5}$ M min^{-1}

(c) 1.73 $10^{\ 4}$ M min^{-1} (d) 1.73 $10^{\ 5}$ M min^{-1}

32. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2 10^4 s. The rate constant of reaction in $\text{s}^{\ 1}$ is **(2003, 1M)**

(a) 2 10^4 (b) 3.45 $10^{\ 5}$

(c) 1.386 $10^{\ 4}$ (d) 2 $10^{\ 4}$

33. Consider the chemical reaction,

$$N_2(g) + 3H_2(g) \qquad 2NH_3(g)$$

The rate of this reaction can be expressed in terms of time derivatives of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions **(2002, 3M)**

(a) Rate $\frac{d[N_2]}{dt} \quad \frac{1}{3}\frac{d[H_2]}{dt} \quad \frac{1}{2}\frac{d[NH_3]}{dt}$

(b) Rate $\frac{d[N_2]}{dt} \quad 3\frac{d[H_2]}{dt} \quad 2\frac{d[NH_3]}{dt}$

(c) Rate $\frac{d[N_2]}{dt} \quad \frac{1}{3}\frac{d[H_2]}{dt} \quad \frac{1}{2}\frac{d[NH_3]}{dt}$

(d) Rate $\frac{d[N_2]}{dt} \quad \frac{d[H_2]}{dt} \quad \frac{d[NH_3]}{dt}$

34. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process. $AB + h \qquad AB^*$, the rate of formation of AB^* is directly proportional to **(2001, 1M)**

(a) C (b) I

(c) I^2 (d) C I

35. The rate constant for the reaction, $2N_2O_5 \qquad 4NO_2 + O_2$ is 3.0 $10^{\ 5}$ $\text{s}^{\ 1}$. If the rate is 2.40 $10^{\ 5}$ mol $\text{L}^{\ 1}$ $\text{s}^{\ 1}$, then the concentration of N_2O_5 (in mol $\text{L}^{\ 1}$) is **(2000, 1M)**

(a) 1.4 (b) 1.2

(c) 0.04 (d) 0.8

36. The half-life period of a radioactive element is 140 days. After 650 days, one gram of the element will reduce to **(1986)**

(a) $\frac{1}{2}$ g (b) $\frac{1}{4}$ g (c) $\frac{1}{8}$ g (d) $\frac{1}{16}$ g

37. A catalyst is a substance which **(1983, 1M)**

(a) increases the equilibrium concentration of the product
(b) changes the equilibrium constant of the reaction
(c) shortens the time to reach equilibrium
(d) supplies energy to the reaction

38. The specific rate constant of a first order reaction depends on the **(1983, 1M)**

(a) concentration of the reactant
(b) concentration of the product
(c) time
(d) temperature

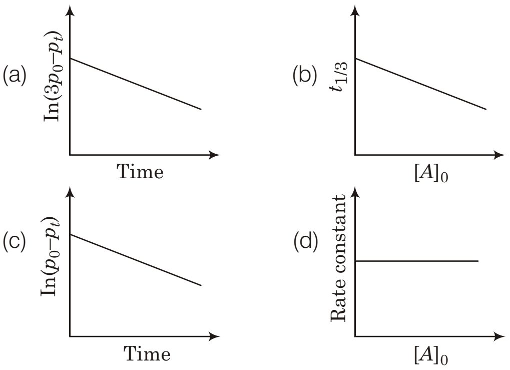
39. The rate constant of a reaction depends on **(1981, 1M)**

(a) temperature
(b) initial concentration of the reactants
(c) time of reaction
(d) extent of reaction

Objective Questions II

(One or more than one correct option)

40. For a first order reaction $A(g) \qquad 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t \quad 0$) and at time t are p_0 and p_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{\text{rd}}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases) **(2018 Adv.)**



41. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. the correct option(s) among the following is(are) **(2017 Adv.)**

(a) The activation energy of the reaction is unaffected by the value of the steric factor
(b) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
(c) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
(d) Since P 4.5, the reaction will not proceed unless an effective catalyst is used

42. According to the Arrhenius equation, **(2016 Adv.)**

(a) a high activation energy usually implies a fast reaction
(b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
(c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
(d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy

43. For the first order reaction,

$$2N_2O_5(g) \qquad 4NO_2(g) + O_2(g) \qquad \textbf{(2011)}$$

(a) the concentration of the reactant decreases exponentially with time
(b) the half-life of the reaction decreases with increasing temperature
(c) the half-life of the reaction depends on the initial concentration of the reactant
(d) the reaction proceeds of 99.6% completion in eight half-life duration

44. The following statement (s) is are correct **(1999, 3M)**

(a) A plot of log K_p *vs* $\frac{1}{T}$ is linear

(b) A plot of log $[X]$ *vs* time is linear for a first order reaction, $x \quad p$

(c) A plot of log p *vs* $\frac{1}{T}$ is linear at constant volume

(d) A plot of p *vs* $\frac{1}{V}$ is linear at constant temperature

45. For the first order reaction, **(1998, 2M)**

(a) the degree of dissociation is equal to $(1 \quad e^{kt})$

(b) a plot of reciprocal concentration of the reactant *vs* time gives a straight line

(c) the time taken for the completion of 75% reaction is thrice the $\frac{1}{2}$ of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, $T^{\ \ 1}$

46. A catalyst **(1984, 1M)**

(a) increases the average kinetic energy of reacting molecules

(b) decreases the activation energy

(c) alters the reaction mechanism

(d) increases the frequency of collisions of reacting species

Numerical Value

47. Consider the following reversible reaction,

$$A(g) + B(g) \rightleftharpoons AB(g)$$

The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol ^{1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of $\ G^{\ominus}$ (in J mol ^{1}) for the reaction at 300 K is ……… .

(Given ; $\ln(2) \quad 0.7\ RT \quad 2500$ J mol ^{1} at 300 K and G is the Gibbs energy) **(2018 Adv.)**

Passage Based Questions

Passage

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N \quad {}_0n^1 \qquad\quad ^{14}_{6}C \quad {}_1p^1$$

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C-14 underoges

$$^{14}_{6}C \qquad\quad ^{14}_{7}N$$

The half-life period of ^{14}C is 5770 yr.

The decay constant ( ) can be calculated by using the following formula $\frac{0.693}{t_{1/2}}$.

The comparison of the activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 yr. The proportion of ^{14}C to ^{12}C in living matter is 1 : 10^{12}. **(2006, 3 4M = 12M)**

48. Which of the following option is correct?

(a) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism

(b) Carbon dating can be used to find out the age of earth crust and rocks

(c) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbons content remains constant in living organisms

(d) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings

49. What should be the age of fossil for meaningful determination of its age?

(a) 6 yr

(b) 6000 yr

(c) 60,000 yr

(d) It can be used to calculate any age

50. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

(a) the age of fossil will increase at the place where explosion has taken place and $T_1 \quad T_2 \quad \frac{1}{\ } \ln \frac{C_1}{C_2}$

(b) the age of fossil will decrease at the place where explosion has taken place and $T_1 \quad T_2 \quad \frac{1}{\ } \ln \frac{C_1}{C_2}$

(c) the age of fossil will be determined to be the same

(d) $\frac{T_1}{T_2} \quad \frac{C_1}{C_2}$

Fill in the Blanks

51. In Arrhenius equation, $k \quad A\exp^{(\ E_a/RT)}$. A may be termed as the rate constant at .... **(1997, 1M)**

52. For the reaction : $N_2(g) + 3H_2(g) \qquad 2NH_3(g)$

Under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg/h ^{1}. The rate of conversion of H_2 under the same condition is .... kg/h ^{1}. **(1994, 1M)**

53. The hydrolysis of ethyl acetate in .... medium is a .... order reaction. **(1986, 1M)**

54. The rate of chemical change is directly proportional to .... **(1985, 1M)**

True/False

55. For a first order reaction, the rate of the reaction doubles as the concentration of the reaction (s) doubles. **(1986, 1M)**

Integer Answer Type Questions

56. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]}$ 10 ? ($\log_{10} 2$ 0.3) **(2012)**

57. The concentration of R in the reaction R P was measured as a function of time and the following data is obtained :

$[R]$ (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is **(2010)**

Subjective Questions

58. $2X(g)$ $3Y(g)$ $2Z(g)$

Time (in min)	0	100	200
Partial pressure of ***X*** (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate
(a) order of reaction
(b) rate constant
(c) time taken for 75% completion of reaction
(d) total pressure when p_x 700 mm **(2005, 4M)**

59. For the given reaction, A B Products

Following data are given

Initial conc. (m/L) $[A]_0$	Initial conc. (m/L) $[B]_0$	Initial rate [$mL^{-1}s^{-1}$]
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) Write the rate equation.
(b) Calculate the rate constant. **(2004, 2M)**

60. ^{64}Cu (half-life = 12.8 h) decays by emission (38%), emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. **(2002)**

61. The rate of first order reaction is 0.04 mol $L^{-1}s^{-1}$ at 10 min and 0.03 mol $L^{-1}s^{-1}$ at 20 min after initiation. Find the half-life of the reaction. **(2001, 5M)**

62. A hydrogenation reaction is carried out at 500 K .If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol ^{1}. **(2000, 3M)**

63. The rate constant for an isomerisation reaction, A B is 4.5 10^{3}min. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. **(1999, 4M)**

64. (i) The rate constant of a reaction is 1.5 10^7 s ^{1} at 50 C and 4.5 10^7 s ^{1} at 100 C. Evaluate the Arrhenius parameters A and E_a. **(1998, 5M)**

(ii) For the reaction, $N_2O_5(g)$ $2NO_2(g) + \frac{1}{2}O_2(g)$, calculate the mole fraction $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

65. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log k(\mathrm{s}^{\ 1}) \quad 14.34 \quad \frac{1.25 \quad 10^4\ \mathrm{K}}{T}$$

(i) What is the energy of activation for the reaction?
(ii) At what temperature will its half-life period be 256 min? **(1997, 5M)**

66. One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half-life of 28.1 yr. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 yr. **(1995, 2M)**

67. At 380 C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol ^{1}. Calculate the time required for 75% decomposition at 450 C. **(1995, 4M)**

68. From the following data for the reaction between A and B

[*A*], (mol/L)	**[*B*]**, (mol/L)	**Initial rate** (mol $L^{-1}s^{-1}$) at 300 K	320 K
2.5 10^{4}	3.0 10^{5}	5.0 10^{4}	2.0 10^{3}
5.0 10^{4}	6.0 10^{5}	4.0 10^{3}	—
1.0 10^{3}	6.0 10^{5}	1.6 10^{2}	—

Calculate

(i) the order of the reaction with respect to A and with respect to B.
(ii) the rate constant at 300 K.
(iii) the pre-exponential factor. **(1994, 5M)**

69. The gas phase decomposition of dimethyl ether follows first order kinetics

$$CH_3—O—CH_3(g) \qquad CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500 C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour. **(1993, 4M)**

70. A first order reaction, $A \quad B$, requires activation energy of 70 kJ mol ^{1}. When a 20% solution of A was kept at 25 C for 20 min, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature. **(1993, 4M)**

71. Two reactions (i) $A \quad$ products (ii) $B \quad$ products, follow first order kinetics.The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K. **(1992, 3M)**

72. The nucleidic ratio, ${}^3_1H$ to ${}^1_1H$ in a sample of water is $8.0 \quad 10^{18}$: 1. Tritium undergoes decay with a half-life period of 12.3 yr. How many tritium atoms would 10.0 g of such a sample contain 40 yr after the original sample is collected. **(1992, 4M)**

73. The decomposition of N_2O_5 according to the equation,

$$2N_2O_5(g) \qquad 4NO_2(g) + O_2(g)$$

is a first order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg. On complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. **(1991, 6M)**

74. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \quad 10^{13}$ s ^{1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 10 min? **(1990, 3M)**

75. An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of ${}_{42}Mo^{99}$, which is a beta emitter, is 66.6 h. Find the minimum amount of ${}_{42}Mo^{99}$ required to carry out the experiment in 6.909 h. **(1989, 5M)**

76. A first order gas reaction has $k \quad 1.5 \quad 10^{6}$ per second at 200 C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction? **(1987, 5M)**

77. While studying the decomposition of gaseous N_2O_5, it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What kinetic parameters can be obtained from this observation? **(1985, 2M)**

78. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr ^{1}) for the decay? What fraction would remain after 11540 yr? **(1984, 3M)**

79. A first order reaction is 20% complete in 10 min. Calculate
(i) the specific rate constant of the reaction, and
(ii) the time taken for the reaction to go to 75% completion. **(1983, 2M)**

80. Rate of reaction, $A \quad B \quad$ products is given below as a function of different initial concentrations of A and B

[A] mol/L	**[B]** (mol/L)	**Initial rate** (mol L^{-1} min^{-1})
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and B. What is the half-life of A in the reaction ? **(1982, 4M)**

Answers

1. (b) **2.** (c) **3.** (d) **4.** (a)
5. (d) **6.** (d) **7.** (b) **8.** (a)
9. (c) **10.** (d) **11.** (b) **12.** (d)
13. (c) **14.** (b) **15.** (c) **16.** (b)
17. (a) **18.** (a) **19.** (d) **20.** (a)
21. (a) **22.** (b) **23.** (d) **24.** (d)
25. (a) **26.** (a) **27.** (d) **28.** (a)
29. (d) **30.** (d) **31.** (a) **32.** (c)
33. (a) **34.** (d) **35.** (d) **36.** (d)
37. (c) **38.** (d) **39.** (a) **40.** (a,d)
41. (a,c) **42.** (b,c,d) **43.** (a,b,d) **44.** (a,b,d)
45. (a,d) **46.** (b,c) **47.** (+8500J/ mol)
48. (c) **49.** (b) **50.** (a) **51.** T
52. 0.0015 **53.** acidic first or basic, second
54. concentration of reactant(s) at that instant
55. T **56.** (9) **57.** (0)
58. (960 mm Hg) **61.** (25 min) **62.** (100 kJ mol ^{1})
63. ($3.26 \quad 10^{3}$ mol L ^{1} min ^{1}) **66.** ($6.1 \quad 10^{7}$ g)
67. (20.74 min) **69.** (0.75 atm) **70.** (67 %)
71. ($3.26 \quad 10^{2}$ min ^{1}) **72.** ($5.6 \quad 10^{5}$)
73. ($5.2 \quad 10^{3}$ min ^{1}) **74.** (311.34 K)
75. ($3.56 \quad 10^{16}$ g) **78.** (0.25)
80. (1.386 min)

Hints & Solutions

1.

> **Key Idea** The rate of a chemical reaction means the speed with which the reaction takes place.
> For $R \quad P$
> Rate of disappearance of R
> $$\frac{\text{Decrease in conc. of } R}{\text{Time taken}} \quad \frac{[R]}{t}$$
> Rate of appearance of P
> $$\frac{\text{Increase in conc. of } P}{\text{Time taken}} \quad \frac{[P]}{t}$$

Given, $[N_2O_5]_{\text{initial}} \quad 3.00 \text{ mol L}^{\ 1}$

After 30 min, $[N_2O_5] \quad 2.75 \text{ mol L}^{\ 1}$

$$2N_2O_5(g) \qquad 4NO_2(g) \quad O_2(g)$$

$t \quad 0 \qquad 3.0\text{ M}$

$t \quad 30 \qquad 2.75\text{ M}$

From the equation, it can be concluded that

$$\frac{1}{2} \quad \frac{[N_2O_5]}{t} \quad \frac{1}{4} \quad \frac{[NO_2]}{t}$$

$$\frac{[N_2O_5]}{t} \quad \frac{(2.75 \quad 3.00)\text{ mol L}^{\ 1}}{30} \quad \frac{0.25}{30}$$

and $$\frac{[NO_2]}{t} \quad 2\frac{(N_2O_5)}{t} \qquad \frac{[NO_2]}{t} \quad 2 \quad \frac{0.25}{30}$$

$$1.667 \quad 10^{\ 2} \text{ mol L}^{\ 1} \text{ min}^{\ 1}$$

2. In the given reaction; $x\ A \qquad y\ B$

$$\log_{10} \frac{d[A]}{dt} \quad \log_{10} \frac{d[B]}{dt} \quad 0.3010$$

Value of $\log 2 \quad 0.3010$

Substituting 0.3010 by $\log 2$

$$\log_{10} \frac{d[A]}{dt} \quad \log_{10} \frac{d[B]}{dt} \quad \log 2$$

Using logarithm rules,

$$\frac{d[A]}{dt} \quad 2 \quad \frac{d[B]}{dt} \qquad \frac{1}{2} \quad \frac{d[A]}{dt} \qquad \frac{d[B]}{dt} \qquad \ldots\text{(i)}$$

Using the rate equation (i) to determine the reaction involved is

$$2A \qquad B$$

Option that fits correct in the above reaction is (c).

$$2C_2H_4 \qquad C_4H_8.$$

3.

> **Key Idea** The Arrhenius equation for rate constants at two different temperatures is
> $$\log \frac{k_2}{k_1} \quad \frac{E_a}{2.303R} \quad \frac{T_2 \quad T_1}{T_1T_2} \qquad [\text{where, } T_2 \quad T_1]$$
> where, k_1 and k_2 are rate constants at temperatures T_1 and T_2, respectively.
> R Gas constant, E_a Activation energy

For the reaction, $H_2 + I_2 \qquad 2HI$

Given $k_1 \quad 2.5 \quad 10^{\ 4} \text{ dm}^3 \text{mol}^{\ 1} \text{s}^{\ 1}$

$T_1 \quad (273 \quad 327)\text{ K} \quad 600\text{ K}$

$k_2 \quad 1 \text{ dm}^3 \text{mol}^{\ 1} \text{ s}^{\ 1}$ at $T_2 \quad (273 \quad 527)\text{ K} \quad 800\text{ K}$

Now, $$\log \frac{k_2}{k_1} \quad \frac{E_a}{2.303R} \quad \frac{T_2 \quad T_1}{T_1T_2}$$

$$\log \frac{1}{2.5 \quad 10^{\ 4}} \quad \frac{E_a}{2.303 \quad 8.314 \quad 10^{\ 3}} \quad \frac{800 \quad 600}{600 \quad 800}$$

$$\log \frac{(10 \quad 10^3)}{2.5} \quad \frac{E_a}{0.019} \quad \frac{200}{48 \quad 10^4}$$

$$\log 4 \quad 3\log 10 \sim E_a \quad 0.022$$

$$E_a \quad \frac{2 \quad \log 2 \quad 3}{0.022}$$

$$\frac{3.6}{0.022} \simeq 163.6 \text{ kJ mol}^{\ 1}$$

4. The expression for bacterial growth is

$$N \quad N_0 e^t$$

$$\frac{N_0}{N} \quad e^{\ t}$$

From 0 to 1 hour $N\ (t) \quad N_0 e^t$

From 1 hour onwards, $\dfrac{dN}{dt} \quad 5N^{\ 2}$

On differentiating the above equation from N to N we get.

$$\int_{eN_0}^{N} N^{\ 2} dN \quad 5\int_{1}^{t} dt \qquad [\because \text{At 1 hour, } N \quad eN_0]$$

$$\frac{1}{N} \quad \frac{1}{eN_0} \qquad 5(t \quad 1)$$

Multiply both sides by N_0, we get

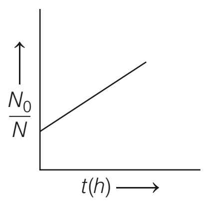
$$\frac{N_0}{N} \quad \frac{1}{e} \qquad 5N_0(t \quad 1) \text{ or, } \frac{N_0}{N} \quad 5N_0(t \quad 1) \quad \frac{1}{e}$$

$$\frac{N_0}{N} \quad 5N_0 t \quad \frac{1}{e} \quad 5N_0$$

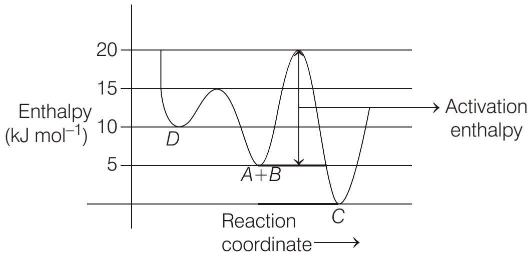
On comparing the above equation with equation of straight line, $y \quad mx \quad c$

We get $m \quad 5N_0,\ c \quad \dfrac{1}{e} \quad 5N_0$

Plot of $\dfrac{N_0}{N}$ vs t is shown aside.



5. Only statement (d) is incorrect. Corrected statement is ''Activation enthalpy to form C is 15 kg mol ^{1} more than 5 kg mol ^{1} that is required to form D.'' It can be easily explained by following graph.



Activation enthalpy (or energy) is the extra energy required by the reactant molecules that result into effective collision between them to form the products.

6. In first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.

$$nR \quad \text{products}$$

$$\frac{d[R]}{dt} \quad k[R]$$

On integration, $\ln[R] \quad kt \quad \ln[R_0]$

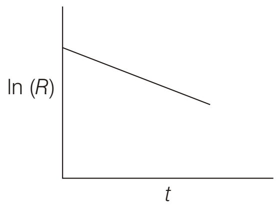
or $\ln(R) \quad \ln(R_0) \quad kt$

$$y \quad c \quad mx$$

$$m \quad \text{slope} \quad k \text{ (negative)}$$

$$c \quad \text{intercept} \quad \ln(r_0)$$

The graph for first order reactions is



In zero order reaction,

$$[R] \quad \text{product}$$

$$\frac{d[R]_t}{dt} \quad k \text{ or } d[R]_t \quad kdt$$

On integrating, $[R]_t \quad kt \quad c$

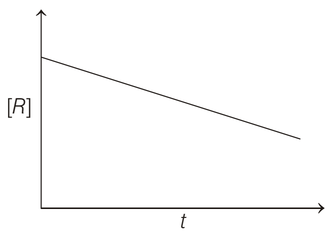
If $t \quad 0, [R]_t \quad [R]_0$

$$[R]_t \quad kt \quad [R]_0$$

$$[R]_t \quad [R]_0 \quad kt$$

Thus, the graph plotted between $[r]_t$ and t gives a straight line with negative slope (k) and intercept equal to $[R]_0$.

The graph for zero order reaction is



7. $A \quad ^{K_1} \quad B \quad ^{K_2} \quad C$

Rate of formation of B is

$$\frac{d[B]}{dt} \quad k_1[A] \quad k_2[B]$$

$$0 \quad k_1[A] \quad k_2[B] \qquad \because \text{Given, } \frac{d[B]}{dt} \quad 0$$

$$k_2[B] \quad k_1[A]$$

Concentration of B, $[B] \quad \frac{k_1}{k_2}[A]$

8. Let the rate equation be $k[A]^x[B]^y$

From Ist values,

$$0.045 \quad k[0.05]^x[0.05]^y \qquad \text{...(i)}$$

From 2nd values,

$$0.090 \quad k[0.10]^x[0.05]^y \qquad \text{...(ii)}$$

From 3rd values,

$$0.72 \quad k[0.20]^x[0.10]^y \qquad \text{...(iii)}$$

On dividing equations (i) by (ii), we get

$$\frac{0.045}{0.09} \quad \frac{0.05}{0.10}^{x}$$

$$\frac{0.05}{0.10}^{1} \quad \frac{0.05}{0.10}^{x}$$

$$x \quad 1$$

Similarly on dividing Eq. (ii) by (iii) we get

$$\frac{0.09}{0.72} \quad \frac{0.1}{0.2}^{x} \quad \frac{0.05}{0.10}^{y}$$

$$\frac{0.01}{0.08} \quad \frac{0.1}{0.2} \quad \frac{0.05}{0.1}^{y}$$

$$0.25 \quad \frac{0.05}{0.10}^{y}$$

$$0.25 \quad [0.5]^y$$

$$[0.5]^2 \quad [0.5]^y$$

$$y \quad 2$$

Hence, the rate law for the reaction

$$\text{Rate} \quad k[A][B]^2$$

9. The temperature dependence of a chemical reaction is expressed by Arrhenius equation,

$$k \quad Ae^{E_a/RT} \qquad \text{...(i)}$$

Taking natural logarithm on both sides, the Arrhenius equation becomes,

$$\ln k \quad \ln A \quad \frac{E_a}{RT}$$

where, $\frac{E_a}{R}$ is the slope of the plot and $\ln A$ gives the intercept.

Eq. (i) at two different temperatures for a reaction becomes,

$$\ln\frac{k_2}{k_1} \quad \frac{E_a}{R} \quad \frac{1}{T_1} \quad \frac{1}{T_2} \qquad \text{...(ii)}$$

In the given problem,

$$T_1 \quad 400\text{K}, T_2 \quad 500\text{K}$$
$$k_1 \quad 10^{\ 5}\text{s}^{\ 1}, k_2 \quad ?$$

$\frac{E_a}{R}$ (Slope) 4606

On substituting all the given values in Eq. (ii), we get

$$\ln \frac{k_2}{10^{\ 5}} \quad 4606 \quad \frac{1}{400} \quad \frac{1}{500}$$

$$\ln \frac{k_2}{10^{\ 5}} \quad 2.303$$

$$\frac{k_2}{10^{\ 5}} \quad 10 \qquad k_2 \quad 10^{\ 4}\text{s}^{\ 1}$$

Therefore, rate constant for the reaction at 500 K is $10^{\ 4}\text{s}^{\ 1}$.

10. Given, rate constant (k) 0.05 g/year

Thus, from the unit of k, it is clear that the reaction is zero order. Now, we know that

half-life ($t_{1/2}$) for zero order reaction $\frac{a_o}{2k}$

where, a_o initial concentration,

k rate constant

$$t_{1/2} \quad \frac{5 \quad \text{g}}{2 \quad 0.05 \quad \text{g / year}} \quad 50 \text{ years}$$

Thus, 50 years are required for the decomposition of 5 g of X into 2.5 g.

11. For zero order reaction,

$$[A_0] \quad [A_t] \quad kt \qquad \text{...(i)}$$

where, $[A_0]$ initial concentration

$[A_t]$ final concentration at time 't'

k rate constant

Also, for zero order reaction, $t_{1/2} \quad \frac{[A_0]}{2k}$

Given, $t_{1/2}$ 6 h and $[A_0]$ 0.2 M

$$6 \quad \frac{0.2}{2k}$$

or, $$k \quad \frac{0.2}{2 \quad 6} \quad \frac{1}{60}$$

Now, from Eq. (i)

$$[A_0] \quad [A_t] \quad kt$$

Given, $[A_0]$ 0.5 M, $[A_t]$ 0.2 M

$$0.5 \quad 0.2 \quad \frac{1}{60} \quad t \qquad \because k \quad \frac{1}{60}$$

$$0.3 \quad \frac{1}{60} \quad t$$

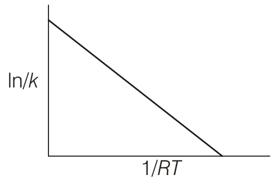
$$t \quad 0.3 \quad 60 \quad 18\text{h}$$

12. The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation as, $k \quad Ae^{\ E \ /RT}$ …(i)

where, A Arrhenius factor or frequency factor or pre-exponential factor

R Gas constant, E_a Activation energy

Taking log on both sides of the Eq. (i), the equation becomes $\ln k \quad \ln A \quad \frac{E_a}{RT}$



On comparing with equation of straight line ($y \quad mx \quad c$), the nature of the plot of ln$k$ vs $\frac{1}{RT}$ will be:

(i) Intercept C $\ln A$

(ii) Slope/gradient m E_a y E_a y

So, the energy required to activate the reactant, (activation energy of the reaction, E_a is y)

13. The elementary reaction, $A_2 \underset{k_{\ 1}}{\overset{k_1}{\rightleftharpoons}} 2A$

follows opposing or reversible kinetics,

(i) Rate of the reaction,

$$r \quad r_{\text{forward}} \quad r_{\text{backward}}$$
$$k_1[A_2] \quad k_{\ 1}[A]^2 \qquad \text{… (i)}$$

(ii) Again, rate of the reaction can be expressed as,

$$r \quad \frac{d[A_2]}{dt} \quad \frac{1}{2}\frac{d[A]}{dt}$$

So, the rate of appearance of A, i.e.

$$\frac{d[A]}{dt} \quad 2r \quad 2k_1[A_2] \quad 2k_{\ 1}[A]^2 \text{ [from Eq. (i)]}$$

14. The Arrhenius equation is,

$$k \quad A.e^{\ E_a/RT}$$

where, k rate constant,

A Arrhenius constant, E_a activation energy,

and T temperature in K

From the equation, it is clear that k decreases exponentially with E_a . So, the plot-I is correct.

In the plot-II, k is plotted with temperature (in °C but not in K). So, at 0°C, k 0 and k will increase exponentially with temperature upto 300°C. Therefore, the plot-II is also correct.

15. For the reaction, $2A \quad B$ products.

Let, the rate expression is

$$r \quad [A]^a[B]^b$$

Expt 1 $\frac{r_2}{r_1} \quad \frac{2A}{A}^{\ a} \quad \frac{2B}{B}^{\ b}$

$$\frac{2.4}{0.3} \quad 2^a \quad 2^b \qquad 2^3 \quad 2^{a \ b}$$

$$3 \quad a \quad b \qquad \text{… (i)}$$

Expt 2 $\frac{r_2}{r_1} \quad \frac{2A}{A}^{\ a} \quad \frac{B}{B}^{\ b}$

$$\frac{0.6}{0.3} \quad 2^a \quad 1 \qquad 2^1 \quad 2^a \qquad a \quad 1 \qquad \text{…(ii)}$$

From Eq. (i), $1 = b - 3 \Rightarrow b = 2$

Order of the reaction $(n) = a + b = 1 + 2 = 3$

Order of the reaction wrt. $A = 1$

Order of the reaction wrt. $B = 2$

16. Let, the rate expression is $r = [A]^a [B]^b$.

From experiment I,

$$\frac{r_2}{r_1} = \left(\frac{0.1}{0.1}\right)^a \left(\frac{0.25}{0.20}\right)^b$$

$$\frac{6.93 \times 10^{-3}}{6.93 \times 10^{-3}} = 1 \times \left(\frac{5}{4}\right)^b$$

$$1 = \left(\frac{5}{4}\right)^b \Rightarrow \left(\frac{5}{4}\right)^0 = \left(\frac{5}{4}\right)^b \Rightarrow b = 0$$

From experiment II, $\dfrac{r_3}{r_1} = \left(\dfrac{0.2}{0.1}\right)^a \left(\dfrac{0.30}{0.20}\right)^b$

$$\frac{1.386 \times 10^{-2}}{0.693 \times 10^{-2}} = (2)^a \times (1.5)^0$$

$$2 = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1$$

So, $r = [A]^1[B]^0 \Rightarrow r = [A]$

Order of the reaction $(n) = 1$

Now, let for the 1st experiment,

$$r_1 = k\,[A]$$

$$k = \frac{r_1}{[A]} = \frac{6.93 \times 10^{-3}}{0.1} = 6.93 \times 10^{-2}\,\text{s}^{-1}$$

$$t_{50} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-2}} = 10\,\text{s}$$

17. From thermodynamics,

$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{...(i)}$$

Mathematically, the equation of straight line is

$$y = c + mx \quad \text{...(ii)}$$

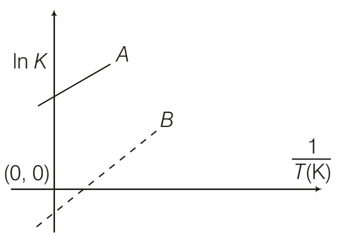
After comparing Eq. (ii) with (i) we get,

slope $= -\dfrac{\Delta H}{R}$ and intercept $= \dfrac{\Delta S}{R}$

Now, we know for exothermic reaction ΔH is negative $(-)$ve. But here,

$$\text{Slope} = -\frac{\Delta H}{R} \text{ is positive}$$

So, lines A and B in the graph represent temperature dependence of equilibrium constant K for an exothermic reaction as shown below



18. For the reaction,

$$CH_3CHO(g) \xrightarrow{\text{Decomposes}} CH_4 + CO$$

Let order of reaction with respect to CH_3CHO is m.

Its given, $r_1 = 1$ torr/sec. when CH_3CHO is 5% reacted i.e. 95% unreacted. Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted i.e., 67% unreacted.

Use the formula, $r = (a - x)^m$

where $(a - x) =$ amount unreacted

so, $\dfrac{r_1}{r_2} = \dfrac{(a - x_1)^m}{(a - x_2)^m}$ or $\dfrac{r_1}{r_2} = \left(\dfrac{a - x_1}{a - x_2}\right)^m$

Now putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m \Rightarrow 2 = (1.41)^m \text{ or } m = 2$$

19. According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where, $A =$ collision number or pre-exponential factor.

$R =$ gas constant

$T =$ absolute temperature

$E_a =$ energy of activation

For reaction R_1, $k_1 = Ae^{-E_{a_1}/RT}$ ...(i)

For reaction R_2, $k_2 = Ae^{-E_{a_2}/RT}$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{-\frac{(E_{a_2} - E_{a_1})}{RT}} \quad \text{...(iii)}$$

[$\because$ Pre-exponential factor 'A' is same for both reactions]

Taking ln on both the sides of Eq. (iii), we get

$$\ln\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{RT}$$

Given, $E_{a_1} = E_{a_2} + 10\,\text{kJ mol}^{-1} \Rightarrow E_{a_2} + 10{,}000\,\text{J mol}^{-1}$

$$\ln\frac{k_2}{k_1} = \frac{10{,}000\,\text{J mol}^{-1}}{8.314\,\text{J mol}^{-1}\text{K}^{-1} \times 300\,\text{K}} = 4$$

20. For first order reaction, $k = \dfrac{2.303}{t}\log\dfrac{a}{a - x}$

Given, $t = 50$ min, $a = 0.5$ M, $a - x = 0.125$ M

$$k = \frac{2.303}{50}\log\frac{0.5}{0.125} = 0.0277\,\text{min}^{-1}$$

Now, as per reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

Rate of reaction, $-\dfrac{d[H_2O_2]}{dt} = k[H_2O_2]$

$$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}k[H_2O_2] \quad \text{...(i)}$$

When the concentration of H_2O_2 reaches 0.05 M,

$$\frac{d[O_2]}{dt} \quad \frac{1}{2} \quad 0.0277 \quad 0.05 \qquad \text{[from Eq. (i)]}$$

or $$\frac{d[O_2]}{dt} \quad 6.93 \quad 10^{\,4} \text{ mol min}^{\,1}$$

Alternative Method

In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M or in one half-life, concentration of H_2O_2 decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2}$ 50 min

$$t_{1/2} \quad 25 \text{ min}$$

$$k \quad \frac{0.693}{25} \quad \text{min}^{\,1}$$

or $$\frac{d[O_2]}{dt} \quad \frac{1}{2}\frac{d[H_2O_2]}{dt} \quad \frac{k[H_2O_2]}{2} \quad 6.93 \quad 10^{\,4} \text{ mol min}^{\,1}$$

21. The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants.

Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.

22. For the elementary reaction, $M \qquad N$

Rate law can be written as

$$\text{Rate} \quad [M]^n$$

$$\text{Rate} \quad k[M]^n \qquad \ldots\text{(i)}$$

When we double the concentration of $[M]$,

rate becomes 8 times, hence new rate law can be written as

$$8 \quad \text{Rate} \quad k[2M]^n \qquad \ldots\text{(ii)}$$

$$\frac{\text{Rate}}{8 \quad \text{Rate}} \quad \frac{k[M]^n}{k[2M]^n} \quad \frac{1}{8} \quad \frac{1}{[2]^n}$$

$$[2]^n \quad 8 \quad [2]^3 \qquad n \quad 3$$

23. This problem can be solved by determining the order of reaction w.r.t. each reactant and then writing rate law equation of the given equation accordingly as

$$R = \frac{dC}{dt} = k[A]^x[B]^y$$

where, x order of reaction w.r.t A

y order of reaction w.r.t B

$$1.2 \quad 10^{\,3} \quad k(0.1)^x(0.1)^y$$

$$1.2 \quad 10^{\,3} \quad k(0.1)^x(0.2)^y$$

$$2.4 \quad 10^{\,3} \quad k(0.2)^x(0.1)^y$$

$$R = k[A]^1[B]^0$$

As shown above, rate of reaction remains constant as the concentration of reactant (B) changes from 0.1 M to 0.2 M and becomes double when concentration of A change from 0.1 to 0.2, (i.e. doubled).

24. PLAN Time of 75% reaction is twice the time taken for 50% reaction if it is first order reaction w.r.t. P. From graph, $[Q]$ decreases linearly with time, thus it is zeroth order reaction w.r.t. Q

$$\frac{dx}{dt} \quad bk[P]^a[Q]^b$$

Order w.r.t $P \quad a \quad 1$

Order w.r.t $Q \quad b \quad 0$

Thus, overall order of the reaction $1 \quad 0 \quad 1$

25. From Arrhenius equation, $\log \frac{k_2}{k_1} \quad \frac{E_a}{2.303\,R} \quad \frac{1}{T_2} \quad \frac{1}{T_1}$

Given, $$\frac{k_2}{k_1} \quad 2 \; T_2 \quad 310 \text{ K}$$

$$T_1 \quad 300 \text{ K}$$

On putting values,

$$\log 2 \quad \frac{E_a}{2.303 \quad 8.314} \quad \frac{1}{310} \quad \frac{1}{300}$$

$$E_a \quad 53.603 \text{ kJ/mol}$$

26. According to Arrehnius equation, rate constant increases exponentially with temperature :

$$k \quad Ae^{\,E_a/RT}$$

27. The logarithmic form of Arrhenius equation is

$$\log k \quad \log A \quad \frac{E_a}{2.303\,RT}$$

Given : $$\log k \quad 6 \quad \frac{2000}{T}$$

Comparing the above two equations :

$$\log A \quad 6 \qquad A \quad 10^6$$

and $$\frac{E_a}{2.303R} \quad 2000$$

$$E_a \quad 2000 \quad 2.303 \quad 8.314 \text{ J}$$

$$38.3 \text{ kJ} \quad \text{mol}^{\,1}$$

28. For first order reaction $t_{1/2} \quad \frac{\ln 2}{k_1} \quad 40\text{s} \qquad \ldots\text{(i)}$

For zero order reaction $t_{1/2} \quad \frac{[A]_0}{2k_0} \quad 20\text{s} \qquad \ldots\text{(ii)}$

Eq. (ii)/(i) $$\frac{1}{2} \quad \frac{[A]_0}{2k_0} \quad \frac{k_1}{\ln 2}$$

$$\frac{k_1}{k_0} \quad \frac{\ln 2}{[A]_0} \quad \frac{0.693}{1.386} \quad 0.5$$

29. Rate $[G]^m[H]^n$

$\because$ Rate is double on doubling the concentration of G and maintaining H constant, m 1, i.e. $R \quad [G]$.

Also, when both concentration of G and H are doubled, rate increases by a factor of 8. Here rate is increasing by a factor of 2 due to G (first order in G), therefore, factor due to H is 4.

$$R \quad [H]^2$$

$$\text{Overall order} \quad m \quad n \quad 1 \quad 2 \quad 3$$

30. Order of a reaction can take any real value, i.e. negative, integer, fraction etc.

31. For first order reaction,

$$k \quad \frac{2.303}{t} \quad \log\frac{a}{a \quad x} \quad \frac{2.303}{40} \log\frac{0.1}{0.025} \quad 3.46 \quad 10^{\,2}$$

Rate $[k]\,A \quad 3.46 \quad 10^{\,2} \quad 0.01 \quad 3.46 \quad 10^{\,4}$

32. For a first order reaction, $kt \quad \ln\frac{[A]_0}{[A]}$

$$k \quad \frac{1}{t}\ln\frac{[A]_0}{[A]} \quad \frac{1}{2 \quad 10^4}\ln\frac{800}{50} \quad \frac{4\ln 2}{2 \quad 10^4}\ \text{s}^{\ \ 1}$$

$$1.386 \quad 10^{\ \ 4}\ \text{s}^{\ \ 1}$$

33. For any general reaction,

$$aA \quad bB \qquad cC \quad dD$$

$$\text{Rate} \quad \frac{1}{a}\frac{d[A]}{dt} \quad \frac{1}{b}\frac{d[B]}{dt}$$

$$\frac{1}{c}\frac{d[C]}{dt} \quad \frac{1}{d}\frac{d[D]}{dt}$$

For $\quad N_2 + 3H_2 \qquad 2NH_3$

$$\text{Rate} \quad \frac{d[N_2]}{dt} \quad \frac{1}{3}\frac{d[H_2]}{dt} \quad \frac{1}{2}\frac{d[NH_3]}{dt}$$

34. Rate will be directly proportional to both concentration and intensity, i.e. rate of formation of $AB^* \quad C \ I$.

35. The unit of rate constant ($t^{\ \ 1}$) indicating that the decomposition reaction following first order kinetics.

$$\text{Rate} \quad k[N_2O_5]$$

$$[N_2O_5] \quad \frac{\text{Rate}}{k} \quad \frac{2.40 \quad 10^{\ \ 5}}{3 \quad 10^{\ \ 5}} \quad 0.8\,\text{M}$$

36. 560 days $\quad \frac{560}{140} \quad$ 4 half-lives.

Amount of reactant remaining after n-half-lives

$$\frac{1}{2}^{\ n} \quad \text{initial amount} \quad \frac{1}{2}^{\ 4} \quad 1.0\ \text{g} \quad \frac{1}{16}\ \text{g}$$

37. A catalyst increases the rate of reaction but by the same factor to both forward and backward directions. Hence, a catalyst shorten the time required to reach the equilibrium.

38. Specific rate constant of reaction depends on temperature.

39. The rate constant (k) of all chemical reactions depends on temperature.

$$k \quad Ae^{\ \ E_a/RT}$$

where, A pre-exponential factor, E_a activation energy.

40. Given for the reaction (at T= 300 K and constant volume = V)

		$A(g)$		$2B(g)$	$C(g)$
at t	0	p_0		–	–
at t	t	$p_0 \quad x$		$2x$	x
at t	$t_{1/3}$	$p_0 \quad \frac{2p_0}{3}$	$\frac{p_0}{3}$	$\frac{4p_0}{3}$	$\frac{2p_0}{3}$

We can calculate,

$$p_t \quad p_0 \quad x \quad 2x \quad x \quad p_0 \quad 2x$$

or $\qquad 2x \quad p_t \quad p_0 \quad$ or $\quad x \quad \frac{p_t \quad p_0}{2}$

Now for first order reaction,

$$t \quad \frac{1}{k}\ln\frac{p_0}{(p_0 \quad x)}$$

Putting the value of x in the equation,

$$t \quad \frac{1}{k}\ln\frac{p_0}{p_0 \quad \frac{p_t \quad p_0}{2}} \quad \frac{1}{k}\ln\frac{2p_0}{2p_0 \quad p_t \quad p_0}$$

or $kt \quad \ln\frac{2p_0}{(3p_0 \quad p_t)}$

or $\qquad kt \quad \ln 2p_0 \quad \ln(3p_0 \quad p_t)$

or $\qquad \ln(3p_0 \quad p_t) \quad kt \quad \ln 2\,p_0$

It indicates graph between ln $(3p_0 \quad p_t)$ *vs* 't' will be a straight line with negative slope , so option (a) is correct

$$t_{1/3} \quad \frac{1}{k}\ln\frac{p_0}{p_0/3} = \frac{1}{k}\ln 3$$

It indicates $t_{1/3}$ is independent of initial concentration so, option (b) is incorrect.

Likewise, rate constant also does not show its dependence over initial concentration. Thus, graph between rate constant and $[A]_0$ will be a straight line parallel to X-axis.

41. If steric factor is considered, the corrected Arrhenius equation will be

$k \quad pAe^{\frac{E_a}{RT}}$ where A frequency factor by Arrhenius.

$\because\ p \quad 1, pA \quad A$ hence, (a) is correct.

Activation energy is not related to steric factor.

42. Rate constant, $\qquad k \quad Ae^{\ \ E_a/RT}$

where, E_a activation energy and A pre-exponential factor

(a) If E_a is high, it means lower value of k hence, slow reaction. Thus, incorrect.

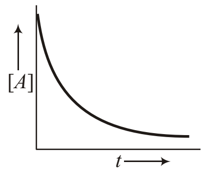
(b) On increasing temperature, molecules are raised to higher energy (greater than E_a), hence number of collisions increases. Thus, correct.

(c) $\log k \quad \log A \quad \frac{E_a}{RT} \qquad \frac{d(\log k)}{dT} \quad \frac{E_a}{RT^2}$

Thus, when E_a is high, stronger is the temperature dependence of the rate constant. Thus, correct.

(d) Pre-exponential factor (A) is a measure of rate at which collisions occur. Thus, correct.

43. (a) For a first order reaction, the concentration of reactant remaining after time t is given by $[A] = [A]_0 e^{-kt}$ Therefore, concentration of reactant decreases exponentially with time.



(b) Rise in temperature increases rate constant (k) and therefore decreases half-life ($t_{1/2}$) as

$$t_{1/2} \quad \frac{\ln 2}{k}$$

(c) Half-life of first order reaction is independent of initial concentration.

(d) For a first order reaction, if 100 moles of reactant is taken initially, after n half-lives, reactant remaining is given by

$$\%A = 100 \quad \frac{1}{2}^{\ n} \quad 100 \quad \frac{1}{2}^{\ 8} \quad 0.3906$$

A reacted $\quad 100 - 0.3906 = 99.6\%$

44. Equilibrium constant is related to temperature

$$\log K_p \quad \text{constant} \quad \frac{H}{2.3\,RT}$$

Plot of $\log K_p$ *vs* $1/T$ will be a straight line.
For the first order reaction $X \quad P$

$$\log \frac{[X]_0}{[X]} \quad \frac{kt}{2.3} \qquad \log[X] \quad \log[X_0] \quad \frac{kt}{2.3},$$

i.e. $\log[X]$ *vs* 't' will give a straight line.
Also at constant temperature, pV constant

Plot of p *vs* $\frac{}{V}$ will give a straight line.

45. For a first order reaction :

$$kt \quad \ln \frac{1}{1} \qquad \text{where,} \qquad \text{degree of dissociation.}$$

$$1 \qquad e^{\;kt} \qquad 1 \quad e^{\;kt}$$

Also $\frac{1}{[A]} \quad \frac{e^{kt}}{[A]_0}$, i.e. plot of reciprocal of concentration of reactant *vs* time will be exponential.

Time for 75% $\frac{1}{k} \ln \frac{100}{100 \quad 75} \quad \frac{2 \ln 2}{k} \quad 2\,(t_{1/2})$

The Arrhenius equation is :

$$\ln k \quad \ln A \quad \frac{E_a}{RT}$$

The dimensions of k and A must be same. For first order reaction, dimensions of k is $t^{\;\;1}$.

46. A catalyst lowers the activation energy by enabling the reaction to continue through an alternative path, i.e. catalyst changes the reaction mechanism. However, catalyst does not affect either average kinetic energies of reactants or the collision frequency.

47. For the reaction,

$$A(g) \quad B(g) \rightleftharpoons AB(g)$$

Given $\quad E_{a_b} \quad E_{a_f} \quad 2RT \quad \text{or} \quad E_{a_b} \quad E_{a_f} \quad 2RT$
Further

$$A_f \quad 4A_b \quad \text{or} \quad \frac{A_f}{A_b} \quad 4$$

Now, rate constant for forward reaction,

$$k_f \quad A_f e^{\;E_{a_f}/RT}$$

Likewise, rate constant for backward reaction,

$$k_b \quad A_b e^{\;E_{a_b}/RT}$$

At equilibrium,
Rate of forward reaction Rate of backward reaction

i.e., $\quad k_f \quad k_b \quad \text{or} \quad \frac{k_f}{k_b} \quad k_{eq}$

so $\quad k_{eq} \quad \frac{A_f e^{\;E_{a_f}/RT}}{A_b e^{\;E_{a_b}/RT}} \quad \frac{A_f}{A_b} e^{\;(E_{a_f} \quad E_{a_b})/RT}$

After putting the given values

$$k_{eq} \quad 4e^2 \quad (\text{as } E_{a_b} \quad E_{a_f} \quad 2RT \text{ and } \frac{A_f}{A_b} \quad 4)$$

Now, $\quad G \quad RT \ln K_{eq} \quad 2500 \ln(4e^2)$

$$2500\,(\ln 4 \quad \ln e^2) \quad 2500\,(1.4 \quad 2)$$

$$2500 \quad 3.4 \quad 8500\ \text{J/mol}$$

Absolute value 8500 J/mol

48. Living plants maintain an equilibrium between the absorption of C^{14} (produced due to cosmic radiation) and the rate of decay of C^{14} present inside the plant. This gives a constant amount of C^{14} per gram of carbon in a living plant.

49. Fossil whose age is closest to half-life of C-14 (5770 yr) will yield the most accurate age by C-14 dating.

50. $T \quad \ln \frac{N_0}{N}$

where N_0 Number of C^{14} in the living matter and N Number of C^{14} in fossil. Due to nuclear explosion, amount of C^{14} in the near by area increases. This will increase N_0 because living plants are still taking C-14 from atmosphere, during photosynthesis, but N will not change because fossil will not be doing photosynthesis.

T (age) determined in the area where nuclear explosion has occurred will be greater than the same determined in normal area.

Also, $\quad T_1 \quad \ln \frac{C_1}{C} \qquad T_2 \quad \ln \frac{C_2}{C} \qquad T_1 \quad T_2 \quad \frac{1}{} \quad \ln \frac{C_1}{C_2}$

C Concentration of C-14 in fossil.

51. $k \quad A e^{\;E_a/RT}$: At $T \quad , k \quad A$

52. $\frac{1}{3} \frac{d[H_2]}{dt} \quad \frac{1}{2} \frac{d[NH_3]}{dt}$

$$\frac{d[H_2]}{dt} \quad \frac{3}{2} \frac{d[NH_3]}{dt} \quad \frac{3}{2} \quad 0.001 \quad 0.0015\ \text{kg h}^{\;\;1}.$$

53. acidic, first or basic, second.

54. Rate is directly proportional to concentration of reactants.

55. $R \quad$ [Reactant]

On doubling the concentration of reactant, rate would be double.

56. For a first order process $\quad kt \quad \ln \frac{[A]_0}{[A]}$

where, $[A]_0$ initial concentration.
$[A]$ concentration of reactant remaining at time "t".

$$kt_{1/8} \quad \ln \frac{[A]_0}{[A]_0/8} \quad \ln 8 \qquad \ldots\text{(i)}$$

and $\quad kt_{1/10} \quad \ln \frac{[A]_0}{[A]_0/10} \quad \ln 10 \qquad \ldots\text{(ii)}$

Therefore, $\quad \frac{t_{1/8}}{t_{1/10}} \quad \frac{\ln 8}{\ln 10} \quad \log 8 \quad 3 \log 2 \quad 3 \quad 0.3 \quad 0.9$

$$\frac{t_{1/8}}{t_{1/10}} \quad 10 \quad 0.9 \quad 10 \quad 9$$

57. Rate of reaction is constant with time.

58. (a) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

(b) $k \quad 100 \quad \ln \frac{800}{400} \quad \ln 2 \qquad k \quad 6.93 \quad 10^{\;3}\ \text{min}^{\;\;1}$

(c) For 75% reaction; time required 2 half-life 200 min

(d) $2X\ (g) \qquad 3Y\ (g) \qquad 2Z\ (g)$

$$800 \quad x \qquad \frac{3}{2}x \qquad x$$

$$\text{Total pressure} \quad 800 \quad \frac{3}{2}x$$

$$\text{Also } 800 \quad x \quad 700 \qquad x \quad 100$$

$$\text{Total pressure} \quad 800 \quad \frac{3}{2} \quad 100 \quad 950 \text{ mm Hg}$$

59. $\dfrac{(\text{Rate})_1}{(\text{Rate})_2} \quad \dfrac{0.05}{0.10} \quad \dfrac{1}{2} \quad \left(\dfrac{1}{2}\right)^a \qquad a \quad 1;$ order w.r.t A.

Order w.r.t B 0

(a) Rate $k\,[A]$

(b) $k \quad \dfrac{\text{Rate}}{[A]} \quad \dfrac{0.05}{0.10} \quad 0.5 \text{ s}^{1}$

60.

$$_{29}\text{Cu}^{64} \xrightarrow[k_1]{38\%} {}_{1}^{0} \quad {}_{30}\text{Zn}^{64}$$

$$_{29}\text{Cu}^{64} \xrightarrow[k_2]{19\%} {}_{1}^{0} \quad {}_{28}\text{Ni}^{64}$$

$$_{29}\text{Cu}^{64} \quad {}_{1}e^{0} \xrightarrow[k_3]{43\%} {}_{28}\text{Ni}^{64}$$

Above are the parallel reactions occurring from Cu^{64}.

$$\frac{k_1}{k_2} \quad \frac{38}{19} \quad 2 \quad \frac{T_2}{T_1} \quad \text{and} \quad \frac{k_1}{k_3} \quad \frac{38}{43} \quad \frac{T_3}{T_1}$$

T_1, T_2 and T_3 are the corresponding partial half-lives.

Also
$$k \quad k_1 \quad k_2 \quad k_3$$

$$\frac{\ln 2}{T} \quad \frac{\ln 2}{T_1} \quad \frac{\ln 2}{T_2} \quad \frac{\ln 3}{T_3}$$

$$\frac{1}{T} \quad \frac{1}{T_1} \quad \frac{1}{T_2} \quad \frac{1}{T_3} \quad \frac{1}{T_1} \quad \frac{1}{2T_1} \quad \frac{43}{38T_1}$$

$$\frac{1}{T_1}\left(1 \quad \frac{1}{2} \quad \frac{43}{38}\right)$$

$$\frac{1}{T_1}\left(\frac{38 \quad 19 \quad 43}{38}\right) \quad \frac{100}{38T_1}$$

$$T_1 \quad \frac{100T}{38} \quad \frac{100}{38} \quad 12.8 \quad 33.68 \text{ h}$$

$$T_2 \quad 2T_1 \quad 67.36 \text{ h}$$

$$T_3 \quad \frac{38T_1}{43} \quad \frac{38 \quad 33.68}{43} \quad 29.76 \text{ h}$$

61.
$$R \quad k\,[A]$$

$$R_1 \quad k\,[A]_1 \quad \text{and} \quad R_2 \quad k\,[A]_2$$

$$\frac{R_1}{R_2} \quad \frac{4}{3} \quad \frac{[A]_1}{[A]_2}$$

$$\text{Also} \qquad k\,(t_2 \quad t_1) \quad \ln\frac{[A]_1}{[A]_2} \quad \ln\frac{4}{3}$$

$$\frac{\ln 2}{t_{1/2}} \quad 10 \quad \ln\frac{4}{3}$$

$$t_{1/2} \quad \frac{10 \log 3}{\log 4 \quad \log 3} \quad \frac{3}{0.6 \quad 0.48} \quad 25 \text{ min}$$

62. $k_{500} \quad A\,e^{\;E_1/RT_1}$

$$k_{400} \quad A\,e^{\;E_2/RT_2}$$

$$\because \qquad k_{500} \quad k_{400}$$

$$\frac{E_1}{RT_1} \quad \frac{E_2}{RT_2} \qquad \frac{E_2}{E_1} \quad \frac{T_2}{T_1} \quad \frac{400}{500} \quad \frac{4}{5}$$

$$\text{Also} \qquad E_1 \quad E_2 \quad 20000 \text{ J}$$

$$\frac{E_1 \quad 20{,}000}{E_1} \quad \frac{4}{5} \qquad E_1 \quad 100{,}000 \text{ J} \quad 100 \text{ kJ mol}^{1}$$

63.
$$kt \quad \ln\frac{[A]_0}{[A]}$$

$$4.5 \quad 10^{3} \quad 60 \quad \ln\frac{1}{[A]} \qquad [A] \quad 0.76 \text{ M}$$

$$\text{Rate} \quad k\,[A] \quad 4.5 \quad 10^{3} \quad 0.76$$

$$3.42 \quad 10^{3} \text{ mol L}^{1} \text{ min}^{1}$$

64. (i) $\ln\dfrac{k_2}{k_1} \quad \dfrac{E_a}{R}\left(\dfrac{T_2 \quad T_1}{T_1T_2}\right)$

$$\ln\left(\frac{4.5 \quad 10^{7}}{1.5 \quad 10^{7}}\right) \quad \frac{E_a}{8.314}\left(\frac{50}{323 \quad 373}\right)$$

$$E_a \quad 22 \text{ kJ}$$

$$\text{Also} \qquad \ln k \quad \ln A \quad \frac{E_a}{RT}$$

$$\text{At } 50°\text{C}: \ \ln A \quad \ln(1.5 \quad 10^{7}) \quad \frac{22 \quad 1000}{8.314 \quad 323} \quad 8.33$$

$$A \quad 4.15 \quad 10^{3} \text{ s}^{1}$$

(ii) $N_2O_5(g) \qquad 2NO_2(g) + \dfrac{1}{2}O_2(g)$

$$600 \quad p \qquad 2p \qquad p/2$$

$$\text{Total pressure} \quad 960 \quad 600 \quad \frac{3}{2}p \qquad p \quad 240 \text{ mm}$$

Partial pressure of $N_2O_5(g)$ remaining = 600 – 240
= 360 mm

$$\text{Mole fraction} \quad \frac{360}{960} \quad 0.375$$

65. (i) The Arrhenius equation is

$$\log k \quad \log A \quad \frac{E_a}{2.303RT}$$

Comparing with the given equation :

$$1.25 \quad 10^{4} \quad \frac{E_a}{2.303R} \qquad E_a \quad 239.33 \text{ kJ mol}^{1}$$

(ii) When half-life 256 min,

$$k \quad \frac{\ln 2}{t_{1/2}} \quad \frac{0.693}{256 \quad 60} \text{ s}^{1} \quad 4.5 \quad 10^{5} \text{ s}^{1}$$

$$\frac{1.25 \quad 10^{4}}{T} \quad 14.34 - \log 4.5 \quad 10^{5} \quad 16.68$$

$$T \quad \frac{1.25 \quad 10^{4}}{16.68} \quad 669 \text{ K}$$

66.
$$k_t \quad \ln\frac{w_0}{w}$$

$$\frac{\ln 2}{28.1} \quad 20 \quad \ln\frac{10^{6} \text{ g}}{w} \qquad w \quad 6.1 \quad 10^{7} \text{ g}$$

67. For 1st order reaction :

$$k \quad \frac{1}{t_{1/2}}$$

$$\ln \frac{k\ (450\ \ C)}{k\ (380\ \ C)} \quad \ln \frac{t_{1/2}\ (380\ \ C)}{t_{1/2}\ (450\ \ C)} \quad \frac{E_a}{R} \frac{450 \quad 380}{727 \quad 653}$$

$$\ln \frac{360}{t_{1/2}\ (450\ \ C)} \quad \frac{200 \quad 10^3}{8.314} \quad \frac{70}{727 \quad 653} \quad 3.54$$

$$t_{1/2}\ (450°C) \quad 10.37 \text{ min}$$

Time for 75% reaction at 450°C

$$2 \quad t_{1/2} \quad 2 \quad 10.37 \quad 20.74 \text{ min}$$

68. Comparing the data of experiment number 2 and 3 :

$$\frac{R_3}{R_2} \quad \frac{1.6 \quad 10^{\ 2}}{4 \quad 10^{\ 3}} \quad \frac{1.0 \quad 10^{\ 3}}{5 \quad 10^{\ 4}}^{\ m}$$

$$m \quad 2, \text{ order w.r.t. } A$$

Now comparing the data of experiment number 1 and 2 :

$$\frac{R_2}{R_1} \quad \frac{4 \quad 10^{\ 3}}{5 \quad 10^{\ 4}} \quad \frac{5 \quad 10^{\ 4}}{2.5 \quad 10^{\ 4}}^{\ 2} \quad \frac{6.0 \quad 10^{\ 5}}{3.0 \quad 10^{\ 5}}^{\ n}$$

$$8 \quad (2)^2\ (2)^n \qquad n \quad 1, \text{ order w.r.t. } B.$$

(i) Order with respect to A 2, order with respect to B 1.

(ii) At 300 K, $R \quad k\,[A]^2\,[B]$

$$k \quad \frac{R}{[A]^2\,[B]} \quad \frac{5.0 \quad 10^{\ 4}}{(2.5 \quad 10^{\ 4})^2\ (3.0 \quad 10^{\ 5})}$$

$$2.66 \quad 10^8 \text{ s}^{\ 1} \text{ L}^2 \text{ mol}^{\ 2}$$

(iii) From first experiment :

Rate (320 K) $\quad k\ (320 \text{ K})\ (2.5 \quad 10^{\ 4})^2\ (3.0 \quad 10^{\ 5})$

$$k\ (320 \text{ K}) \quad \frac{2 \quad 10^{\ 3}}{(2.5 \quad 10^{\ 4})^2\ (3.0 \quad 10^{\ 5})}$$

$$1.066 \quad 10^9 \text{ s}^{\ 1} \text{ L}^2 \text{ mol}^{\ 2}.$$

$$\ln \frac{k\ (320 \text{ K})}{k\ (300 \text{ K})} \quad \frac{E_a}{R} \frac{T_2 \quad T_1}{T_1 T_2}$$

$$\ln \frac{1.066 \quad 10^9}{2.66 \quad 10^8} \quad \frac{E_a}{8.314} \frac{20}{300 \quad 320}$$

$$E_a \quad 55.42 \text{ kJ mol}^{\ 1}$$

Now $\quad \ln k \quad \ln A \quad \dfrac{E_a}{RT}$

At 300 K : $\ln (2.66 \quad 10^8) \quad \ln A \quad \dfrac{55.42 \quad 10^3}{8.314 \quad 300}$

Solving : $\quad \ln A \quad 41.62 \qquad A \quad 1.2 \quad 10^{18}$

69. $CH_3 \quad O \quad CH_3(g) \qquad CH_4(g) + H_2(g) + CO\ (g)$

At 12 min : $\quad 0.40 \quad p \qquad p \qquad p \qquad p$

Total pressure $\quad 0.4 \quad 2p$

Also $\quad k \quad 12 \quad \ln \dfrac{0.40}{0.40 \quad p} \quad \dfrac{\ln 2}{14.5} \quad 12 \quad 1.77 \qquad p \quad 0.175$

Total pressure $\quad 0.4 + 2p = 0.4 + 2 \quad 0.175 = 0.75$ atm

70. $\ln \dfrac{k\ (40\ \ C)}{k\ (25\ \ C)} \quad \dfrac{E_a}{R} \dfrac{15}{298 \quad 313}$

$$\frac{70 \quad 1000}{8.314} \quad \frac{15}{298 \quad 313} \quad 1.35$$

$$\frac{k\ (40\ \ C)}{k\ (25\ \ C)} \quad 3.87$$

Also $\quad k\ (25°C) \quad \dfrac{1}{20} \ln \dfrac{100}{75} \quad \dfrac{1}{20} \ln \dfrac{4}{3}$

$$k\ (40\ \ C) \quad 3.87 \quad k\ (25°C)$$

$$3.87 \quad \frac{1}{20} \ln \frac{4}{3} \quad 55.66 \quad 10^{\ 3} \text{ min}^{\ 1}$$

Now $\qquad k\ (40°C) \quad 20 \quad \ln \dfrac{100}{100 \quad x}$

$$55.66 \quad 10^{\ 3} \quad 20 \quad \ln \frac{100}{100 \quad x} \qquad x \quad 67\%$$

71. (i) $A \quad \overset{k_A}{} \quad$ Product

(ii) $B \quad \overset{k_B}{} \quad$ Product

For (i) $\qquad \dfrac{E_a}{R} \dfrac{10}{300 \quad 310} \qquad \ln 2$

$$E_a\ \text{(i)} \qquad 9300\ R \ln 2 \quad 53.6 \text{ kJ}$$

$$E_a\ \text{(ii)} \qquad \frac{E_a\ \text{(i)}}{2} \quad 26.8 \text{ kJ}$$

At 310 K $\quad t_{1/2}$ (i) $\quad$ 30 min

$\because \quad$ Rate of (ii) $\qquad$ 2 rate of (i)

$t_{1/2}$ (ii) $\quad$ 15 min

Now for reaction (ii) :

$$\ln \frac{k_B\ (310)}{k_B\ (300)} \quad \ln \frac{t_{1/2}\ (300)}{t_{1/2}\ (310)} \quad \frac{E_a\ \text{(ii)}}{R} \frac{10}{300 \quad 310}$$

$$\ln \frac{t_{1/2}\ (300)}{15} \quad \frac{\ln 2}{2} \qquad t_{1/2}\ (300) \quad 21.2 \text{ min}$$

$$k_B\ (300) \quad \frac{\ln 2}{t_{1/2}} \quad \frac{0.693}{21.2} \quad 3.26 \quad 10^{\ 2} \text{ min}^{\ 1}$$

72. Initially :

$$N\ ({}_1H^3 \quad {}_1H^1) \quad \frac{10}{8} \quad 2 \quad 6 \quad 10^{23} \quad \frac{20}{3} \quad 10^{23}$$

$$1 \quad \frac{N\ ({}_1H^1)}{N\ ({}_1H^3)} \quad \frac{20 \quad 10^{23}}{3N\ ({}_1H^3)}$$

$$1 \quad \frac{1}{8 \quad 10^{\ 18}} \quad \frac{20 \quad 10^{23}}{3N\ ({}_1H^3)} \quad 1.25 \quad 10^{17}$$

$$N\ ({}_1H^3) \quad \frac{20 \quad 10^{23}}{3 \quad 1.25 \quad 10^{17}} \quad 5.33 \quad 10^6$$

$$kt \quad \ln \frac{N_0}{N} \qquad \frac{\ln 2}{12.3} \quad 40 \quad \ln \frac{5.33 \quad 10^6}{N}$$

$$N \quad 5.6 \quad 10^5$$

73. For the reaction :

$$2N_2O_5 \qquad 4NO_2 + O_2$$

If p_0 is the initial pressure, the total pressure after completion of reaction would be $\dfrac{5}{2}\,p_0$.

$$584.5 \quad \frac{5}{2}p_0 \qquad p_0 \quad 233.8 \text{ mm}$$

Let the pressure of N_2O_5 decreases by 'p' amount after 30 min. Therefore,

$$2N_2O_5 \qquad 4NO_2 + O_2$$

At 30 min : $\quad p_0 \quad p \qquad 2p \qquad \frac{p}{2}$

$$\text{Total pressure} \quad p_0 \quad \frac{3}{2}p \quad 284.5$$

$$p \quad \frac{2}{3}(284.5 \quad 233.8) \quad 33.8$$

$$\text{Now,} \qquad kt \quad \ln\frac{p_0}{p_0 \quad p}$$

$$k \quad \frac{1}{30}\ln\frac{233.8}{233.8 \quad 33.8}\text{ min}^{\ 1} \quad 5.2 \quad 10^{\ 3}\text{ min}^{\ 1}$$

74. Arrhenius equation is :

$$\log k \quad \log A \quad \frac{E_a}{2.303\,RT}$$

$$\text{when } t_{1/2} \quad 10 \text{ min, } k \quad \frac{\ln 2}{t_{1/2}} \quad \frac{0.693}{10 \quad 60} \quad 1.115 \quad 10^{\ 3}\text{ s}^{\ 1}$$

$$\frac{E_a}{2.303RT} \quad \log A \quad \log k$$

$$\log\frac{A}{k} \quad \log\frac{4 \quad 10^{13}}{1.115 \quad 10^{\ 3}} = 16.54$$

$$T \quad \frac{E_a}{2.303R \quad 16.54} \quad \frac{98.6 \quad 1000}{2.303 \quad 16.54 \quad 8.314}$$

$$311.34 \text{ K}$$

75. The minimum rate of decay required after 6.909 h is 346 particles min ^{1}.

$$\text{Rate} \quad kN$$

$$N \quad \frac{\text{Rate}}{k} \quad \frac{346 \quad 66.6 \quad 60}{0.693} \quad 1.995 \quad 10^6 \text{ atoms}$$

$$kt \quad \ln\frac{N_0}{N} \qquad \frac{\ln 2}{66.6} \quad 6.909 \quad \ln\frac{N_0}{N} \quad 0.0715$$

$$\frac{N_0}{N} \quad 1.074$$

$$N_0 \quad 1.074 \quad N \quad 1.074 \quad 1.995 \quad 10^6$$

$$2.14 \quad 10^6 \text{atoms of Mo}$$

$$\text{Mass of Mo required} \quad \frac{2.14 \quad 10^6}{6.023 \quad 10^{23}} \quad 99 \quad 3.56 \quad 10^{\ 16}\text{ g}$$

76. $k \quad 1.5 \quad 10^{\ 6}\text{ s}^{\ 1}$

$$kt \quad \ln\frac{100}{100 \quad x}$$

$$\ln\frac{100}{100 \quad x} \quad 1.5 \quad 10^{\ 6}\text{ s}^{\ 1} \quad 10 \quad 60 \quad 60 \text{ s} \quad 0.0054$$

$$\frac{100}{100 \quad x} \quad 1.055$$

x 5.25% reactant is converted into product.

$$\text{Half-life} \quad \frac{\ln 2}{k} \quad \frac{0.693}{1.5 \quad 10^{\ 6}} \quad 462000 \text{ s} \quad 128.33 \text{ h}$$

77. For a first order process : $\ln\frac{[A]_0}{[A]} \quad kt \qquad \ln[A] \quad \ln[A]_0 \quad kt$

If the reactant is in gaseous state

$$\text{and } kt_{1/10} \quad \ln\frac{[A]_0}{[A]_0/10} \quad \ln 10 \qquad \ldots\text{(ii)}$$

$$\text{Therefore, } \frac{t_{1/8}}{t_{1/10}} \quad \frac{\ln 8}{\ln 10} \quad \log 8 \quad 3\log 2 \quad 3 \quad 0.3 \quad 0.9$$

$$\frac{t_{1/8}}{t_{1/10}} \quad 10 \quad 0.9 \quad 10 \quad 9$$

$$\ln p \quad \ln p_0 \quad kt \qquad \ldots\text{(i)}$$

where p is the partial pressure of reactant remaining unreacted at instant 't' and p_0 is its initial partial pressure.

Also, from equation (i), ln p *vs* t would give a straight line. Therefore, decomposition of N_2O_5 following first order kinetics.

78. $k \quad \frac{\ln 2}{t_{1/2}} \quad \frac{0.693}{5770}\text{ yr}^{\ 1} \quad 1.2 \quad 10^{\ 4}\text{ yr}^{\ 1}$

$$\text{Also} \quad kt \quad \ln\frac{1}{f} \quad \frac{\ln 2}{5770} \quad 11540 \quad \ln 4 \qquad f \quad \frac{1}{4} \quad 0.25$$

79. For a first order reaction,

$$kt \quad \ln\frac{[A]_0}{[A]}$$

where $[A]_0$ Initial concentration of reactant
$[A]$ Concentration of reactant remaining unreacted at time t.

$$\text{(i)} \qquad k \quad \frac{1}{t}\ln\frac{[A]_0}{[A]} \quad \frac{1}{10}\ln\frac{100}{100 \quad 20} \quad \frac{1}{10}\ln\frac{5}{4}$$

$$\frac{2.303\,(\log 5 \quad 2\log 2)}{10}\text{ min}^{\ 1} \quad 0.023 \text{ min}^{-1}$$

$$\text{(ii)} \qquad t \quad \frac{1}{k}\ln\frac{100}{25} \quad \frac{2\ln 2}{k} \quad \frac{2 \quad 0.693}{0.023} \quad 60 \text{ min}$$

80. Looking at the rate data of experiment number 1 and 2 indicates that rate is doubled on doubling concentration of A while concentration of B is constant. Therefore, order with respect to A is 1. Similarly, comparing data of experiment number 1 and 3, doubling concentration of B, while concentration of A is constant, has no effect on rate.

Therefore, order with respect to B is zero.

$$\text{Rate} \quad k[A]$$

$$k \quad \frac{0.005}{0.010} \quad 0.5 \text{ min}^{\ 1} \quad \frac{0.693}{t_{1/2}}$$

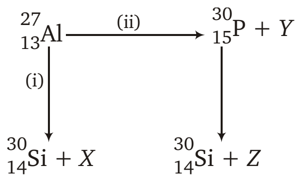
$$t_{1/2} \quad \frac{0.693}{0.5} \quad 1.386 \text{ min}$$

12

Nuclear Chemistry

Objective Questions I (Only one correct option)

1. Bombardment of aluminium by -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively, are **(2011)**



(a) proton, neutron, positron (b) neutron, positron, proton
(c) proton, positron, neutron (d) positron, proton, neutron

2. A positron is emitted from $^{23}_{11}$Na. The ratio of the atomic mass and atomic number of the resulting nuclide is **(2007, 3M)**
(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12

3. ^{23}Na is the more stable isotope of Na. Find out the process by which $^{24}_{11}$Na can undergo radioactive decay. **(2003, 1M)**
(a) -emission (b) -emission
(c) -emission (d) K-electron capture

4. The number of neutrons accompanying the formation of $^{139}_{54}$Xe and $^{94}_{38}$Sr from the absorption of a slow neutron by $^{235}_{92}$U, followed by nuclear fission is **(1999, 2M)**
(a) 0 (b) 2 (c) 1 (d) 3

5. $^{27}_{13}$Al is a stable isotope. $^{29}_{13}$Al is expected to decay by **(1996, 1M)**
(a) -emission (b) -emission
(c) positron emission (d) proton emission

6. The radiation from a naturally occurring radioactive substance, as seen after deflection by a magnet in one direction, are **(1984, 1M)**
(a) definitely alpha rays (b) definitely beta rays
(c) both alpha and beta rays (d) either alpha rays or beta rays

7. An isotope of Ge^{76}_{32} is **(1984, 1M)**
(a) Ge^{77}_{32} (b) As^{77}_{33} (c) Se^{77}_{34} (d) Se^{78}_{34}

8. If uranium (mass number 238 and atomic number 92) emits an -particle, the product has mass number and atomic number **(1981, 1 M)**
(a) 236 and 92 (b) 234 and 90
(c) 238 and 90 (d) 236 and 90

Objective Questions II
(One or more than one correct option)

9. A plot of the number of neutrons (n) against the number of protons (p) of stable nuclei exhibits upward deviation from linearity for atomic number, $Z > 20$. For an unstable nucleus having n/p ratio less than 1, the possible mode(s) of decay is (are) **(2016 Adv.)**
(a) - decay (- emission) (b) orbital or K-electron capture
(c) neutron emission (d) -decay (positron emission)

10. In the nuclear transmutation, $^{9}_{4}$Be X $^{8}_{4}$Be Y
X and Y are **(2013 Adv.)**
(a) (, n) (b) (p, D) (c) (n, D) (d) (, p)

11. Decrease in atomic number is observed during **(1998, 2M)**
(a) alpha emission (b) beta emission
(c) positron emission (d) electron capture

12. The nuclear reactions accompanied with emission of neutron(s) are **(1988, 1 M)**
(a) $^{27}_{13}$Al + $^{4}_{2}$He $^{30}_{15}$P (b) $^{12}_{6}$C + $^{1}_{1}$H $^{13}_{7}$N
(c) $^{30}_{15}$P $^{30}_{14}$Si + $^{0}_{1}e$ (d) $^{241}_{96}$Cm + $^{4}_{2}$He $^{244}_{97}$Bk + $^{0}_{1}e$

Assertion and Reason

Read the following questions and answer as per the direction given below:

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

13. **Statement I** The plot of atomic number (y-axis) *versus* number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as the atomic number is increased.
Statement II Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons and neutrons in heavier nuclides. **(2008)**

14. **Statement I** Nuclide $^{30}_{13}$Al is less stable than $^{40}_{20}$Ca.
Statement II Nuclides having odd number of protons and neutrons are generally unstable. **(1998)**

Fill in the Blanks

15. (a) $^{235}_{92}U$ $\quad {}_0n^1$ $\quad ^{137}_{52}A$ $\quad ^{97}_{40}B$ $\quad$ ......

(b) $^{82}_{34}Se$ $\quad 2 \quad {}_1e^0$ $\quad$ ...... **(2005, 1M 2 = 2M)**

16. A radioactive nucleus decays by emitting one alpha and two beta particles, the daughter nucleus is.... of the parent. **(1989, 1M)**

17. The number of neutrons in the parent nucleus which gives N^{14} on beta emission is .... **(1985, 1M)**

18. Elements of the same mass number but different atomic number are known as ……… **(1983, 1M)**

19. An element ${}_ZM^A$ undergoes an -emission followed by two successive -emissions. The element formed is …… **(1982, 1M)**

Integer Answer Type Questions

20. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table? **(2012)**

$$^{63}_{29}Cu + {}^1_1H \qquad 6{}^1_0n + {}^4_2 \quad + 2{}^1_1H + X$$

21. The number of neutrons emitted when $^{235}_{92}U$ undergoes controlled nuclear fission to $^{142}_{54}Xe$ and $^{90}_{38}Sr$ is **(2010)**

Subjective Questions

22. The total number of and particles emitted in the nuclear reaction ${}_{92}U^{238}$ $\quad {}_{82}Pb^{214}$ is ..... . **(2009)**

23. ${}_{92}X^{234}$ $\quad \begin{matrix}7\\6\end{matrix} \quad Y$. Find out atomic number, mass number of Y and identify it. **(2004)**

24. ${}_{92}U^{238}$ is radioactive and it emits and particles to form ${}_{82}Pb^{206}$. Calculate the number of and particles emitted in this conversion.

An ore of ${}_{92}U^{238}$ is found to contain ${}_{92}U^{238}$ and ${}_{82}Pb^{206}$ in the weight ratio of 1 : 0.1. The half-life period of ${}_{92}U^{238}$ is 4.5 $\quad 10^9$ yr. Calculate the age of the ore. **(2000)**

25. Write a balanced equation for the reaction of N^{14} with -particle.

26. ${}_{90}Th^{234}$ disintegrates to give ${}_{82}Pb^{206}$ as the final product. How many alpha and beta particles are emitted during this process? **(1986, 2M)**

Answers

1. (a)	**2.** (c)	**3.** (a)	**4.** (b)	**16.** isotope	**17.** eight	**18.** isobars	**19.** ${}_ZM^{A\ \ 4}$
5. (b)	**6.** (c)	**7.** (a)	**8.** (b)	**20.** (8)	**21.** 3	**22.** (8)	**23.** ${}_{84}PO^{206}$
9. (b, d)	**10.** (a, b)	**11.** (a, c, d)	**12.** (a, d)	**24.** (7.12 $\quad 10^8$yr)		**26.** (13)	
13. (a)	**14.** (b)	**15.** $2\,{}_0n^1$, ${}_{36}Kr^{82}$					

Hints & Solutions

1. (i) $^{27}_{13}Al + {}^4_2He \qquad {}^{30}_{14}Si + {}^1_1X$

X is proton ^1_1H.

(ii) $^{27}_{13}Al + {}^4_2He\,(\ \ ) \qquad {}^{30}_{15}P + {}^1_0Y$

Y is neutron, ^1_0n.

$$^{30}_{15}P \qquad {}^{30}_{14}Si + {}^0_1Z$$

Z is positron, $^{0}_{+1}e$.

2. The required nuclear reaction is

$${}_{11}Na^{23} \qquad {}_1e^0 \quad {}_{10}Na^{23}$$

3. In stable isotope of Na, there are 11 protons and 12 neutrons. In the given radioactive isotope of sodium (Na^{24}), there are 13 neutrons, one neutron more than that required for stability. A neutron rich isotope always decay by -emission as

$${}_0n^1 \qquad {}_1{}^0 \quad {}_1H^1$$

4. The balanced nuclear reaction is

$$2{}_0n^1 \quad {}_{92}U^{235} \qquad {}_{54}Xe^{139} + {}_{38}Sr^{94}$$

5. ${}_{13}Al^{29}$ is neutron rich isotope, will decay by -emission converting some of its neutron into proton as

$${}_0n^1 \qquad {}_1{}^0 \quad {}_1H^1$$

6. Both -rays and - rays are deflected by magnetic field.

7. Isotopes have same atomic number (Z) but different mass number (A). Therefore, ${}_{32}Ge^{76}$ and ${}_{32}Ge^{77}$ are isotopes.

8. The nuclear reaction is

$${}_{92}U^{238} \qquad {}_2He^4(\ \ ) \quad {}_{90}Th^{234}$$

9. For the elements with atomic number (Z) larger than 20,

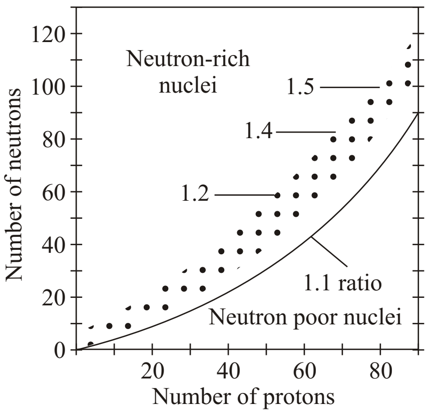
Neutrons (n) > Protons (p); Thus, $n/p \quad 1$
Thus, there is upward deviation from linearity.
If $n < p$, Thus $n/p \quad 1$, then

(a) By - decay, $^1_0n \qquad {}^1_1p \quad {}^0_1e$ neutron changes to proton. Thus, (n/p) ratio further decreases below 1. Thus, this decay is not allowed.

(b) By orbital or K- electron capture, $^1_1p \quad {}^0_1e \qquad {}^1_0n$ proton changes to neutron, hence, (n/p) ratio increases. Thus stability increases. Thus correct.

(c) Neutron emission further decreases n/p ratio.

(d) By -emission, $^1_1p \qquad {}^1_0n \quad {}^0_1e$ proton changes to neutron. Hence, n/p ratio increases. Thus correct.



Plot of the number of neutrons against the number of protons in stable nuclei (shown by dots).

10. **PLAN** ${}^{9}_{4}\text{Be}$ ${}^{b}_{a}X$ ${}^{8}_{4}\text{Be}$ ${}^{d}_{c}Y$

Atomic number same

$$4 \quad a \quad 4 \quad c$$
$$9 \quad b \quad 8 \quad d$$

If X ${}^{0}_{0}$ a 0, b 0

Y ${}^{1}_{0}n$ c 0, d 1

If X ${}^{1}_{1}p$ a 1, b 1

Y ${}^{2}_{1}\text{D}$ c 1, d 2

$${}^{9}_{4}\text{Be} \quad {}^{0}_{0} \qquad {}^{8}_{4}\text{Be} \quad {}^{1}_{0}n$$
$${}^{9}_{4}\text{Be} \quad {}^{1}_{1}p \qquad {}^{8}_{4}\text{Be} \quad {}^{2}_{1}\text{D}$$

11. In the following nuclear reactions, there occur decrease in atomic number (Z)

$${}_{Z}X^{A} \qquad {}_{2}\text{He}^{4} \quad {}_{Z\ 2}Y^{A\ 4}, \quad \text{- emission}$$
$${}_{Z}X^{A} \qquad {}_{1}e^{0} \quad {}_{Z\ 1}Y^{A}, \text{ positron emission}$$
$${}_{Z}X^{A} \qquad {}_{1}e^{0} \qquad {}_{Z\ 1}Y^{A}, \text{ electron capture}$$

In beta emission, increase in atomic number is observed.

$${}_{Z}X^{A} \qquad {}_{1}e^{0} \quad {}_{Z\ 1}Y^{A}, \quad \text{-emission}$$

12. If sum of mass number of product nuclides is less than the sum of parent nuclides, then neutron emission will occur. In both (a) and (d), sum of mass number of product nuclides is one unit less than the sum of parent nuclides, neutron emission will balance the mass number.

13. After atomic number 20, proton-proton repulsion increases immensely, more neutrons are required to shield this electrostatic repulsion, curve of stability incline towards neutron axis.

14. Upto atomic number of 20, stable nuclei possess neutron to proton ratio (n/p) 1.

$$\frac{n}{p}({}_{13}\text{Al}^{30}) \quad \frac{17}{13} \quad 1.3 > 1, \text{ unstable, } \text{-emitters.}$$
$$\frac{n}{p}({}_{20}\text{Ca}^{40}) \quad \frac{20}{20} \quad 1, \text{ stable.}$$

Also, nuclei with both neutrons and protons odd are usually unstable but it does not explain the assertion appropriately.

15. (a) ${}_{92}\text{U}^{235}$ ${}_{0}n^{1}$ ${}_{52}A^{137}$ ${}_{40}B^{97}$ $2\ {}_{0}n^{1}$

(b) ${}_{34}\text{Se}^{82}$ $2\ {}_{1}e^{0}$ ${}_{36}\text{Kr}^{82}$

16. Isotope : ${}_{Z}X^{A}$ ${}_{2}\text{He}^{4}$ $2\ {}_{1}e^{0}$ ${}_{Z}Y^{A\ 4}$

17. 8 : ${}_{6}\text{C}^{14}$ ${}_{7}\text{N}^{14}$ ${}_{1}e^{0}$

18. Isobars have same mass number but different atomic number.

19. ${}_{Z}M^{A\ 4}$: ${}_{Z}M^{A}$ ${}_{2}\text{He}^{4}$ $2\ {}_{1}e^{0}$ ${}_{Z}M^{A\ 4}$

20. Balancing the given nuclear reaction in terms of atomic number (charge) and mass number:

$${}_{29}\text{Cu}^{63} \quad {}_{1}\text{H}^{1} \qquad 6_{0}n^{1} \quad {}_{2}\text{He}^{4}(\ ) \quad 2_{1}\text{H}^{1} \quad {}_{26}X^{52}$$

The atomic number 26 corresponds to transition metal Fe which belongs to 8th group of modern periodic table.

21. ${}_{92}\text{U}^{235}$ ${}_{54}\text{Xe}^{142}$ ${}_{38}\text{Sr}^{90}$ $3_{0}n^{1}$

22. ${}_{92}\text{U}^{238}$ ${}_{82}\text{Pb}^{214}$ $6\ {}_{2}\text{He}^{4}$ $2\ {}_{1}e^{0}$

Number of ( ) 6 2 8

23. ${}_{92}X^{234}$ $7\ {}_{2}\text{He}^{4}$ $6\ {}_{1}e^{0}$ ${}_{84}Y^{206}$

Y is ${}_{84}\text{Po}^{206}$.

24. ${}_{92}\text{U}^{238}$ $\quad {}_{82}\text{Pb}^{206} + 8\ {}_{2}\text{He}^{4} + 6\ {}_{1}e^{0}$

Present : $N_0 \quad N \qquad N$

Given, $\dfrac{w(\text{U})}{w(\text{Pb})} \quad \dfrac{1}{0.1} \quad 10$

$$\frac{N\,(\text{U})}{N\,(\text{Pb})} \quad \frac{10}{238} \quad \frac{206}{1} \quad \frac{N_0 \quad N}{N}$$

$$\frac{N}{N_0 \quad N} \quad \frac{238}{2060} \qquad \frac{N_0}{N_0 \quad N} \quad 1 \quad \frac{238}{2060} \quad \frac{2298}{2060}$$

Now, applying first order rate law

$$\frac{\ln 2}{t_{1/2}} \quad t \quad \ln \frac{N_0}{N_0 \quad N} \qquad t \quad \frac{(t_{1/2})}{\log 2} \log \frac{N_0}{N_0 \quad N}$$

$$\frac{4.5 \quad 10^{9}}{0.3} \log \frac{2298}{2060} \quad 7.12 \quad 10^{8} \text{ yr}$$

25. ${}_{7}\text{N}^{14}$ ${}_{2}\text{He}^{4}$ ${}_{9}\text{F}^{18}$

26. ${}_{90}\text{Th}^{234}$ ${}_{82}\text{Pb}^{206}$ $7\ {}_{2}\text{He}^{4}$ $6\ {}_{1}e^{0}$

Download Chapter Test
http://tinyurl.com/y3qvab9f *or*

13

Surface Chemistry

Objective Questions I (Only one correct option)

1. Among the following, the incorrect statement about colloids is **(2019 Main, 12 April II)**

(a) They can scatter light

(b) They are larger than small molecules and have high molar mass

(c) The osmotic pressure of a colloidal solution is of higher order than the true solution at the same concentration

(d) The range of diameters of colloidal particles is between 1 and 1000 nm

2. Peptisation is a **(2019 Main, 12 April I)**

(a) process of bringing colloidal molecule into solution

(b) process of converting precipitate into colloidal solution

(c) process of converting a colloidal solution into precipitate

(d) process of converting soluble particles to form colloidal solution

3. The correct option among the following is **(2019 Main, 10 April II)**

(a) colloidal medicines are more effective, because they have small surface area.

(b) brownian motion in colloidal solution is faster if the viscosity of the solution is very high.

(c) addition of alum to water makes it unfit for drinking.

(d) colloidal particles in lyophobic sols can be precipitated by electrophoresis.

4. A gas undergoes physical adsorption on a surface and follows the given Freundlich adsorption isotherm equation

$$\frac{x}{m} \quad Kp^{0.5}$$

Adsorption of the gas increases with **(2019 Main, 10 April I)**

(a) increase in p and increase in T

(b) increase in p and decrease in T

(c) decrease in p and decrease in T

(d) decrease in p and increase in T

5. Match the catalysts Column I with products Column II. **(2019 Main, 9 April I)**

	Column I (Catalyst)		**Column II** (Product)
(A)	V_2O_5	(i)	Polyethlyene
(B)	$TiCl_4$ / $Al(Me)_3$	(ii)	Ethanal
(C)	$PbCl_2$	(iii)	H_2SO_4
(D)	Iron oxide	(iv)	NH_3

(a) (A)-(ii), (B)-(iii), (C)-(i), (D)-(iv)

(b) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i)

(c) (A)-(iii), (B)-(i), (C)-(ii), (D)-(iv)

(d) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)

6. The number of water molecule(s) not coordinated to copper ion directly in $CuSO_4 \; 5H_2O$, is **(2019 Main, 9 April I)**

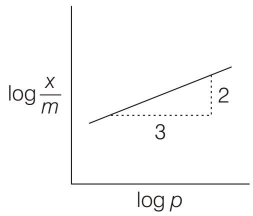
(a) 2 (b) 3 (c) 1 (d) 4

7. The aerosol is a kind of colloid in which **(2019 Main, 9 April I)**

(a) gas is dispersed in liquid (b) gas is dispersed in solid

(c) liquid is dispersed in water (d) solid is dispersed in gas

8. Adsorption of a gas follows Freundlich adsorption isotherm. x is the mass of the gas adsorbed on mass m of the adsorbent. The plot of $\log \frac{x}{m}$ *versus* $\log p$ is shown in the given graph. $\frac{x}{m}$ is proportional to **(2019 Main, 8 April I)**



(a) $p^{2/3}$ (b) $p^{3/2}$ (c) p^3 (d) p^2

9. Among the following, the false statement is **(2019 Main, 12 Jan II)**

(a) Tyndall effect can be used to distinguish between a colloidal solution and a true solution

(b) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane

(c) Lyophilic sol can be coagulated by adding an electrolyte

(d) Latex is a colloidal solution of rubber particles which are positively charged

10. Given, Gas : H_2, CH_4, CO_2, SO_2

Critical temperature/K 33 190 304 630

On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal? **(2019 Main, 12 Jan I)**

(a) CH_4 (b) SO_2 (c) CO_2 (d) H_2

11. Among the colloids cheese (C), milk (M) and smoke (S), the correct combination of the dispersed phase and dispersion medium, respectively is **(2019 Main, 11 Jan II)**

(a) C : liquid in solid; M : liquid in liquid; S : solid in gas
(b) C : solid in liquid; M : liquid in liquid; S : gas in solid
(c) C : liquid in solid; M : liquid in solid; S : solid in gas
(d) C : solid in liquid; M : solid in liquid; S : solid in gas

12. An example of solid sol is **(2019 Main, 11 Jan I)**

(a) gem stones (b) hair cream
(c) butter (d) paint

13. Haemoglobin and gold sol are examples of **(2019 Main, 10 Jan II)**

(a) negatively and positively charged sols, respectively
(b) negatively charged sols
(c) positively charged sols
(d) positively and negatively charged sols, respectively

14. Which of the following is not an example of heterogeneous catalytic reaction? **(2019 Main, 10 Jan I)**

(a) Haber's process
(b) Combustion of coal
(c) Hydrogenation of vegetable oils
(d) Ostwald's process

15. The correct match between item-I and Item-II is **(2019 Main, 9 Jan II)**

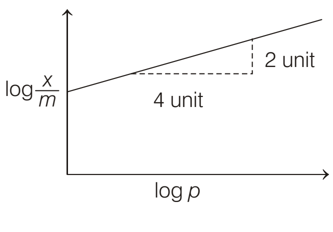
A. Benzaldehyde	P. Dynamic phase
B. Alumina	Q. Adsorbent
C. Acetonitrile	R. Adsorbate

(a) (A) (R) ; (B) (Q); (C) (P)
(b) (A) (P); (B) (R); (C) (Q)
(c) (A) (Q); (B) (P); (C) (R)
(d) (A) (Q); (B) (R); (C) (P)

16. Which of the salt-solution is most effective for coagulation of arsenious sulphide? **(2019 Main, 9 Jan II)**

(a) $BaCl_2$ (b) $AlCl_3$
(c) Na_3PO_4 (d) $NaCl$

17. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p $\frac{x}{m}$ is proportional to **(2019 Main, 9 Jan I)**



(a) p^2 (b) $p^{1/4}$ (c) $p^{1/2}$ (d) p

18. The Tyndall effect is observed only when following conditions are satisfied **(2017 Main)**

1. The diameter of the dispersed particles is much smaller than the wavelength of the light used.
2. The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
3. The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
4. The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

(a) 1 and 4 (b) 2 and 4 (c) 1 and 3 (d) 2 and 3

19. For a linear plot of log (x/m) *versus* log p in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants) **(2016 Main)**

(a) $1/n$ appears as the intercept
(b) Only $1/n$ appears as the slope
(c) $\log \frac{1}{n}$ appears as the intercept
(d) Both k and $1/n$ appear in the slope term

20. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is **(2013 Adv.)**

(a) the adsorption requires activation at 25°C
(b) the adsorption is accompanied by a decreases in enthalpy
(c) the adsorption increases with increase of temperature
(d) the adsorption is irreversible

21. The coagulating power of electrolytes having ions Na^+, Al^3 and Ba^{2+} for arsenic sulphide sol increases in the order **(2013 Main)**

(a) Al^{3+} Ba^2 Na^+ (b) Na^+ Ba^{2+} Al^{3+}
(c) Ba^{2+} Na^{2+} Al^{3+} (d) Al^{3+} Na^+ Ba^{2+}

22. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is **(2009, 1M)**

(a) Na_2SO_4 (b) $CaCl_2$
(c) $Al_2(SO_4)_3$ (d) NH_4Cl

23. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions, is **(2008, 3M)**

(a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br$ (b) $CH_3(CH_2)_{11}OSO_3Na^+$
(c) $CH_3(CH_2)_6COO\ Na^+$ (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br$

24. Lyophilic sols are **(2005, 1M)**

(a) irreversible sols
(b) prepared from inorganic compounds
(c) coagulated by adding electrolytes
(d) self-stabilising

25. Spontaneous adsorption of a gas on solid surface is an exothermic process, because **(2004, 1M)**

(a) H increases for system (b) S increases for gas
(c) S decreases for gas (d) G increases for gas

26. Rate of physisorption increases with **(2003, 1M)**

(a) decrease in temperature (b) increase in temperature
(c) decrease in pressure (d) decrease in surface area

27. When the temperature is increased, surface tension of water **(2002, 1M)**

(a) increases (b) decreases
(c) remains constant (d) shows irregular behaviour

Objective Questions II

(One or more than one correct option)

28. The correct statement(s) about surface properties is(are) **(2017 Adv.)**

(a) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen of same amount of activated charcoal at a given temperature

(b) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium

(c) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system

(d) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution

29. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The true statement(s) regarding this adsorption is (are) **(2015 Adv.)**

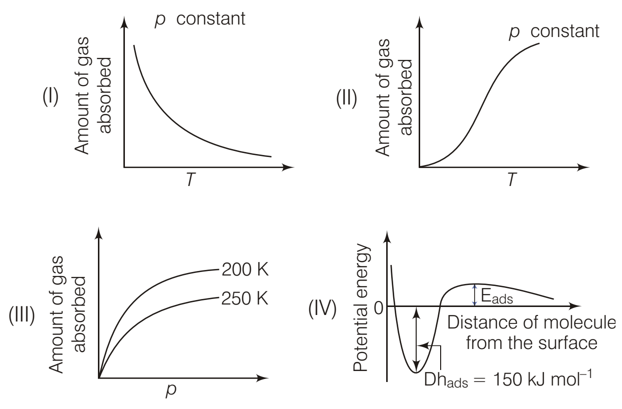
(a) O_2 is physisorbed

(b) heat is released

(c) occupancy of $2p$ of O_2 is increased

(d) bond length of O_2 is increased

30. The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct? **(2012)**



(a) I is physisorption and II is chemisorption

(b) I is physisorption and III is chemisorption

(c) IV is chemisorption and II is chemisorption

(d) IV is chemisorption and III is chemisorption

31. Choose the correct reason(s) for the stability of the lyophobic colloidal particles. **(2012)**

(a) Preferential adsorption of ions on their surface from the solution

(b) Preferential adsorption of solvent on their surface from the solution

(c) Attraction between different particles having opposite charges on their surface

(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

32. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) **(2011)**

(a) Adsorption is always exothermic

(b) Physisorption may transform into chemisorption at high temperature

(c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature

(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation

Assertion and Reason

Read the following questions and answer as per the direction given below:

(a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

33. **Statement I** Micelles are formed by surfactant molecules above the critical micelle concentration (CMC).

Statement II The conductivity of a solution having surfactant molecules decreases sharply at the CMC **(2007)**

Answers

1. (c)	**2.** (b)	**3.** (d)	**4.** (b)	**21.** (b)	**22.** (c)	**23.** (a)	**24.** (d)
5. (c)	**6.** (c)	**7.** (d)	**8.** (a)	**25.** (c)	**26.** (a)	**27.** (b)	**28.** (a, c)
9. (d)	**10.** (d)	**11.** (a)	**12.** (a)	**29.** (b, c, d)	**30.** (a, c)	**31.** (a, d)	**32.** (a, b, d)
13. (d)	**14.** (b)	**15.** (a)	**16.** (b)	**33.** (b)			
17. (c)	**18.** (b)	**19.** (b)	**20.** (b)				

Hints & Solutions

1. Statement (c) is incorrect about colloids. Colligative properties such as relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure of a colloidal solution is of low order than the true solution at the same concentration.

2. Peptisation is a process of converting precipitate into colloidal solution. This process involves the shaking of precipitate with the dispersion medium in the presence of small amount of electrolyte. The electrolyte added is called **peptising agent**.

During peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately breakup into smaller particles of the size of a colloid.

3. The explanation of the given statements are as follows :

(a) Colloidal medicines are more effective because they (dispersed phase) have larger surface area.

Thus, option (a) is incorrect.

(b) Brownian motion of dispersed phase particles in colloidal solution is faster if the viscosity of the solution is very low. Thus, option (b) is incorrect.

(c) Addition of alum(K_2SO_4 $Al_2(SO_4)_3$ $24H_2O$), an electrolyte to water makes it fit for drinking purposes because alum coagulates mud particles from water.

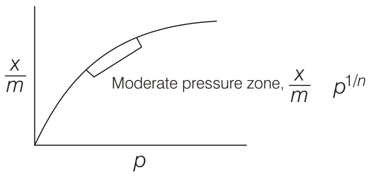
Thus, option (c) is incorrect.

(d) Precipitation of lyophobic solution particles by electrophoresis is called cottrell precipitation.

Thus, option (d) is correct.

4. For physisorption or physical adsorption,

Adsorption isotherm (Temperature, T constant) is shown below:



where, x amount of adsorbate, m amount of adsorbent,

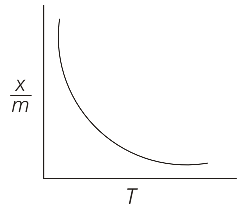
$\frac{x}{m}$ degree of adsorption

$\frac{1}{n}$ order of the reaction, where, $0 \quad \frac{1}{n} \quad 1$ and so, $1 \quad n$

Here, $\frac{x}{m} \quad Kp^{\frac{1}{2}}$,

i.e. $\frac{x}{m} \quad p^{\frac{1}{2}}$

Adsorption isobar (Pressure, $p =$ constant)



So, the rate of physical adsorption of the gas, increases with p (when, T is constant) and decreases with T (when p is constant).

5. Correct match is

(A) (iii); (B) (i); (C) (ii); (D) (iv)

(i) $TiCl_4$ $AlCl_3$ (*Ziegler- Natta* catalyst) is used to prepare polyethylene from ethene.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow{\text{Ziegler-Natta catalyst}} \underset{\text{Polyethylene}}{-\!\!\left(CH_2{-}CH_2\right)_n\!\!-}$$

(ii) V_2O_5 (Vanadium pentoxide) is used as catalyst to prepare H_2SO_4 from contact process. Reaction involved is

$$2SO_2(g) \quad O_2(g) \quad \xrightarrow{V_2O_5} \quad 2SO_3(g)$$

It is the key step in the manufacture of H_2SO_4.

(iii) Fe (Iron) is used as catalyst in Haber's process for the manufacture of ammonia.

$$N_2(g) \quad 3H_2(g) \quad \xrightarrow{Fe(s)} \quad 2NH_3(g)$$

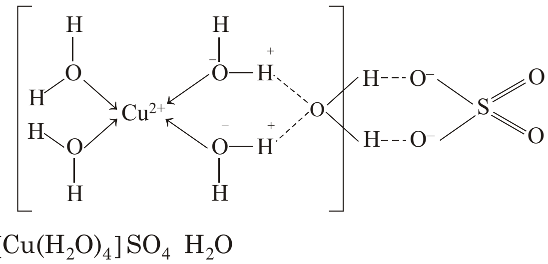
(iv) Pd (Palladium) is used to prepare ethanal. Reaction involved is

$$H_2C{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2/CuCl_2} CH_3CHO$$

This reaction is also known as Wacker's process.

6. In $CuSO_4$ $5H_2O$, one molecule of water is indirectly connected to Cu. In this molecule, four water molecules form coordinate bond with Cu^{2} ion while one water molecule is associated with H-bond with SO_4^{2} .

Structure of $CuSO_4$ $5H_2O$



$[Cu(H_2O)_4]SO_4$ H_2O

7. The aerosol is a kind of colloid in which solid is dispersed in gas. e.g. smoke, dust.

8. **Key Idea** According to Freundlich,

$$\frac{x}{m} \quad Kp^{1/n} [n \quad 1]$$

where, m mass of adsorbent, x mass of the gas adsorbed, $\frac{x}{m}$ amount of gas adsorbed per unit mass of solid adsorbent, p pressure, K and n constants.

The logarithm equation of Freundlich adsorption isotherm is

$$\log \frac{x}{m} \quad \log K \quad \frac{1}{n} \log p$$

On comparing the above equation with straight line equation, $(y \quad mx \quad c)$

we get

$$m \quad \text{slope} \quad \frac{1}{n} \quad \text{and} \quad c \quad \log K$$

From the given plot,

$$m \quad \frac{y_2 \quad y_1}{x_2 \quad x_1} \quad \frac{1}{n} \quad \frac{2}{3}$$

$$\frac{x}{m} \quad Kp^{2/3}$$

9. Statement given as statement (d) is incorrect. Latex is a stable dispersion, i.e. emulsion of polymer microparticles in an aqueous medium.

These microparticles belong to rubber and are negatively charged in nature. Natural latex contains some amount of sugar, resin, protein and ash as well.

The closest synthetic latex that can be associated with the properties of natural latex is SBR, i.e. **Styro Butane Rubber.**

Rest of all the statements are correct.

10. Same adsorbant (charcoal in this case) at same temperature will adsorb different gases to different extent. The extent to which gases are adsorbed is proportional to the critical temperature of gas.

$$\because \qquad T_c \quad \frac{8a}{27Rb}$$

where, a is the magnitude of intermolecular forces between gaseous molecules.

Thus, higher the cirtical temperature more is the gas adsorbed. Among the given gases, H_2 has the minimum critical temperature, i.e. 33K thus, it shows least adsorption on a definite amount of charcoal.

11.

Dispersed phase	Dispersion medium	Type of colloid	Examples
Liquid	Solid	Gel	Cheese (C), butter, jellies
Liquid	Liquid	Emulsion	Milk (M), hair cream
Solid	Gas	Aerosol	Smoke (S), dust

Thus, C : liquid in solid, M : liquid in liquid and S : solid in gas.

12. Solid sol consists of solid as both dispersed phase and dispersion medium. In gemstones, metal crystals (salt and oxides of metals) are dispersed in solid (stone) medium. Hair cream is an emulsion (liquid in liquid). Butter is a colloidal solution of liquid in solid. Paint is also sol (solid in liquid).

13. Haemoglobin and gold sol both are colloids and always carry an electric charge. Haemoglobin is a positively charged sol, because in haemoglobin, Fe^{2} ion is the central metal ion of the octahedral complex.

All metal sols like, Au-sol, Ag-sol etc; are negatively charged sols.

14. In heterogeneous catalytic reactions, physical state of reactants and that of catalyst(s) used are different.

Haber's process, hydrogenation of vegetable oils and Ostwald's process all are heterogeneous process. Combustion of coal is not a heterogeneous catalytic reaction.

- In Haber's process

$$N_2(g) \quad 3H_2(g) \xrightarrow{Fe(s),\ Mo(s)} 2NH_3(g)$$

- Hydrogenation of vegetable oils,

$$\underset{\text{(Unsaturated)}}{\text{Vegetable oil}(l)} \xrightarrow[\text{or Ni }(s)]{[(Ph_3P)_3Rh]\ Cl} \text{Vanaspati}(s)$$

- Ostwald's process,

$$4NH_3(g) \quad 5O_2(g) \xrightarrow[V_2O_5(s)]{Pt(s)} 4NO(g) \quad 6H_2O(g)$$

- No catalyst is used in combustion of coal. The reaction is highly spontaneous in nature.

$$\underset{\text{(Coal)}}{C} \quad O_2 \qquad CO_2$$

15. Using the principle of adsorption chromatography, qualitative and quantitative analysis of benzaldehyde can be done from its mixture with acetonitrile. Here, a mobile phase moves over a stationary phase (adsorbent). Adsorbents used are alumina (Al_2O_3) and silica gel. The sample solution of benzaldehyde and acetonitrile when comes in contact with the adsorbent, benzaldehyde gets adsorbed on the surface of the adsorbent. So, benzaldehyde acts as absorbate whereas acetonitrile starts moving as mobile phase over the stationary phase of the adsorbate. Hence, act as dynamic phase.

16. Arsenious sulphide sol is a negative colloid, $As_2S_3.(S^{2}\ )$. So, it will be coagulated by the cation of an electrolyte.

According to the Hardy-Schulze rule, the higher the charge of the ion, the more effective it is in bringing about coagulation. Here, the cations available are Al^{3} (from $AlCl_3$), Ba^{2} (from $BaCl_2$) and Na (from Na_3PO_4 and NaCl). So, their power to coagulate $As_2S_3.(S^{2}\ )$ will follow the order as

$$Al^{3+} > Ba^{2+} > Na^{+}$$

17. According to Freundlich adsorption isotherm,

$$\frac{x}{m} \quad p^{1/n} \qquad \frac{x}{m} \quad Kp^{1/n}$$

On taking log on both sides, we get

$$\log \frac{x}{m} \quad \log K \quad \frac{1}{n} \log p$$

On comparing with equation of straight line, $y \quad mx \quad c$, plot of $\log \frac{x}{m}$ *vs* $\log p$ gives,

$$\text{Slope} \; \frac{(y_2 \quad y_1)}{(x_2 \quad x_1)} \quad \frac{1}{n} \quad \frac{2}{4} \quad \frac{1}{2}$$

$$\frac{x}{m} \quad p^{1/2}$$

18. Colloidal solutions show Tyndall effect due to scattering of light by colloidal particles in all directions in space. It is observed only under the following conditions.

(i) The diameter of the colloids should not be much smaller than the wavelength of light used.

(ii) The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude.

19. According to Freundlich adsorption isotherm, $\frac{x}{m} \quad kp^{1/n}$

On taking logarithm of both sides, we get

$$\log \frac{x}{m} \quad \log k \quad \log p^{1/n}$$

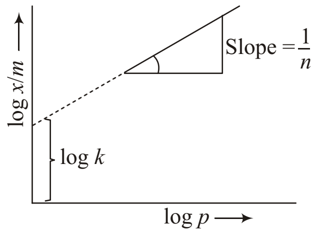
$$\text{or } \log \frac{x}{m} \quad \log k \quad \frac{1}{n} \log p$$

$$y \quad c \quad mx$$

$$y \quad \log \frac{x}{m},$$

$$c \quad \text{intercept} \quad \log k$$

$$m \quad \text{slope} \quad \frac{1}{n} \text{ and } x \quad \log p$$



20. Physical adsorption takes place with decrease in enthalpy thus exothermic change. It is physical adsorption and does not require activation. Thus, (*a*) is incorrect.

Being physical adsorption H 0 thus, (*b*) is correct. Exothermic reaction is favoured at low temperature thus (c) is incorrect. Physical adsorption is always reversible, thus (d) is incorrect.

21. According to Hardy Schulze rule, greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ \quad Ba^{2+} \quad Al^{3+}$.

22. Sb_2S_3 is a negative (anionic) sol. According to Hardy Schulze rule, greater the valency of cationic coagulating agent, higher its coagulating power. Therefore, $Al_2(SO_4)_3$ will be the most effective coagulating agent in the present case.

23. Larger the hydrophobic fragment of surfactant, easier will be the micellisation, smaller the crticial micelle concentration. Therefore, $CH_3(CH_2)_{15}N^+ (CH_3)_3Br$ will have the lowest crticial micelle concentration.

24. Lyophilic sols are reversible, not easily coagulated because it is self-stabilising.

25. $G \quad H \quad T \; S$

As gas is adsorbed on surface of solid, entropy decreases, i.e. S 0. Therefore, for G 0, H must be negative.

26. It is an exothermic process, according to Le-Chatelier's principle, lowering temperature drive the process in forward direction.

27. As temperature increases surface tension of liquid decreases.

28. (a) Higher the critical temperature, greater the extent of adsorption.

(c) $\underset{\text{Adsorbent}}{P(s)} \quad \underset{\text{Adsorbate}}{Q(g)} \quad PQ(s)$

As gaseous adsorbate is adsorbed on solid surface, entropy decreases, S 0. Also formation of bond between P and Q results in release of energy, hence H 0.

29. Since, adsorption involves electron transfer from metal to O_2, it is chemical adsorption not physical adsorption, hence (*a*) is incorrect. Adsorption is spontaneous which involves some bonding between adsorbent and adsorbate, hence exothermic. The last occupied molecular orbital in O_2 is $^*2p$. Hence, electron transfer from metal to oxygen will increase occupancy of $^*2p$ molecular orbitals. Also increase in occupancy of $^*2p$ orbitals will decrease bond order and hence increase bond length of O_2.

30. **Graph-I** represents physisorption as in physisorption, absorbents are bonded to adsorbate through weak van der Waals' force.

Increasing temperature increases kinetic energy of adsorbed particles increasing the rate of desorption, hence amount of adsorption decreases.

Graph-II represents chemisorption as it is simple activation energy diagram of a chemical reaction.

Graph-III also represents physical adsorption as extent of adsorption increasing with pressure.

Graph-IV represents chemisorption as it represents the potential energy diagram for the formation of a typical covalent bond.

31. Lyophobic sol, which is otherwise unstable, gets stabilised by preferential adsorption of ions on their surface, thus developing a potential difference between the fixed layer and the diffused layer. Thus, option (a) and (d) are correct.

32. (a) In the process of adsorption, a bond is formed between adsorbate and adsorbent, hence always exothermic.

(b) Physisorption require very low activation energy while chemisorption require high activation energy. Therefore a physisorption may transform into chemisorption but only at high temperature.

(c) It is wrong statement as at higher temperature, physically adsorbed substance starts desorbing.

(d) In physical adsorption, van der Waals' force hold the adsorbate and adsorbent together which is a weak electrostatic attraction. In chemisorption, strong chemical bond binds the adsorbate to the adsorbent. Therefore, chemisorption is more exothermic than physical adsorption.

33. Both statements are independently correct but Statement II does not explain Statement I. Critical micelle concentration is the minimum concentration of surfactant at which micelle formation commences first. At critical micelle concentration, several molecules of surfactant coalesce together to form one single micelle molecule. This decreases the apparent number of molecule suddenly lowering conductivity sharply.

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http://tinyurl.com/y6lc4mog *or*

14

s-Block Elements

Topic 1 Group I Elements

Objective Questions I (Only one correct option)

1. The temporary hardness of a water sample is due to compound X. Boiling this sample converts X to compound Y. X and Y, respectively, are **(2019 Main, 12 April II)**

(a) $Mg(HCO_3)_2$ and $Mg(OH)_2$
(b) $Ca(HCO_3)_2$ and $Ca(OH)_2$
(c) $Mg(HCO_3)_2$ and $MgCO_3$
(d) $Ca(HCO_3)_2$ and CaO

2. The incorrect statement is **(2019 Main, 12 April II)**

(a) lithium is the strongest reducing agent among the alkali metals.
(b) lithium is least reactive with water among the alkali metals.
(c) $LiNO_3$ decomposes on heating to give $LiNO_2$ and O_2.
(d) LiCl crystallise from aqueous solution as $LiCl\ \ 2H_2O$.

3. The metal that gives hydrogen gas upon treatment with both acid as well as base is **(2019 Main, 12 April I)**

(a) magnesium (b) mercury
(c) zinc (d) iron

4. The correct statements among (a) to (d) are: **(2019 Main, 8 April II)**

1. Saline hydrides produce H_2 gas when reacted with H_2O.
2. Reaction of $LiAlH_4$ with BF_3 leads to B_2H_6.
3. PH_3 and CH_4 are electron rich and electron precise hydrides, respectively.
4. HF and CH_4 are called as molecular hydrides.

(a) (1), (2), (3) and (4) (b) (1), (2) and (3) only
(c) (3) and (4) only (d) (1), (3) and (4) only

5. The strength of 11.2 volume solution of H_2O_2 is [Given that molar mass of $H\ \ 1\,g\,mol^{\ 1}$ and $O\ \ 16\,g\,mol^{\ 1}$] **(2019 Main, 8 April II)**

(a) 1.7% (b) 34% (c) 13.6% (d) 3.4%

6. The correct order of hydration enthalpies of alkali metal ions is **(2019 Main, 8 April I)**

(a) $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$
(b) $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$
(c) $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$
(d) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

7. The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are **(2019 Main, 12 Jan II)**

I. They activate many enzymes.
II. They participate in the oxidation of glucose to produce ATP.
III. Along with sodium ions, they are responsible for the transmission of nerve signals.

(a) I, and III only (b) I, II and III
(c) I and II only (d) III only

8. A metal on combustion in excess air forms X. X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is **(2019 Main, 12 Jan I)**

(a) Li (b) Mg (c) Rb (d) Na

9. The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing is
(Molar mass of $CaSO_4\ \ 136\ g\ mol^{\ 1}$) **(2019 Main, 12 Jan I)**

(a) 100 ppm (b) 10 ppm (c) 50 ppm (d) 90 ppm

10. The hydride that is not electron deficient is **(2019 Main, 11 Jan II)**

(a) AlH_3 (b) B_2H_6 (c) SiH_4 (d) GaH_3

11. The correct statements among (a) to (d) regarding H_2 as a fuel are : **(2019 Main, 11 Jan I)**

I. It produces less pollutants than petrol.
II. A cylinder of compressed dihydrogen weights ~ 30 times more than a petrol tank producing the same amount of energy.
III. Dihydrogen is stored in tanks of metal alloys like $NaNi_5$.
IV. On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.

(a) I, II and III only (b) II, III and IV only
(c) II and IV only (d) I and III only

12. NaH is an example of **(2019 Main, 11 Jan I)**

(a) metallic hydride (b) electron-rich hydride
(c) saline hydride (d) molecular hydride

13. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of **(2019 Main, 10 Jan II)**

(a) sodium ammonia complex (b) sodium ion-ammonia complex
(c) sodamide (d) ammoniated electrons

14. The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are **(2019 Main, 10 Jan I)**

(a) 2 and 1 (b) 3 and 2 (c) 2 and 0 (d) 3 and 1

15. The chemical nature of hydrogen peroxide is **(2019 Main, 10 Jan I)**
(a) oxidising and reducing agent in both acidic and basic medium
(b) oxidising and reducing agent in acidic medium, but not in basic medium
(c) reducing agent in basic medium, but not in acidic medium
(d) oxidising agent in acidic medium, but not in basic medium

16. The metal that forms nitride by reacting directly with N_2 of air, is **(2019 Main, 9 Jan II)**
(a) Rb (b) K (c) Cs (d) Li

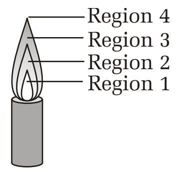
17. What is reason of temporary hardness of water? **(2019 Main, 9 Jan II)**
(a) Na_2SO_4 (b) $CaCl_2$ (c) NaCl (d) $Ca(HCO_3)_2$

18. The isotopes of hydrogen are **(2019 Main, 9 Jan I)**
(a) deuterium and tritium only
(b) protium and deuterium only
(c) protium, deuterium and tritium
(d) tritium and protium only

19. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4}$ to $[Fe(CN)_6]^{3}$ in acidic medium but reduces $[Fe(CN)_6]^{3}$ to $[Fe(CN)_6]^{4}$ in alkaline medium. The other products formed are, respectively. **(2018 Main)**
(a) $(H_2O + O_2)$ and H_2O (b) $(H_2O + O_2)$ and $(H_2O + OH\ )$
(c) H_2O and $(H_2O + O_2)$ (d) H_2O and $(H_2O + OH\ )$

20. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is **(2017 Main)**
(a) Both form basic carbonates
(b) Both form soluble bicarbonates
(c) Both form nitrides
(d) nitrates of both Li and Mg yield NO_2 and O_2 on heating

21. The hottest region of Bunsen flame shown in the figure given below is **(2016 Main)**



(a) region 2 (b) region 3 (c) region 4 (d) region 1

22. Which one of the following statements about water is false? **(2016 Main)**
(a) Water can act both as an acid and as a base
(b) There is extensive intramolecular hydrogen bonding in the condensed phase
(c) Ice formed by heavy water sinks in normal water
(d) Water is oxidised to oxygen during photosynthesis

23. The main oxides formed on combustion of Li, Na and K in excess of air respectively are **(2016 Main)**
(a) LiO_2, Na_2O_2 and K_2O (b) Li_2O_2, Na_2O_2 and KO_2
(c) Li_2O, Na_2O_2 and KO_2 (d) Li_2O , Na_2O and KO_2

24. Which of the following atoms has the highest first ionisation energy? **(2016 Main)**
(a) Na (b) K (c) Sc (d) Rb

25. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a **(2014 Adv.)**
(a) reducing agent, oxidising agent
(b) reducing agent, reducing agent
(c) oxidising agent, oxidising agent
(d) oxidising agent, reducing agent

26. In which of the following reactions H_2O_2 acts as a reducing agent? **(2014 Main)**

I. $H_2O_2 \quad 2H \quad 2e \qquad 2H_2O$
II. $H_2O_2 \quad 2e \qquad O_2 + 2H$
III. $H_2O_2 \quad 2e \qquad 2OH$
IV. $H_2O_2 + 2OH \quad 2e \qquad O_2 + 2H_2O$

(a) I and II (b) III and IV (c) I and III (d) II and IV

27. A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is **(2004, 1M)**
(a) SO_4^2 (b) HCO_3 (c) CO_3^2 (d) NO_3

28. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are respectively **(1996, 1M)**
(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na (c) O_2, Na (d) $S_2O_8^{2-}$, H_2

29. Hydrolysis of one mole of peroxodisulphuric acid produces **(1996, 1M)**
(a) two moles of sulphuric acid
(b) two moles of peroxomono sulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomono sulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomono sulphuric acid and one mole of hydrogen peroxide

30. The species that do not contain peroxide ions, is **(1992, 1M)**
(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2

31. The metallic lustre exhibited by sodium metal is explained by **(1987, 1M)**
(a) diffusion of sodium ions
(b) oscillation of loose electron
(c) excitation of free protons
(d) existence of body centred cubic lattice

32. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at cathode and anode are respectively **(1987, 1M)**
(a) H_2, O_2 (b) O_2, H_2 (c) O_2, Na (d) O_2, SO_2

33. Nitrogen dioxide cannot be obtained by heating **(1985, 1M)**
(a) KNO_3 (b) $Pb(NO_3)_2$ (c) $Cu(NO_3)_2$ (d) $AgNO_3$

34. The oxide that gives H_2O_2 on treatment with a dilute acid is **(1985, 1M)**
(a) PbO_2 (b) Na_2O_2
(c) MnO_2 (d) TiO_2

35. Molecular formula of Glauber's salt is **(1985, 1M)**
(a) $MgSO_4\ 7H_2O$ (b) $CuSO_4\ 5H_2O$
(c) $FeSO_4\ 7H_2O$ (d) $Na_2SO_4\ 10H_2O$

36. Heavy water is **(1983, 1M)**
(a) H_2O^{18}
(b) water obtained by repeated distillation
(c) D_2O
(d) water at 4°C

37. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of **(1981, 1M)**
(a) sodium atoms (b) sodium hydride
(c) sodium amide (d) solvated electrons

38. The temporary hardness of water is due to calcium bicarbonate can be removed by adding **(1979, 1M)**
(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) $CaCl_2$ (d) HCl

Objective Questions II
(One or more than one correct option)

39. The pair(s) of reagents that yield paramagnetic species is/are
(a) Na and excess of NH_3 (b) K and excess of O_2
(c) Cu and dilute HNO_3 (d) O_2 and 2-ethylanthraquinol

40. The compound(s) formed upon combustion of sodium metal in excess air is (are) **(2007, 2M)**
(a) Na_2O_2 (b) Na_2O (c) NaO_2 (d) NaOH

41. Sodium nitrate decomposes above 800°C to give **(1998, 2M)**
(a) N_2 (b) O_2
(c) NO_2 (d) Na_2O

42. Highly pure dilute solution of sodium in liquid ammonia **(1998, 2M)**
(a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amide
(d) produces hydrogen gas

43. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with **(1990, 1M)**
(a) H^+ ions (b) SO_4^{2-} ions (c) Mg^{2+} ions (d) OH ions

44. Sodium sulphate is soluble in water, whereas barium sulphate is sparingly soluble because **(1989, 1M)**
(a) the hydration energy of sodium sulphate is more than its lattice energy
(b) the lattice energy of barium sulphate is more than its hydration energy
(c) the lattice energy has no role to play in solubility
(d) the hydration energy of sodium sulphate is less than its lattice energy

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

45. **Statement I** Alkali metals dissolve in liquid ammonia to give blue solution.
Statement II Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]$ (M alkali metals). **(2007, 3M)**

46. **Statement I** LiCl is predominantly a covalent compound.
Statement II Electronegativity difference between Li and Cl is too small. **(1998, 2M)**

47. **Statement I** The alkali metals can form ionic hydrides which contain the hydride ion, H .
Statement II The alkali metals have low electronegativity, their hydrides conduct electricity when fused and liberate hydrogen gas at the anode. **(1994, 2M)**

Fill in the Blanks

48. Hydrogen gas is liberated by the action of aluminium with concentrated solution of .... **(1987, 1M)**

49. Sodium dissolved in liquid ammonia conducts electricity because of ...... **(1985, 1M)**

50. The adsorption of hydrogen by palladium is commonly known as ...... **(1983, 1M)**

51. Iodine reacts with hot NaOH solution. The products are NaI and ...... **(1980, 1M)**

True/False

52. Sodium when burnt in excess of oxygen gives sodium oxide. **(1987, 1M)**

Subjective Questions

53. A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
(i) Identify the substance and explain with balanced equation.
(ii) Explain what would happen to the red litmus if the white solid were the other compound. **(1999, 4M)**

54. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations. **(1998, 4M)**

55. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide gas. Identify A, B, C and D. **(1997, 3M)**

56. Complete and balance the following chemical reaction.
Anhydrous potassium nitrate is heated with excess of metallic potassium
$KNO_3(s) \quad K(s) \quad \ldots \ldots$ **(1992, 1M)**

57. Give reasons in one or two sentences for the following:
"H_2O_2 is a better oxidising agent than H_2O." **(1986, 1M)**

58. Sodium carbonate is prepared by Solvay process but the same process is not extended to the manufacture of potassium carbonate, explain. **(1981, 1M)**

59. Water is a liquid, while H_2S is a gas at ordinary temperature. Explain . **(1978, 1M)**

Topic 2 Group II Elements

Objective Questions I (Only one correct option)

1. In comparison to boron, berylium has **(2019 Main, 12 April II)**
(a) lesser nuclear charge and lesser first ionisation enthalpy
(b) greater nuclear charge and lesser first ionisation enthalpy
(c) greater nuclear charge and greater first ionisation enthalpy
(d) lesser nuclear charge and greater first ionisation enthalpy

2. The correct sequence of thermal stability of the following carbonates is **(2019 Main, 12 April I)**
(a) $BaCO_3$ $CaCO_3$ $SrCO_3$ $MgCO_3$
(b) $MgCO_3$ $CaCO_3$ $SrCO_3$ $BaCO_3$
(c) $MgCO_3$ $SrCO_3$ $CaCO_3$ $BaCO_3$
(d) $BaCO_3$ $SrCO_3$ $CaCO_3$ $MgCO_3$

3. A hydrated solid X on heating initially gives a monohydrated compound Y.
Y upon heating above 373 K leads to an anhydrous white powder Z. X and Z, respectively, are **(2019 Main, 10 April II)**
(a) baking soda and soda ash
(b) washing soda and soda ash
(c) baking soda and dead burnt plaster
(d) washing soda and dead burnt plaster

4. The alloy used in the construction of aircrafts is **(2019 Main, 10 April I)**
(a) Mg-Zn (b) Mg-Mn (c) Mg-Sn (d) Mg-Al

5. The structures of beryllium chloride in the solid state and vapour phase, respectively are **(2019 Main, 9 April II)**
(a) dimeric and dimeric (b) chain and chain
(c) dimeric and chain (d) chain and dimeric

6. Magnesium powder burns in air to give **(2019 Main, 9 April I)**
(a) MgO and Mg_3N_2 (b) $Mg(NO_3)_2$ and Mg_3N_2
(c) MgO only (d) MgO and $Mg(NO_3)_2$

7. The covalent alkaline earth metal halide (X = Cl, Br, I) is **(2019 Main, 8 April II)**
(a) SrX_2 (b) CaX_2 (c) MgX_2 (d) BeX_2

8. Match the following items in Column I with the corresponding items in Column II. **(2019 Main, 11 Jan II)**

	Column I		Column II
(i)	Na_2CO_3 $10H_2O$	A.	Portland cement ingredient
(ii)	$Mg(HCO_3)_2$	B.	Castner-Kellner process
(iii)	NaOH	C.	Solvay process
(iv)	$Ca_3Al_2O_6$	D.	Temporary hardness

(a) (i) - (D); (ii) - (A); (iii) - (B); (iv) - (C)
(b) (i) - (B); (ii) - (C); (iii) - (A); (iv) - (D)
(c) (i) - (C); (ii) - (B); (iii) - (D); (iv) - (A)
(d) (i) - (C); (ii) - (D); (iii) - (B); (iv) - (A)

9. The amphoteric hydroxide is **(2019 Main, 11 Jan I)**
(a) $Be(OH)_2$ (b) $Ca(OH)_2$ (c) $Sr(OH)_2$ (d) $Mg(OH)_2$

10. The metal used for making X-ray tube window is **(2019 Main, 10 Jan I)**
(a) Na (b) Be (c) Mg (d) Ca

11. The alkaline earth metal nitrate that does not crystallise with water molecules, is **(2019 Main, 9 Jan I)**
(a) $Ca(NO_3)_2$ (b) $Sr(NO_3)_2$
(c) $Ba(NO_3)_2$ (d) $Mg(NO_3)_2$

12. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **(2015 Main)**
(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

13. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order.
K_2CO_3 (I), $MgCO_3$ (II), $CaCO_3$ (III), $BeCO_3$ (IV)
(a) I < II < III < IV (b) IV < II < III < I **(1996, 1M)**
(c) IV < II < I < III (d) II < IV < III < I

14. The oxidation state of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 are **(1991, 1M)**
(a) 0 and –1 (b) –1 and –2
(c) –2 and 0 (d) –2 and –1

15. Calcium is obtained by **(1980, 1M)**
(a) electrolysis of molten $CaCl_2$
(b) electrolysis of solution of $CaCl_2$ in water
(c) reduction of $CaCl_2$ with carbon
(d) roasting of limestone

Objective Questions II
(One or more than one correct option)

16. The reagent(s) used for softening the temporary hardness of water is(are) **(2010)**
(a) $Ca_3(PO_4)_2$ (b) $Ca(OH)_2$
(c) Na_2CO_3 (d) NaOCl

17. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula? **(2006, 3M)**
(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_3$
(c) $MgCl_2$ $MgSO_4$ (d) $MgSO_4$

18. The material used in solar cells contains **(1993, 1M)**
(a) Cs (b) Si (c) Sn (d) Ti

Fill in the Blank

19. Anhydrous $MgCl_2$ is obtained by heating the hydrated salt with …… **(1980, 1M)**

True/False

20. $MgCl_2$ $6H_2O$ on heating gives anhydrous $MgCl_2$. **(1982, 1M)**

Subjective Questions

21. Identify (X) in the following synthetic scheme and write their structures.

$Ba\overset{*}{C}O_3 + H_2SO_4$ X (gas) (C* denotes C^{14}) **(2001, 1M)**

22. Give reasons for the following in one or two sentences only :
"$BeCl_2$ can be easily hydrolysed." **(1999, 2M)**

23. The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why? **(1997, 2M)**

24. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas *A* and an alkaline solution. The solution on exposure to air produces a thin solid layer of *B* on the surface. Identify the compounds *A* and *B*. **(1996, 3M)**

25. Arrange the following in increasing order of basic strength :

$MgO, SrO, K_2O, NiO, Cs_2O$ **(1991, 1M)**

Answers

Topic 1

1. (a)	**2.** (c)	**3.** (c)	**4.** (a)
5. (d)	**6.** (d)	**7.** (b)	**8.** (c)
9. (a)	**10.** (c)	**11.** (a)	**12.** (c)
13. (d)	**14.** (d)	**15.** (a)	**16.** (d)
17. (d)	**18.** (c)	**19.** (c)	**20.** (a)
21. (a)	**22.** (b)	**23.** (c)	**24.** (c)
25. (a)	**26.** (d)	**27.** (b)	**28.** (a)
29. (c)	**30.** (a)	**31.** (b)	**32.** (a)
33. (a)	**34.** (b)	**35.** (d)	**36.** (c)
37. (d)	**38.** (b)	**39.** (a, b, c)	**40.** (a, b)
41. (a, b, d)	**42.** (a, b)	**43.** (a, d)	**44.** (a, b)
45. (b)	**46.** (c)	**47.** (a)	**48.** NaOH
49. solvated electrons		**50.** occlusion	**51.** $NaIO_3$
52. F			

Topic 2

1. (d)	**2.** (b)	**3.** (b)	**4.** (d)
5. (c)	**6.** (a)	**7.** (d)	**8.** (d)
9. (a)	**10.** (b)	**11.** (c)	**12.** (b)
13. (b)	**14.** (d)	**15.** (a)	**16.** (b, c, d)
17. (a)	**18.** (b)	**19.** dry HCl	**20.** F

Hints & Solutions

Topic 1 Group I Elements

1. The temporary hardness of a water sample is due to compound *X* [i.e. $Mg(HCO_3)_2$]. Boiling of this sample converts *X*[i.e. $Mg(HCO_3)_2$] to compound *Y*[i.e. $Mg(OH)_2$]. Generally, temporary hardness is due to presence of magnesium and calcium hydrogen carbonates. It can be removed by boiling. During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ changed to insoluble $CaCO_3$. These precipitates can be removed by filteration.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \quad 2CO_2$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \quad H_2O \quad CO_2$$

2. Statement (c) is incorrect. $LiNO_3$(Lithium nitrate) on heating gives a mixture of Li_2O, NO_2 and O_2.

$$4LiNO_3 \quad 2Li_2O \quad 4NO_2 \quad O_2$$

Among the alkali metals, lithium is the strongest reducing agent.

3. Metal that gives hydrogen gas upon treatment with both acid as well as base is zinc. Hence, it is amphoteric in nature.
Reactions involved are as follows:

$$Zn \quad \text{Dil. NaOH} \quad Na_2ZnO_2 \quad H_2$$

$$Zn \quad 2HCl(\text{dil.}) \quad ZnCl_2 \quad H_2$$

4. The explanation of given statements are as follows :

1. Saline or ionic hydrides produce H_2 with H_2O.

$$M\overset{\ominus}{H} + H_2O \quad H_2 \quad + MOH$$

Thus, statement (1) is correct.

2. $$3LiAlH_4 + 4BF_3 \xrightarrow{\text{Ether}} \underset{\text{(Diborane)}}{2B_2H_6} + 3LiF + 3AlF_3$$

Thus, statement (2) is correct.

3. PH_3 and CH_4 are covalent hydrides and in both of the hydrides, octet of P and C have been satisfied. But P in PH_3 has one lone pair of electrons and C in CH_4 does not have so PH_3 (group 15) and CH_4 (group 14) are electron rich and electron precise hydrides, respectively.

Thus, statement (3) is correct.

4. HF and CH_4 are called as molecular hydrides because of their discrete and sterically symmetrical structure.

Thus, statement (4) is also correct.

5. 11.2 volume of H_2O_2 means that 1 mL of this H_2O_2 will give 11.2 mL of oxygen at STP.

$$\underset{2 \quad 34\text{ g}}{2H_2O_2(l)} \quad \underset{22.4\text{ L at STP}}{O_2(g)} \quad 2H_2O(l)$$

22.4 L of O_2 at STP is produced from H_2O_2 68 g

11.2 L of O_2 at STP is produced from

$$H_2O_2 \quad \frac{68}{22.4} \quad 11.2 \quad 34\text{ g}$$

34 g of H_2O_2 is present in 1000 g of solution

$$\% \ w/w \quad \frac{34}{1000} \quad 100 \quad 3.4\%$$

6. **Key Idea** The amount of energy released when one mole of gaseous ions combine with water to form hydrated ions is called hydration enthalpy.

The correct order of hydration enthalpies of alkali metal ions is

$$Li \quad Na \quad K \quad Rb \quad Cs$$

Li possesses the maximum degree of hydration due to its small size. As a consequence of hydration enthalpy, their mobility also get affected. Cs^+ has highest and Li has lowest mobility in aqueous solution.

7. All the statements are correct. K being metallic unipositive ions work as enzyme activators. These also participate in many reactions of glycolysis and Kreb's cycle to produce ATP from glucose.

Being unipositive these are also equally responsible for nerve signal transmission along with Na . (Na ion-pump theory)

8. Metal (*A*) is rubidium (Rb). In excess of air, it forms $RbO_2(X)$.
X is a superoxide that have O_2 ion. It is due to the stabilisation of large anion by large cations through lattice energy effects. $RbO_2\,(X)$ gets easily hydrolysed by water to form the hydroxide, H_2O_2 and O_2.
The reaction involved are as follows:

$$Rb + O_2 \qquad \underset{(X)}{RbO_2} \text{ (superoxide)}$$

$$\underset{(X)}{2RbO_2} + 2H_2O \qquad 2RbOH + H_2O_2 + O_2$$

9. Hardness of water sample can be calculated in terms of ppm concentration of $CaCO_3$.

Given, molarity $10\ ^{3}$M

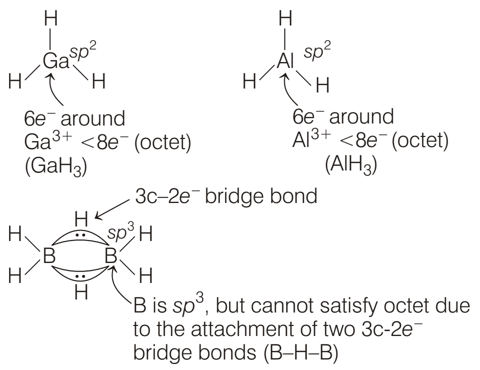
i.e. 1000 mL of solution contains $10\ ^{3}$ mole of $CaCO_3$.

$$\text{Hardness of water} \quad \text{ppm of } CaCO_3$$

$$\frac{10\ ^{3}\quad 1000}{1000} \quad 10^6$$

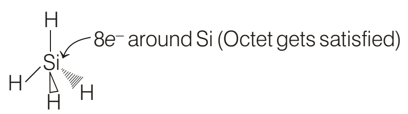
$$100\,\text{ppm}$$

10. GaH_3, AlH_3 and B_2H_6 are the hydrides of group-13 (ns^2np^1), whereas SiH_4 is an hydride of group 14.



So, B_2H_6, AlH_3 and GaH_3 are electron deficient hydrides.

But, SiH_4 is an electron precise hydride of group-14 (ns^2np^2), i.e. these hydrides can have the required number of electrons to write their conventional Lewis structures.



11. (I) H_2 is a 100% pollution free fuel. So, statement (I) is correct.

(II) Molecular weight of H_2(2u).

$\frac{1}{29}$ molecular weight of butane,

C_4H_{10} (LPG) [58u].

So, compressed H_2 weighs ~30 times more than a petrol tank and statement (II) is correct.

(III) $NaNi_5$, $Ti\text{-}TiH_2$ etc. are used for storage of H_2 in small quantities. Thus, statement (III) is correct.

(IV) On combustion values of energy released per gram of liquid dihydrogen (H_2) : 142 kJ g ^{1}, and for LPG : 50 kJ g ^{1}. So, staement (IV) is incorrect.

12. $\overset{\oplus}{Na}\overset{\ominus}{H}$ is an example of ionic or saline hydride. These hydrides are formed when hydrogen combines with metals having less electronegativity and more electropositive character with respect to hydrogen.

Except Be and Mg, all *s*-block metals form saline hydrides.

Hydrides of *p*-block elements are covalent in nature, *viz*, electron deficient hydrides (by group-13 elements), electron-precise hydrides (by group-14 elements), and electron-rich hydrides (by group 15-17 elements). Hydrides of d, f-block metals are called interstitial or metallic hydrides.

13. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of ammoniated electrons. The reaction is represented as follows:

$$Na(s) \quad (x \quad y)\,NH_3(l) \qquad \underset{\substack{\text{[Ammoniated Na}\\\text{or expanded Na]}}}{[Na(NH)_x]} \quad \underset{\substack{\text{[Ammoniated}\\\text{electrons]}}}{[e_{(NH_3)_y}]}$$

Ammoniated (solvated) electrons show electronic transition in visible region and the solution becomes deep blue coloured.

This deep blue solution also shows the following properties due to the presence of ammoniated electrons.

(i) It is strongly reducing in nature.
(ii) It is paramagnetic.
(iii) It is a good conductor of electricity.

14. Hydrogen has three isotopes:

	^1_1H	^2_1H	^3_1H
	Protium (P)	**Deuterium (D)**	**Tritium (T)**
p	1	1	1
n	0	1	2
$\frac{n}{p}$	0	1	2

Only tritium (T) is radioactive, because of its very high $\frac{n}{p}$ value, $\frac{n}{p}\quad 2$.

15. H_2O_2 can act as both oxidising and reducing agents in both acidic and basic medium.

H_2O_2 as oxidising agent

- In acidic medium: $H_2O_2 + 2H^+ + 2e \qquad 2H_2O$

- In basic medium : $H_2O_2 + 2O\,H + 2e \qquad 2H_2O + 2O^2$

H_2O_2 as reducing agent

- In acidic medium : $H_2O_2 \qquad O_2 \quad 2H \quad 2e$

In basic medium :

$H_2O_2 + 2OH \qquad O_2 \quad 2H_2O \quad 2e$

16. Among the group-1 metals, only Li is able to form its nitride, Li_3N. [All alkaline earth metals of group-2 form their nitride, M_3N_2]

$6Li + \underset{(Air)}{N_2} \qquad 2Li_3N$ (Ruby red solid)

$[3\overset{I}{M} + N_2 \qquad \overset{II}{M_3}N_2]$

Li is the smallest metal ion of group-1. Smaller size of Li and larger size of nitride ion, N^3, enable Li to polarise the spherical electron cloud of N^3 and it gives higher stability to Li_3N.

17. Temporary hardness of water is due to presence of soluble $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$.

Permanent hardness of water is due to the presence of $CaCl_2$ or $CaSO_4$ or $MgCl_2$ or $MgSO_4$.

Temporary hardness of water is also called carbonate hardness which can be easily removed by boiling or by treatment with $Ca(OH)_2$ (Clark's method).

18. There are three known isotopes of hydrogen, each possessing an atomic number 1 and atomic masses 1, 2 and 3 respectively. These are named as protium (^1H), deuterium (^2H or D) and tritium (^3H or T)

The most common isotope is the ordinary hydrogen usually called protium. It consists of one proton in the nucleus and an electron revolving around it.

The second isotope of hydrogen is called heavy hydrogen or deuterium. It consists of one proton and one neutron in the nucleus and an electron revolving around it. The third isotope of hydrogen is called tritium. It consists of one proton and two neutrons in the nucleus and an electron revolving around it.

19. Both reactions in their complete format are written below

(i) In acidic medium,

$[Fe^{2+}(CN)_6]^4 + H_2\overset{1}{O_2} + 2H^+ \qquad [Fe^{3+}(CN)_6]^3 + 2H_2\overset{2}{O}$

(ii) In alkaline medium,

$[Fe^{3+}(CN)_6]^3 \quad H_2\overset{1}{O_2} \quad 2OH$

$[Fe^2\ (CN)_6]^4 \quad O_2 \quad 2H_2O$

Hence, H_2O (for reaction (i)) and $O_2 + H_2O$ (for reaction (ii)) are produced as by product.

20. **Mg** can form basic carbonate while **Li** cannot.

$5\,Mg^{2+} \quad 6\,CO_3^{2-} \quad 7H_2O \qquad 4MgCO_3\ \ Mg(OH)_2$

$5H_2O + 2\,HCO_3$

21. Region 1 (Pre-heating zone)
Region 2 (Primary combustion zone, hottest zone)
Region 3 (Internal zone)
Region 4 (Secondary reaction zone)

22. There is extensive intermolecular H-bonding in the condensed phase.

23. $2Li + \frac{1}{2}\underset{(Excess)}{O_2(g)} \qquad Li_2O$

$2Na + \underset{(Excess)}{O_2(g)} \qquad Na_2O_2;\ K + \underset{(Excess)}{O_2(g)} \qquad KO_2$

24. Order of first ionisation energy is Sc > Na > K > Rb.

Due to poor shielding effect, removal of one electron from 4*s* orbital is difficult as compared to 3*s*-orbital.

25. **PLAN** This problem can be solved by using concept of oxidant and reductant.

Oxidant Oxidant increases the oxidation number of the species with which it is reacted.

Reductant Reductant decreases the oxidation number of the species with which it is reacted.

H_2O_2 reacts with KIO_4 in the following manner:

$K\overset{7}{I}O_4 + H_2O_2 \qquad K\overset{5}{I}O_3 + H_2O + O_2$

On reaction of KIO_4 with H_2O_2, oxidation state of I varies from +7 to +5, i.e. decreases. Thus, KIO_4 gets reduced hence, H_2O_2 is a reducing agent here.

With NH_2OH, it given following reaction:

$\overset{1}{N}H_2OH + H_2O_2 \qquad \overset{3}{N_2}O_3 + H_2O$

In the above reaction, oxidation state of N varies from –1 to +3. Here, oxidation number increases, hence H_2O_2 is acting as an oxidising agent here.

Hence, (a) is the correct choice.

26. Release of electron is known as reduction. So, H_2O_2 acts as reducing agent when it releases electrons.

Here, in reaction (II) and (IV), H_2O_2 releases two electron, hence reaction (II) and (IV) is known as **reduction**.

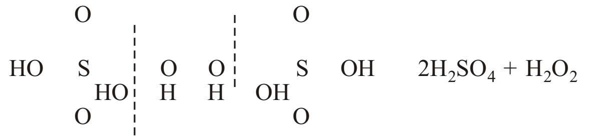
In reaction (I) and (III), two electrons are being added, so (I) and (III) represents **oxidation.**

27. $Mg(HCO_3)_2$ on boiling decomposes to give white precipitate of $MgCO_3$ as:

$Mg(HCO_3)_2\ (aq) \xrightarrow{Heat} MgCO_3 + H_2O + CO_2$

28. Electrolysis of aqueous Na_2SO_4 gives $H_2\ (g)$ at cathode and $O_2(g)$ at anode.

29. Peroxodisulphuric acid ($H_2S_2O_8$) on complete hydrolysis gives two moles of H_2SO_4 and one mole of H_2O_2 as



On partial hydrolysis, it gives one mole of H_2SO_4 and one mole of peroxomonosulphuric acid as

HO S O ¦ O S OH $\quad H_2SO_4$
(with O above and below each S; H ¦ OH under the O–O bond)

$+ HO \; S \; O \; O \; H$ (with O above and below S)

Peroxomonosulphuric acid

30. In PbO_2, Pb is in +4 oxidation state and oxygen is in –2 oxidation state. In all other case, peroxide ion (O_2^{2}) is present.

31. Metallic lustre of any metal is due to oscillation of free electrons present in the metal.

32. H_2O is reduced as well as oxidised giving $H_2(g)$ at cathode and $O_2(g)$ at anode.

33. KNO_3 and other nitrates of alkli metals (except $LiNO_3$) are thermally stable.

34. Sodium peroxide on treatment with dilute acid gives H_2O_2

$$Na_2O_2 + H_2SO_4 \qquad Na_2SO_4 + H_2O_2$$

35. Glauber's salt is $Na_2SO_4 \;\; 10H_2O$.

36. D_2O is commonly known as heavy water.

37. Presence of solvated electrons makes solution of alkali metal in liquid ammonia makes them strongly reducing agent.

38. Lime treatment remove bicarbonate hardness by forming insoluble $CaCO_3$ as

$$Ca(HCO_3)_2 + Ca(OH)_2 \qquad 2CaCO_3 \quad + 2H_2O$$

39. **PLAN** Paramagnetic character of species can be easily explained on the basis of presence of unpaired electrons, i.e. compounds containing unpaired electron(s) is/are paramagnetic.

Reaction of alkali metals with ammonia depends upon the physical state of ammonia whether it is in gaseous state or liquid state. If ammonia is considered as a gas then reaction will be

(a) $Na + \underset{\text{(Excess)}}{NH_3} \qquad NaNH_2 + \frac{1}{2}H_2$

($NaNH_2$ + 1/2 H_2 are diamagnetic)

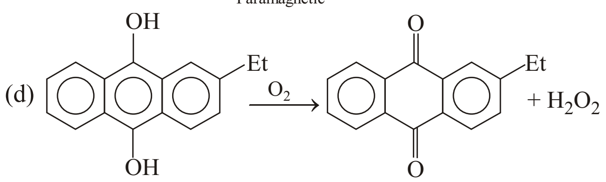
If ammonia is considered as a liquid then reaction will be

$$M \quad (x \quad y)NH_3 \qquad [M(NH_3)_x] \quad [e(NH_3)_y]$$

Ammoniated electron
Blue colour
Paramagnetic
Very strong reducing agent

(b) $K \quad \underset{\text{(Excess)}}{O_2} \qquad \underset{\text{Potassium superoxide paramagnetic}}{KO_2(K \;\; , O_2\;)}$

(c) $3Cu + 8HNO_3 \qquad \underset{\text{Paramagnetic}}{3Cu(NO_3)_2} \quad \underset{\text{Paramagnetic}}{2NO} \quad 4H_2O$

(d) 

2-ethylanthraquinol $\qquad$ 2-ethylanthraquinone

Hence, option (a), (b) and (c) are correct choices.

40. When sodium metal is burnt in excess of air, mainly sodium peroxide (Na_2O_2) with little sodium oxide (Na_2O) are formed.

41. $NaNO_3$ when heated, it decomposes in two stages as:

$$NaNO_3 \xrightarrow{T < 500\,C} NaNO_2 + \frac{1}{2}O_2$$

$$NaNO_2 \xrightarrow{T > 800\,C} Na_2O + N_2 + O_2$$

42. In dilute solution of Na in liquid ammonia, solvated electrons are present whose emission spectrum gives blue colouration to solution.

$$Na + NH_3 \qquad Na^+ + \underset{\text{Solvated electron}}{NH_3\,(e\;\;)}$$

Also, presence of solvated electrons and solvated Na^+ ion makes solution highly conducting.

43. Zeolite acts as ion exchange resin and its Na^+ is exchanged with H^+ and Mg^{2+} ions present in hard water.

44. Solubility of a salt is influenced by two major factors, lattice energy and hydration energy. For greater solubility, there should be smaller lattice energy and greater hydration energy.

45. Both statements are correct but blue colour is due to presence of solvated electron NH_3 (e).

46. Statement I is correct. Small size of Li^+ makes it highly polarising, introduces predominant covalency in LiCl. Statement II is incorrect, there is very large difference in electronegativity of Li and Cl.

47. Alkali metal forms *M*H in which hydrogen is in –1 oxidation state. Both statements are correct and statement –2 is correct explanation of statement I.

48. Al + conc. NaOH $\qquad NaAlO_2 + H_2$

49. Na in liquid ammonia contain $NH_3(e\;\;)$ which possesses charge and conduct electricity.

50. Occlusion is a phenomena in which particles are physically trapped in voids.

51. I_2 disproportionate in alkali giving NaI and $NaIO_3$.

52. Sodium when burnt in excess of oxygen, gives sodium peroxide as major product.

$$Na + O_2 \qquad \underset{\text{Major}}{Na_2O_2} + \underset{\text{Minor}}{Na_2O}$$

53. The substance is Na_2O_2. When Na_2O_2 is dissolved in water, it forms NaOH and H_2O_2. In this case, NaOH is a strong base while H_2O_2 is a weak acid.

(i) $Na_2O_2 + 2H_2O \qquad 2NaOH + H_2O_2$

H_2O_2 decolourises red litmus paper due to its bleaching action which is due to its oxidising character.

$$H_2O_2 \qquad H_2O + \underset{\text{Bleaches colour of red litmus}}{[O]}$$

(ii) If the compound is Na_2O, it will hydrolyse to form NaOH.

$$Na_2O + H_2O \qquad 2NaOH$$

NaOH solution formed above will change colour of red litmus paper into blue.

54. $\underset{\text{OA}}{KMnO_4} + \underset{\text{RA}}{H_2O_2} \qquad MnO_2 + KOH + O_2$

$\underset{\text{RA}}{FeSO_4} + \underset{\text{OA}}{H_2O_2} \qquad Fe^{3+} + H_2O$

55. $\underset{A}{3M} + N_2 \qquad \underset{B}{M_3N_2}$

$\underset{B}{M_3N_2} + 6H_2O \qquad \underset{C}{3M(OH)_2} + \underset{D}{2NH_3}$

$\underset{C}{M(OH)_2} + CO_2 \qquad \underset{\text{Milkyness}}{MCO_3}$

M can be either Ca or Ba but essentially not Mg because $Mg(OH)_2$ is very sparingly soluble in water.

56. $2KNO_3(s) + 10K(s) \qquad 6K_2O(s) + N_2(g)$

57. In H_2O_2, the peroxide ion (O_2^{2}) is unstable, has tendency to pass into stable oxide state (O^{2}). Hence, H_2O_2 is a good oxidising agent while H_2O is stable.

58. In Solvay process, $NaHCO_3$ is extracted from the solution by fractional crystallisation, which is then heated to convert it into Na_2CO_3. $KHCO_3$, being more soluble than $NaHCO_3$, cannot be extracted by fractional crystallisation. Hence, Solvay process fails in production of K_2CO_3.

59. Water forms stronger intermolecular H-bonds, therefore it is liquid at room temperature while H_2S cannot form such strong intermolecular bonds, gas at room temperature.

Topic 2 Group II Elements

1. In comparison to boron, beryllium has lesser nuclear charge and greater first ionisation enthalpy.

Electronic configuration of Be(4) $1s^2, 2s^2$.

It possess completely filled *s*-orbitals. Hence, high amount of energy is required to pull the electron from the gaseous atom. Beryllium (4) lies left to the boron (5) and on moving from left to right an electron is added due to which nuclear charge increases from Be to B.

2. The correct sequence of thermal stability of carbonates is

$MgCO_3 \quad CaCO_3 \quad SrCO_3 \quad BaCO_3$

On moving down the group, i.e. from Mg to Ba, atomic radius generally increases. It is due to the addition of shell. As a result, the atomic size increases. CO_3^{2} is a large anion. Hence, more stabilised by Ba^{2} (large cation) and less stabilised by Mg^{2}. Therefore, $BaCO_3$ has highest thermal stability followed by $SrCO_3$, $CaCO_3$ and $MgCO_3$.

3. Baking soda ($NaHCO_3$) is not a hydrated solid. Thus, (X) is not baking soda. Thus, option (a) and (c) are incorrect. Dead burnt plaster ($CaSO_4$) is obtained from gypsum *via* the formation of plaster of Paris.

$$\underset{\text{Gypsum}}{CaSO_4 \ 2H_2O} \xrightarrow[1/2\,H_2O]{380\text{-}393\text{ K}} \underset{\text{Plaster of Paris}}{CaSO_4 \ \frac{1}{2}H_2O} \xrightarrow[\frac{1}{2}H_2O]{>393\text{K}} \underset{\text{Dead burnt plaster (anhydrous)}}{CaSO_4}$$

Therefore, the reaction takes place as follows :

$$\underset{\text{Washing soda }(X)}{Na_2CO_3 \ 10H_2O} \xrightarrow[9H_2O]{<373\text{K}} \underset{\text{Monohydrate }(Y)}{Na_2CO_3 \ H_2O} \xrightarrow[H_2O]{>373\text{K}} \underset{\text{Anhydrous white powder (soda ash) }(Z)}{Na_2CO_3}$$

4. Names of magnesium alloys are given by two letters followed by two numbers. The common alloying elements are A (Aluminium), Z (zinc), T (tin), M (manganese) etc. Numbers indicate respective nominal compositions of main alloying elements, e.g. 'AZ 91' implies the composition of the alloy as : Al = 9%, Zn = 1% and Mg = 100 – (9 + 1) = 90%

Among the alloys given, Mg – Al (Magnalium ; Mg = 5%, Al =95%) is being light, tough and strong, hence it is used in aircrafts.

5. The structures of beryllium chloride in the solid state and vapour phase, respectively are dimeric and chain. In vapour phase at above 900°C, $BeCl_2$ is monomeric having a linear structure Cl Be Cl. The bonding in $BeCl_2$ is covalent and Be atom accommodates 2 2 4 electrons in the two *sp*-hybrid orbitals. Below 900°C, beryllium chloride in vapour phase exists as a mixture of monomer $BeCl_2$ and dimer Be_2Cl_4.

6. Magnesium powder burns in air to give MgO and Mg_3N_2. MgO does not combine with excess oxygen to give any superoxide. Mg reacts with nitrogen to form magnesium nitride (Mg_3N_2).

$Mg \quad O_2 \qquad MgO$

$3Mg \quad N_2 \qquad Mg_3N_2$

7. **Key Idea** According to Fajan's rule, degree of covalency (ionic potential), -polarisation power of the cation charge on the cation $\dfrac{1}{\text{size of the cation}}$.

Alkaline earth metals contains bipositive (H^{2}) ions in their compounds.

So, here

(i) Charge on cation, i.e. 2 is constant.

(ii) Halide present (X) is also constant.

So, the covalent character depends on the size of alkaline earth metal. As we move down the group, size of metal ion increases.

$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$

So, Be^{2} readily forms covalent compounds like BeX_2, because of very high positive charge density over its small size, so that it readily polarises anionic spherical electron cloud.

8. (i) Washing soda ($Na_2CO_3 \ 10H_2O$) is manufactured in Solvay process. In this method, CO_2 gas is passed through a conc. solution of NaCl saturated with NH_3. It gives ammonium carbonate followed by ammonium hydrogen carbonate.

The obtained NH_4HCO_3 is treated with solution of NaCl which result in the formation of $NaHCO_3$. The crystal obtained are heated to obtain Na_2CO_3.

$NaCl \quad NH_3 \quad CO_2 \quad H_2O \qquad NaHCO_3 \quad NH_4Cl$

$$2NaHCO_3 \xrightarrow[H_2O,\ CO_2]{} Na_2CO_3 \xrightarrow{\text{Crystallisation}} Na_2CO_3 \ 10H_2O$$

(ii) $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ cause temporary hardness to water that can be easily removed by boiling.

(iii) NaOH is manufactured by Castner-Kellner process.

In this reaction, Na amalgam flows out and treated with water to give NaOH and H_2 gas. During electrolysis, hydrogen is evolved at cathode and chlorine is evolved at anode, which are the by product of this process.

$$2NaCl(aq) \xrightarrow{\text{Electrolysis}} \begin{cases} \boxed{\text{Carbon anode}}\ 2Cl^{-} - 2e \longrightarrow Cl_2\uparrow \\ \boxed{\text{Hg cathode}}\ 2Na^{+} + 2e \end{cases}$$

$$\downarrow$$

$$2Na\ (Na/Hg)$$

$$\downarrow H_2O$$

$$2NaOH(aq) + H_2\uparrow$$

(iv) Portland cement constitutes, tricalcium aluminosilicate, $3CaO\ Al_2O_3.\ SiO_2$, i.e. $Ca_3Al_2O_6\ \ SiO_2$.

9. For group-2 metal hydroxides, basicity increases down the group, as:

$Be(OH)_2\quad Mg(OH)_2\quad Ca(OH)_2\quad Sr(OH)_2\quad Ba(OH)_2$

This is because as the size of metal atom increases, *M*—OH bond length increases or *M*—OH bond become weaker thus readily breaks to release OH ions which are responsible for the basicity of these solutions.

But $Be(OH)_2$ shows amphoteric (basic as well as acidic) character as it reacts with acid and alkali both which is shown in the following reactions. $Be(OH)_2$ as a base :

$$Be(OH)_2\quad 2HCl\qquad BeCl_2\quad 2H_2O$$

$Be(OH)_2$ as an acid :

$$Be(OH)_2\quad 2NaOH\qquad Na_2[Be(OH)_4]$$

10. Among the four elements given, Na, Be, Mg and Ca, Be has highest IE value because of its smallest size and $2s^2$ valence shell configuration.

So, *X*-ray cannot cause ionisation from the material used, i.e. Be in the tube window, which may cause interference in the study.

11. A saturated aqueous solution of $\overset{\text{I}}{M}(NO_3)_2$ on crystallisation will produce hydrated crystal, $\overset{\text{II}}{M}(NO_3)_2\ \ nH_2O$ only when hydration enthalpy (H_{hyd}) of M^{2} ion will be appreciably more negative.

Hydration of an ion depends on its size. Smaller the size of an ion, higher will be its charge density and as a result it will remain more solvated (hydrated) through ion dipole interaction.

Size of group-2 metal ions increases on going down the group. So, their ability to form hydrated crystals follows the order:

$$Be^{2}\qquad Mg^{2}\qquad Ca^{2}\qquad Sr^{2}\qquad Ba^{2}$$

Thus, $Ba(NO_3)_2$ is slightly or almost insoluble in water.

12. As we move down the group, size of metal increases. Be has lower size while SO_4^{2} has bigger size, that's why $BeSO_4$ breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases. On the other hand, rest of the metals, i.e. Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time saving technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy. Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, $BeSO_4$ is the right response.

13. Thermal stability of salts with common anion depends on polarising power of cation. Greater the polarising power, lower be their thermal stability. Hence,

$BeCO_3$ (IV) < $MgCO_3$ (II) < $CaCO_3$ (III) < K_2CO_3 (I)

14. The reaction involved is

$$BaO_2 + H_2SO_4\qquad BaSO_4 + H_2O_2$$

The most electronegative atom, oxygen, in $BaSO_4$ and H_2O_2 has 2 and 1 oxidation state respectively.

15. Electrolysis of molten $CaCl_2$ gives calcium at cathode

$$Ca^{2+} + 2e\qquad Ca\quad \text{(at cathode)}$$

In case of electrolysis in aqueous medium, less electropositive H^{+} is reduced at cathode rather than Ca^{2+}.

16. $Ca(OH)_2 + Ca(HCO_3)_2\qquad 2CaCO_3\quad + \quad \underset{\text{(Clark's method)}}{2H_2O}$

$$NaOCl + H_2\qquad NaOH + HOCl$$

$$HO\ \ + HCO_3\qquad CO_3^{2}\ \ + H_2O$$

$$Ca(HCO_3)_2 + Na_2CO_3\qquad CaCO_3\quad + 2NaHCO_3$$

17. Magnesium ammonium phosphate is precipitated out.

$MgSO_4 + NH_4OH + Na_2HPO_4\qquad Mg(NH_4)PO_4\quad + Na_2SO_4$

18. Si is used in solar cells, because of its semi-conductor properties.

19. Anhydrous $MgCl_2$ is obtained by heating hydrated salt in stream of dry HCl.

20. Heating $MgCl_2\ \ 6H_2O$ brings about partial dehydration as

$$MgCl_2\ \ 6H_2O\qquad Mg(OHCl) + HCl + 5H_2O$$

21. $Ba\overset{*}{C}O_3 + H_2SO_4\qquad BaSO_4 + H_2O + \overset{*}{C}O_2\qquad (\overset{*}{C}\quad C^{14})$

22. Be in $BeCl_2$ is electron deficient, short of two lone pair of electrons from stable octet. H_2O has lone pair of electrons, reacts with $BeCl_2$.

23. Alkaline earth metal salts have M^{2+} ions which has very high polarising power compared to polarising power of monovalent metal ion (M^{+}) of alkali metal. Due to high polarising power of M^{2+}, it associate more water than M^{+}.

24. *A* NH_3, *B* $CaCO_3$.

Reactions involved are :

$$3Ca + N_2\ \xrightarrow{\text{Heat}}\ Ca_3N_2$$

$$Ca_3N_2 + 6H_2O\qquad 3Ca(OH)_2 + \underset{A}{2NH_3}$$

$$Ca(OH)_2 + \underset{\text{(From air)}}{CO_2}\qquad \underset{B}{CaCO_3} + H_2O$$

25. Basic strength (i) decreases from left to right in period and (ii) increases from top to bottom in group. Therefore,

$$NiO < MgO < SrO < K_2O < Cs_2O\quad \text{Basic strength}$$

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15

p-Block Elements-I

Topic 1 Group 13 Elements

Objective Questions I

(Only one correct option)

1. The correct statements among I to III regarding group 13 element oxides are: **(2019 Main, 9 April II)**

I. Boron trioxide is acidic.

II. Oxides of aluminium and gallium are amphoteric.

III. Oxides of indium and thallium are basic.

(a) I, II and III (b) I and III only
(c) I and II only (d) II and III only

2. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively. **(2019 Main, 8 April I)**

(a) B_2O_3 and H_3BO_3 (b) B_2O_3 and $[BH_4]$
(c) H_3BO_3 and B_2O_3 (d) HBO_2 and H_3BO_3

3. The relative stability of 1 oxidation state of group 13 elements follows the order **(2019 Main, 11 Jan II)**

(a) Al < Ga < Tl < In (b) Al < Ga < In < Tl
(c) Tl < In < Ga < Al (d) Ga < Al < In < Tl

4. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are **(2019 Main, 10 Jan II)**

(a) 4 and 2 (b) 2 and 4
(c) 2 and 2 (d) 2 and 1

5. The electronegativity of aluminium is similar to **(2019 Main, 10 Jan I)**

(a) lithium (b) carbon
(c) beryllium (d) boron

6. Aluminium is usually found in 3 oxidation state. In contrast, thallium exists in 1 and 3 oxidation states. This is due to **(2019 Main, 9 Jan I)**

(a) lattice effect (b) lanthanoid contraction
(c) inert pair effect (d) diagonal relationship

7. The increasing order of atomic radii of the following Group 13 elements is **(2016 Adv.)**

(a) Al < Ga < In < Tl
(b) Ga < Al < In < Tl
(c) Al < In < Ga < Tl
(d) Al < Ga < Tl < In

8. $B(OH)_3 \quad NaOH \rightleftharpoons NaBO_2 \quad Na[B(OH)_4] \quad H_2O$

How can this reaction is made to proceed in forward direction? **(2006, 3M)**

(a) Addition of *cis* 1, 2-diol
(b) Addition of borax
(c) Addition of *trans* 1, 2-diol
(d) Addition of Na_2HPO_4

9. H_3BO_3 is **(2003, 1M)**

(a) monobasic acid and weak Lewis acid
(b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid
(d) tribasic and weak Bronsted acid

10. In compounds of type ECl_3, where E B, P, As or Bi, the angles Cl E Cl for different E are in the order **(1999, 2M)**

(a) B > P = As = Bi (b) B > P > As > Bi
(c) B < P = As = Bi (d) B < P < As < Bi

11. Moderate electrical conductivity is shown by **(1982, 1M)**

(a) silica (b) graphite
(c) diamond (d) None of these

Objective Questions II

(One or more than one correct option)

12. Among the following, the correct statement(s) is(are) **(2017 Adv.)**

(a) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure
(b) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$
(c) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure
(d) BH_3 has the three-centre two-electron bonds in its dimeric structure

13. The crystalline form of borax has **(2016 Adv.)**

(a) tetranuclear $[B_4O_5(OH)_4]^2$ unit
(b) all boron atoms in the same plane
(c) equal number of sp^2 and sp^3 hybridised boron atoms
(d) one terminal hydroxide per boron atom

14. The correct statement(s) for orthoboric acid is/are **(2014 Adv.)**

(a) It behaves as a weak acid in water due to self ionisation
(b) Acidity of its aqueous solution increases upon addition of ethylene glycol
(c) It has a three-dimensional structure due to hydrogen bonding
(d) It is a weak electrolyte in water

15. In the reaction, $2X + B_2H_6 \quad [BH_2(X)_2]^+[BH_4]$ the amine(s) X is/are **(2009)**

(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

16. **Statement I** Boron always forms covalent bond.

Statement II The small size of B^{3} favours formation of covalent bond. **(2007, 3M)**

17. **Statement I** In water, orthoboric acid behaves as a weak monobasic acid.

Statement II In water, orthoboric acid acts as a proton donor. **(2007, 3M)**

18. **Statement I** $Al(OH)_3$ is amphoteric in nature.

Statement II Al O and O H bonds can be broken with equal ease in Al $(OH)_3$. **(1998 , 2M)**

Match the Column

19. Match the following. **(2006, 6M)**

	Column I		Column II
A.	Bi^{3} (BiO)	p.	Heat
B.	$[AlO_2]$ $Al(OH)_3$	q.	Hydrolysis
C.	SiO_4^{4} $Si_2O_7^{6}$	r.	Acidification
D.	$(B_4O_7^{2})$ $[B(OH)_3]$	s.	Dilution by water

Fill in the Blank

20. The two types of bonds present in B_2H_6 are covalent and ……… **(1994, 1M)**

True/False

21. The basic nature of hydroxide of group 13 (group IIIA) decreases progressively down the group. **(1993, 1M)**

22. All the Al Cl bonds in Al_2Cl_6 are equivalent. **(1989, 1M)**

Integer Answer Type Question

23. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is **(2015 Adv.)**

24. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is **(2010)**

Subjective Questions

25. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3, AlF_3 is precipitated. Write the balanced chemical equations. **(2004, 2M)**

26. (i) How is boron obtained from borax? Give chemical equations with reaction conditions.

(ii) Write the structure of B_2H_6 and its reaction with HCl. **(2002)**

27. Compound X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air.

Draw the structure of Y. **(2001, 5M)**

28. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. **(1997, 2M)**

29. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.

(Ionisation energy for Al 5137 kJ mol^{-1}

$H_{\text{hydration}}$ for $Al^{3+} = -4665$ kJ mol^{-1}

$H_{\text{hydration}}$ for Cl 381 kJ mol ^{1} **(1997, 2M)**

Topic 2 Group 14 Elements

Objective Questions I (Only one correct option)

1. The C C bond length is maximum in **(2019 Main, 12 April II)**

(a) graphite (b) C_{70}
(c) C_{60} (d) diamond

2. The basic structural unit of feldspar, zeolites, mica and asbestos is **(2019 Main, 12 April I)**

(a) $(SiO_3)^{2}$ (b) SiO_2 (c) $(SiO_4)^{4}$

(d) $(\underset{R}{\overset{R}{\text{Si}}}\ \ O)_n$ $(R$ Me)

3. The correct order of catenation is **(2019 Main, 10 April I)**

(a) $C > Sn > Si \quad Ge$ (b) $Si > Sn > C > Ge$
(c) $C > Si > Ge \quad Sn$ (d) $Ge > Sn > Si > C$

4. The amorphous form of silica is **(2019 Main, 9 April II)**

(a) tridymite (b) kieselguhr
(c) cristobalite (d) quartz

5. C_{60} an allotrope of carbon contains **(2019 Main, 9 April I)**

(a) 16 hexagons and 16 pentagons
(b) 20 hexagons and 12 pentagons
(c) 12 hexagons and 20 pentagons
(d) 18 hexagons and 14 pentagons

6. The element that does not show catenation is **(2019 Main, 12 Jan II)**

(a) Ge (b) Sn (c) Si (d) Pb

7. The element that shows greater ability to form p -p multiple bonds, is **(2019 Main, 12 Jan II)**

(a) Ge (b) Si (c) Sn (d) C

8. The chloride that cannot get hydrolysed is **(2019 Main, 11 Jan I)**

(a) $SnCl_4$ (b) CCl_4
(c) $PbCl_4$ (d) $SiCl_4$

9. Correct statements among (I) to (IV) regarding silicones are: **(2019 Main, 9 Jan I)**

I. They are polymers with hydrophobic character.
II. They are biocompatible.
III. In general, they have high thermal stability and low dielectric strength.
IV. Usually, they are resistant to oxidation and used as greases.

(a) I and II only (b) I, II, III only
(c) I, II, III and IV (d) I, II and IV only

10. Name the structure of silicates in which three oxygen atoms of $[SiO_4]^{4}$ are shared is **(2005, 1M)**

(a) pyrosilicate (b) sheet silicate
(c) linear chain silicate (d) three-dimensional silicate

11. Me_2SiCl_2 on hydrolysis will produce **(2003, 1M)**

(a) $(Me)_2Si(OH)_2$ (b) $(Me)_2Si{=}O$
(c) $[\quad O \quad (Me)_2Si \quad O \quad]_n$ (d) $Me_2SiCl(OH)$

12. Identify the correct order of acidic strength of CO_2, CuO, CaO, H_2O. **(2002, 3M)**

(a) $CaO < CuO < H_2O < CO_2$
(b) $H_2O < CuO < CaO < CO_2$
(c) $CaO < H_2O < CuO < CO_2$
(d) $H_2O < CO_2 < CaO < CuO$

13. Which one of the following oxides is neutral ? **(1996, 1M)**

(a) CO (b) SnO_2 (c) ZnO (d) SiO_2

14. Which of the following halides is least stable and has doubtful existence? **(1996, 1M)**

(a) CCl_4 (b) GeI_4 (c) SnI_4 (d) PbI_4

Objective Question II

(One or more than one correct option)

15. With respect to graphite and diamond, which of the statement(s) given below is/are correct? **(2012)**

(a) Graphite is harder than diamond
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C C bond order than diamond

Assertion and Reason

(a) Statement I is correc;t Statement II is correct Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

16. **Statement I** Pb^{4} compounds are stronger oxidising agents than Sn^{2} compounds.

Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **(2008, 3M)**

17. **Statement I** Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.

Statement II $SiCl_4$ is ionic and CCl_4 is covalent. **(2001, S, 1M)**

Fill in the Blanks

18. A liquid which is permanently supercooled is frequently called ……… . **(1997, 1M)**

19. The recently discovered allotrope of carbon (e.g. C_{60}) is commonly known as ……… . **(1994, 1M)**

20. The hydrolysis of trialkyl chlorosilane R_3SiCl, yields ……… . **(1994, 1M)**

21. The hydrolysis of alkyl substituted chlorosilanes gives ……… . **(1991, 1M)**

True/False

22. The tendency for catenation is much higher for C than for Si. **(1993, 1M)**

23. Diamond is harder than graphite. **(1993, 1M)**

24. Graphite is a better lubricant on the moon than on the earth. **(1987, 1M)**

25. Carbon tetrachloride burns in air when lighted to give phosgene gas. **(1983, 1M)**

Subjective Questions

26. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (give reactions only).
(i) Silicon
(ii) Linear silicon containing methyl group only
(iii) Na_2SiO_3 **(2001, 5M)**

27. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling. **(1998, 4M)**

28. Write the balanced equation for the preparation of crystalline silicon from $SiCl_4$. **(1990, 1M)**

29. Each entry in column *X* is in some way related to the entries in columns *Y* and *Z*. Match the appropriate entries.

X	*Y*	*Z*
Yeast	Fermentation	Ethanol
Mica	Graphite	Abrasive
Superphosphate	Crystalline cubic	Insulator
Carbon fibres	Layer structure	Fertiliser
Rock salt	Diamond structure	Reinforced plastics
Carborundum	Bone ash	Preservative

(1989, 3M)

30. Give reasons for the following in one or two sentences : "Graphite is used as a solid lubricant." **(1985, 1M)**

31. Give reason for the following in one or two sentences : "Solid carbon dioxide is known as dry ice." **(1983, 1M)**

32. Carbon acts as an abrasive and also as a lubricant, explain. **(1981, 1M)**

Answers

Topic 1

1. (a) **2.** (a) **3.** (b) **4.** (a)
5. (c) **6.** (c) **7.** (b) **8.** (a)
9. (a) **10.** (b) **11.** (b) **12.** (a, b, c)
13. (a, c, d) **14.** (b, d) **15.** (a, b, c) **16.** (a)
17. (a) **18.** (a)
19. A q; B r; C p ; D q, r
20. Three centre two electron bond or banana bond.
21. F **22.** F **23.** (3) **24.** (3)

Topic 2

1. (d) **2.** (c) **3.** (c) **4.** (b)
5. (b) **6.** (d) **7.** (d) **8.** (b)
9. (d) **10.** (a) **11.** (c) **12.** (a)
13. (a) **14.** (d) **15.** (b, d) **16.** (a)
17. (c) **18.** glass **19.** Buckminster
20. $(R_3SiO)_2$ **21.** silicones **22.** T **23.** T
24. T **25.** F

Hints & Solutions

Topic 1 Group 13 Elements

1. All the given statements are correct. For group 13 elements, the acidic nature of oxides decreases and the basic nature of oxides increases on moving from B to Tl. This is because as we move down the group, the atomic size of elements goes on increasing, whereas the ionisation energy decreases, due to which the strength of metal oxide (MO) bond goes on decreasing. Thus, boron trioxide or boron oxide is acidic and reacts with basic oxides to give metal borates. Aluminium and gallium oxides are amphoteric while oxides of indium and thallium are basic in nature.

2. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce B_2O_3 and H_3BO_3 respectively. Diborane is a colourless, highly toxic gas, having boiling point 180 K. Because of its inflammable nature, it catches fire spontaneously when exposed to air and burns in oxygen releasing an enormous amount of energy as:

$$B_2H_6 \quad 3O_2 \qquad B_2O_3 \quad 3H_2O \quad 1976\,\text{kJ/mol}$$

It gets hydrolysed readily to give boric acid.

$$\underset{\text{Borane}}{B_2H_6} \quad 6H_2O \qquad \underset{\text{Orthoboric acid}}{2H_3BO_3} \quad \underset{\text{Dihydrogen}}{6H_2}$$

3. The stability order of 3 and 1 oxidation states of group 13 elements will be:

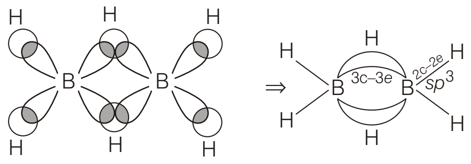
$$B^3 > Al^3 > Ga^3 > In^3 >> Tl^3$$
(order of 3 oxidation state)

$$B << Al < Ga < In < Tl$$
(order of 1 oxidation state)

The presence of two oxidation states in *p*-block elements is due to the inert pair effect.

Because of the presence of poor shielding *d* and *f*-orbitals, as we move from Ga to Tl, effective nuclear charge of these elements increases so as to hold the valence ns^2 electrons tightly. It causes difficulty to the ionisation of ns^2-electrons and it remains inert, only np^1-electron ionises to give 1 oxidation state.

4. The structure of B_2H_6 can be shown as :



In B_2H_6, four 2-centre-2-electron (2*c* 2*e*) bonds are present in the same plane and two 3-centre-2-electron (3*c* 2*e*) bonds are present in another plane.

5. Let, us consider the electronegativity values of the given elements,

	Group-1	Group-2	Group-13	Group-19
Period 2	Li (1.0)	Be (1.5)	B (2.0)	C (2.5)
Period 3			Al (1.5)	

Be and Al show diagonal relationship which is based on their same $\frac{Z}{r}$ value (Z^* is effective nuclear charge, r atomic radius). So, they have similar electronegativity.

6. Due to inert pair effect, group-13 elements (ns^2np^1) show 3 and 1 oxidation states in their compounds. Stability order of these oxidation states will be as,

- **3 oxidation states**

$$B^3 > Al^3 > Ga^3 > In^3 > Tl^3$$

B^3 does not exist in free states. All B(III) compounds are covalent.

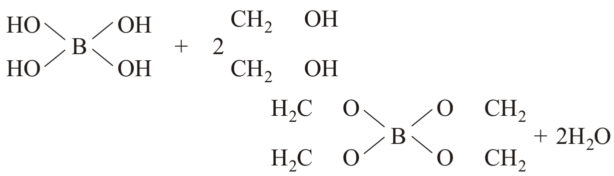
- **1 oxidation states**

B Al Ga In Tl

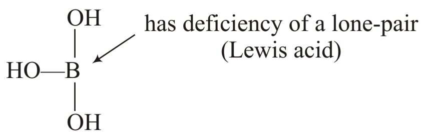
B does not exist in ionic as well covalent compounds.

7. Due to poor shielding of *d*-orbital in Ga, atomic radius of Ga is smaller than that of Al. Thus, Ga < Al < In < Tl.

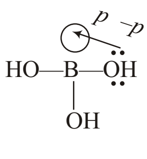
8. Orthoboric acid is a very weak acid, direct neutralisation does not complete. However, addition of *cis*-diol allow the reaction to go to completion by forming a stable complex with $[B(OH)_4]$ as:



9. Orthoboric acid is a weak, monobasic, Lewis acid.



p -p backbonding between 'B' and 'O' decreases acid strength greatly :



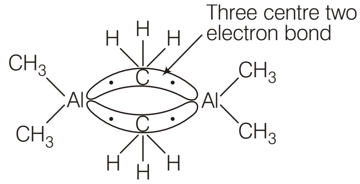
10. In BCl_3, bond angle 120 .

In PCl_3, $AsCl_3$ and $BiCl_3$, central atom is sp^3 hybridised. Since P, As and Bi are from the same group, bond angle decreases down the group. Hence, overall order of bond angle is :

$$B > P > As > Bi$$

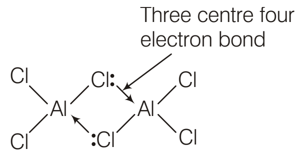
11. Graphite has layered structure and conducted electricity moderately. Silica and diamond have 3-dimensional network structures and non-conducting.

12. (a)

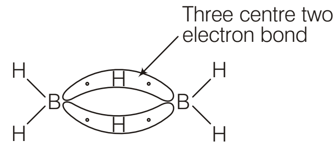


(b) BCl_3 is stronger Lewis acid than $AlCl_3$ due to greater extent of p p back bonding in $AlCl_3$.

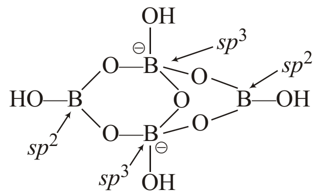
(c)



(d)



13. $Na_2B_4O_7$ $10H_2O$ (borax) is actually made of two tetrahedral and two triangular units, and is actually written as$Na_2[B_4O_5(OH)_4]$ $5H_2O$.



(a) Thus, correct.

(b) Boron atoms are in different planes thus, incorrect.

(c) Two sp^2 and two sp^3-hybridised B atoms thus, correct.

(d) Each boron has one OH group thus, correct.

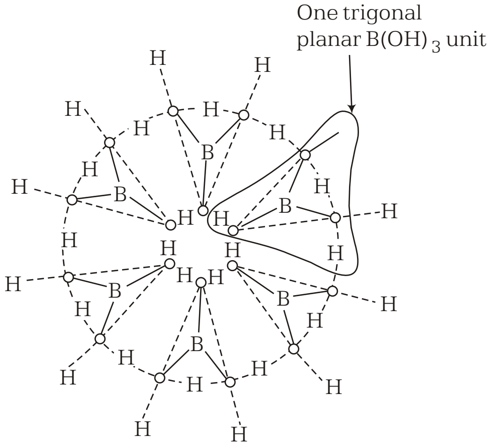
14. (a) It does not undergo self ionisation in water but accepts an electron pair from water, so it behaves as weak monobasic acid.

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4 \quad H$$

Hence, (a) is incorrect.

(b) When treated with 1, 2-dihydroxy or polyhydroxy compounds, they form chelate (ring complex) which effectively remove $[B(OH)_4]$ species from solution and thereby produce maximum number of H_3O or H ions, i.e. results in increased acidity.

(c) Boric acid crystallises in a layer structure in which planar triangular BO_3^3 ` ions are bonded together through hydrogen bonds.

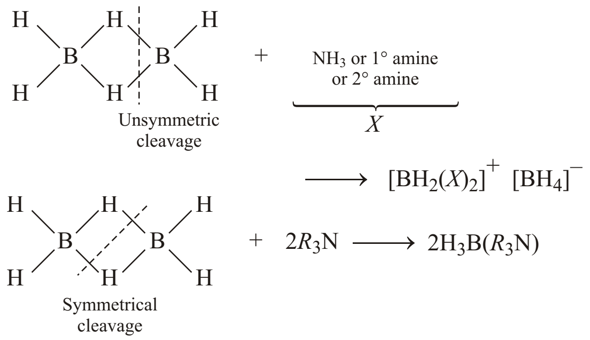


(d) In water the pK_a value of H_3BO_3 is 9.25.

$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4 \quad H$; pK_a 9.25

So, it is a weak electrolyte in water.

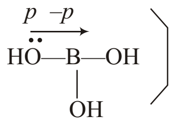
15. Diborane (B_2H_6) undergoes unsymmetric cleavage with NH_3, primary and secondary amine while tertiary amine brings about symmetrical cleavage of B_2H_6 as :



16. Small size and high charge on B^{3+} makes it highly polarising. Therefore, in most of its compounds, boron forms covalent bonds.

Hence, both statement I and statement II are correct and statement II is a correct explanation of statement I.

17. Orthoboric acid is a weak, monobasic, Lewis acid and the poor acidic character is due to $p \quad p$ backbondings as:



Backbonding decreases electron deficiency at boron, decreases its Lewis acid strength.

18. Due to small size and high charge on Al in $Al(OH)_3$ the fission ability of Al—O and O—H bonds become comparable and compound can give both H^+ and HO under appropriate reaction conditions as:

$$\underset{\text{Base}}{Al(OH)_3} + 3HCl \qquad AlCl_3 + 3H_2O$$

$$\underset{\text{Acid}}{Al(OH)_3} + NaOH \qquad Na[Al(OH)_4]$$

Therefore, both statements are correct and statement II is a correct explanation of statement I.

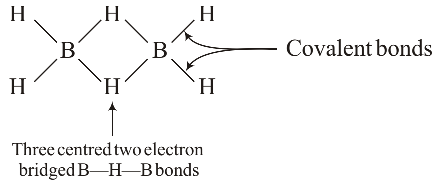
19. (A) Bi^{3+} hydrolysis to $(BiO)^+$ *q*.

(B) $[AlO_2]$ exist in basic medium, on acidification gives $Al(OH)_3$ *r*.

(C) Orthosilicate (SiO_4^4) on heating changes into pyrosilicate $Si_2O_7^6$ *p*.

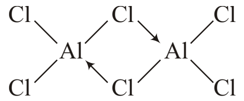
(D) Tetraborate ion $[B_4O_7^2\ ]$ on treatment with dil. acid hydrolysis gradually to orthoboric acid *q*, *r*.

20. Three centred two electron bonds.



12. The basic nature of hydroxide of group-13 increases from top to bottom due to increase in electropositive character.

22. In Al_2Cl_6, Al–Cl bonds are not equivalent :



The bridged Al—Cl bonds are different from terminal Al—Cl bonds.

23. $B_2H_6 \quad 6\ CH_3OH \qquad 2[B(OCH_3)_3] \quad 6H_2$

Therefore, from 3 moles of B_2H_6, 6 moles of $B(OCH_3)_3$ will be

24. $Be_nAl_2Si_6O_{18}$, $2n \quad 6 \quad 24 \quad 36 \quad 0 \qquad n \quad 3$

25. $3KF + AlF_3 \qquad B_2H_5Cl + H_2$

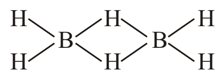
$K_3AlF_6 + 3BF_3 \qquad \underset{\text{ppt}}{AlF_3} + 3KBF_4$

26. (i) $Na_2B_4O_7 + HCl \qquad NaCl + H_3BO_3$

$H_3BO_3 + HCl \qquad BCl_3 + H_2O$

$BCl_3 + Al \qquad B + AlCl_3$

(ii) B_2H_6 :



It has 4 terminal B—H bonds. There are two B—H—B, three centred two electron bridged bonds.

$B_2H_6 + HCl \qquad B_2H_5Cl + H_2$

27. Compound $X \overset{LiAlH_4}{\quad} Y$ a hydride + other compound. Hydride *Y* contains 21.72% hydrogen.

$$Y \quad O_2 \qquad B_2O_3 + H_2O$$

Therefore, *Y* is a hydride of boron and it is obtained by reduction of *X* with $LiAlH_4$. So, *X* is either BCl_3 or BF_3.

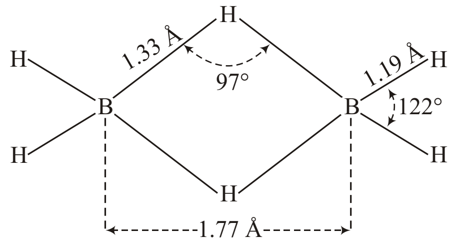
$$\underset{X}{4BCl_3} + LiAlH_4 \qquad \underset{Y}{B_2H_6} + \underbrace{3AlCl_3 + 3LiCl}_{\text{Other products}}$$

Molar mass of $B_2H_6 = 2 \quad 11 + 6 = 28$

% of H in $B_2H_6 = \frac{6}{28}$ 100 = 21.5 21.72

$\underset{Y}{B_2H_6} + 3O_2 \quad\quad B_2O_3 + 3H_2O$ + Heat

Structure of *Y* (B_2H_6)



(a) There are 4 terminal B—H bonds.
(b) There are two 3-centre-2-electron B—H—B bridged bonds.
(c) Terminal H—B—H planes are perpendicular to bridged B—H—B bonds.

28. $Al_2S_3 + 6H_2O \quad\quad 2Al(OH)_3 + \underset{\text{Foul odour}}{3H_2S(g)}$

Foul odour on damping of Al_2S_3 is due to the formation of H_2S gas as shown above.

29. The total hydration energy of $AlCl_3$

= Hydration energy of Al^{3+} + 3 Hydration energy of Cl

4665 3 (381) kJ/mol

5808 kJ/mol

The above hydration energy is more than the energy required for ionisation of $AlCl_3$ into Al^{3+} and 3Cl .

Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqueous solution, it is ionised completely as

$AlCl_3 + 6H_2O \quad\quad [Al(H_2O)_6]^{3+} + 3Cl$

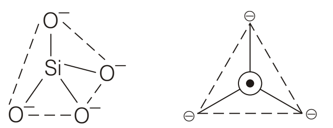
Topic 2 Groups 14 Elements

1. The C C bond length is maximum in diamond having value 154 pm. Here, each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. It has a rigid three-dimensional network of carbon atoms.

C C bond length within the layers of graphite is 141.5 pm. In C_{60}, C C distances between single and double bonds are 143.5 pm and 138.3 pm respectively.

2. The basic structural unit of feldspar, zeolites, mica and asbestos is $(SiO_4)^4$. These all are silicates. All silicates involve two types of Si O bonds.

(i) Terminal Si O bonds in which oxygen is bonded to a silicon and not other atom.
(ii) Bridging Si O Si bonds in which oxygen is bonded to two silicon atoms.



In SiO_4^4 ion, each Si atom is bonded to four oxygen atoms tetrahedrally.

3. Catenation property is an unique property of group 14 elements. Down the group 14, catenation power decreases as:

C Si Ge Sn

Pb does not show catenation.

4. Silica occurs in nature in several amorphous and crystalline forms. Kieselguhr is the amorphous form of silica. Quartz, tridymite and cristobalite are crystalline forms of silica.

5. C_{60} is aromatic allotrope of carbon containing 12 pentagons and 20 hexagons. It is a fullerene having a shape like soccer ball and called Buckminster fullerene.

6. The property of self-linking of atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called catenation. Down the group, catenation tendency decreases due to decrease in element bond strength. Carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) are group-14 elements.

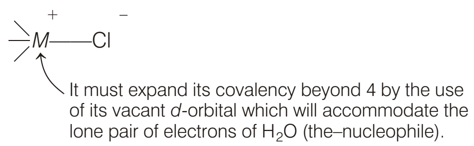
Catenation tendency is highest in carbon while silicon has second highest tendency of catenation among all elements of family due to higher bond energy. The decreasing tendency of catenation among group 14 elements is as follows:

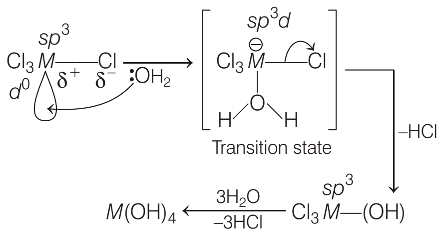
C >> Si > Ge Sn

However, Pb does not show catenation.

7. Carbon (C) has greatest ability to form stable *p* -*p* multiple bonds. 2*p*-orbitals of this element participate in the process. The stability of multiple bonds of C is attributed to their closeness with C-nucleus. Thus, the smaller size of C plays a significant role in the process.

8. The compounds given are the tetrahalides (MCl_4) of group 14 elements. For the hydrolysis, (nucleophilic substitution) of MCl_4 the nature of the *M*—Cl bond should be as:





Here, *M* can be Si, Sn and Pb because they have vacant *nd*-orbital. But, carbon is a member of second period (*n* 2, *l* 0, 1),
it does not have *d*-orbital (*l* 2). So, CCl_4 will not be hydrolysed and correct option is (b).

9. Silicones are polysiloxanes with general chemical formula, $[R_2SiO]_n$, where *R* is an organic group such as:

CH_3, C_2H_5, C_6H_5 etc.

Silicones have many useful properties:

(i) They repel water and form watertight seals.

(ii) They are heat resistant because of constancy of properties over a wide range of temperature (100 to 250 C).

(iii) Silicones are non-toxic.

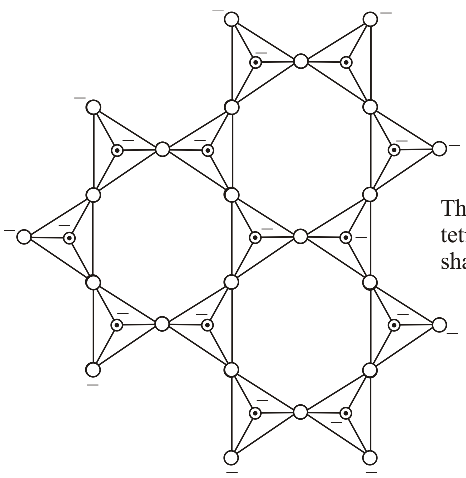
(iv) Silicones are biocompatible because these do not support microbiological growth and these have high gas permeability at room temperature.

(v) They are resistant to O_2, O_3 and UV-radiation.

(vi) Silicones are formulated to be electrically insulative.

(vii) Silicone grease is typically used as a lubricant for brake components in automobiles, since it is stable at high temperature, is not water soluble and is a odourless viscous liquid.

10. In sheet silicates, three out of four oxygen of SiO_4^4 unit are shared as shown below :



In pyrosilicates, there is only one shared oxygen, in linear chain silicates, two oxygen per tetrahedra are shared while in three-dimensional silicates, all four oxygens are shared.

11. Me_2SiCl_2 on hydrolysis yields a linear chain silicone as :

$$\begin{array}{ccc} & CH_3 & \\ Cl & Si & Cl + 2H_2O \\ & CH_3 & \end{array} \qquad \begin{array}{ccc} & CH_3 & \\ HO & Si & OH \quad 2HCl \\ & CH_3 & \end{array}$$

$$\begin{array}{ccc} & CH_3 & \\ nHO & Si & OH \\ & CH_3 & \end{array} \xrightarrow{\text{Polymerisation}} \begin{array}{ccc} & CH_3 & \\ [\ O & Si & O\ ]_n \\ & CH_3 & \end{array}$$

12. CO_2 is acidic oxide, H_2O is neutral, CaO is strongly basic and CuO is weakly basic. Therefore, order of acid strength is :

$$CaO < CuO < H_2O < CO_2$$

13. Carbon monoxide is a neutral oxide, all others are amphoteric :

$$SnO_2 + 4HCl \qquad SnCl_4 + 2H_2O$$

$$ZnO + 2HCl \qquad ZnCl_2 + H_2O$$

$$SiO_2 + 2NaOH \qquad Na_2SiO_3 + H_2O$$

SnO_2 and ZnO also react with NaOH. SiO_2 is also attacked by H_3PO_4.

14. PbI_4 is least stable, has doubtful existence. It is due to inert pair effect, the stable oxidation state of lead is 2.

15. Diamond has a three-dimensional network structure, a hard substance where graphite is soft due to layered structure.

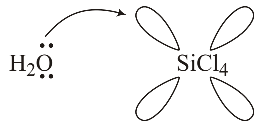
In graphite, only three valence electrons are involved in bonding and one electron remain free giving electrical conductivity. In diamond, all the four valence electrons are covalently bonded hence, insulator.

Diamond is better thermal conductor than graphite. Electrical conductivity is due to availability of free electrons, thermal conduction is due to transfer of thermal vibrational energy from one atom to another atom. A compact and precisely aligned crystals like diamond thus facilitate better movement of heat.

In graphite C C bond acquire some double bond character, hence, higher bond order than in diamond.

16. In group 13, 14, 15 as we descend down in group, the higher oxidation state becomes less tenable due to inert pair effect. Therefore, lead show 2 as stable oxidation state. Hence, Pb^{4+} act as a strong oxidising agent, itself reduced to Pb^{2+} very easily. Both statement I and statement II are correct and statement II is a correct explanation of statement I.

17. $SiCl_4$ reacts with water due to vacant *d*-orbitals available with Si as:



No such vacant *d*-orbitals are available with carbon, hence CCl_4 does not react wtih water. Otherwise, both $SiCl_4$ and CCl_4 are covalent.

Statement I is correct but statement II is incorrect.

18. Glass is commonly known as supercooled liquid.

19. Buckminster fullerene is the name of recently discovered allotrope of carbon.

20. After dimerisation, no reactive function group remains.

$$R_2SiCl + H_2O \xrightarrow[HCl]{} \begin{array}{ccc} & R & \\ R & Si & OH \\ & R & \end{array}$$

$$\begin{array}{ccccc} & R & & R & \\ R & Si & O & Si & R \\ & R & & R & \end{array}$$

Dimeric silicone

21. Silicones are organosilicon polymers, obtained by hydrolysis of alkyl substituted chlorosilanes.

22. Due to smaller size of carbon than silicon, C—C bond is stronger than Si—Si bond, hence former is more likely to extend than later.

23. Graphite has a layered structure of hexagonal carbon rings stacked one over other which makes it slippery.

On the other hand, in diamond, each carbon is tetrahedrally bond to other four carbons extended in three dimensional space, giving a giant, network structure. Due to this reason, diamond is harder than graphite.

24. Graphite is better lubricant on moon than on earth because of absence of gravitational pull on the moon.

25. Phosgene gas is obtained by treatment of CCl_4 with superheated steam :

$$CCl_4 + H_2O\text{ (vapour)} \longrightarrow COCl_2 + 2HCl$$

26. (i) $3SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$;

Mg or Zn can also be used.

(ii) $SiCl_4 + 2CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + 2MgCl_2$

$$(CH_3)_2SiCl_2 + H_2O \xrightarrow{HCl} CH_3-\underset{OH}{\overset{OH}{Si}}-CH_3$$

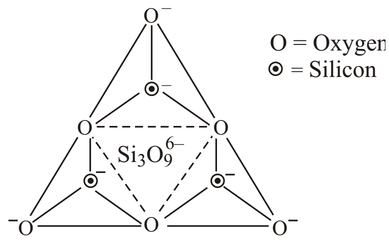
$$-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-$$

(iii) $SiCl_4 + 4H_2O \longrightarrow \underset{\text{Unstable}}{Si(OH)_4} + 4HCl$

$$Si(OH)_4 \xrightarrow{heat} SiO_2 + 2H_2O$$

$$SiO_2 \quad Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

27.



28. $\underset{\text{Vapour}}{3SiCl_4} + \underset{\text{Molten}}{4Al} \longrightarrow \underset{\text{Volatilizes}}{4AlCl_3} + \underset{\text{Crystalline}}{3Si}$

29.

X	*Y*	*Z*
Yeast	Fermentation	Ethanol
Mica	Layered structure	Insulator
Superphosphate	Bone ash	Fertiliser
Carbon fibres	Graphite	Reinforced plastics
Rock salt	Crystalline cubic	Preservative
Carborundum	Diamond structure	Abrasive

30. Graphite has layered structure and the adjacent layers are weakly associated giving slippery nature, used as solid lubricant.

31. Carbon dioxide solidifies at very low temperature, hence solid CO_2 is very cold, commonly known as dry ice. Also solid carbon dioxide sublime, without passing through liquid state.

32. The two common allotropes of carbon are diamond and graphite. Diamond is the hardest, natural, substance, used as an abrasive while graphite is soft, used as a lubricant.

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http://tinyurl.com/y3ctmvau *or*

16
p-Block Elements-II

Topic 1 Elements and Compounds of Group 15 and 16

Objective Questions I (Only one correct option)

1. The correct statement among the following is **(2019 Main, 12 April I)**
(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.
(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.
(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.
(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

2. The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are **(2019 Main, 10 April II)**
(a) 20 and 3 (b) 12 and 4
(c) 20 and 4 (d) 12 and 3

3. The oxoacid of sulphur that does not contain bond between sulphur atoms is **(2019 Main 10 April I)**
(a) $H_2S_2O_3$ (b) $H_2S_2O_4$
(c) $H_2S_2O_7$ (d) $H_2S_4O_6$

4. The correct order of the oxidation states of nitrogen in NO, NO_2, NO_2 and N_2O_3 is **(2019 Main, 9 April I)**
(a) NO_2 NO N_2O_3 N_2O (b) N_2O NO N_2O_3 NO_2
(c) O_2 N_2O_3 NO N_2O (d) N_2O N_2O_3 NO NO_2

5. The pair that contains two P H bonds in each of the oxoacids is **(2019 Main, 10 Jan II)**
(a) $H_4P_2O_5$ and $H_4P_2O_6$ (b) H_3PO_3 and H_3PO_2
(c) $H_4P_2O_5$ and H_3PO_3 (d) H_3PO_2 and $H_4P_2O_5$

6. When the first electron gain enthalpy $_{eg}H$) of oxygen is 141 kJ/ mol, its second electron gain enthalpy is **(2019 Main, 9 Jan II)**
(a) a positive value
(b) a more negative value than the first
(c) almost the same as that of the first
(d) negative, but less negative than the first

7. Good reducing nature of H_3PO_2 is attributed to the presence of **(2019 Main, 9 Jan II)**
(a) two P H bonds (b) one P H bond
(c) two P OH bonds (d) one P OH bond

8. The compound that does not produce nitrogen gas by the thermal decomposition is **(2018 Main)**
(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$
(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

9. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ is **(2017 Adv.)**
(a) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$
(b) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$
(c) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$
(d) $H_3PO_3 > H_3PO_2$ $H_3PO_4 > H_4P_2O_6$

10. The species in which the N-atom is in a state of *sp* hybridisation is **(2016 Main)**
(a) NO_2 (b) NO_3
(c) NO_2 (d) NO_2

11. The pair in which phosphorus atoms have a formal oxidation state of 3 is **(2016 Main)**
(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids

12. The product formed in the reaction of $SOCl_2$ with white phosphorus is **(2014 Adv.)**
(a) PCl_3 (b) SO_2Cl_2
(c) SCl_2 (d) $POCl_3$

13. Which of the following properties is not shown by NO? **(2014 Main)**
(a) It is paramagnetic in liquid state
(b) It is a neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) Its bond order is 2.5

14. Concentrated nitric acid upon long standing, turns yellow-brown due to the formation of **(2013 Main)**
(a) NO (b) NO_2
(c) N_2O (d) N_2O_4

15. Which of the following is the wrong statement? **(2013 Main)**
(a) ONCl and ONO   are not isoelectronic
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas

16. The reaction of white phosphorus with aqueous NaOH gives phosphine alongwith another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are **(2012)**
(a) redox reaction,   3 and   5
(b) redox reaction, 3 and   5
(c) disproportionation reaction,   3 and   5
(d) disproportionation reaction,   3 and   3

17. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? **(2012)**
(a) HNO_3, NO, NH_4Cl, N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2

18. Extra pure N_2 can be obtained by heating **(2011)**
(a) NH_3 with CuO
(b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$
(d) $Ba(N_3)_2$

19. The reaction of P_4 with X leads selectively to P_4O_6. The X, is **(2009)**
(a) dry O_2
(b) a mixture of O_2 and N_2
(c) moist O_2
(d) O_2 in the presence of aqueous NaOH

20. The percentage of *p*-character in the orbitals forming P—P bonds in P_4 is **(2007, 3M)**
(a) 25 (b) 33 (c) 50 (d) 75

21. Which of the following is not oxidised by O_3? **(2005, 1M)**
(a) KI
(b) $FeSO_4$
(c) $KMnO_4$
(d) K_2MnO_4

22. Which gas is evolved when PbO_2 is treated with concentrated HNO_3? **(2005)**
(a) NO_2
(b) O_2
(c) N_2
(d) N_2O

23. A pale blue liquid obtained by equimolar mixture of two gases at – 30°C is **(2005, 1M)**
(a) N_2O
(b) N_2O_3
(c) N_2O_4
(d) N_2O_5

24. Which of the following isomers of phosphorus is thermodynamically most stable? **(2005, 1M)**
(a) Red
(b) White
(c) Black
(d) Yellow

25. Which of the following has —O—O— linkage? **(2004, 3M)**
(a) $H_2S_2O_6$
(b) $H_2S_2O_8$
(c) $H_2S_2O_3$
(d) $H_2S_4O_6$

26. For H_3PO_3 and H_3PO_4, the correct choice is **(2003, 1M)**
(a) H_3PO_3 is dibasic and reducing
(b) H_3PO_3 is dibasic and non-reducing
(c) H_3PO_4 is tribasic and reducing
(d) H_3PO_3 is tribasic and non-reducing

27. Polyphosphates are used as water softening agents because they **(2002, 3M)**
(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitate cationic species

28. The number of S   S bonds in sulphur trioxide trimer, (S_3O_9) is **(2001, 1M)**
(a) three
(b) two
(c) one
(d) zero

29. Ammonia can be dried by **(2000, 1M)**
(a) conc. H_2SO_4
(b) P_4O_{10}
(c) CaO
(d) anhydrous $CaCl_2$

30. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is **(2000, 1M)**
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight

31. The correct order of acidic strength is **(2000, 1M)**
(a) $Cl_2O_7 > SO_2 > P_4O_{10}$
(b) $CO_2 > N_2O_5 > SO_3$
(c) $Na_2O > MgO > Al_2O_3$
(d) $K_2O > CaO > MgO$

32. The number of P   O   P bonds in cyclic metaphosphoric acid is **(2000, 1M)**
(a) zero (b) two (c) three (d) four

33. One mole of calcium phosphide on reaction with excess water gives **(1999, 2M)**
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentaoxide

34. Sodium thiosulphate is prepared by **(1996, 1M)**
(a) reducing Na_2SO_4 solution with H_2S
(b) boiling Na_2SO_3 solution with S in alkaline medium
(c) neutralising $H_2S_2O_3$ solution with NaOH
(d) boiling Na_2SO_3 solution with S in acidic medium

35. There is no S   S bond in **(1991, 1M)**
(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$ (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$

36. Which one of the following is the strongest base? **(1989, 2M)**
(a) AsH_3 (b) NH_3 (c) PH_3 (d) SbH_3

37. Amongst the trihalides of nitrogen, which one is least basic? **(1987, 1M)**
(a) NF_3
(b) NCl_3
(c) NBr_3
(d) NI_3

38. Which of the following oxides of nitrogen is a coloured gas ? **(1987,1M)**
(a) N_2O
(b) NO
(c) N_2O_4
(d) NO_2

39. The bonds present in N_2O_5 are **(1986, 1M)**
(a) only ionic
(b) covalent and coordinate
(c) only covalent
(d) covalent and ionic

40. A gas that cannot be collected over water is **(1985, 1M)**
(a) N_2 (b) O_2 (c) SO_2 (d) PH_3

41. Ammonia gas can be dried by **(1978, 1M)**

(a) conc H_2SO_4 (b) P_2O_5
(c) $CaCl_2$ (d) quicklime

42. Which of the following is incorrect statement? **(1978, 1M)**

(a) NO is heavier than O_2
(b) The formula of heavy water is D_2O
(c) N_2 diffuses faster than oxygen through an orifice
(d) NH_3 can be used as a refrigerant

Objective Questions II
(One or more than one correct option)

43. The compound(s) which generate (s) N_2 gas upon thermal decomposition below 300 C is (are) **(2018 Adv.)**

(a) NH_4NO_3 (b) $(NH_4)_2Cr_2O_7$
(c) $Ba(N_3)_2$ (d) Mg_3N_2

44. Based on the compounds of group 15 elements, the correct statement(s) is (are) **(2018 Adv.)**

(a) Bi_2O_5 is more basic than N_2O_5
(b) NF_3 is more covalent than BiF_3
(c) PH_3 boils at lower temperature than NH_3
(d) The N—N single bond is stronger than the P—P single bond

45. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} **(2016 Adv.)**

(a) can also be prepared by reaction of P_4 and HNO_3
(b) is diamagnetic
(c) contains one N N bond
(d) reacts with Na metal producing a brown gas

46. The correct statement(s) about O_3 is/are **(2013 Adv.)**

(a) O—O bond lengths are equal
(b) thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure

47. The nitrogen oxide(s) that contain(s) N—N bond(s) is/are **(2009)**

(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) 2 5

48. Ammonia, on reaction with hypochlorite anion, can form **(1999, 3M)**

(a) NO (b) NH_4Cl
(c) N_2H_4 (d) HNO_2

49. White phosphorus (P_4) has **(1998, 2M)**

(a) six P P single bonds
(b) four P P single bonds
(c) four lone pairs of electrons
(d) P P P angle of 60°

50. Nitrogen (I) oxide is produced by **(1989, 1M)**

(a) thermal decomposition of NH_4NO_3
(b) disproportionation of N_2O_4
(c) thermal decomposition of NH_4NO_2
(d) interaction of hydroxylamine and nitrous acid

Numerical Value

51. The total number of compounds having at least one bridging oxo group among the molecules given below is ……… .

N_2O_3, N_2O_5, P_4O_6, P_4O_7, $H_4P_2O_5$, $H_5P_3O_{10}$, $H_2S_2O_3$, $H_2S_2O_5$

(2018 Adv.)

Assertion and Reason

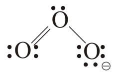
Read the following questions and answer as per the direction given below:

(a) Statement I is correct, Statement II is correct, Statement II is the correct explanation of Statement I
(b) Statement I is correct, Statement II is correct, Statement II is not the correct explanation of Statement I
(c) Statement I is correct, Statement II is incorrect
(d) Statement I is incorrect, Statement II is correct

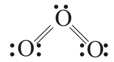
52. **Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Statement II The reaction between nitrogen and oxygen requires high temperature. **(1998, 2M)**

53. **Statement I** The electronic structure of O_3 is



Statement II The following structure is not allowed because octet around O cannot be expanded.



(1998, 2M)

54. **Statement I** HNO_3 is a stronger acid than HNO_2.

Statement II In HNO_3, there are two nitrogen to oxygen bonds whereas in HNO_2 there is only one. **(1998, 2M)**

55. **Statement I** Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.

Statement II Phosphorus has lower electronegativity than nitrogen. **(1994, 2M)**

Passage Based Questions

Passage

Upon heating $KClO_3$ in presence of catalytic amount of MnO_2, a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure HNO_3 gives Y and Z. **(2017 Adv.)**

56. Y and Z are, respectively

(a) N_2O_4 and HPO_3 (b) N_2O_4 and H_3PO_3
(c) N_2O_3 and H_3PO_4 (d) N_2O_5 and HPO_3

57. W and X are, respectively

(a) O_2 and P_4O_{10} (b) O_2 and P_4O_6
(c) O_3 and P_4O_6 (d) O_3 and P_4O_{10}

Passage

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus. **(2008, 3 4M = 12M)**

58. Among the following, the correct statement is
(a) Phosphates have no biological significance in humans
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
(d) Oxidation of nitrates is possible in soil

59. Among the following, the correct statement is
(a) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional
(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3-orbital and is more directional
(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3-orbital and is more directional
(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional

60. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(a) dimerisation reaction (b) disproportionation reaction
(c) condensation reaction (d) precipitation reaction

Match the Columns

61. The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns. **(2013 Adv.)**

	Column I		Column II
P.	PbO_2 H_2SO_4 ? $PbSO_4$ O_2 other product	1.	NO
Q.	$Na_2S_2O_3$ H_2O ? $NaHSO_4$ other product	2.	I_2
R.	N_2H_4 ? N_2 other product	3.	Warm
S.	XeF_2 ? Xe other product	4.	Cl_2

Codes

	P	Q	R	S		P	Q	R	S
(a)	4	2	3	1	(b)	3	2	1	4
(c)	1	4	2	3	(d)	3	4	2	1

Fill in the Blanks

62. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence of ....as catalyst. **(1992, 1M)**

63. In P_4O_{10}, the number of oxygen atoms bonded to each phosphorus atom is .... **(1992, 1M)**

64. The basicity of phosphorus acid (H_3PO_3) is .... **(1990, 1M)**

65. .... phosphorus is reactive because of its highly strained tetrahedral structure. **(1987, 1M)**

True/False

66. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. **(1991, 1M)**

67. The H N H bond angle in NH_3 is greater than the H As H bond angle in AsH_3. **(1984, 1M)**

68. In aqueous solution, chlorine is a stronger oxidising agent than fluorine. **(1984, 1M)**

69. Dilute HCl oxidises metallic Fe to Fe^{2} . **(1983, 1M)**

Integer Answer Type Question

70. The total number of lone pair of electrons in N_2O_3 is **(2015 Adv.)**

71. Among the following, the number of compounds that can react with PCl_5 to give $POCl_3$ is O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}. **(2011)**

72. The total number of diprotic acids among the following is

H_3PO_4	H_2SO_4	H_3PO_3
H_2CO_3	$H_2S_2O_7$	H_3BO_3
H_3PO_2	H_2CrO_4	H_2SO_3

(2010)

Subjective Questions

73. Draw the structure of P_4O_{10}. **(2005)**

74. Arrange the following oxides in the increasing order of Bronsted basicity.

Cl_2O_7, BaO, SO_3, CO_2, B_2O_3 **(2004)**

75. Identify the compounds *A, B, C, D*

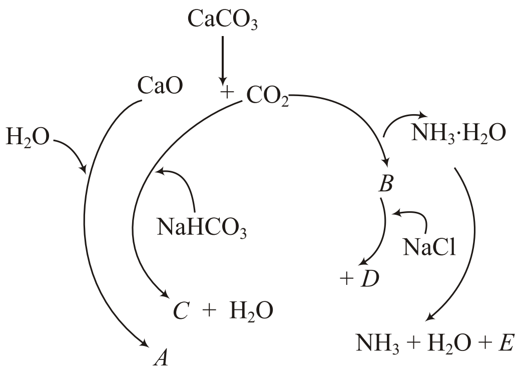
$Na_2CO_3 \; ^{SO_2} \; A \; ^{Na_2CO_3} \; B \; ^{\text{Elemental S}} \; C \; ^{I_2} \; D$

and give oxidation state of sulphur in each compounds. **(2003, 4M)**

76. Write the balanced equations for the reactions of the following compounds with water:
(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4 **(2002, 5M)**

77. Give reason(s), why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule? **(2000, 2M)**

78. The Haber's process can be represented by the following scheme.



Identify *A, B, C, D* and *E*. **(1999, 5M)**

79 (a) In the following equation

$$A \quad 2B \quad H_2O \qquad C \quad 2D$$

($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$).

Identify *D*. Draw the structures of *A*, *B*, *C* and *D*.

(b) In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2? **(1999, 10M)**

80. Complete and balance the following chemical equations.

(i) $P_4O_{10} + PCl_5$

(ii) $SnCl_4 + C_2H_5Cl + Na$ **(1998, 1M 2 2M)**

81. (a) Thionyl chloride can be synthesised by chlorinating SO_2 using PCl_5. Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2,2-dimethoxypropane. Discuss all this using balanced chemical equations.

(b) Reaction of phosphoric acid with $Ca_3(PO_4)_2$ yields a fertiliser "triple superphosphate" represent the same through balanced chemical equation. **(1998, 5M)**

82. A soluble compound of a poisonous element *M*, when heated with Zn/H_2SO_4, gives a colourless and extremely poisonous gaseous compound *N*, which on passing through a heated tube gives a silvery mirror of element *M*. Identify *M* and *N*. **(1997, 2M)**

83. Write balanced equations for the following.

(i) Phosphorus is treated with concentrated nitric acid.

(ii) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.

(iii) Manufacture of phosphoric acid from phosphorus.

(iv) Reaction of aluminium with aqueous sodium hydroxide. **(1997, 1M 4 4M)**

84. Draw the structure of P_4O_{10} and identify the number of single and double P O bonds. **(1996, 3M)**

85. Account for the following. Write the answers in four or five sentences only.

(i) The experimentally determined N F bond lengths in NF_3 is greater than the sum of the single bond covalent radii of N and F.

(ii) Mg_3N_2 when reacted with water gives of NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature.

(iii) $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$. **(1995, 2M 3 = 6M)**

86. Complete and balance the following reactions. **(1994, 1M)**

$$Ca_5(PO_4)_3F + H_2SO_4 + H_2O \quad \text{Heat}$$

$$\ldots + 5CaSO_4 \quad 2H_2O + \ldots$$

87. In the following reaction, identify the compounds *A* and *B*

$$PCl_5 + SO_2 \qquad A \quad B$$ **(1994, 1M)**

88. Complete and balance the following reaction.
Red phosphorus is reacted with iodine in the presence of water.

$$P + I_2 + H_2O \qquad \ldots + \ldots$$ **(1992, 1M)**

89. Give reasons in two or three sentences only.Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. **(1992, 2M)**

90. Draw the two resonance structures of ozone which satisfy the octet rule. **(1991, 1M)**

91. Give reasons in one or two sentences.

Ammonium chloride is acidic in liquid ammonia solvent. **(1991, 1M)**

92. Write the balanced chemical equations for the following.

(i) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda.

(ii) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate.

(iii) Elemental phosphorus reacts with concentrated HNO_3 to give phosphoric acid.

(iv) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution.

(v) Carbon dioxide is passed through a suspension of limestone in water. **(1991, 1 5 5M)**

93. Write the balanced chemical equation for the following reactions.

(i) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution.

(ii) Sodium iodate is added to a solution of sodium bisulphite **(1990, 2M)**

94. Write the two resonance structures of N_2O that satisfy the octet rule. **(1990, 2M)**

95. Draw balanced equations for
(i) the preparation of phosphine from CaO and white phosphorus.
(ii) the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. **(1990, 2M)**

96. Explain the following **(1989, 2M)**
(i) H_3PO_3 is a dibasic acid.
(ii) Phosphine has lower boiling point than ammonia.

97. Write the balanced chemical equations for the following.
(i) Hypophosphorous acid is heated.
(ii) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium.

98. Arrange the following as indicated. $CO_2, N_2O_5, SiO_2, SO_3$ in the order of increasing acidic character.

99. Give balanced equations for the following.
(i) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
(ii) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. **(1988, 3M)**

100. Give reason for "valency of oxygen is generally two, whereas sulphur shows valency of two, four and six." **(1988, 1M)**

101. Explain the following in one or two sentences.
(i) Magnesium oxide is used for the lining of steel making furnace.
(ii) The mixture of hydrazine and hydrogen peroxide with a copper (II) catalyst is used as a rocket fuel.
(iii) Orthophosphorous acid is not tribasic acid.
(iv) The molecule of magnesium chloride is linear, whereas that of stannous chloride is angular. **(1987, 4M)**

102. Write balanced equations for the following. **(1987, 2M)**
(i) Phosphorus is reacted with boiling aqueous solution of sodium hydroxide in an inert atmosphere.
(ii) Dilute nitric acid is slowly reacted with metallic tin.

103. Complete and balance the following reactions.
(i) $S + OH^- \quad S^{2-} + S_2O_3^{2-} + ...$
(ii) $ClO_3^- + I^- + H_2SO_4 \quad Cl^- + HSO_4^- + ... + ...$
(1986, 2M)

104. Write down the balanced equation for the reactions when
(i) calcium phosphate is heated with a mixture of sand and carbon.
(ii) ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. **(1985, 2M)**

105. Draw the resonance structures of nitrous oxide. **(1985, 90, 2M)**

106. Show with balanced chemical reaction what happens when following are mixed?
Aqueous solution of ferric sulphate and potassium iodide. **(1984, 1M)**

107. Write the matched set (of three) for each entry in Column *A*

A	*B*	*C*
Asbestos	Paramagnetic	Air pollutant
Lithium metal	Silicates of Ca and Mg	Electron donor
Nitric oxide	Reducing agent	

(1984, 2M)

108. Complete and balance the following reactions.
(i) $HNO_3 + HCl \quad NO + Cl_2$
(ii) $Ce^{3+} + S_2O_8^{2-} \quad SO_4^{2-} + Ce^{4+}$
(iii) $Cl_2 + OH^- \quad Cl^- + ClO^-$ **(1983, 3M)**

109. Explain, "orthophosphoric acid, H_3PO_4 is tribasic but phosphorous acid, H_3PO_3 is dibasic". **(1982, 1M)**

110. Give structural formula for the following.
(i) Phosphorous acid, H_3PO_3
(ii) Pyrophosphoric acid, $H_4P_2O_7$ **(1981, 2M)**

111. Sulphur melts to a clear mobile liquid at 119°C, but on further heating above 160° C, it becomes viscous, explain. **(1981, 1M)**

112. Explain the following in not more than two sentences .
(i) Conc. HNO_3 turns yellow in sunlight.
(ii) Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. **(1980, 2M)**

Topic 2 Elements and Compounds of Group 17 and 18

Objective Questions I (Only one correct option)

1. The noble gas that does not occur in the atmosphere is **(2019 Main, 10 April II)**
(a) Ra (b) Kr
(c) He (d) Ne

2. Chlorine on reaction with hot and concentrated sodium hydroxide gives **(2019 Main, 12 Jan II)**
(a) Cl and ClO (b) Cl and ClO_3
(c) ClO_3 and ClO_2 (d) Cl and ClO_2

3. Iodine reacts with concentrated HNO_3 to yield *Y* along with other products. The oxidation state of iodine in *Y*, is **(2019 Main, 12 Jan I)**
(a) 1 (b) 3
(c) 7 (d) 5

4. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is **(2019 Main, 10 Jan II)**
(a) $H_2 + Cl_2 \quad 2HCl$ (b) $H_2 + I_2 \quad 2HI$
(c) $H_2 + F_2 \quad 2HF$ (d) $H_2 + Br_2 \quad 2HBr$

5. The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are **(2019 Main, 10 Jan I)**
(a) sp^3d^2 and 1 (b) sp^3d and 2
(c) sp^3d and 1 (d) sp^3d^2 and 2

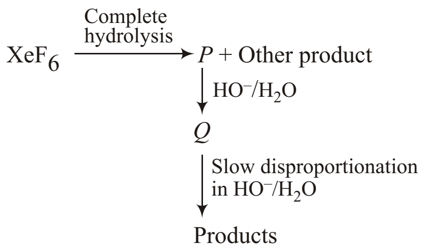
6. Which of the following reactions is an example of a redox reaction? **(2017 Main)**
(a) XeF_4 O_2F_2 XeF_6 O_2
(b) XeF_2 PF_5 $[XeF]^+PF_6$
(c) XeF_6 H_2O $XeOF_4$ 2HF
(d) XeF_6 $2H_2O$ XeO_2F_2 4HF

7. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are **(2017 Main)**
(a) ClO and ClO_3 (b) ClO_2 and ClO_3
(c) Cl and ClO (d) Cl and ClO_2

8. Which among the following is the most reactive? **(2015 Main)**
(a) Cl_2 (b) Br_2 (c) I_2 (d) ICl

9. Which one has highest boiling point? **(2015 Main)**
(a) He (b) Ne (c) Kr (d) Xe

10. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is **(2014 Adv.)**



(a) 0 (b) 1 (c) 2 (d) 3

11. Among the following oxoacids, the correct decreasing order of acidic strength is **(2014 Main)**
(a) $HOCl > HClO_2 > HClO_3 > HClO_4$
(b) $HClO_4 > HOCl > HClO_2 > HClO_3$
(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

12. The shape of XeO_2F_2 molecule is **(2012)**
(a) trigonal bipyramidal (b) square planar
(c) tetrahedral (d) *see-saw*

13. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives **(2008, 3M)**
(a) $Na_2S_4O_6$ (b) $NaHSO_4$
(c) NaCl (d) NaOH

14. When I is oxidised by $KMnO_4$ in alkaline medium, I converts into **(2004, 1M)**
(a) IO_3 (b) I_2
(c) IO_4 (d) IO

15. The set with correct order of acidic strength is **(2001, 1M)**
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

16. Which one of the following species is not a pseudo halide? **(1997, 1M)**
(a) CNO^- (b) *R*COO (c) OCN (d) NNN

17. The following acids have been arranged in the order of decreasing acidic strength. Identify the correct order.
ClOH (I), BrOH (II), IOH (III) **(1996, 1M)**
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

18. KF combines with HF to form KHF_2. The compound contains the species **(1996, 1M)**
(a) K^+, F and H^+ (b) K^+, F^- and HF
(c) K and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

19. Bromine can be liberated from potassium bromide solution by the action of **(1987, 1M)**
(a) iodine solution (b) chlorine water
(c) sodium chloride (d) potassium iodide

20. Chlorine acts as a bleaching agent only in the presence of **(1983, 1M)**
(a) dry air (b) moisture
(c) sunlight (d) pure oxygen

21. HBr and HI reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce **(1981, 1M)**
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) None of these

Objective Questions II
(One or more than one correct option)

22. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is (are) **(2017 Adv.)**
(a) The central atom in both $HClO_4$ and HClO is sp^3-hybridised
(b) $HClO_4$ is formed in the reaction between Cl_2 and H_2O
(c) The conjugate base of $HClO_4$ is weaker base than H_2O
(d) $HClO_4$ is more acidic than HClO because of the resonance stabilisation of its anion

23. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to **(2017 Adv.)**
(a) decrease in * * gap down the group
(b) decrease in ionisation energy down the group
(c) the physical state of X_2 at room temperature changes from gas to solid down the group
(d) decreases in HOMO-LUMO gap down the group

24. The compound(s) with two lone pairs of electrons on the central atom is (are) **(2016 Adv.)**
(a) BrF_5 (b) ClF_3
(c) XeF_4 (d) SF_4

25. The correct statement(s) regarding,

(i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$ is (are)

(a) the number of Cl O bonds in (ii) and (iii) together is two
(b) the number of lone pair of electrons on Cl in (ii) and (iii) together is three
(c) the hybridisation of Cl in (iv) is sp^3
(d) amongst (i) to (iv), the strongest acid is (i)

Passage Based Questions

Passage 1

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, *P* and *Q*, respectively. The Cl_2 gas reacts with SO_2 gas in the presence of charcoal, to give a product *R*. *R* reacts with white phosphorus to give a compound *S*. On hydrolysis, *S* gives an oxoacid of phosphorus *T*. **(2013 Adv.)**

26. *P* and *Q* respectively, are the sodium salts of
(a) hypochlorous and chloric acids
(b) hypochlorous and chlorous acids
(c) chloric and perchloric acids
(d) chloric and hypochlorous acids

27. *R, S* and *T*, respectively, are
(a) SO_2Cl_2, PCl_5 and H_3PO_4 (b) SO_2Cl_2, PCl_3 and H_3PO_3
(c) $SOCl_2$, PCl_3 and H_3PO_2 (d) $SOCl_2$, PCl_5 and H_3PO_4

Passage 2

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. **(2012)**

28. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is
(a) 0.48 M (b) 0.96 M
(c) 0.24 M (d) 0.024 M

29. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
(a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

Passage 3

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers 2, 4 and 6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. **(2007, 3 4M = 12M)**

30. Argon is used in arc welding because of its
(a) low reactivity with metal
(b) ability to lower the melting point of metal
(c) flammability
(d) high calorific value

31. The structure of XeO_3 is
(a) linear (b) planar
(c) pyramidal (d) T-shaped

32. XeF_4 and XeF_6 are expected to be
(a) oxidising (b) reducing
(c) unreactive (d) strongly basic

Match the Columns

33. All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II. **(2010)**

	Column I		Column II
A.	$(CH_3)_2SiCl_2$	p.	Hydrogen halide formation
B.	XeF_4	q.	Redox reaction
C.	Cl_2	r.	Reacts with glass
D.	VCl_5	s.	Polymerisation
		t.	O_2 formation

Fill in the Blanks

34. The increase in solubility of iodine in aqueous solution of KI is due to the formation of ….. **(1982, 94, 1M)**

True/False

35. HBr is a stronger acid than HI because of hydrogen bonding. **(1993, 1M)**

Integer Answer Type Questions

36. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is **(2011)**

Subjective Questions

37. Write the balanced equation for the reaction of the following compound with water.

XeF_4 **(2002, 5M)**

38. Draw molecular structures of XeF_2, XeF_4 and XeO_2F_2, indicating the locations of lone pair(s) of electrons. **(2000, 3M)**

39. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. **(2000, 2M)**

40. Work out the following using chemical equations

"Chlorination of calcium hydroxide produces bleaching powder." **(1998, 2M)**

41. Complete the following chemical equations:
(i) $KI + Cl_2$ (ii) $KClO_3 + I_2$ **(1996, 2M)**

42. Give reasons in two or three sentences only for
(i) Bond dissociation energy of F_2 is less than that of Cl_2.
(ii) Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. **(1992, 2M)**

43. Write the balanced chemical equation for the following:
Sodium bromate reacts with fluorine in the presence of alkali.

44. Arrange the following as indicated. HOCl, $HOClO_2$, $HOClO_3$, HOClO in increasing order of thermal stability **(1988, 2M)**

45. Give balanced equation for the following:
Iodate ion reacts with bisulphite ion to liberate iodine. **(1988, 3M)**

46. Mention the products formed in the following
"Chlorine gas is bubbled through a solution of ferrous bromide." **(1986, 2M)**

47. Complete and balance the following reaction:
$ClO_3^- \quad I^- \quad H_2SO_4 \qquad Cl^- \quad HSO_4^-$ .... **(1986, 2M)**

48. Arrange the following in the order of
(i) increasing bond strength HCl, HBr, HF, HI
(ii) increasing oxidation number of iodine
I_2, HI, HIO_4, ICl **(1986, 2M)**

49. Give reason in one or two sentences.
Fluorine cannot be prepared from fluorides by chemical reduction method. **(1985, 1M)**

50. Complete and balance the following reaction.
$Cl_2 \quad OH^- \qquad Cl^- \quad ClO^-$ **(1983, 3M)**

51. Explain the following in not more than two sentences.
Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. **(1980, 2M)**

52. Give reasons for the following in one or two sentences.
(i) Hydrogen bromide cannot be prepared by the action of conc. sulphuric acid on sodium bromide.
(ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised. **(1979, 2M)**

53. Write the balanced equations involved in the preparation of
(i) bleaching powder from slaked lime **(1979, 10M)**
(ii) nitric oxide from nitric acid
(iii) chlorine from sodium chloride
(iv) anhydrous aluminium chloride from alumina

Answers

Topic 1

1. (a)	**2.** (b)	**3.** (c)	**4.** (b)
5. (d)	**6.** (a)	**7.** (a)	**8.** (d)
9. (b)	**10.** (d)	**11.** (d)	**12.** (a)
13. (a)	**14.** (b)	**15.** (c)	**16.** (c)
17. (b)	**18.** (d)	**19.** (b)	**20.** (d)
21. (c)	**22.** (b)	**23.** (b)	**24.** (c)
25. (b)	**26.** (a)	**27.** (c)	**28.** (d)
29. (c)	**30.** (a)	**31.** (a)	**32.** (c)
33. (c)	**34.** (b)	**35.** (d)	**36.** (b)
37. (a)	**38.** (d)	**39.** (b)	**40.** (c)
41. (d)	**42.** (a)	**43.** (b,c)	**44.** (a,b,c)
45. (b, d)	**46.** (a, c, d)	**47.** (a, b, c)	**48.** (c)
49. (a, c, d)	**50.** (a, d)	**51.** (6)	**52.** (a)
53. (a)	**54.** (a)	**55.** (b)	**56.** (a)
57. (b)	**58.** (c)	**59.** (c)	**60.** (b)
61. (d)	**62.** NO_2	**63.** Four	**64.** Two
65. white	**66.** T	**67.** T	**68.** F
69. T	**70.** (8)	**71.** 4	**72.** 6

Topic 2

1. (a)	**2.** (b)	**3.** (d)	**4.** (b)
5. (a)	**6.** (a)	**7.** (c)	**8.** (d)
9. (d)	**10.** (c)	**11.** (c)	**12.** (a)
13. (a)	**14.** (a)	**15.** (a)	**16.** (b)
17. (a)	**18.** (c)	**19.** (b)	**20.** (b)
21. (d)	**22.** (a, c, d)	**23.** (b, c)	**24.** (b, c)
25. (b, c)	**26.** (a)	**27.** (a)	**28.** (c)
29. (a)	**30.** (a)	**31.** (c)	**32.** (a)

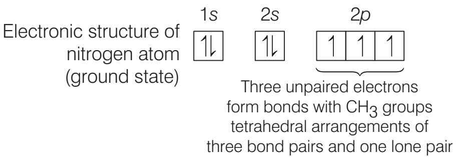
33. A p, s B p, q, r, t C p, q, t D p

34. KI_3	**35.** F	**36.** 5

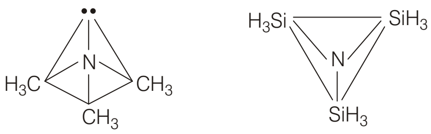
Hints & Solutions

Topic 1 Elements and Compounds of Group 15 and 16

1. The correct statement is that $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae, but have totally different structures. In trimethylamine the arrangement of electrons is as follows :

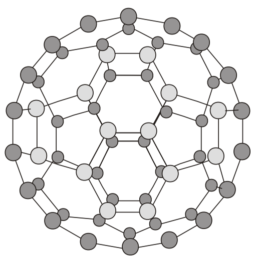


In trisilylamine, three sp^2 orbitals are used for -bonding, giving a plane triangular structure.

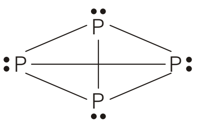


$N(CH_3)_3$ molecule $N(SiH_3)_3$ molecule

2. In C_{60} (Buckminster fullerene) twenty hexagons and twelve pentagons are present which are interlocked resulting a shape of soccer ball. Every ring in this structure is aromatic.

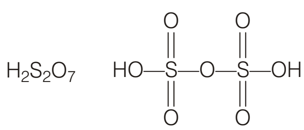


Phosphorus has large atomic size and less electronegativity, so it forms single bond instead of p -p multiple bond. So, it consists of discrete tetrahedral P_4 molecule as shown below :



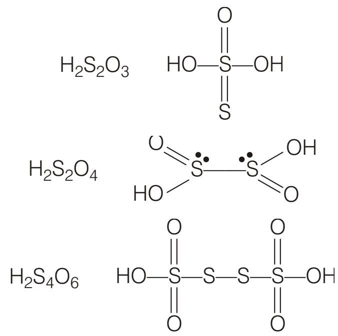
Number of trigons (triangles) 4

3. S S bond is not present in $H_2S_2O_7$ (pyrosulphuric acid or oleum).



While the other given oxoacids of sulphur, i.e.

$H_2S_2O_3$ (thiosulphuric acid), $H_2S_2O_4$ (hyposulphurous or dithionous acid) and $H_2S_4O_6$ (tetrathionic acid) contains S S bonds.



4. The correct increasing order of oxidation state of nitrogen for nitrogen oxides is

$$\overset{1}{N}_2O < \overset{+2}{N}O < \overset{+3}{N}_2O_3 \quad \overset{4}{N}O_2$$

- Oxidation state of N in N_2O is

$$2(x) \quad 2 \quad 0$$
$$x \quad \frac{2}{2} \quad 1$$

- Oxidation state of N in NO is

$$x \quad 2 \quad 0$$
$$x \quad 2$$

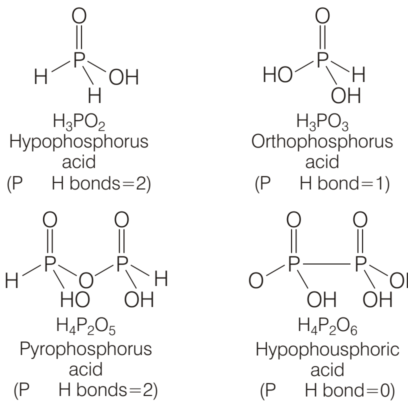
- Oxidation state of N in N_2O_3 is

$$2x \quad 3(\ 2) \quad 0$$
$$x \quad \frac{6}{2} \quad 3$$

- Oxidation state of N in NO_2 is

$$x \quad 2(\ 2) \quad 0$$
$$x \quad 4 \quad 0$$
$$x \quad 4$$

5. Let us consider the structure of the phosphorus oxyacids,



6. As given, the first electron gain enthalpy of oxygen can be shown as,

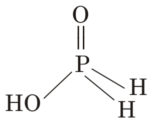
$$O(g) + e \qquad O \ (g) \quad \Delta_{eg}H_1 \qquad 141 \text{kJ/mol}$$

The expression of second electron gain enthalpy of oxygen will be,

$$O\ (g) + e \quad\quad O^{2}\ (g), \quad \Delta_{eg}H_2 \quad \text{ve}$$

$\Delta_{eg}H_2$ of oxygen is positive, i.e. endothermic, because a strong electrostatic repulsion will be observed between highy negative O and the incoming electron (e). A very high amount of energy will be consumed (endothermic) by the system to overcome the electrostatic repulsion.

7. The structure of H_3PO_2 (hypophosphorous) acid is



Due to the presence of two P H bonds, H_3PO_2 acts a strong reducing agent. e.g.

$$4\overset{+1}{Ag}NO_3 \quad H_3\overset{+1}{P}O_2 \quad 2H_2O \quad\quad 4\overset{0}{Ag} \quad H_3\overset{+5}{P}O_4 \quad 4HNO_3$$

8. The thermal decomposition of given compounds is shown below

$$(NH_4)_2Cr_2O_7 \quad\quad N_2 + 4H_2O + Cr_2O_3$$

$$NH_4NO_2 \quad\quad N_2 + 2H_2O$$

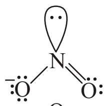
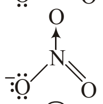
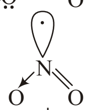
$$(NH_4)_2SO_4 \quad\quad 2NH_3 + H_2SO_4$$

$$Ba(N_3)_2 \quad\quad Ba + 3N_2$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating (It give NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

9. $H_3\overset{5}{P}O_4 \quad H_4\overset{4}{P_2}O_6 \quad H_3\overset{3}{P}O_3 \quad H_3\overset{1}{P}O_2$

10.

Species	Hybridisation
	sp^2
	sp^2
	sp^2
$O{=}\overset{+}{N}{=}O$	sp

11. Orthophosphorous acid, H_3PO_3 : HO P OH (with O above P and H below P)

$H_3\overset{x}{P}O_3 = 3 \quad x \quad 3(\ 2) \quad 0$ or $x \quad 3$

Pyrophosphorous acid, $H_4P_2O_5$:

```
      O       O
HO    P   O   P    OH
      H       H
```

$H_4\overset{x}{P_2}O_5 \quad 4 \quad 2x \quad 5(\ 2) \quad 0$

$4 \quad 2x \quad 10 \quad 0, \ x \quad 3$

12. **PLAN** This problem is based on chemical properties of phosphorus.

White phosphorus on reaction with thionyl chloride ($SOCl_2$) produces phosphorus trichloride.

$$P_4(s) \quad 8SOCl_2(l) \quad\quad 4PCl_3(l) \quad 4SO_2(g) \quad 2S_2Cl_2(g)$$

But if amount of thionyl chloride ($SOCl_2$) is in excess then it produces phosphorus pentachloride.

$$P_4 + 10SOCl_2(l) \quad\quad 4PCl_5 + 10SO_2$$

13. NO is paramagnetic in gaseous state because in gaseous state, it has one unpaired electron.

Total number of electrons present $\ 7 \quad 8 \quad 15\,e$

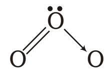
Hence, there must be the presence of unpaired electron in gaseous state while in liquid state, it dimerises due to unpaired electron.

14. NO_2 is a brown coloured gas and imparts this colour to concentrated HNO_3 during long standing.

$$4HNO_3 \quad\quad 2H_2O \quad 2NO_2 \quad 3O_2$$

15. (a) ONCl $\ 8 \quad 7 \quad 17 \quad 32e$

ONO $\ 8 \quad 7 \quad 8 \quad 1 \quad 24e$ (correct)

(b) 

Central O-atom is sp^2-hybridised with 1 lone pair, so bent shape (correct).

(c) In solid state, ozone is violet-black. Ozone does not exist in solid state, thus incorrect.

(d) O_3 has no unpaired electrons, so diamagnetic (correct).

Hence, (c) is the correct.

16. The reaction of white phosphorus with aqueous alkali is

$$P_4 + 3NaOH + 3H_2O \quad\quad PH_3 + NaH_2PO_2$$

In the above reaction, phosphorus is simultaneously oxidised $[P_4(0) \quad\quad NaH_2\overset{+1}{P}O_2]$ as well as reduced $[P_4(0) \quad\quad \overset{3}{P}H_3]$. Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in PH_3 is $\ 3$ and in NaH_2PO_2 is $\ 1$. However, $\ 1$ oxidation number is not given in any option, one might think that NaH_2PO_2 has gone to further decomposition on heating.

$$2NaH_2PO_2 \quad\quad Na_2H\overset{+5}{P}O_4 + PH_3$$

17. Let oxidation number of N be x.

In HNO_3, $\ 1 \quad x \quad 3(\ 2) \quad 0 \quad\quad x \quad 5$

In NO, $\quad x \quad 2 \quad 0 \quad\quad x \quad 2$

In N_2, $\quad x \quad 0$

In NH_4Cl, $\quad x \quad 4 \quad 1 \quad 0 \quad\quad x \quad 3$

18. $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by product

alongwith gaseous nitrogen, hence no additional step of separation is required.
Other reactions are

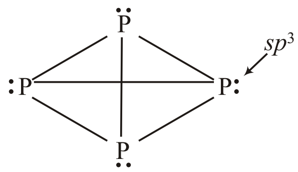
$$NH_4NO_3 \quad ^{\text{Heat}} \quad N_2O + 2H_2O$$

$$2NH_3 \quad 3CuO \quad ^{\text{Heat}} \quad 3Cu + 3H_2O + N_2$$

$$(NH_4)_2Cr_2O_7 \quad ^{\text{Heat}} \quad Cr_2O_3 \quad 4H_2O + N_2$$

19. In limited supply of oxygen, phosphorus is oxidised to its lower oxide P_4O_6 while excess of oxygen gives P_4O_{10}. A mixture of O_2 and N_2 is used for controlled oxidation of phosphorus into P_4O_6.

20. In P_4, all phosphorus are sp^3-hybridised and has 75% *p*-character.



21. In $KMnO_4$, Mn is already in its highest oxidation state (+7), cannot be oxidised by any oxidising agent.

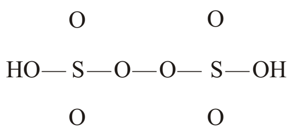
22. $PbO_2 + HNO_3 \qquad Pb(NO_3)_2 + H_2O + O_2$

23. Equimolar amounts of NO and NO_2 at –30°C gives $N_2O_3(l)$ which is a blue liquid.

$$NO(g) + NO_2(g) \quad ^{30\ C} \quad \underset{\text{(Blue)}}{N_2O_3(l)}$$

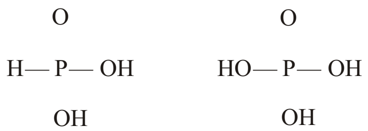
24. Black phosphorus is thermodynamically most stable allotrope of phosphorus.
It is due to three dimensional, network structure of polymeric black phosphorus.

25. $H_2S_2O_8$ is a peroxy acid, has—O—O—linkage



Peroxodisulphuric acid

26. H_3PO_3 is a dibasic, reducing acid. H_3PO_4 is tribasic, non-reducing acid.

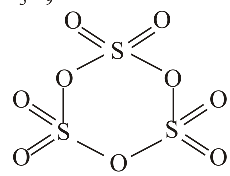


Dibasic, reducing Tribasic, non-reducing

27. Polyphosphates are used as water softening agents because they form soluble complexes with cationic species of hard water.

$$Na_2[Na_4(PO_3)_6] + CaSO_4 \qquad \underset{\text{Soluble complex}}{Na_2[(Ca_2(PO_3)_6]} + Na_2SO_4$$

28. The structure of S_3O_9 is



It has no S—S linkage.

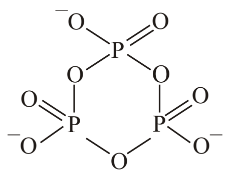
29. CaO, a basic oxide, is most suitable for drying of basic ammonia.

30. H_2O, due to its ability to form intermolecular H-bonds.

31. Corresponding acids are $HClO_4$, H_2SO_3 and H_3PO_4. Hence, the order of acidic strength is

$$Cl_2O_7 > SO_2 > P_4O_{10}$$

32. The structure of cyclic metaphosphate is

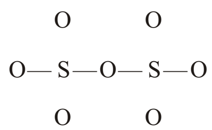


There is three P—O—P bonds.

33. $Ca_3P_2 \quad 6H_2O \qquad 3Ca(OH)_2 \quad 2PH_3$

34. $Na_2SO_3 + S \quad ^{OH} \quad Na_2S_2O_3$

35. $S_2O_7^2$ has no S—S linkage.



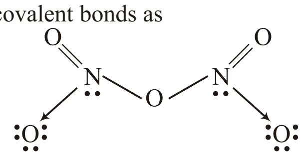
All others have atleast one S—S linkage.

36. Amongst XH_3 where 'X' is group-15 elements, basic strength decreases from top to bottom. Hence, NH_3 is strongest base.

37. The electron withdrawing inductive effect of halogen decreases electron density on nitrogen, lowers basic strength. Since, fluorine is most electronegative, NF_3 is least basic.

38. $NO_2(g)$ is deep brown coloured.

39. In N_2O_5, there are (sigma) covalent bonds, (pi) bonds and coordinate covalent bonds as



40. SO_2 cannot be collected over water because it reacts with water forming H_2SO_3.

$$SO_2 + H_2O \qquad H_2SO_3$$

41. Quicklime (CaO) is used for drying NH_3 gas because both are basic, do not react. On the other hand, H_2SO_4 and P_2O_5 are acidic, reacts with ammonia forming salts. $CaCl_2$ forms complex with ammonia.

42. NO is lighter than O_2.

D_2O is commonly known as heavy water.

N_2 is lighter than O_2, effuse at faster rate under identical experimental conditions. NH_3 liquefies at very low temperature. Therefore, liquid NH_3 is used as a refrigerant.

43. Among the given compounds, those which generate N_2 on thermal decomposition below 300°C are **ammonium dichromate** i.e., $(NH_4)_2Cr_2O_7$ and **barium azide** or nitride i.e., $Ba(N_3)_2$. Reactions of their thermal decomposition are given below

(i) $(NH_4)_2Cr_2O_7 \xrightarrow[\text{Below 300 C}]{} N_2 \quad Cr_2O_3 \quad 4H_2O$

It is an exothemic reaction with

$$H \quad 429.1 \quad 3 \text{ kcal/mol.}$$

(ii) $Ba(N_3)_2 \xrightarrow[\text{Around 160 and above}]{} Ba \quad 3N_2$

Ammonium nitrate (NH_4NO_3) on heating below 300°C gives N_2O as

$$NH_4NO_3 \xrightarrow[\text{below 300 C}]{} N_2O \quad 2H_2O$$

However, on rapid heating or explosion (i.e. above 300°C) it gives off nitrogen as

$$2NH_4NO_3 \xrightarrow[\text{or explosion}]{\text{Rapid heating}} 2N_2 \quad O_2 \quad 4H_2O$$

Magnesium nitride (Mg_3N_2) does not decompose at lower temperatures being comparatively more stable. Its thermal decomposition requires a minimum temperature of 700°C and proceeds as

$$Mg_3N_2 \xrightarrow{700 \quad 1500\,C} 3Mg \quad N_2$$

44. Statement wise explanation is

(i) **Statement (a)** Bi_2O_5 is a metallic oxide while N_2O_5 is a non-metallic oxide.

Metallic oxides being **ionic** are **basic in nature** while non metallic oxides being **covalent** are **acidic in nature**. This confirms more basic nature of Bi_2O_5 in comparison to N_2O_5. Hence, this is a correct statement.

(ii) **Statement (b)** The electronegativity difference between N(3) and F(4) is less as compared to the electronegativity difference between Bi (1.7) and F(4). More electronegativity difference leads to ionic compounds. Thus, NF_3 must be more covalent in nature as compared to BiF_3. Hence, this statement is also correct.

(iii) **Statement (c)** In NH_3 intermolecular hydrogen bonding is present, which is altogether absent in PH_3. Thus, PH_3 boils at lower temperature than NH_3.

Hence, this is also a correct statement.

(iv) **Statement (d)** Due to smaller size of N the lone pair-lone pair repulsion is more in N—N single bond as compared to O—P single bond. This results to weaker N—N single bond as compared to P—P single bond. Hence, this statement is incorrect.

45. P_4O_{10} is a dehydrating agent and converts HNO_3 into N_2O_5

$$2HNO_3 \qquad N_2O_5 + H_2O$$

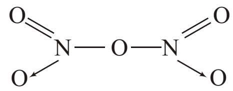
$$P_4O_{10} + 6H_2O \qquad 4H_3PO_4$$

(a) $P_4 + 20HNO_3 \qquad 4H_3PO_4 + 20NO_2 + 4H_2O$

Thus, (a) is incorrect.

(b) N_2O_5 has no unpaired electron and is thus, diamagnetic thus, (b) is correct.

(c)



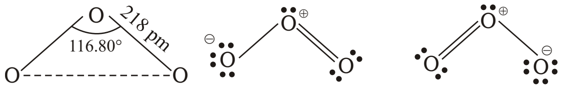
There is no N—N bond, thus, (c) is incorrect.

(d) $N_2O_5 + Na \qquad NaNO_3 + NO_2$

N_2O_5 vapours are of brownish colour. Thus, (d) is correct.

46. **Plan** Due to resonance, bond lengths between two atoms are equal. Species is said to be diamagnetic if all electrons are paired.

Process is endothermic if it takes place with absorption of heat.



bent molecule all electrons paired thus, diamagnetic

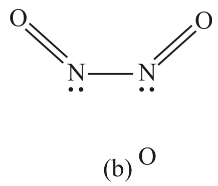
$$2O_3 \qquad 3O_2 \quad H \qquad 142 \text{ kJ mol}^{1}$$

Exothermic

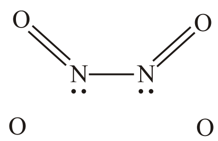
Thus, (b) is incorrect. (a, c, d) are correct.

47. The structures of these oxides are

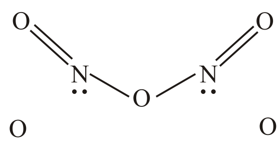
(a)



(b)



(c)

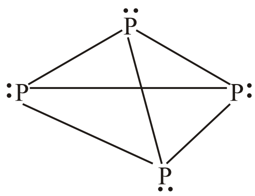


(d)

(a), (b), (c) have N—N bonds.

48. $2NH_3 + OCl \qquad H_2N—NH_2 + H_2O + Cl$

49. The structure of P_4 is



It has six P—P single bonds.

There are four lone pairs on four phosphorus. P—P—P bond angles are of 60°.

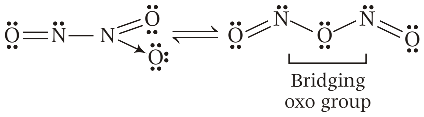
50. $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$

$NH_2OH \;\; HCl + NaNO_2 \qquad NaCl + 2H_2O + N_2O$

However, NH_4NO_2 on heating gives N_2.

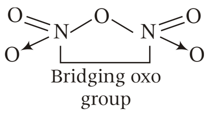
51. The structures of various molecules given in problem are discussed below—

1. $\mathbf{N_2O_3}$ It is the tautomeric mixture of following two structures—



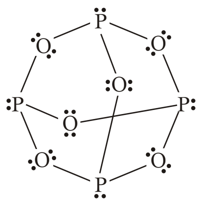
Conclusion 1 bridging oxo group is present in the compound.

2. $\mathbf{N_2O_5}$ It has following structure.



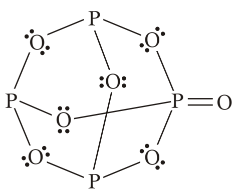
Conclusion 1 bridging oxo group is present in the compound.

3. $\mathbf{P_4O_6}$



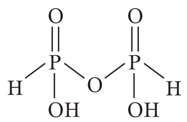
Conclusion 6 bridging oxo groups are present in the compound.

4. $\mathbf{P_4O_7}$



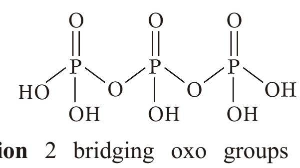
Conclusion 6 bridging oxo groups are present in the compound.

5. $\mathbf{H_4P_2O_5}$



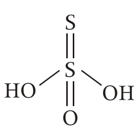
Conclusion 1 bridging oxo group is present in the compound.

6. $H_5P_3O_{10}$



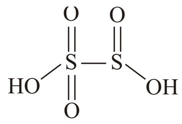
Conclusion 2 bridging oxo groups are present in the compound.

7. $\mathbf{H_2S_2O_3}$



Conclusion This compound does not contain any bridging oxo group.

8. $\mathbf{H_2S_2O_5}$

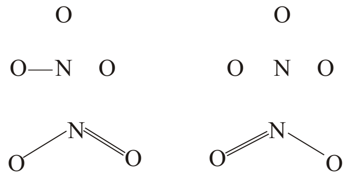


Conclusion This compound also does not contain any bridging oxo group.

52. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

53. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

54. Both Statement I and Statement II are true and Statement II explains the Statement I appropriately. Nitrate ion (NO_3) is more stable than nitrite ion :



(Resonance structure)

(Resonance structure)

55. Both Statement I and Statement II are independently correct but reason is not the correct explanation of Statement I. Nitrogen does not has any vacant *d*-orbitals, it cannot expand its valence shell beyond eight electrons, i.e. it cannot violate octet. Therefore, nitrogen forms only trihalides (NX_3 with eight electrons in valence shell of N).

Phosphorus has vacant 3*d*-orbitals, it can expand its valence shell beyond eight electrons, its both trihalides and pentahalides exist.

Passage

$$KClO_3 \xrightarrow{MnO_2} KCl + \underset{W}{O_2}$$

$$O_2 + P_4 \quad \underset{X}{P_4O_{10}} \xrightarrow{HNO_3} \underset{Y}{N_2O_5} + \underset{Z}{HPO_3}$$

56. (a)

57. (b)

Passage

58. Due to greater solubility in water and prone to microbial attack, nitrates are less abundant in earth's crust.

59. NH_3 is stronger Lewis base than PH_3. In a group of hydrides, basic strength decreases down the group.

60. White phosphorus undergo disproportionation in alkaline medium.

$$P_4 + NaOH \quad PH_3 + NaH_2PO_2$$

61. (P) $2PbO_2 \quad 2H_2SO_4 \xrightarrow{\text{Warm (3)}} 2PbSO_4 \quad O_2 \quad 2H_2O$

(Q) $Na_2S_2O_3 \quad H_2O \xrightarrow{Cl_2(4)} NaHSO_4 \quad HCl$

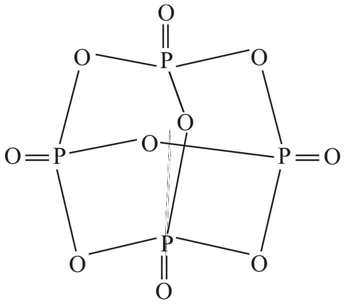
(R) $N_2H_4 \xrightarrow{I_2(2)} N_2 \quad HI$

(S) $XeF_2 \quad \overset{NO(1)}{\quad} \quad Xe \quad NOF$

Thus, P—(3), Q—(4), R—(2), S—(1)

62. $NO_2: \; 2SO_2(g) + O_2(g) \quad \underset{(NO_2)}{\overset{\text{Oxides of } N_2}{\quad}} \quad 2SO_3(g)$

63.



Here four oxygen atoms are bonded to each phosphorus atom.

64. $H_3PO_3 \; [O{=}PH(OH)_2]$ is a dibasic acid.

65. White phosphorus has highly strained, tetrahedral structure, therefore highly reactive.

66. In liquid state, nitric oxide (NO) dimerises into $(NO)_2$ and odd electrons disappear giving diamagnetic property.

$$\underset{\text{Paramagnetic}}{2NO} \qquad \underset{\text{Diamagnetic}}{O{=}N{-}N{=}O\,(l)}$$

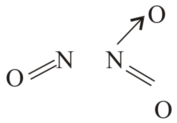
67. Both 'N' and 'As' in corresponding hydrides are sp^3-hybridised. If central atoms are from same group, bond angle decreases from top to bottom if all other things are similar. Hence, H—N—H bond angle in NH_3 is greater than H—As—H bond angle in AsH_3.

68. Halogens are all good oxidising agent and their oxidising power decreases from top to bottom (F_2 to I_2) in group. Any halogen above in group oxidises halides down in group from their aqueous solution. Hence, Cl_2 can oxidise Br to Br_2, I to I_2 but cannot oxidise F to F_2 rather F_2 can oxidise Cl to Cl_2.

69. Fe is more electropositive than hydrogen, displaces H ions from acid solution as :

$$Fe + 2HCl \qquad FeCl_2 + H_2$$

70. N_2O_3 has two proposed structures.

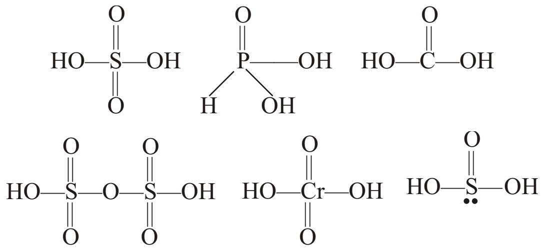
O N O N O and 

In both cases, number of lone pair of electrons are eight.

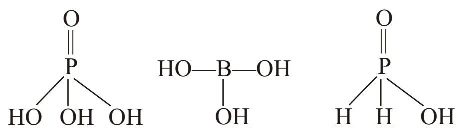
71. PCl_5 produces $POCl_3$ with the following reagents

$$PCl_5 + SO_2 \qquad POCl_3 + SOCl_2$$
$$PCl_5 + H_2O \qquad POCl_3 + 2HCl$$
$$2PCl_5 + H_2SO_4 \qquad SO_2Cl_2 + 2POCl_3 + 2HCl$$
$$6PCl_5 + P_4O_{10} \qquad 10POCl_3$$

72. Diprotic acids 6

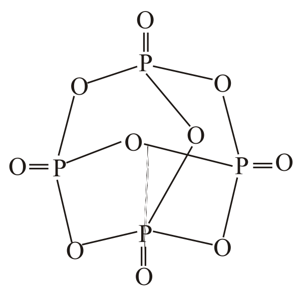


Others are



Triprotic — Monobasic Lewis acid — Monoprotic

73.



(P_4O_{10})

74. $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$

75. $A = NaH\overset{+4}{S}O_3$; $B = Na_2\overset{+4}{S}O_3$; $C = Na_2\overset{+2}{S_2}O_3$; $D = Na_2\overset{+2.5}{S_4}O_6$

76. (i) $Al_4C_3 + 12H_2O \qquad 4Al(OH)_3 + 3CH_4$

(ii) $CaNCN + 5H_2O \qquad CaCO_3 + 2NH_4OH$

(iii) $4BF_3 + 3H_2O \qquad H_3BO_3 + 3HBF_4$

(iv) $NCl_3 + 3H_2O \qquad NH_3 + 3HOCl$

(v) $2XeF_4 + 3H_2O \qquad Xe + XeO_3 + F_2 + 6HF$

77. Nitrogen in N_2 are bonded by one sigma and two pi bonds. Phosphorus and other elements of this period, due to larger size, are very less likely to form pi bonds, hence P_4 is formed in which there is no pi bonds.

78. In given scheme : *A* $Ca(OH)_2$

B NH_4HCO_3, *C* Na_2CO_3

D NH_4Cl and E $CaCl_2$

79. (a) $\underset{A}{HNO_2} + \underset{B}{2H_2SO_3} + H_2O \qquad \underset{C}{NH_2OH} + \underset{D}{2H_2SO_4}$

(b) In $SO_3 + H_2O \qquad H_2SO_4$, sulphuric acid is obtained in misty form and the reaction is explosive. By adding H_2SO_4, above reaction is prevented :

$$H_2SO_4 + SO_3 \qquad H_2S_2O_7 \text{ (oleum)}$$
$$H_2S_2O_7 + H_2O \qquad 2H_2SO_4$$

In the contact process, V_2O_5 is used as catalyst.

80. (i) $P_4O_{10} + 6PCl_5 \qquad 10\,POCl_3$

(ii) $SnCl_4 + 2C_2H_5Cl + 2Na \qquad Na_2SnCl_4 + C_4H_{10}$

81. (a) $PCl_5 + SO_2 \quad POCl_3 + SOCl_2$

(b) $Ca_3(PO_4)_2 + 4H_3PO_4 \quad \underset{\text{triple superphosphate}}{3Ca(H_2PO_4)_2}$

82. The poisonous element *M* may be As. On the basis of given information

$$AsCl_3 + 6H \quad ^{Zn/HCl} \quad \underset{N}{AsH_3} + 3HCl$$

$$2AsH_3 \quad \underset{M}{2As} + 3H_2$$

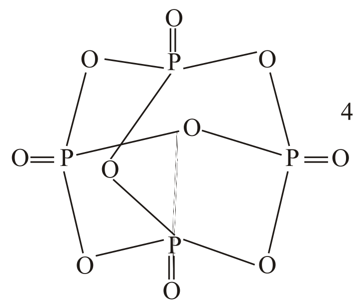
83. (i) $P_4 + 20HNO_3 \quad 4H_3PO_4 + 20NO_2 + 4H_2O$

(ii) $3KMnO_4 + 5H_2O_2 + 3H_2SO_4 \quad K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$

(iii) $P_4 + 20HNO_3 \quad 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $2Al + 2NaOH + 2H_2O \quad 2NaAlO_2 + 3H_2$

84.



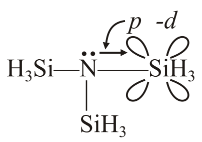
4 P=O bonds

85. (i) The size of both nitrogen and fluorine are very small as well as they have very high electron density. Thus in NF_3, N and F repel each other stretching the N—F bond. Hence, in NF_3, N—F bond lengths are greater than the sum of their single bond covalent radii.

(ii) $Mg_3N_2 + 6H_2O \quad 3Mg(OH)_2 + 2NH_3$

$MgCl_2$ is a salt of strong acid HCl and strong base $Mg(OH)_2$ and therefore, not hydrolysed in aqueous solution.

(iii) In $(SiH_3)_3N$, the lone pair of nitrogen is involved in *p* -*d* bonding, less available on nitrogen for donation to a Lewis acid, a weaker Lewis base



Carbon does not have any vacant *d*-orbitals, no such *p* -*d* bonding occur in trimethyl amine, lone pair of nitrogen is available for donation to Lewis acid, hence a stronger Lewis base.

86. $Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \quad ^{Heat} \quad 3H_3PO_4 + 5CaSO_4 \; 2H_2O + HF$

87. $PCl_5 + SO_2 \quad \underset{A}{POCl_3} + \underset{B}{SOCl_2}$

88. Red phosphorus reacts with iodine in the presence of water to form H_3PO_3 and HI as–

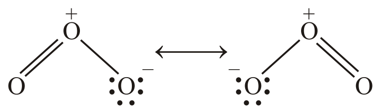
$$2P + 3I_2 + 6H_2O \quad 2H_3PO_3 + 6HI$$

89. SO_2 acts as reducing agent on account of following reaction :

$$SO_2 + 2OH \quad SO_4^{2} + 2H^+ + 2e$$

Hence, the above reaction proceeds in forward direction on increasing concentration of HO ion. H^+ is on product side, adding H^+ retards the reaction by sending it in backward direction.

90.



91. Ammonia, in liquid state undergo self-ionisation as :

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2$$

Thus, addition of NH_4Cl to liquid ammonia increases concentration of NH_4^+ in solution and NH_4Cl act as acid.

92. (i) $Na_2CO_3 + NO + NO_2 \quad 2NaNO_2 + CO_2$

(ii) $2KMnO_4 + 2NH_3 \quad 2MnO_2 + 2KOH + 2H_2O + N_2$

(iii) $P_4 + 20HNO_3 \quad 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $2H_2S + NaHSO_3 \quad H^+ \quad 3S + 3H_2O + Na^+$

(v) $CaCO_3 + CO_2 + H_2O \quad Ca(HCO_3)_2$

93. (i) $NaNO_2 + Zn + NaOH \quad 3Na_2ZnO_2 + NH_3 + H_2O$

(ii) $2NaIO_3 + 5NaHSO_3 \quad 3NaHSO_4 + 2Na_2SO_4 + I_2 + H_2O$

94. N N—O N=N=O

95. (i) $15CaO + 4P_4 \quad 5Ca_3P_2 + 3P_2O_5$

$[Ca_3P_2 + 6H_2O \quad 3Ca(OH)_2 + 2PH_3 \;]\; 5$

$15CaO + 4P_4 + 30H_2O \quad 15Ca(OH)_2 + 3P_2O_5 \quad + 10PH_3$

(ii) $2NH_3 + CO_2 + H_2O \quad (NH_4)_2CO_3$

$\underset{\text{gypsum}}{CaSO_4} + (NH_4)_2CO_3 \quad CaCO_3 \quad + (NH_4)_2SO_4$

$CaSO_4 + 2NH_3 + CO_2 + H_2O \quad CaCO_3 \quad (NH_4)_2SO_4$

96. (i) In H_3PO_3, there is only two replaceable H, hence dibasic

O

H—P—OH H—of OH are acidic, dibasic.

OH

(ii) NH_3 molecules are associated by intermolecular H—bonds.

97. (i) $\underset{\text{hypophosphorus acid}}{2H_3PO_2} \quad PH_3 + H_3PO_4$ (Disproportionation)

(ii) $NaClO_3 \quad SO_2 \quad ^{10H} \quad NaCl \quad S \quad 5H_2O$

98. $SiO_2 < CO_2 < N_2O_5 < SO_3$

99. (i) $4P + 10HNO_3 + H_2O \quad 5NO + 5NO_2 + 4H_3PO_4$

(ii) $NaCl + NH_4OH + CO_2 \quad NH_4Cl + NaHCO_3$

100. Oxygen lacks empty *d*-orbitals in its valence shell, cannot violate octet rule, hence in most of its compound it show only divalency. On the other hand, sulphur has vacant 3*d*-orbitals in its valence shell, can violate octet rule, show di, tetra and hexa valency.

101. (i) MgO is used for the lining of steel making furnace because it forms slag with impurities, and thus helps in removing them from iron.

(ii) The mixture of N_2H_4 and H_2O_2 (in presence of Cu(II) catalyst) is used as a rocket propellant because the reaction is highly exothermic and large volumes of gases is evolved.

$$N_2H_4(l) + 2H_2O_2(l) \qquad N_2(g) + 4H_2O(g)$$

(iii) In orthophosphorus acid (H_3PO_3) only two of the three H are replaceable as

O

H—P—OH

OH

(Only H of —OH are acidic)

(iv) In $MgCl_2$, Mg is *sp*-hybridised while in $SnCl_2$, Sn is sp^2-hybridised with a lone pair at Sn. Hence, $MgCl_2$ is linear while $SnCl_2$ is angular.

102. (i) $P_4 + 3NaOH + 3H_2O \xrightarrow{\text{Inert atm.}} \underset{\text{(phosphine)}}{3NaH_2PO_2 + PH_3}$

(ii) $4Sn + \underset{\text{dil}}{10HNO_3} \qquad 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

103. (i) $4S \; + 6OH \qquad 2S^2 \; + S_2O_3^2 \; + 3H_2O$

(ii) $ClO_3^- \; + 6I^- \quad 6H_2SO_4 \qquad Cl^- \quad 6HSO_4^- \quad 3I_2 \quad 3H_2O$

104. (i) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \qquad 6CaSiO_3 + 10CO + \underset{\text{(white)}}{P_4}$

(ii) $(NH_4)_2SO_4 + NO + NO_2 \qquad 2N_2 + 3H_2O + H_2SO_4$

105. N N—O   N═N═O

106. $Fe_2(SO_4)_3 + 2KI \qquad 2FeSO_4 + K_2SO_4 + I_2$

In the above reaction, strong reducing agent, iodide, reducing ferric salt into ferrous salt.

107.

A	*B*	*C*
Asbestos	Silicates of Ca and Mg	Donar
Lithium metal	Reducing agent	Electron donor
Nitric oxide	Paramagnetic	Air pollutant

108. (i) $2HNO_3 + 6HCl \qquad 2NO + 3Cl_2 + 4H_2O$

(ii) $2Ce^{3+} + S_2O_8^2 \qquad 2SO_4^2 \; + 2Ce^{4+}$

(iii) $Cl_2 + 2OH \qquad Cl \; + ClO \; + H_2O$

109. Orthophosphoric acid (H_3PO_4) has three replaceable (acidic) hydrogen while orthophosphorus acid (H_3PO_3) has only two replaceable hydrogen.

O

HO—P—OH

OH

orthophosphoric acid
(it has three acidic H)

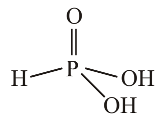
O

O—P—OH

OH

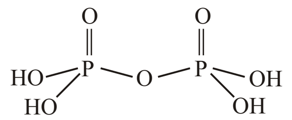
orthophosphorus acid
(only two acidic H, H directly bonded to P is not acidic)

110. (i)



phosphorus acid
(P is sp^3-hybridised)

(ii)



(pyrosphosphoric acid)

111. Rhombic sulphur has a eight membered puckered ring structure.

On heating ring tends to break and linear chain sulphur is formed. When sulphur melts, the S_8 rings slip and roll over one another very easily. It gives rise to a clear mobile liquid. When liquid sulphur is further heated to higher temperature, rings are broken giving long chain sulphur molecules. This long chain molecules of sulphur gets entangled into one another increasing viscosity of melt.

112. (i) In the presence of sunlight, concentrated nitric acid decomposes partially as

$$\text{Conc. } HNO_3 \xrightarrow{h} NO_2 + H^+ + O_2$$

It is the NO_2 which impart yellow colouration to nitric acid.

(ii) The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

Topic 2 Element and Compound of Group 17 and 18

1. Radium (Ra) is a radioactive element. Ra belongs to group 2 (alkaline earth metals), it is not a noble gas.

Note In question noble gas which does not exist in the atmosphere is asked and answer is Ra. But Ra (radium) is an alkaline earth metal and not noble gas. It can be Rn (radon) and is misprint in JEE Main Paper.

2. Halogens form halates and halides with hot and concentrated solution of NaOH as :

$$3X_2 \quad 6NaOH \qquad 5NaX \quad NaXO_3 \quad 3H_2O$$

So, Cl_2 will also give Cl (as NaCl) and ClO_3 (as $NaClO_3$) in the above reaction.

Thus, option (b) is correct.

Note When halogens react with cold and dilute solution of NaOH, hypohalites and halides are produced as:

$$X_2 \quad 2NaOH \qquad NaX \quad NaXO \quad H_2O$$

3. Iodine reacts with concentrated HNO_3 to yield HIO_3 along with NO_2 and H_2O. The reaction involved in as follows :

$$I_2 + 10HNO_3 \qquad 2HIO_3 + 10NO_2 + 4H_2O$$

The oxidation state of 'I' in HIO_3 is 5 as calculated below :

$$1 \quad x \quad 3(\;2) \quad 0$$

$$x \quad 5 \quad 0, x \quad 5$$

4. Chemical reactivity of halogens decreases down the group. The chemical reactivity follows the order.

$$F_2 > Cl_2 > Br_2 > I_2.$$

The highest reactivity of fluorine is attributed to two factors:

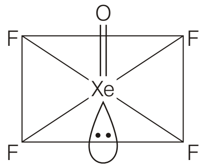
(i) The low dissociation energy of F F bond (which results in low attraction energy for the reaction).

(ii) Very strong bonds which are formed. Both properties arise from, small size of fluorine. I_2 is being the least reactive halogen, it requires a catalyst for the reaction.

$$H_2 + I_2 \quad 2HI$$

5. In $XeOF_4$, Xe is sp^3d^2-hybridised. Geometry of the molecule is octahedral, but shape of the molecule is square pyramidal.

According to VSEPR, theory it has one bond. Remaining six electron pairs form an octahedron with one position occupied by a lone pair.



[Number of *bp* = 5
Number of *lp* = 1]

Here, Xe contains one lone pair of electrons.

6. The reaction in which oxidation and reduction occur simultaneously are termed as redox reaction.

$$\overset{+4}{XeF_4} \quad \overset{1}{O_2}\ (\ F_2) \qquad \overset{6}{X\,eF_6} \quad \overset{0}{O_2}$$

Since, Xe undergoes oxidation while O undergoes reduction. So, it is an example of redox reaction.

7. Cl_2, Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalies while a mixture of halides and haloate when react with concentrated cold alkalies.

$$\underset{\text{Cold and dilute}}{Cl_2 \quad 2NaOH} \qquad NaCl \quad NaClO \quad H_2O$$

Cl and ClO are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

8. Interhalogen compounds are generally more reactive than halogens (except fluorine).

9. Xe has highest boiling point.

10. **PLAN** This problem can be solved by using concept involved in chemical properties of xenon oxide and xenon fluoride.

XeF_6 on complete hydrolysis produces XeO_3.

XeO_3 on reaction with OH produces $HXeO_4$ which on further treatment with OH undergo slow disproportionation reaction and produces XeO_6^{4} along with Xe(g), $H_2O(l)$ and $O_2(g)$ as a by-product.

Oxidation half-cell in basic aqueous solution

$$HXeO_4 \quad 5OH \qquad XeO_6^{4} \quad 3H_2O \quad 2e^-$$

Reduction half-cell in basic aqueous solution

$$HXeO_4 \quad 3H_2O \quad 6e \qquad Xe \quad 7OH$$

Balanced overall disproportionation reaction is

$$4HXeO_4 \quad 8OH \qquad \underbrace{3XeO_6^{4} \quad Xe}_{\text{2 products}} + 6H_2O$$

Complete sequence of reaction can be shown as

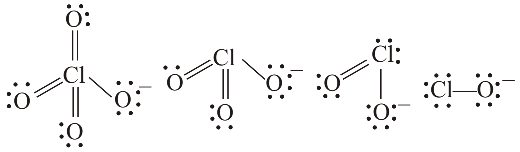
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 3H_2F_2$$
$$\downarrow OH^-$$
$$HXeO_4^-$$
$$\downarrow OH^-/H_2O \text{ (disproportionation)}$$
$$XeO_6^{4-}(s) + Xe(g) + H_2O(l) + O_2(g)$$

Thus, (c) is the correct answer.

11. Decreasing order of strength of oxoacids

$$HClO_4 > HClO_3 > HClO_2 > HOCl$$

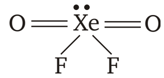
Reason Consider the structures of conjugate bases of each oxyacids of chlorine.



Negative charge is more delocalised on ClO_4 due to resonance, hence, ClO_4 is more stable (and less basic).

Hence, we can say as the number of oxygen atom(s) around Cl-atom increases as oxidation number of Cl-atom increases and thus, the ability of loose the H increases.

12. In XeO_2F_2, the bonding arrangement around the central atom Xe is

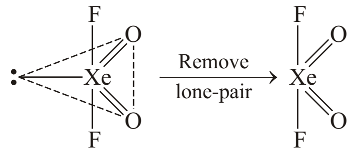


4 bonds 1.0 lp 5

Hybridisation of Xe sp^3d

sp^3d-hybridisation corresponds to trigonal bipyramidal geometry.

Also, in trigonal bipyramidal geometry, lone pairs remain present on equatorial positions in order to give less electronic repulsion.



See-saw shape

NOTE According to Bent's rule, the more electronegative atoms must be present on axial position. Hence, F are kept on axial positions.

13. Sodium thiosulphate, $Na_2S_2O_3$ gets oxidised by chlorine water as $Na_2S_2O_3 \quad 4Cl_2 \quad 5H_2O \qquad 2NaHSO_4 \quad 8HCl$

$FeCl_3$ oxidises $Na_2S_2O_3$ to $Na_2S_4O_6$.

14. I^- is oxidised by MnO_4^- in alkaline medium to form IO_3^-

$2KMnO_4 \quad KI \quad H_2O \qquad 2KOH \quad 2MnO_2 \quad KIO_3$

15. Amongst oxyacids of a given halogen, higher the oxidation number of halogen, stronger the acid. Hence,

$$HOCl < HClO_2 < HClO_3 < HClO_4.$$

16. Pseudo halides must contain atleast one nitrogen atom.

17. Among oxyacids of halogens, if there are same number of oxygens bonded to central atom, higher the electronegativity of halogen, stronger the acid. Hence,

$$IOH < BrOH < ClOH$$

18. All others has at least one S-S linkage.

$$KF + HF \quad K^+ + HF_2$$

19. Among halogens, oxidising power decreases from top to bottom. Hence, the upper halogen oxidises lower halides from aqueous solution. Chlorine will oxidise bromide into bromine.

20. Moist chlorine gives nascent oxygen, act as oxidising agent :

$$Cl_2 + H_2O \quad HCl + HOCl$$

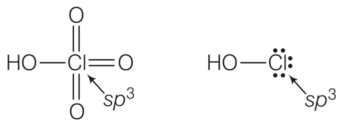
$$HOCl \quad HCl + \underset{\text{(bleaching action)}}{\underset{\text{nascent oxygen}}{[O]}}$$

21. Fluorine, being the most electronegative, its size is very small. Therefore, it does not have a tendency to loose electrons. Hence, HF does not act as a reducing agent.

22. (a) ClO_4 is more stable than ClO .

(b) Incorrect : $Cl_2 \quad H_2O \quad HCl \quad HOCl$

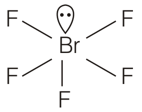
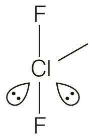
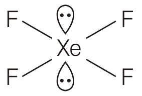
(c)



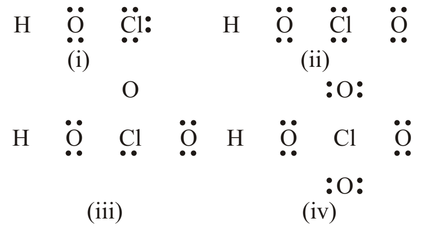
(d) $HClO_4$ is stronger acid than H_2O.

23. Colour of halogen arises due to transition from HOMO to LUMO in the visible region. On moving down a group, the difference in energy between HOMO and LUMO decreases electronic transition occur more easily and colour intensity increases.

24.

Compounds	Hydridisation	Structures	Lone pair on central atom
BrF_5	sp^3d^2		1
ClF_3	sp^3d		2
XeF_4	sp^3d^2		2
SF_4	sp^3d		1

25.



(*a*) Number of Cl ═ O bonds in (ii) and (iii) together is three. Hence, wrong.

(*b*) Number of Lone Pair on Cl in (ii) and (iii) together is three. Hence, correct.

(*c*) In (iv), Cl is sp^3-hybridised. Hence, correct.

(*d*) Amongst (i) to (iv), the strongest acid is (iv). Hence, wrong.

Passage 1 Q. Nos. (**26-27**)

$$2NaOH \quad Cl_2 \xrightarrow{\text{Cold}} NaCl \quad \underset{P}{NaOCl} \quad H_2O$$

$$6NaOH \quad 3Cl_2 \xrightarrow{\text{hot}} 5NaCl \quad \underset{Q}{NaClO_3} \quad 3H_2O$$

$$\underset{\text{hypochlorous acid}}{HOCl} \xrightarrow{NaOH} \underset{P}{NaOCl}$$

$$\underset{\text{chloric acid}}{HClO_3} \xrightarrow{NaOH} \underset{Q}{NaClO_3}$$

$$Cl_2 \quad SO_2 \quad \underset{R}{SO_2Cl_2}$$

$$10\,\underset{R}{SO_2Cl_2} \quad P_4 \quad \underset{S}{4PCl_5} \quad 10\,SO_2$$

$$PCl_5 \quad 4H_2O \quad \underset{T}{H_3PO_4} \quad 5\,HCl$$

Passage 2 Q.Nos. (**28-29**)

28. The involved redox reactions are :

$$2H^+ + OCl \ + 2I \quad Cl \ + I_2 + H_2O \qquad \ldots(i)$$

$$I_2 + 2S_2O_3^2 \quad 2I \ + S_4O_6^2 \qquad \ldots(ii)$$

Also the *n*-factor of $S_2O_3^2$ is one as

$$2S_2O_3^2 \quad S_4O_6^2 \quad 2e$$

[one '*e*' is produced per unit of $S_2O_3^2$]

Molarity of $Na_2S_2O_3$ = 0.25 N 1 = 0.25 M

m mol of $Na_2S_2O_3$ used up 0.25 48 12

Now from stoichiometry of reaction (ii)

12 m mol of $S_2O_3^2$ would have reduced 6 m mol of I_2.

From stoichiometry of reaction (i)

m mol of OCl reduced = m mol in I_2 produced 6

Molarity of household bleach solution $\frac{6}{25}$ 0.24 M

Shortcut Method

Milliequivalent of $Na_2S_2O_3$ = milliequivalent of OCl

= 0.25 48 = 12

Also *n*-factor of OCl 2 [Cl Cl , gain of 2*e*]

m mol of OCl $\frac{12}{2}$ 6 m mol. Remaining part is solved in the same manner.

29. Bleaching powder is Ca(OCl)Cl. Therefore, the oxoacid whose salt is present in bleaching powder is HOCl. Anhydride of HOCl is Cl_2O as

$$2\,HOCl \quad Cl_2O + H_2O$$

NOTE The oxidation number of element in anhydride and oxoacid remains the same.

Passage 3 Q.Nos. (**30-32**)

30. Ar, being inert, provide inert atmosphere in arc welding, and prevent from undesired oxidation.

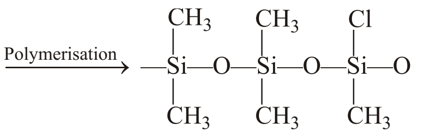
31. O Xe O

O

Xe is sp^3-hybridised with one lone pair. Hence, molecule of XeO_3 has pyramidal shape.

32. Both XeF_4 and XeF_6 are strong oxidising agent.

33. $(CH_3)_2SiCl_2 + H_2O \quad (CH_3)_2Si(OH)_2 + 2HCl$



silicone

$3XeF_4 + 6H_2O \quad XeO_3 + 2Xe + 12HF + \frac{3}{2}O_2$

$Cl_2 + H_2O \quad HCl + HOCl \quad HCl + \frac{1}{2}O_2$

$VCl_5 + H_2O \quad VOCl_3 + 2HCl$

34. $KI + I_2 \quad KI_3$

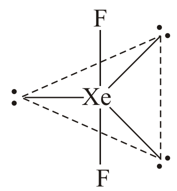
35. Among H*X*, acidic strength increases from HF to HI.

36. Br_2 is disproportionated in basic medium as

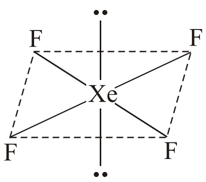
$3Br_2 + 3Na_2CO_3 \quad 5NaBr + NaBrO_3 + 3CO_2$

37. $2XeF_4 + 3H_2O \quad Xe + XeO_3 + F_2 + 6HF$

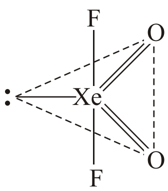
38.



linear



square planar



see-saw shaped

39. Halogen above in the group oxidises halide below to it from their aqueous solution, e.g.

$Cl_2 + 2I\ (aq) \quad 2Cl \ + I_2$

40. $Ca(OH)_2 + Cl_2 \quad 40\ C \quad CaOCl_2 + H_2O$

41. (i) $2KI + Cl_2 \quad 2KCl + I_2$

(ii) $2KClO_3 + I_2 \quad 2KIO_3 + Cl_2$

42. (i) Due to small size and high electron density of fluorine atom, there exist a significant repulsions between fluorine atoms in F_2, they have greater tendency to get apart. Hence, bond energy of F_2 is less than that of Cl_2. This is against to bond-length bond-energy relationship,.

(ii) Sulphur dioxide is a more powerful reducing agent in alkaline medium because nascent hydrogen is produced in the presence of moisture

i.e. $SO_2 \quad 2H_2O \quad H_2SO_4 \quad 2H$

And alkaline solution neutralises the acid i.e. H_2SO_4 and shift the equilibrium in the forward direction producing more nascent hydrogen. But in acidic medium the equilibrium will suppressed resulting in a lesser amount of nascent hydrogen.

43. $NaBrO_3 + 3F_2 \quad 3F_2O + NaBr$

44. $HOCl < HOClO < HOClO_2 < HOClO_3$

45. $2IO_3 + 5HSO_3 \quad I_2 + H_2O + 3HSO_4 + 2SO_4^2$

46. $Cl_2 + FeBr_2 \quad FeCl_3 + Br_2$

47. $ClO_3 + 6I + 6H_2SO_4 \quad Cl + 6HSO_4 + 3I_2 + 3H_2O$

48. (i) Bond strength is inversely related to bond length. Hence, bond energy : HI < HBr < HCl < HF

(ii) $HI(-1) < I_2(0) < ICl(+1) < HIO_4\ (+7)$

49. F_2 itself, is the strongest oxidising agent. Therefore, chemical reagent cannot oxidise fluoride to fluorine.

50. Complete and balance the following reactions

$Cl_2 + 2OH \quad Cl \ + ClO \ + H_2O$

51. The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

52. (i) HBr is a stronger reducing agent, reduces concentrated H_2SO_4 to SO_2. Hence, HBr cannot be prepared by heating bromide salts with concentrated H_2SO_4.

(ii) Hypochlorous acid is acidic in nature, therefore it turns blue litmus paper into red. However, HOCl is also an oxidising acid (bleaching), it bleaches red colour to finally colourless.

53. (i) $Ca(OH)_2 + Cl_2 \quad 40\ C \quad CaOCl_2 + H_2O$

(ii) $3Cu + 8HNO_3\ (dil) \quad 3Cu(NO_3)_2 + 4H_2O + 2NO$

(iii) $2NaCl + 2H_2SO_4 + MnO_2 \quad Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

(iv) $Al_2O_3 + 3C + 3Cl_2 \quad 2AlCl_3 + 3CO$

Download Chapter Test
http://tinyurl.com/y2yzc2dp *or*

17

Transition and Inner-Transition Elements

Objective Questions I (Only one correct option)

1. Thermal decomposition of a Mn compound (X) at 513 K results in compound (Y), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z. X, Y and Z, respectively, are **(2019 Main, 12 April II)**

(a) K_3MnO_4, K_2MnO_4 and Cl_2 (b) K_2MnO_4, $KMnO_4$ and SO_2
(c) $KMnO_4$, K_2MnO_4 and Cl_2 (d) K_2MnO_4, $KMnO_4$ and Cl_2

2. The pair that has similar atomic radii is

(a) Mn and Re (b) Ti and Hf
(c) Sc and Ni (d) Mo and W

3. The correct order of the first ionisation enthalpies is **(2019 Main, 10 April II)**

(a) Mn < Ti < Zn < Ni (b) Ti < Mn < Zn < Ni
(c) Zn < Ni < Mn < Ti (d) Ti < Mn < Ni < Zn

4. The highest possible oxidation states of uranium and plutonium, respectively, are **(2019 Main, 10 April II)**

(a) 7 and 6 (b) 6 and 7
(c) 6 and 4 (d) 4 and 6

5. Consider the hydrated ions of Ti^{2} , V^{2} , Ti^{3} and Sc^{3} . The correct order of their spin-only magnetic moment is **(2019 Main, 10 April I)**

(a) $Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$ (b) $Sc^{3+} < Ti^{3+} < V^{2+}$ Ti^{2+}
(c) Ti^{3} Ti^{2} Sc^{3+} V^{2} (d) V^{2} Ti^{2} Ti^{3} Sc^{3}

6. The maximum number of possible oxidation states of actinoides are shown by **(2019 Main, 9 April II)**

(a) berkelium, (Bk) and californium (Cf)
(b) nobelium (No) and lawrencium (Lr)
(c) actinium (Ac) and thorium (Th)
(d) neptunium (Np) and plutonium (Pu)

7. The lanthanide ion that would show colour is **(2019 Main, 8 April I)**

(a) Gd^{3} (b) Sm^{3}
(c) La^{3} (d) Lu^{3}

8. The correct order of atomic radii is **(2019 Main, 12 Jan II)**

(a) Ho > N > Eu > Ce (b) N > Ce > Eu > Ho
(c) Eu > Ce > Ho > N (d) Ce > Eu > Ho > N

9 $\underline{A} \xrightarrow{4\,KOH,\,O_2} 2\underline{B}$ $2H_2O$
(Green)

$3\underline{B} \xrightarrow{4\,HCl} 2\underline{C}$ MnO_2 $2H_2O$
(Purple)

$2\underline{C} \xrightarrow{H_2O,\,KI} 2\underline{A}$ $2KOH$ $\underline{D}$

In the above sequence of reactions, $\underline{A}$ and $\underline{D}$, respectively, are **(2019 Main, 11 Jan II)**

(a) KI and $KMnO_4$ (b) MnO_2 and KIO_3
(c) KI and K_2MnO_4 (d) KIO_3 and MnO_2

10. The element that usually does not show variable oxidation states is **(2019 Main, 11 Jan I)**

(a) Sc (b) Cu (c) Ti (d) V

11. The 71^{st} electron of an element X with an atomic number of 71 enters into the orbital **(2019 Main, 10 Jan II)**

(a) $4f$ (b) $6p$ (c) $5d$ (d) $6s$

12. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means **(2019 Main, 10 Jan I)**

(a) increase in atomic radii and decrease in ionic radii
(b) decrease in both atomic and ionic radii
(c) increase in both atomic and ionic radii
(d) decrease in atomic radii and increase in ionic radii

13. The transition element having least enthalpy of atomisation is **(2019 Main, 9 Jan II)**

(a) Zn (b) V (c) Fe (d) Cu

14. In the following reactions, ZnO is respectively acting as a/an **(2017 Main)**

(i) $ZnO + Na_2O$ Na_2ZnO_2
(ii) $ZnO + CO_2$ $ZnCO_3$

(a) base and acid (b) base and base
(c) acid and acid (d) acid and base

15. Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4. 'X' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. 'X' is **(2017 Main)**

(a) C_6H_5COONa (b) HCOONa
(c) CH_3COONa (d) $Na_2C_2O_4$

16. Which of the following combination will produce H_2 gas? **(2017 Adv.)**
(a) Fe metal and conc. HNO_3
(b) Cu metal and conc. HNO_3
(c) Au metal and NaCN (*aq*) in the presence of air
(d) Zn metal and NaOH (*aq*)

17. Which of the following compounds is metallic and ferromagnetic? **(2016 Main)**
(a) CrO_2 (b) VO_2
(c) MnO_2 (d) TiO_2

18. The reaction of zinc with dilute and concentrated nitric acid, respectively, produce **(2016 Main)**
(a) NO_2 and NO (b) NO and N_2O
(c) NO_2 and N_2O (d) N_2O and NO_2

19. The geometries of the ammonia complexes of Ni^{2} , Pt^{2} and Zn^{2} , respectively, are **(2016 Main)**
(a) octahedral, square planar and tetrahedral
(b) square planar, octahedral and tetrahedral
(c) tetrahedral, square planar and octahedral
(d) octahedral, tetrahedral and square planar

20. Which of the following compounds is not yellow coloured? **(2015 Main)**
(a) $Zn_2[Fe(CN)_6]$ (b) $K_3[Co(NO_2)_6]$
(c) $(NH_4)_3[As(Mo_3O_{10})_4]$ (d) $BaCrO_4$

21. Which series of reactions correctly represents chemical relations related to iron and its compound? **(2014 Main)**
(a) $Fe \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$
(b) $Fe \xrightarrow{O_2, \text{Heat}} FeO \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$
(c) $Fe \xrightarrow{Cl_2, \text{Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
(d) $Fe \xrightarrow{O_2, \text{Heat}} Fe_3O_4 \xrightarrow{CO, 600 C} FeO \xrightarrow{CO, 700 C} Fe$

22. Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest $E_{M^{3+}/M^{2+}}$ value? **(2013 Main)**
(a) Cr (Z = 24) (b) Mn (Z = 25)
(c) Fe (Z = 26) (d) Co (Z = 27)

23. Consider the following reaction, **(2013 Main)**

$$xMnO_4 \quad yC_2O_4^{2} \quad zH^+ \qquad xMn^{2+} \quad 2yCO_2 \quad \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively
(a) 5, 2 and 16 (b) 2, 5 and 8
(c) 2, 5 and 16 (d) 5, 2 and 8

24. Which of the following arrangements does not represent the correct order of the property stated against it? **(2013 Main)**
(a) V^{2+} Cr^{2+} Mn^{2+} Fe^{2+}: paramagnetic behaviour
(b) Ni^{2+} Co^{2+} Fe^{2+} Mn^{2+} : ionic size
(c) Co^{3+} $Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(d) Sc < Ti < Cr < Mn : number of oxidation states

25. The colour of light absorbed by an aqueous solution of $CuSO_4$ is **(2012)**
(a) orange-red (b) blue-green
(c) yellow (d) violet

26. Which of the following will not be oxidised by O_3? **(2005)**
(a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4

27. Which of the following pair is expected to exhibit same colour in solution? **(2005, 1M)**
(a) $VOCl_2$; $FeCl_2$ (b) $CuCl_2$; $VOCl_2$
(c) $MnCl_2$; $FeCl_2$ (d) $FeCl_2$; $CuCl_2$

28. When I is oxidised by MnO_4 in alkaline medium, I converts into **(2004)**
(a) IO_3 (b) I_2 (c) IO_4 (d) IO

29. The pair of compounds having metals in their highest oxidation state is **(2004, 1M)**
(a) MnO_2, $FeCl_3$ (b) $[MnO_4]$, CrO_2Cl_2
(c) $[Fe(CN)_6]^{3}$, $[Co(CN)_3]$ (d) $[NiCl_4]^{2}$, $[CoCl_4]$

30. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by **(2004, 1M)**
(a) heating NH_4NO_2
(b) heating NH_4NO_3
(c) Mg_3N_2 H_2O
(d) Na(comp.) + H_2O_2

31. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is **(2003, 1M)**
(a) K_2MnO_4, purple green (b) $KMnO_4$, purple
(c) Mn_2O_3, brown (d) Mn_3O_4, black

32. Amongst the following, identify the species with an atom in + 6 oxidation state **(2000, 1M)**
(a) MnO_4 (b) $Cr(CN)_6^{3}$ (c) NiF_6^{2} (d) CrO_2Cl_2

33. On heating ammonium dichromate, the gas evolved is **(1999, 2M)**
(a) oxygen (b) ammonia
(c) nitrous oxide (d) nitrogen

34. In the dichromate dianion **(1999, 2M)**
(a) 4 Cr—O bonds are equivalent
(b) 6 Cr—O bonds are equivalent
(c) all Cr—O bonds are equivalent
(d) all Cr—O bonds are non-equivalent

35. Which of the following compounds is expected to be coloured? **(1997, 1M)**
(a) Ag_2SO_4 (b) CuF_2 (c) MgF_2 (d) CuCl

36. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is **(1997, 1M)**
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) CO

37. The reaction which proceed in the forward direction is **(1991, 1M)**
(a) $Fe_2O_3 + 6HCl \qquad 2FeCl_3 + 3H_2O$
(b) $NH_3 + H_2O + NaCl \qquad NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 \qquad SnCl_2 + 2HgCl_2$
(d) $2CuI + I_2 + 4H^+ \qquad 2Cu^{2+} + 4KI$

38. Zinc-copper couple that can be used as a reducing agent is obtained by **(1984, 1M)**
(a) mixing of zinc dust and copper gauge
(b) zinc coated with copper
(c) copper coated with zinc
(d) zinc and copper wires welded together

39. How many unpaired electrons are present in Ni^{2+}? **(1981, 1M)**
(a) 0 (b) 2
(c) 4 (d) 8

40. One of the constituent of German silver is **(1980, 1M)**
(a) Ag (b) Cu (c) Mg (d) Al

41. Which of the following dissolves in concentrated NaOH solution? **(1980, 1M)**
(a) Fe (b) Zn (c) Cu (d) Ag

Objective Questions II

(One or more than one correct option)

42. The correct statement(s) about Cr^{2} and Mn^{3} is/are [atomic number of Cr 24 and Mn 25] **(2015 Adv.)**
(a) Cr^{2} is a reducing agent
(b) Mn^{3} is an oxidising agent
(c) both Cr^{2} and Mn^{3} exhibit d^4 electronic configuration
(d) when Cr^{2} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

43. Fe^{3} is reduced to Fe^{2+} by using **(2015 Adv.)**
(a) H_2O_2 in presence of NaOH
(b) Na_2O_2 in water
(c) H_2O_2 in presence of H_2SO_4
(d) Na_2O_2 in presence of H_2SO_4

44. Which of the following halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$?
(a) HCl (b) HF (c) HBr (d) HI

45. Reduction of the metal centre in aqueous permanganate ion involves **(2011)**
(a) three electrons in neutral medium
(b) five electrons in neutral medium
(c) three electrons in alkaline medium
(d) five electrons in acidic medium

46. Which of the following statement (s) is/are correct? **(1998)**
(a) The electronic configuration of Cr is [Ar] $3d^5 4s^1$ (Atomic number of Cr = 24)
(b) The magnetic quantum number may have a negative value
(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (Atomic number of Ag = 47)
(d) The oxidation state of nitrogen in HN_3 is – 3

47. Which of the following statement(s) is/are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4? **(1998, 2M)**
(a) A deep red vapours is formed
(b) Vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(c) Chlorine gas is evolved
(d) Chromyl chloride is formed

48. Which of the following alloys contains Cu and Zn? **(1993, 1M)**
(a) Bronze (b) Brass
(c) Gun metal (d) Type metal

49. The aqueous solution of the following salts will be coloured in case of **(1990, 1M)**
(a) $Zn(NO_3)_2$ (b) $LiNO_3$ (c) $Co(NO_3)_2$ (d) $CrCl_3$
(e) potash alum

50. Potassium manganate (K_2MnO_4) is formed when **(1988, 2M)**
(a) chlorine is passed into aqueous $KMnO_4$ solution
(b) manganese dioxide is fused with KOH in air
(c) formaldehyde reacts with potassium permanganate in the presence of strong alkali
(d) potassium permanganate reacts with conc. H_2SO_4

Assertion and Reason

Read the following questions and answer as per the direction given below :
(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

51. **Statement I** Zn^{2+} is diamagnetic.
Statement II The electrons are lost from 4*s* orbital to form Zn^{2+}. **(1998, 2M)**

52. **Statement I** To a solution of potassium chromate if a strong acid is added, it changes its colour from yellow to orange.
Statement II The colour change is due to the change in oxidation state of potassium chromate. **(1988, 2M)**

Fill in the Blanks

53. The compound $YBa_2Cu_3O_7$ which show super conductivity has copper in oxidation state …… assuming that the rare earth element Yttrium in its usual +3 oxidation state. **(1994, 1M)**

54. The outermost electronic configuration of Cr is …… **(1994, 1M)**

55. Fehling's solution *A* consists of an aqueous solution of copper sulphate while Fehling's solution *B* consists of an alkaline solution of …… **(1990, 1M)**

56. The salts ……… and …… are isostructural. ($FeSO_4$ $7H_2O$, $CuSO_4$ $5H_2O$, $MnSO_4$ $4H_2O$, $ZnSO_4$ $7H_2O$ **(1990, 1M)**

57. Mn^{2+} can be oxidised to MnO_4 by ……… (SnO_2, PbO_2, BaO_2) **(1981, 1M)**

True/False

58. Dipositive zinc exhibit paramagnetism due to loss of two electrons from $3d$-orbitals of neutral atom. **(1987, 1M)**

59. Copper metal reduces Fe^{2+} in an acidic medium. **(1982, 1M)**

Integer Answer Type Question

60. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitative oxidise thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is ... . **(2016 Adv.)**

61. In dilute aqueous H_2SO_4 the complex diaquadioxalatoferrate (II) is oxidised by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4\ ]$ is **(2015 Adv.)**

62. Consider the following list of reagents, acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is **(2014 Adv.)**

Subjective Questions

63. $\underset{\text{White fumes with pungent smell}}{(B)} \quad \overset{\text{Moist air}}{\quad} \quad \underset{(M\ =\text{Transition element colourless})}{MCl_4} \quad \overset{\text{Zn}}{\quad} \quad \underset{\text{(purple colour)}}{(A)}$

Identify the metal M and hence MCl_4. Explain the difference in colours of MCl_4 and A. **(2005)**

64. Give reasons : CrO_3 is an acid anhydride. **(1999, 2M)**

65. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion of the compound. **(1997)**

66. Write balanced equations for the following

(i) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.

(ii) Reaction of zinc with dilute nitric acid. **(1997, 2M)**

67. Complete and balance the following reactions

(i) $[MnO_4]^2 \quad H^+ \quad ..... \quad [MnO_4] \quad H_2O$

(ii) $SO_2(aq) \quad Cr_2O_7^2 \quad 2H^+ \quad \ldots + \ldots +$ **(1994, 2M)**

68. Complete and balance the following reaction.

$(NH_4)_2S_2O_8 \quad H_2O \quad MnSO_4 \quad \ldots\ldots + \ldots\ldots + \ldots\ldots$ **(1993, 1M)**

69. Write the balanced chemical equations for the following reactions.

(i) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4.

(ii) Potassium permanganate is added to a hot solution of manganous sulphate. **(1990, 2M)**

70. Complete and balance the following reactions.

(i) $Mn^{2+} \quad PbO_2 \quad MnO_4 \quad H_2O$

(ii) $Ag^+ \quad AsH_3 \quad H_3AsO_3 \quad H^+$ **(1987, 2M**

71. Give reason in one or two sentences
"Most transition metal compounds are coloured." **(1986, 1M)**

72. Show with balanced equations for the reactions when

(i) potassium permanganate interacts with manganese dioxide in the presence of potassium hydroxide.

(ii) potassium ferricyanide is heated with concentrated sulphuric acid. **(1985, 2M)**

73. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

"Potassium permanganate from manganese dioxide" **(1983, 1M)**

74. Complete and balance the following reactions **(1983, 2M)**

(i) $Zn \quad NO_3 \quad Zn^{2+} \quad NH_4^+$

(ii) $Cr_2O_7^2 \quad C_2H_4O \quad C_2H_4O_2 \quad Cr^{3+}$

Answers

1. (c)	**2.** (d)	**3.** (d)	**4.** (b)
5. (a)	**6.** (d)	**7.** (b)	**8.** (c)
9. (b)	**10.** (a)	**11.** (c)	**12.** (b)
13. (a)	**14.** (d)	**15.** (d)	**16.** (d)
17. (a)	**18.** (d)	**19.** (a)	**20.** (a)
21. (d)	**22.** (d)	**23.** (c)	**24.** (a)
25. (a)	**26.** (c)	**27.** (b)	**28.** (a)
29. (b)	**30.** (a)	**31.** (a)	**32.** (d)
33. (d)	**34.** (b)	**35.** (b)	**36.** (b)
37. (a)	**38.** (b)	**39.** (b)	**40.** (b)
41. (b)	**42.** (a, b, c)	**43.** (a, b)	**44.** (a, c, d)
45. (a, c, d)	**46.** (a, b, c, d)	**47.** (a, b, d)	**48.** (b, c)
49. (c, d)	**50.** (b, c)	**51.** (b)	**52.** (c)
53. $x \quad 7/3$	**54.** $3d^5 4s^1$	**55.** Rochelle salt	
56. $FeSO_4 \ 7H_2O$ and $ZnSO_4 \ 7H_2O$			**57.** PbO_2
58. F	**59.** F	**60.** (6)	**61.** (8)
62. (7)			

Hints & Solutions

1. Thermal decomposition of Mn compound (X), i.e. $KMnO_4$ at 513 K results in compound Y(i.e. K_2MnO_4), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z(i.e. Cl_2). The reactions involved are as follows :

$$\underset{(X)}{2KMnO_4} \quad ^{513\text{ K}} \quad \underset{(Y)}{K_2MnO_4} \quad MnO_2 \quad O_2(g)$$

$$MnO_2 \quad 4NaCl \quad 4\,H_2SO_4$$
$$MnCl_2 \quad 4NaHSO_4 \quad 2H_2O \quad \underset{(Z)}{Cl_2(g)}$$

Pungent gas.

2. The pair that has similar atomic radii is Mo and W. It is due to lanthanoid contraction. The factor responsible for lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals. Shielding of $4f$ is very less due to its diffused shape. As a result, nuclear charge increases. Hence, Mo and W have similar atomic radii.

3. The $3d$-transition series is

	Sc	$\boxed{\text{Ti}}$	V	Cr	$\boxed{\text{Mn}}$	Fe	Co	$\boxed{\text{Ni}}$	Cu	$\boxed{\text{Zn}}$
Atomic number	21	22	23	24	25	26	27	28	29	30
Outermost Electronic Configuration		$3d^2 4s^2$			$3d^5 4s^2$			$3d^8 4s^2$		$3d^{10} 4s^2$

In 1st ionisation, one electron will be removed from $4s^2$ subshell/orbital.

With increase in atomic number (Z), i.e. with increase in number of protons in the nucleus, effective nuclear charge (Z^*) also increases from Sc to Zn.

$$\text{IE} \quad Z^*$$

So, IE order of the given elements will be,

$$\text{Ti} < \text{Mn} < \text{Ni} < \text{Zn}$$

4. Actinoids show a variety of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ energy levels.

In the actinoids family ($5f$-block), uranium (U) neptunium (Np), plutonium (Pu) and americium (Am) have highest possible oxidation states of 6, 7, 7 and 6 respectively.

5. The spin only magnetic moment ( ) of each ion can be calculated as :

$$\sqrt{n\,(n \quad 2)}\ \text{BM}$$

[$\because n$ No. of unpaired electron(s)] n, i.e. higher the number of unpaired electron, higher will be the value of .

Metal ion	Z	n (for metal ion)	M (BM)	Nature
Ti^2	22	2 ($3d^2$)	$\sqrt{8}$	Paramagnetic
V^2	23	3 ($3d^3$)	$\sqrt{15}$	Paramagnetic
Ti^3	22	1 ($3d^1$)	$\sqrt{3}$	Paramagnetic
Sc^3	21	0 ($3d^0$)	0	Diamagnetic

Thus, the correct order of spin only magnetic moments of given hydrated ions will be

$$Sc^3 \quad Ti^3 \quad Ti^2 \quad V^2$$

6. The maximum number of possible oxidation states of actinoids are shown by neptunium (Np) and plutonium (Pu). These actinoids exhibit oxidation states of 3, 4, 5 and 6.

7. The lanthanide ion that would show colour is Sm^3 . Colour of a compound depends on the number of electrons in $4f$-orbitals.

Electronic configuration of given lanthanides are as follows:

$$Gd^3 \quad 4f^7$$
$$Sm^3 \quad 4f^5$$
$$La^3 \quad 4f^0$$
$$Lu^3 \quad 4f^{14}$$

Gd^3 have half-filled $4f$-orbitals.

La^3 have no electron in $4f$-orbitals.

Lu^3 have fully-filled $4f$-orbitals.

Only Sm^3 contain $4f^5$. The electrons can easily undergoes excitation. That result in a formation of colour.

8. The correct order of atomic radii is

$$\underbrace{\text{Europium (Eu)}}_{199\text{ pm}} > \underbrace{\text{Cerium (Ce)}}_{183\text{ pm}} > \underbrace{\text{Holmium (Ho)}}_{176\text{ pm}} > \underbrace{\text{Nitrogen (N)}}_{65\text{ pm}}$$

Note

(i) N being the member of p-block and second period, have the smallest radii.

(ii) Rest of all the 3 members are lanthanides with Eu having stable half-filled configuration thus with bigger size than rest two.

(iii) Among Ce and Ho, Ce has larger size which can be explained on the basis of **"Lanthanoid contraction".**

9. When MnO_2(A) is fused with alkali in presence of air then potassium manganate (B) is formed. Potassium manganate (B) is of green colour which disproportionate in a neutral or acidic solution to produce potassium permanganate (C). Potassium permanganate (C) in presence of acidic medium oxidises iodide to iodate.

The reaction can be shown as:

(i) $$\underset{(A)}{2\overset{4}{Mn}O_2} \quad 4\text{ KOH}, \overset{0}{O_2} \quad \underset{\substack{(B)\\ \text{Potassium manganate}\\ \text{(Green)}}}{2K_2\overset{+6}{Mn}\overset{2}{O_4}} \quad 2H_2\overset{2}{O}$$

(ii) $$\underset{(B)}{3K_2\overset{6}{Mn}O_4} \quad 4HCl \quad \underset{\substack{(C)\\ \text{Potassium}\\ \text{permanganate}\\ \text{(purple)}}}{2K\overset{7}{Mn}O_4} \quad \overset{7}{Mn}O_2 + 2H_2O + 4KCl$$

(iii) $$\underset{(C)}{2K\overset{7}{Mn}O_4} \quad K\overset{1}{I}, H_2O \quad \underset{(A)}{2\overset{4}{Mn}O_2} \quad 2KOH \quad \underset{(D)}{K\overset{5}{I}O_3}$$

Thus, A and D are MnO_2 and KIO_3 respectively.

10. The most stable oxidation states in the compounds of the given transition metals of $3d$-series are,

Sc : 3; Ti : 3, 4; V : 2, 3, 4, 5; Cu : 1, 2

The electronic configuration of Sc ($Z = 21$) is [Ar] $3d^1, 4s^2$. Due to the presence of only one $3d$-electron (no pairing energy) and two $4s$-electrons, they easily ionise to achieve most stable   3 oxidation state.

11. In the lanthanoid series, atomic number of fourteen $4f$-block elements ranges from 58 (Ce) to 71 (Lu).

Ytterbium, Yb(Z 70) has electronic configuration : $[Xe]4f^{14}6s^2$. So, the 71nth electron of lutetium, Lu (Z 71) should enter into $5d$ orbital and its (here, Lu is 'X') electronic configuration will be : $[Xe]4f^{14}5d^16s^2$. It happens so, because f-block elements have general electronic configuration, $(n \;\; 2)f^{1 \;\; 14}(n \;\; 1)d^{1 \;\; 10}ns^2$. Therefore, option (c) is correct.

12. Lanthanoid contraction in the lanthanoid series takes place due to the presence of electron(s) in the $4f$-orbitals. f-orbitals have poor shielding effect. As a result, the effective nucleur charge will be more experienced by the $5d$ and $6s$- electrons and it will cause contraction or decrease in both atomic and ionic radii.

13. For transition metals,

$H_{\text{Atomisation}}$ Strength of metallic bonding

  Number of unpaired electrons in the metal atom

For the given $3d$-transition metals,

V	Fe	Cu	Zn
$3d^34s^2$	$3d^64s^2$	$3d^{10}4s^1$	$3d^{10}4s^0$
n 3	n 4	n 0	n 0

[$\because n$ no. of unpaired electrons]

$H_{\text{Atomisation}}$ (kJ mol ^{1}) = 515   418   339   130

So, absence of unpaired d-electrons and larger size of Zn atoms, make the crystal lattice of Zn less closely packed.

14. Zinc oxide (ZnO) when react with Na_2O it act as acid while with CO_2 it act as base. Therefore, it is an amphoteric oxide.

$$\underset{\text{Acid}}{ZnO} + \underset{\text{Base}}{Na_2O} \quad \underset{\text{Salt}}{Na_2ZnO_2}$$

$$\underset{\text{Base}}{ZnO} + \underset{\text{Acid}}{CO_2} \quad \underset{\text{Salt}}{ZnCO_3}$$

15. The reaction takes place as follows

$$\underset{(X)}{Na_2C_2O_4} + \underset{\text{(Conc.)}}{H_2SO_4} \quad Na_2SO_4 + H_2O \underset{\text{Effervescence}}{+ CO} + CO_2$$

$$\underset{(X)}{Na_2C_2O_4} + CaCl_2 \quad \underset{\text{White ppt.}}{CaC_2O_4} + 2NaCl$$

$$5CaC_2O_4 \quad \underset{\text{Purple}}{2KMnO_4} \quad 8H_2SO_4 \quad K_2SO_4 \quad 5CaSO_4$$

$$\underset{\text{Colourless}}{2MnSO_4} \quad 10CO_2 \quad 8H_2O$$

Hence, X is $Na_2C_2O_4$.

16. $\underset{\text{Amphoteric}}{Zn} \quad 2NaOH \quad Na_2ZnO_2 \quad H_2$

17. Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO_2 is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

18. $Zn + \underset{\text{(Conc.)}}{4HNO_3} \quad Zn(NO_3)_2 + 2H_2O + 2NO_2$

$4Zn + \underset{\text{(Dil.)}}{10HNO_3} \quad 4Zn(NO_3)_2 + N_2O + 5H_2O$

19. $[Ni(NH_3)_6]^{2+}$ sp^3d^2 octahedral

$[Pt(NH_3)_4]^{2+}$ dsp^2 square planar

$[Zn(NH_3)_4]^{2+}$ sp^3 tetrahedral

20. $Zn_2[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$ and $(NH_4)_3As[Mo_3O_{10}]_4$ show colour due to d-d transition while $BaCrO_4$ is coloured due to charge transfer phenomenon.

Further according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO_2, NH_4, O^2 etc., ligands show yellow colour while CN   forces the complex to impart white colour.

Spectrochemical series

I   Br S^2 SCN   Cl NO_3 N_3 F   OH $C_2O_4^2$ H_2O NCS CH_3CN py NH_3 en   bipy   Phen NO_2 PPh_3 CN   CO

21. **PLAN** Analyse each reaction given in the question and choose the correct answer on the basis of oxidation state and stability of iron compounds. Use the concept of Ellingham diagram to solve this problem.

The correct reactions are as follows:

(a) $Fe + \text{dil. } H_2SO_4 \quad FeSO_4 + H_2$

$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \quad Fe_2(SO_4)_3 + H_2O$$

$$Fe_2(SO_4)_3 \quad Fe_2O_3(s) + 3SO_3$$

The given reaction is incorrect in question

22. SRP value normally increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. e.g.

$$E_{Mn^{3+}/Mn^{2+}} \quad 1.57\text{ V}; E_{Co^{3+}/Co^2} \quad 1.97\text{ V}$$

Thus, $E_{M^{3+}/M^{2+}}$ is highest for Co.

23. The half equations of the reaction are

$$MnO_4 \quad Mn^{2+}$$

$$C_2O_4^2 \quad CO_2$$

The balanced half equations are

$$MnO_4 \quad 8H \quad 5e \quad Mn^{2+} \quad 4H_2O$$

$$C_2O_4^2 \quad 2CO_2 \quad 2e$$

On equating number of electrons, we get

$$2MnO_4 \quad 16H \quad 10e \quad 2Mn^{2+} \quad 8H_2O$$

$$5C_2O_4^2 \quad 10CO_2 \quad 10e$$

On adding both the equations, we get

$$2MnO_4 \quad 5C_2O_4 \quad 16H \quad 2Mn^{2+} \quad 2 \quad 5CO_2 \quad \frac{16}{2}H_2O$$

Thus x, y and z are 2, 5 and 16 respectively.

24. (a) V^2 3 unpaired electrons

Cr^2 4 unpaired electrons

Mn^2 5 unpaired electrons

Fe^2 4 unpaired electrons

Hence, the order of paramagnetic behaviour should be

$$V^2 \quad Cr^2 \; < Fe^{2+} \quad Mn^{2+}$$

(b) Ionic size decreases from left to right in the same period.

(c) (As per data from NCERT)

Co^{3} / Co^{2+} 1.97;

Fe^{3+} / Fe^{2+} 0.77;

Cr^{3+} / Cr^{2+} 0.41

Sc^{3+} is highly stable (It does not show 2).

(d) The oxidation states increases as we go from group 3 to group 7 in the same period.

25. The aqueous solution of $CuSO_4$ consist of the complex $[Cu(H_2O)_4]^{2+}$ ion which absorbed in orange-red region and impart deep blue colouration to solution.

26. $KMnO_4$ is itself a very strong oxidising agent, O_3 cannot oxidise it.

27. In $CuCl_2$, Cu^{2+} has d^9 configuration, exhibit *d-d* transition and show colour. Similarly in $VOCl_2$, V^{4+} has d^1 configuration, can exhibit *d-d* transition and show colour.

28. $MnO_4 + I \quad + OH \qquad MnO_4^2 \ + IO_3$

29. In MnO_4, Mn^{7+} is in highest oxidation state possible for Mn. In CrO_2Cl_2, Cr^{6+} is in highest oxidation state possible for Cr.

30. Ammonium dichromate on heating produces $N_2(g)$. NH_4NO_2 also gives N_2 on heating :

$$(NH_4)_2Cr_2O_7 \qquad N_2 + Cr_2O_3 + 4H_2O$$

$$NH_4NO_2 \qquad N_2 + 2H_2O$$

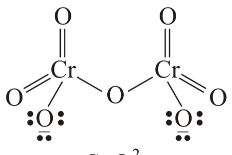
31. K_2MnO_4 (purple green) is formed which is the first step of preparation of $KMnO_4$.

$$2MnO_2 + 4KOH + O_2 \qquad \underset{\text{Purple green}}{K_2MnO_4} + 2H_2O$$

32. In CrO_2Cl_2, Cr is in + 6 oxidation state because Cl is in (–1) and, oxygen is in (–2) oxidation states.

33. $(NH_4)_2Cr_2O_7 \overset{\text{Heat}}{\quad} N_2 + Cr_2O_3 + 4H_2O$

34. The structure of dichromate ion is :



$Cr_2O_7^{2-}$

Exhibit resonance phenomena. Except the bridged Cr—O—Cr, all Cr—O bonds are equivalent.

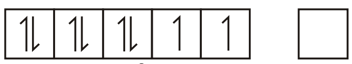
35. $Cu^{2+}(3d^9)$ undergo *d-d* transition, exhibit colour.

36. Ammonium dichromate $[(NH_4)_2Cr_2O_7]$ on heating decomposes producing green powder of Cr_2O_3 and $N_2(g)$ is evolved.

37. Fe_2O_3 is a basic oxide, neutralised by HCl spontaneously forming $FeCl_3$ and water.

38. Zinc coated with copper is used as a reducing agent.

39. The valence shell electronic configuration of Ni^{2+} is :

[Ar]  ; two unpaired electrons

$3d^8$ $4s^0$

40. German silver is an alloy of copper (56%), Zn (24%) and Ni(20%).

41. Zn being amphoteric, dissolves in both acid and base :

$$Zn + 2NaOH \qquad Na_2ZnO_2 + H_2$$

42. In aqueous solution Cr^{2} $(3d^4)$ acts as a reducing agent, oxidising itself to Cr^{3} $(3d^3)$ that gives a completely half-field t_{2g} level in octahedral ligand field of H_2O.

(*b*) Mn^{3} $(3d^4)$ is an oxidising agent as it is reduced to Mn^{2} $(3d^5)$, a completely half-filled stable configuration.

(*c*) Both Cr^{2+} and Mn^{3+} have d^4 configuration.

(*d*) $3d^4\ Cr^{2+}(aq) \overset{\text{R.A}}{\quad} Cr^{3+}(aq) + e^-$

Hence (*d*) is wrong statement.

43. H_2O_2 is alkaline medium acts as reducing agent, reduces Fe^{3+} to Fe^{2+}. In acidic medium the same H_2O_2 oxidises Fe^{2+} to Fe^{3+}.

44. Solubilities of silver halides in water decreases from fluoride (AgF) to iodide (AgI). Silver fluoride is readialy soluble in water, hence when $AgNO_3$ solution is added to HF solution (HF being weak acid, its solution maintain very low concentration of F) no precipitate of AgF is formed.

HCl, HBr and HI being all strong acid, forms precipitates of AgCl, AgBr and AgI when $AgNO_3$ solution is added to their aqueous solution.

$$HCl(aq) + AgNO_3(aq) \qquad \underset{\text{Curdy white}}{AgCl\ (s)} + HNO_3(aq)$$

$$HBr\ (aq) + AgNO_3(aq) \qquad \underset{\text{Pale yellow}}{AgBr\ (s)} + HNO_3(aq)$$

$$Hl\ (aq) + AgNO_3(aq) \qquad \underset{\text{Yellow}}{AgI\ (s)} + HNO_3(aq)$$

The solubilities decreases from AgCl to AgI, AgCl dissolves in aqueous ammonia, AgBr dissolves only slightly in concentrated ammonia while AgI does not dissolve in ammonia solution.

$Na_2S_2O_3$ solution dissolve all three, AgCl, AgBr, AgI by forming complex $[Ag(S_2O_3)_2]^3$ as $S_2O_3^2$ is a stronger complexing agent than ammonia.

45. In neutral medium

$$MnO_4^- \qquad MnO_2\ (Mn^{7+} + 3e^- \qquad Mn^{4+})$$

In alkaline medium

$$MnO_4^- \qquad MnO_2\ (Mn^{7+} + 3e^- \qquad Mn^{4+})$$

In acidic medium

$$MnO_4^- \qquad Mn^{2+}\ (Mn^{7+} + 5e^- \qquad Mn^{2+})$$

46. Cr : $[Ar]3d^5 4s^1$

Magnetic quantum number : $-l \ldots\ldots 0 \ldots\ldots + l$.

$Ag(4d^{10}5s^1)$ All paired electrons have opposite spin. The last one has unpaired spin.

47. $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \qquad \underset{\substack{\text{Chromyl chloride} \\ \text{(red vapour)}}}{2CrO_2Cl_2}$

$+ 4NaHSO_4 + 2KHSO_4 + 3H_2O$

$$CrO_2Cl_2 + 4NaOH \qquad \underset{\text{yellow solution}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

48. Brass = Cu and Zn Gun metal = Cu, Sn, Zn
Bronze = Cu and Sn Type metal = Pb, Sn, Sb

49. Co^{2+} ($3d^7$) and Cr^{3+} ($3d^3$) have allowed *d-d* transition, therefore produces coloured aqueous solution.

50. $2KOH + MnO_2 + O_2 \quad K_2MnO_4 + H_2O$

$HCHO + KMnO_4 + 2KOH \quad K_2MnO_4 + H_2O + HCOOH$

51. Both Statement I and Statement II are independently true but Statement II is not the correct explanation of Statement I. Diamagnetism is due to lack of unpaired electron in Zn^{2+} ($3d^{10}$).

52. Statement I is true but Statement II is false :

$$\underset{\text{Yellow}}{K_2CrO_4} + H_2SO_4 \quad \underset{\text{Orange}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$$

In both K_2CrO_4 and $K_2Cr_2O_7$, chromium is in +6 oxidation state.

53. $Y = +3$, $2Ba \quad 2 \quad 2 \quad 4$

7 'O' $\quad 7 \quad (\ 2) \quad 14$

$3 \quad 4 \quad (\ 14) \quad 3x \quad 0 \qquad x \quad \frac{7}{3}$

54. $3d^5 4s^1$

55. Rochelle salt.

56. $FeSO_4 \quad 7H_2O$ and $ZnSO_4 \quad 7H_2O$

57. PbO_2, a strong oxidising agent, oxidises Mn^{2+} to MnO_4.

58. Zn^{2+} ($3d^{10}$) has no unpaired electron–diamagnetic.

59. Cu cannot reduce Fe^{2+}

60. In neutral or faintly alkaline solution, MnO_4 is reduced to MnO_2 and $S_2O_3^2$ is oxidised to SO_4^2 .

Change in ON = 4 units

$$\underset{+7}{MnO_4^-} + 1/2\ \underset{+2}{S_2O_3^{2-}} \longrightarrow \underset{+6}{SO_4^{2-}} + \underset{+4}{MnO_2}$$

Change in ON = 3 units

Thus, $4MnO_4 + \frac{3}{2} S_2O_3^2 \qquad 3SO_4^2 \quad 4MnO_2$

or $8MnO_4 + 3S_2O_3^2 \qquad 6SO_4^2 + 8MnO_2$

Thus, moles of SO_4^2 formed by 8 moles of $MnO_4 \quad 6$

61. The balanced redox reaction is

$MnO_4 \quad [Fe(H_2O)_2(C_2O_4)_2]^2 \quad 8H^+ \qquad Mn^2 \quad Fe^3 \quad 4CO_2 \quad 6H_2O$

$$\frac{r[H\ \ ]}{r[MnO_4^-]} \quad \frac{8}{1} \quad 8$$

62. Acidified $K_2Cr_2O_7$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$ and HNO_3 oxidise aq. iodide to iodine. Alkaline $KMnO_4$ oxidise aq. iodide to IO_3.

$Na_2S_2O_3$ is a strong reducing agent which on reaction with I_2 produces I .

$$Na_2S_2O_3 + I_2 \quad 2I \quad Na_2S_4O_6$$

Therefore, no reaction takes place between $Na_2S_2O_3$ and iodide ion.

Hence, correct integer is (7).

63. $A = [Ti(H_2O)_6]^{3+}$ and M = Ti, $B = TiO_2$, Ti(IV) has no electron in 3*d*-orbital, no *d-d* transition is possible, therefore MCl_4 is colourless. In *A*, there is one electron in 3*d*-orbital and its *d-d* transition is responsible for colour.

64. CrO_3 is anhydride of chromic acid :

$$CrO_3 + H_2O \qquad \underset{\text{Chromic acid}}{H_2CrO_4}$$

65. $\sqrt{n(n \quad 2)}$ BM where '*n*' is number of unpaired electrons.

$$1.73 \quad \sqrt{n(n \quad 2)} \qquad n \quad 1;\ V^4 \quad 3d^1$$

66. (i) $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \qquad K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$

(ii) $4Zn + 10HNO_3 \qquad 4Zn(NO_3)_2 + N_2O + 5H_2O$

67. (i) $3MnO_4^2 + 4H^+ \qquad MnO_2 + 2MnO_4 + 2H_2O$

(ii) $3SO_2(aq) + Cr_2O_7^2 + 2H^+ \qquad 3SO_4^2 + 2Cr^{3+} + H_2O$

68. $(NH_4)_2S_2O_8 \quad 2H_2O \quad MnSO_4 \qquad MnO_2 \quad 2H_2SO_4 \quad (NH_4)_2SO_4$

69. (i) $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \qquad 2CrO_2Cl_2 + 4NaHSO_4 + 3H_2O + 2KHSO_4$

(ii) $2KMnO_4 + 3MnSO_4 + 2H_2O \qquad 5MnO_2 + K_2SO_4 + 2H_2SO_4$

70. (i) $2Mn^{2+} + 5PbO_2 + 4H^+ \qquad 2MnO_4 + 2H_2O + 5Pb^{2+}$

(ii) $6Ag^+ + AsH_3 + 3H_2O \qquad 6Ag + H_3AsO_3 + 6H^+$

71. Most transition metals have partially filled *d*-orbitals which absorb in visible region and undergo *d-d* transition, which is responsible for colour.

72. (i) $2KMnO_4 + 4KOH + MnO_2 \qquad 3K_2MnO_4 + 2H_2O$

(ii) $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \qquad 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

73. Potassium permanganate can be prepared from MnO_2 under the following conditions :

$$MnO_2 + KOH + O_2 \xrightarrow{\text{Heat}} K_2MnO_4 + H_2O$$

$$K_2MnO_4 + Cl_2 \qquad KMnO_4 + KCl$$

74. (i) $4Zn + NO_3 + 10H^+ \qquad 4Zn^{2+} + NH_4^+ + 3H_2O$

(ii) $Cr_2O_7^2 + 3C_2H_4O + 8H^+ \qquad 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

18

Coordination Compounds

Topic 1 Nomenclature and Isomerism of Coordination Compounds

Objective Questions I (Only one correct option)

1. The coordination numbers of Co and Al in $[CoCl(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$, respectively, are (en ethane-1, 2-diamine) **(2019 Main, 12 April II)**

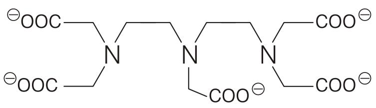
(a) 5 and 3 (b) 3 and 3 (c) 6 and 6 (d) 5 and 6

2. The species that can have a *trans*-isomer is (en ethane -1, 2-diamine, ox oxalate) **(2019 Main, 10 April I)**

(a) $[Pt(en)Cl_2]$ (b) $[Cr(en)_2(ox)]$

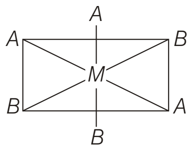
(c) $[Pt(en)_2Cl_2]^2$ (d) $[Zn(en)Cl_2]$

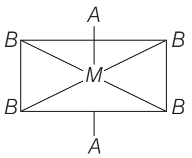
3. The maximum possible denticities of a ligand given below towards a common transition and inner-transition metal ion, respectively, are **(2019 Main, 9 April II)**

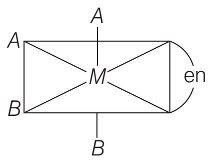


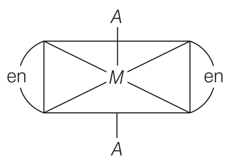
(a) 8 and 8 (b) 8 and 6 (c) 6 and 6 (d) 6 and 8

4. The one that will show optical activity is (en = ethane-1, 2-diamine) **(2019 Main, 9 April I)**

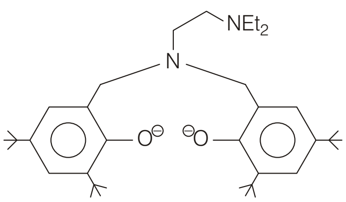
(a)


(b)


(c)


(d)


5. The following ligand is



(2019 Main, 8 April I)

(a) hexadentate (b) tetradentate

(c) bidentate (d) tridentate

6. The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is **(2019 Main, 10 Jan I)**

(a) 12 (b) 16 (c) 4 (d) 8

7. The oxidation states of Cr, in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are **(2018 Main)**

(a) 3, 4 and 6 (b) 3, 2 and 4

(c) 3, 0 and 6 (d) 3, 0 and 4

8. Consider the following reaction and statements :

$[Co(NH_3)_4Br_2]^+ + Br \qquad [Co(NH_3)_3Br_3] + NH_3$

I. Two isomers are produces if the reactant complex ion is a *cis*-isomer.

II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.

III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.

IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are **(2018 Main)**

(a) (I) and (II) (b) (I) and (III)

(c) (III) and (IV) (d) (II) and (IV)

9. Which one of the following complexes shows optical isomerism? **(2016 Main)**

(a) *cis* $[Co(en)_2Cl_2]Cl$ (b) *trans* $[Co(en)_2Cl_2]Cl$

(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

10. The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]$ is (py pyridine). **(2015 Main)**

(a) 2 (b) 3 (c) 4 (d) 6

11. Which of the following complex species is not expected to exhibit optical isomerism? **(2013 Main)**

(a) $[Co(en)_3]^3$ (b) $[Co(en)_2Cl_2]$

(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)Cl_2]$

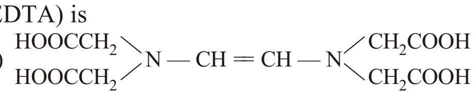
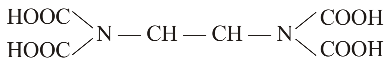
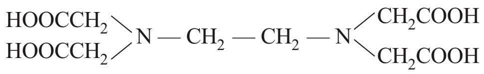
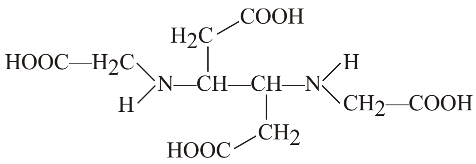
12. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is **(2012)**

(a) tetraaquadiaminecobalt (III) chloride

(b) tetraaquadiamminecobalt (III) chloride

(c) diaminetetraaquacobalt (III) chloride
(d) diamminetetraaquacobalt (III) chloride

13. Geometrical shapes of the complexes formed by the reaction of Ni^{2} with Cl , CN and H_2O, respectively, are **(2011)**
(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral

14. The correct structure of ethylenediaminetetraacetic acid (EDTA) is **(2010)**
(a) 
(b) 
(c) 
(d) 

15. The ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is **(2010)**
(a) $[Cr(H_2O)_4(O_2N)]Cl_2$ (b) $[Cr(H_2O)_4Cl_2](NO_2)$
(c) $[Cr(H_2O)_4Cl(ONO)]Cl$ (d) $[Cr(H_2O)_4Cl_2(NO_2)]$ H_2O

16. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is **(2008, 3M)**
(a) Tetrachloronickel (II)-tetraamminenickel (II)
(b) Tetraamminenickel (II)-tetrachloronickel (II)
(c) Tetraamminenickel (II)-tetrachloronickelate (II)
(d) Tetrachloronickel (II)-tetraamminenickelate (0)

17. Which kind of isomerism is shown by $Co(NH_3)_4Br_2Cl$? **(2005, 1M)**
(a) Geometrical and ionisation (b) Optical and ionisation
(c) Geometrical and optical (d) Geometrical only

Objective Questions II
(One or more than one correct option)

18. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is/are **(2013 Adv.)**
(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$
(b) $[Co(NH_3)_4Cl_2]$ and $[Pt(NH_3)_2(H_2O)Cl]$
(c) $[CoBr_2Cl_2]^{2}$ and $[PtBr_2Cl_2]^{2}$
(d) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

19. The compound(s) that exhibit(s) geometrical isomerism is/are **(2009)**
(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$
(c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2]Cl_2$

Assertion and Reason

Read the following questions and answer as per the direction given below :
(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

20. **Statement I** The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.
Statement II Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. **(2008, 3M)**

Passage Based Question

Passage

The coordination number of Ni^{2} is 4.

$NiCl_2$ KCN (excess) A (cyano complex)

$NiCl_2$ conc. HCl (excess) B (chloro complex)

21. The IUPAC name of A and B are **(2006, 3 4M = 12M)**
(a) potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)
(b) tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)
(c) tetracyanonickel (II), tetrachloronickel (II)
(d) potassium tetracyanonickel (II), potassium tetrachloronickel (II)

Fill in the Blank

22. The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is … **(1994, 1M)**

Integer Answer Type Questions

23. The possible number of geometrical isomers for the complex $[CoL_2Cl_2]$ (L $H_2NCH_2CH_2O$) is (are) ... **(2016 Adv.)**

24. Among the complex ions,
$[Co(NH_2CH_2CH_2\ \ NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^3$,
$[Fe(H_2O)_4(OH)_2]$, $[Fe(NH_3)_2(CN)_4]$,
$[Co(NH_2\ \ CH_2\ \ CH_2\ \ NH_2)_2(NH_3)Cl]^2$ and
$[Co(NH_3)_4(H_2O)Cl]^2$ the number of complex ion(s) that show(s) *cis-trans* isomerism is **(2015 Adv.)**

25. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to **(2011)**

26. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is **(2010)**

Subjective Questions

27. Write the formulae of the following complexes :
(i) Pentamminechlorocobalt (III) ion
(ii) Lithium tetrahydridoaluminate (III) **(1997, 2M)**

28. Write the IUPAC name for $[Cr(NH_3)_5CO_3]Cl$. **(1996, 1M)**

29. Write the IUPAC name of the following compounds :
(i) $[Co(NH_3)_5ONO]Cl_2$
(ii) $K_3[Cr(CN)_6]$ **(1995, 2M)**

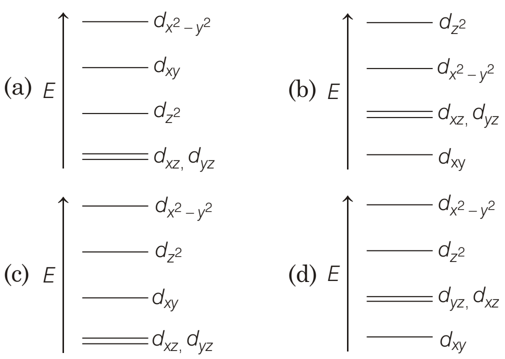
Topic 2 Bonding and Important Property of Coordination Compounds

Objective Questions I (Only one correct option)

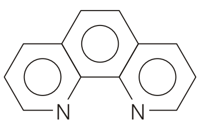
1. The compound used in the treatment of lead poisoning is **(2019 Main, 12 April II)**

(a) D-penicillamine (b) desferrioxime-B
(c) *cis*-platin (d) EDTA

2. Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale). **(2019 Main, 12 April I)**



3. The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to 3 state is

(Phen = 

Ignore pairing energy **(2019 Main, 12 April I)**

(a) $[Co(phen)_3]^2$ (b) $[Ni(phen)_3]^2$
(c) $[Zn(phen)_3]^2$ (d) $[Fe(phen)_3]^2$

4. The crystal field stabilisation energy (CFSE) of $[Fe(H_2O)_6]Cl_2$ and $K_2[NiCl_4]$, respectively, are **(2019 Main, 10 April II)**

(a) 0.4 $_o$ and 1.2 $_t$ (b) 0.4 $_o$ and 0.8 $_t$
(c) 2.4 $_o$ and 1.2 $_t$ (d) 0.6 $_o$ and 0.8 $_t$

5. The incorrect statement is **(2019 Main, 10 April II)**

(a) the gemstone, ruby, has Cr^3 ions occupying the octahedral sites of beryl
(b) the color of $[CoCl(NH_3)_5]^2$ is violet as it absorbs the yellow light
(c) the spin only magnetic moments of $Fe(H_2O)_6]^2$ and $[Cr(H_2O)_6]^2$ are nearly similar
(d) the spin only magnetic moment of $[Ni(NH_3)_4(H_2O)_2]^2$ is 2.83 BM

6. Three complexes, $[CoCl(NH_3)_5]^2$ (I), $[Co(NH_3)_5 H_2O]^3$ (II) and $[Co(NH_3)_6]^3$ (III) absorb light in the visible region. The correct order of the wavelength of light absorbed by them is **(2019 Main, 10 April I)**

(a) II > I > III (b) I > II > III
(c) III > I > II (d) III > II > I

7. The degenerate orbitals of $[Cr(H_2O)_6]^3$ are **(2019 Main, 9 April I)**

(a) d_{z^2} and d_{xz} (b) d_{xz} and d_{yz}
(c) $d_{x^2 \; y^2}$ and d_{xy} (d) d_{yz} and d_{z^2}

8. The calculated spin only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$, respectively, are **(2019 Main, 8 April II)**

(a) 0 and 4.9 (b) 2.84 and 5.92
(c) 0 and 5.92 (d) 4.9 and 0

9. The compound that inhibits the growth of tumors is **(2019 Main, 8 April II)**

(a) *trans*-$[Pt(Cl)_2(NH_3)_2]$ (b) *cis*-$[Pd(Cl)_2(NH_3)_2]$
(c) *cis*-$[Pt(Cl)_2(NH_3)_2]$ (d) *trans*-$[Pd(Cl)_2(NH_3)_2]$

10. The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[V(CN)_6]^4$, $[Fe(CN)_6]^4$, $[Ru(NH_3)_6]^3$, and $[Cr(NH_3)_6]^2$, is **(2019 Main, 8 April I)**

(a) $Cr^{2+} > Ru^{3+} > Fe^{2+} > V^{2+}$
(b) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$
(c) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$
(d) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$

11. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is

(a) CN (b) ethylenediamine
(c) NCS (d) CO

12. The pair of metal ions that can given a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is **(2019 Main, 12 Jan I)**

(a) Co^2 and Fe^{2+} (b) Cr^{2+} and Mn^{2+}
(c) V^{2+} and Co^{2+} (d) V^{2+} and Fe^{2+}

13. The metal d-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are **(2019 Main, 12 Jan I)**

(a) d_{xz}, d_{yz} and d_{z^2} (b) $d_{x^2 \; y^2}$ and d_{z^2}
(c) d_{xy}, d_{xz} and d_{yz} (d) d_{xz} and $d_{x^2 \; y^2}$

14. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of **(2019 Main, 12 Jan I)**

(a) Mn C bond (b) Mn O bond
(c) C O bond (d) Mn Mn

15 The number of bridging CO ligand(s) and Co Co bond(s) in $Co_2(CO)_8$, respectively are **(2019 Main, 11 Jan II)**

(a) 2 and 0 (b) 0 and 2 (c) 4 and 0 (d) 2 and 1

16. The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is ($C_2O_4^2$ Oxalato) **(2019 Main, 11 Jan II)**

(a) 14 (b) 10 (c) 8 (d) 6

17. Match the metals (Column I) with the coordination compound(s)/enzyme(s) (Column II). **(2019 Main, 11 Jan I)**

Column I		Column II	
(A)	Co	(i)	Wilkinson catalyst
(B)	Zn	(ii	Chlorophyll
(C)	Rh	(iii)	Vitamin B_{12}
(D)	Mg	(iv)	Carbonic anhydrase

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(i)	(ii)
(c)	(iii)	(iv)	(i)	(ii)
(d)	(ii)	(i)	(iv)	(iii)

18. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is **(2019 Main, 10 Jan II)**
(a) Mn^{2} (b) Fe^{2} (c) Ni^{2} (d) Co^{2}

19. A reaction of cobalt (III) chloride and ethylene diamine in a 1 : 2 mole ratio generates two isomeric products *A* (violet coloured) and *B* (green coloured). *A* can show optical activity, but *B* is optically inactive. What type of isomers does *A* and *B* represent ? **(2019 Main, 10 Jan II)**
(a) Ionisation isomers (b) Coordination isomers
(c) Geometrical isomers (d) Linkage isomers

20. Wilkinson catalyst is **(2019 Main, 10 Jan I)**
(a) $[(Et_3P)_3RhCl]$ (b) $[(Et_3P)_3IrCl](Et \quad C_2H_5)$
(c) $[(Ph_3P)_3RhCl]$ (d) $[(Ph_3P)_3IrCl]$

21. Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is **(2019 Main, 9 Jan II)**
(a) $L_1 \quad L_2 \quad L_3$ (b) $L_2 \quad L_1 \quad L_3$
(c) $L_3 \quad L_1 \quad L_2$ (d) $L_3 \quad L_2 \quad L_1$

22. The complex that has highest crystal field splitting energy ( ), is **(2019 Main, 9 Jan II)**
(a) $[Co(NH_3)_5Cl]\ Cl_2$ (b) $[Co(NH_3)_5(H_2O)]Cl_3$
(c) $K_3[Co(CN)_6]$ (d) $K_2[CoCl_4]$

23. The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complexes is **(2019 Main, 9 Jan I)**
(a) 5.92 (b) 3.87 (c) 6.93 (d) 4.90

24. Two complexes $[Cr(H_2O)_6]Cl_3$ (*A*) and $[Cr(NH_3)_6]Cl_3$ (*B*) are violet and yellow coloured, respectively. The incorrect statement regarding them is **(2019 Main, 9 Jan I)**
(a) $_o$ value for (*A*) is less than that of (*B*)
(b) both absorb energies corresponding to their complementary colours
(c) $_o$ values of (*A*) and (*B*) are calculated from the energies of violet and yellow light, respectively
(d) both are paramagnetic with three unpaired electrons

25. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting $[3Ca_3(PO_4)_2 \quad Ca(OH)_2]$ to : **(2018 Main)**
(a) $[CaF_2]$ (b) $[3(CaF_2) \quad Ca(OH)_2]$
(c) $[3Ca_3(PO_4)_2 \quad CaF_2]$ (d) $[3\{Ca_3(PO_4)_2\} \quad CaF_2]$

26. On treatment of 100 mL of 0.1 M solution of $CoCl_3.6H_2O$ with excess of $AgNO_3$; $1.2 \quad 10^{22}$ ions are precipitated. The complex is **(2017 Main)**
(a) $[Co(H_2O)_4Cl_2]\ Cl \quad 2H_2O$ (b) $[Co(H_2O)_3Cl_3] \quad 3H_2O$
(c) $[Co(H_2O)_6]Cl_3$ (d) $[Co(H_2O)_5Cl]\ Cl_2 \quad H_2O$

27. The pair having the same magnetic moment is [at. no. Cr 24, Mn 25, Fe 26 and Co 27] **(2016 Main)**
(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2}$
(c) $[CoCl_4]^{2}$ and $[Fe(H_2O)_6]^{2}$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2}$

28. Among $[Ni(CO)_4]$, $[NiCl_4]^{2}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is **(2016 Adv.)**
(a) 2 (b) 3 (c) 4 (d) 5

29. The colour of $KMnO_4$ is due to **(2015 Main)**
(a) *M* *L* charge transfer transition
(b) *d* *d* transition
(c) *L* *M* charge transfer transition
(d) transition

30. The equation which is balanced and represents the correct product(s) is **(2014 Main)**
(a) $Li_2O + 2KCl \quad 2LiCl + K_2O$
(b) $[CoCl(NH_3)_5] \quad + 5H^+ \quad Co^{2+} \quad 5NH_4 \quad + Cl$
(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4} \xrightarrow{\text{Excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(d) $CuSO_4 + 4KCN \quad K_2\ [Cu(CN)_4] + K_2SO_4$

31. The octahedral complex of a metal ion M^{3} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is **(2014 Main)**
(a) $L_4 < L_3, L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

32. Consider the following complex ions, *P*, *Q* and *R*.
$P \quad [FeF_6]^{3}$, $Q \quad [V(H_2O)_6]^{2}$ and $R \quad [Fe(H_2O)_6]^{2}$
The correct order of the complex ions, according to their spin-only magnetic moment values (in BM) is **(2013 Adv.)**
(a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$

33. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic) the coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states respectively, are **(2012)**
(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

34. Among the following complexes *(K-P)*, **(2011)**

$K_3[Fe(CN)_6]$ (K), $[Co(NH_3)_6]Cl_3$ (L),

$Na_3[Co(ox)_3]$ (M), $[Ni(H_2O)_6]Cl_2$ (N),

$K_2[Pt(CN)_4]$(O), $[Zn(H_2O)_6](NO_3)_2$ (P)

the diamagnetic complexes are

(a) *K, L, M, N* (b) *K, M, O, P*

(c) *L, M, O, P* (d) *L, M, N, O*

35. The complex showing a spin only magnetic moment of 2.82 BM is **(2010)**

(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2}$

(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)_4]^{2}$

36. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is **(2009)**

(a) 0 (b) 2.84

(c) 4.90 (d) 5.92

37. Among the following, the coloured compound is **(2008, 3M)**

(a) CuCl

(b) $K_3[Cu(CN)_4]$

(c) CuF_2

(d) $[Cu(CH_3CN)_4]BF_4$

38. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2}$ are diamagnetic. The hybridisations of nickel in these complexes respectively, are **(2008, 3M)**

(a) sp^3, sp^3 (b) sp^3, dsp^2

(c) dsp^2, sp^3 (d) dsp^2, dsp^2

39. Among the following metal carbonyls, the C—O bond order is lowest in **(2007, 3M)**

(a) $[Mn(CO)_6]$ (b) $[Fe(CO)_5]$

(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]$

40. If the bond length of CO bond in carbon monoxide is 1.128 Å, then what is the value of CO bond length in $Fe(CO)_5$? **(2006)**

(a) 1.15 Å (b) 1.128 Å

(c) 1.72 Å (d) 1.118 Å

41. Spin only magnetic moment of the compound $Hg[Co(SCN)_4]$ is **(2004, 1M)**

(a) $\sqrt{3}$ (b) $\sqrt{15}$

(c) $\sqrt{24}$ (d) $\sqrt{8}$

42. The compound having tetrahedral geometry is **(2004, 1M)**

(a) $[Ni(CN)_4]^{2-}$ (b) $[Pd(CN)_4]^{2-}$

(c) $[PdCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$

43. Mixture X = 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L of solution.

1 L of mixture X + excess $AgNO_3$ Y

1 L of mixture X + excess $BaCl_2$ Z

Number of moles of Y and Z are **(2003)**

(a) 0.01, 0.01 (b) 0.02, 0.01

(c) 0.01, 0.02 (d) 0.02, 0.02

44. The complex ion which has no 'd'-electrons in the central metal atom is **(2001, 1M)**

(a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$

(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

45. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are **(1999, 2M)**

(a) both square planar

(b) tetrahedral and square planar, respectively

(c) both tetrahedral

(d) square planar and tetrahedral, respectively

46. Which of the following is formed when excess of KCN is added to aqueous solution of copper sulphate? **(1996, 1M)**

(a) $Cu(CN)_2$

(b) $K_2[Cu(CN)_4]$

(c) $K[Cu(CN)_2]$

(d) $K_3[Cu(CN)_4]$

47. Among the following ions, which one has the highest paramagnetism? **(1993, 1M)**

(a) $[Cr(H_2O)_6]^{3}$ (b) $[Fe(H_2O)_6]^{2+}$

(c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$

48. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$ **(1991, 1M)**

(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

(b) $[NiCl_4]^{2}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2}$ is paramagnetic

(d) $Ni(CO)_4$ is diamagnetic and $[NiCl_4]^{2}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

49. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by **(1988, 2M)**

(a) $MnSO_4$ $4H_2O$ (b) $CuSO_4$ $5H_2O$

(c) $FeSO_4$ $6H_2O$ (d) $NiSO_4$ $6H_2O$

Objective Question II

(One or more than one correct option)

50. The correct statement (s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers : Fe = 26, Ni = 28) **(2018 Adv.)**

(a) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16

(b) These are predominantly low spin in nature

(c) Metal-carbon bond strengthens when the oxidation state of the metal is lowered

(d) The carbonyl C—O bond weakens when the oxidation state of the metal is increased

51. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^3$ (en $H_2NCH_2CH_2NH_2$) is (are) **(2018 Adv.)**

(a) It has two geometrical isomers

(b) It will have three geometrical isomers, if bidentate 'en' is replaced by two cyanide ligands

(c) It is paramagnetic

(d) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^3$

52. Addition of excess aqueous ammonia to a pink coloured aqueous solution of MCl_2 $6H_2O(X)$ and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue colured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whersas it is zero for complex Y.

Among the following options, which statement(s) is (are) correct? **(2017 Adv.)**

(a) The hybridisation of the central metal ion in Y is d^2sp^3

(b) Addition of silver nitrate to Y given only two equivalents of silver chloride

(c) When X and Y are in equilibrium at 0°C, the colour of the solution is pink

(d) Z is a tetrahedral complex

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

53. Statement I $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

Statement II The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. **(2008, 3M)**

Passage Based Questions

The coordination number of Ni^2 is 4.

$NiCl_2$ KCN (excess) A (cyano complex)

$NiCl_2$ conc. HCl (excess) B (chloro complex)

54. Predict the magnetic nature of A and B.

(a) Both are diamagnetic

(b) A is diamagnetic and B is paramagnetic with one unpaired electron

(c) A is diamagnetic and B is paramagnetic with two unpaired electrons

(d) Both are paramagnetic

55. The hybridisation of A and B are

(a) dsp^2, sp^3 (b) sp^3, sp^3

(c) dsp^2, dsp^2 (d) sp^3d^2, d^2sp^3

Match the Columns

56. Match each set of hybrid orbitals from List–I with complexes given in List-II.

List–I		List–II	
P.	dsp^2	1.	$[FeF_6]^4$
Q.	sp^3	2.	$[Ti(H_2O)_3Cl_3]$
R.	sp^3d^2	3.	$[Cr(NH_3)_6]^3$
S.	d^2sp^3	4.	$[FeCl_4]^2$
		5.	$[Ni(CO)_4]$
		6.	$[Ni(CN)_4]^2$

The correct option is **(2018 Adv.)**

(a) P 5; Q 4, 6; R 2, 3; S 1

(b) P 5,6; Q 4; R 3; S 1,2

(c) P 6; Q 4, 5; R 1; S 2, 3

(d) P 4,6; Q 5, 6; R 1,2; S 3

57. Match each coordination compound in Column I with an appropriate pair of characteristics from Column II and select the correct answer using the codes given below the Columns (en $H_2NCH_2CH_2NH_2$; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78) **(2014 Adv.)**

	Column I		Column II
(A)	$[Cr(NH_3)_4Cl_2]Cl$	1.	Paramagnetic and exhibits ionisation isomerism
(B)	$[Ti(H_2O)_5Cl](NO_3)_2$	2.	Diamagnetic and exhibits *cis-trans* isomerism
(C)	$[Pt(en)(NH_3)Cl]NO_3$	3.	Paramagnetic and exhibits *cis-trans* isomerism
(D)	$[Co(NH_3)_4(NO_3)_2]NO_3$	4.	Diamagnetic and exhibits ionisation isomerism

Codes

	A	B	C	D		A	B	C	D
(a)	4	2	3	1	(b)	3	1	4	2
(c)	2	1	3	4	(d)	1	3	4	2

58. Match the complexes in Column I with their properties listed in Column II. **(2007, 6M)**

	Column I		Column II
(A)	$[Co(NH_3)_4(H_2O)_2]Cl_2$	p.	Geometrical isomers
(B)	$[Pt(NH_3)_2Cl_2]$	q.	Paramagnetic
(C)	$[Co(H_2O)_5Cl]Cl$	r.	Diamagnetic
(D)	$[Ni(H_2O)_6]Cl_2$	s.	Metal ion with +2 oxidation state

Fill in the Blanks

59. The IUPAC name of $[Co(NH_3)_6]Cl_3$ is …… **(1994, 1M)**

True/False

60. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. **(1989, 1M)**

61. The electron density in the *xy* plane in $3d_{x^2 \; y^2}$ orbital is zero. **(1986, 1M)**

Integer Answer Type Questions

62. For the octahedral complexes of Fe^{3+} in SCN (thiocyanato-S) and in CN ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [atomic number of Fe 26] **(2015 Adv.)**

63. In the complex acetylbromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe C bond (s) is **(2015 Adv.)**

64. $EDTA^{4}$ is ethylenediaminetetraacetate ion. The total number of N Co O bond angles in [Co(EDTA)] complex ion is **(2013 Adv.)**

Subjective Questions

65. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red colour.

(a) Draw its structure and show H-bonding

(b) Give oxidation state of Ni and its hybridisation

(c) Predict whether it is paramagnetic or diamagnetic **(2004, 4M)**

66. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex $= 1.73$ BM. Give the structure of anion. **(2003, 4M)**

67. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. **(2002, 5M)**

68. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms *A* and *B*. The form *A* reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas *B* gives a pale yellow precipitate soluble in concentrated ammonia.

Write the formula of *A* and *B* and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). **(2001, 5M)**

69. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. **(2000, 4M)**

70. *A*, *B* and *C* are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands.

Complex *A* does not react with concentrated H_2SO_4, whereas complexes *B* and *C* lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify *A*, *B* and *C*. **(1999, 2M)**

71. Identify the complexes which are expected to be coloured. Explain **(1994, 2M)**

(i) $[Ti(NO_3)_4]$ (ii) $[Cu(NCCH_3)]^+ BF_4$

(iii) $[Cr(NH_3)_6] Cl_3$ (iv) $K_3[VF_6]$

72. Give reasons in two or three sentences only for the following :

"The species $[CuCl_4]^{2-}$ exists, while $[CuI_4]^{2-}$ does not exist." **(1992, 1M)**

Answers

Topic 1

1. (d)	**2.** (c)	**3.** (d)	**4.** (c)
5. (b)	**6.** (a)	**7.** (c)	**8.** (b)
9. (a)	**10.** (b)	**11.** (c)	**12.** (d)
13. (b)	**14.** (c)	**15.** (b)	**16.** (c)
17. (a)	**18.** (b,d)	**19.** (c,d)	**20.** (b)
21. (a)	**22.** paramagnetism		**23.** (5)
24. (6)	**25.** (6)	**26.** (3)	

Topic 2

1. (d)	**2.** (a)	**3.** (d)	**4.** (b)
5. (a)	**6.** (b)	**7.** (b)	**8.** (a)
9. (c)	**10.** (b)	**11.** (c)	**12.** (c)
13. (b)	**14.** (a)	**15.** (d)	**16.** (b)
17. (c)	**18.** (d)	**19.** (c)	**20.** (c)
21. (c)	**22.** (c)	**23.** (a)	**24.** (c)
25. (c)	**26.** (d)	**27.** (a)	**28.** (b)
29. (c)	**30.** (b)	**31.** (b)	**32.** (b)
33. (c)	**34.** (c)	**35.** (b)	**36.** (a)
37. (c)	**38.** (b)	**39.** (b)	**40.** (a)
41. (b)	**42.** (d)	**43.** (a)	**44.** (a)
45. (c)	**46.** (d)	**47.** (b)	**48.** (c)
49. (b)	**50.** (b, c)	**51.** (a, b, d)	**52.** (a, b, d)
53. (a)	**54.** (c)	**55.** (a)	**56.** (c)
57. (b)	**58.** A p, q, s B p, r, s C q, s D q, s		
59. hexaammine cobalt (III) chloride			**60.** F
61. F	**62.** (4)	**63.** (3)	**64.** (8)

Hints & Solutions

Topic 1 Nomenclature and Isomerism of Coordination Compounds

1. **Key Idea** The total number of ligands to which the metal is directly attached is called coordination number.

The coordination numbers of Co and Al in $[Co(Cl)(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$ are 5 and 6 respectively.

In first complex, 'en' is a didentate ligand and 'Cl' is a unidentate ligand.

$[Co(Cl)(en)_2]Cl$, coordination number 1 2 2 1 4 5

So, the coordination number is 5.

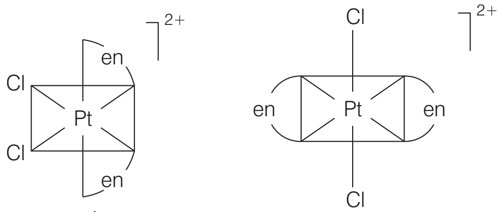
For $K_3[Al(C_2O_4)_3]$, '$C_2O_4^{2}$' is a didentate ligand.

Coordination number 3 2 6.

Hence, coordination number is 6.

2. **Key Idea** Square planar complexes of general formulae : $[M(a\quad a)b_2]$ and $[M(a\quad a)(b\quad b)]$ do not show geometrical isomerism. Whereas, an octahedral complex of general formula $[M(a\quad a)_2b_2]$ can show geometrical (*cis-trans*) isomerism.

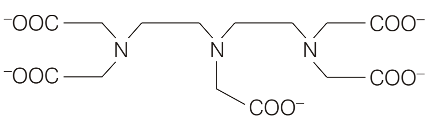
$[Pt(en)_2(Cl_2)]^{2}$ with formula $[M(a\quad a)_2b_2]$ will show geometrical isomerism as follows:



cis- (optically active) (I)

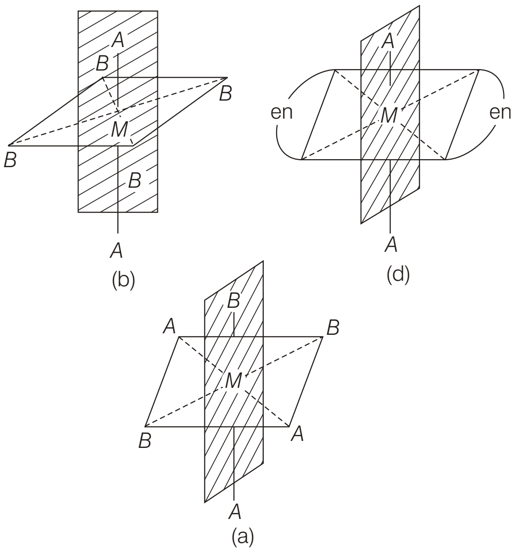
trans- (optically inactive)

3. The maximum possible denticities of given ligand towards a common transition and inner transition metal ion, are 6 and 8 respectively.



The given ligand act as hexadentate ligand in transition metal ion because the common oxidation state shown by them is 3. Whereas in case of inner transition metal ion, its denticity is 8 because their common oxidation state is 4.

4. Optical activity is the ability of a chiral molecule to rotate the plane of polarised light, measured by a polarimeter. A chiral molecule does not have any plane of symmetry. If a molecule possess any plane of symmetry, then it is an achiral molecule. Given options (a), (b) and (d) possess plane of symmetry.

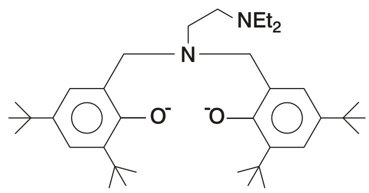


Only molecule (c) does not possess any plane of symmetry. Hence, it is a chiral molecule and shows optical activity.

5. **Key Idea** Denticity of ligand is defined as donor sites or number of ligating groups.

The given ligand is tetradentate. It contains four donor atoms. It can bind through two nitrogen and two oxygen atom to the central metal ion.

Ligand bound to the central atom or ion through coordinate bond in the coordination entity. It act as a Lewis base. The attacking site of the given ligand is given in bold.



6. A square planar complex of general formula, M_{abcd} gives three geometrical isomers only.

Let, a F , b Cl , c S CN , d NO_2

SCN and NO_2 are ambidentate ligands and they also show linkage isomerism (structural). Considering both linkage and geometrical isomerism.

Total number of possible isomers given by the complex,

$$3\quad(2\quad 2)\quad 12$$

7. Let the oxidation state of Cr in all cases is 'x'

(i) Oxidation state of Cr in $[Cr(H_2O)_6]Cl_3$

$$x\quad(0\quad 6)\quad(\ 1\quad 3)\quad 0$$

or $\quad x\quad 0\quad 3\quad 0$ or $x\quad 3$

(ii) Oxidation state of Cr in $[Cr(C_6H_6)_2]$

$$x\quad(2\quad 0)\quad 0\ \text{ or }\ x\quad 0$$

(iii) Oxidation state of Cr in

$K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$

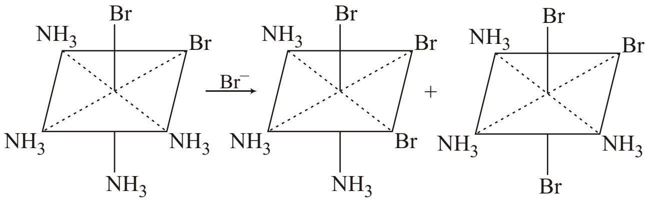
1 2 x (1 2) (2 2) (2) 0 0

or 2 x 2 4 2 0 or x 6 0

hence x 6

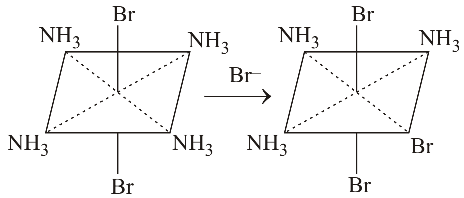
Thus, 3, 0 and 6 is the answer.

8. If the reactant is *cis* isomer than following reaction takes place.



Cis-isomer Facial Meridonial

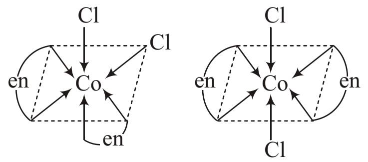
i.e. two isomers are produced. If the reactant is *trans* isomer than following reaction takes place.



Trans Meridonial

i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

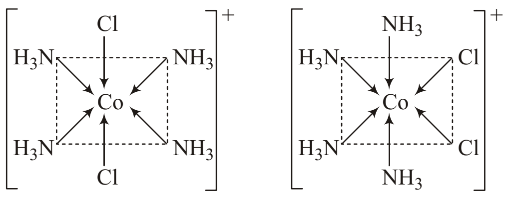
9.



cis-$[Co(en)_2Cl_2]Cl$ (optically active)

trans-$[Co(en)_2Cl_2]Cl$ (optically inactive due to plane of symmetry)

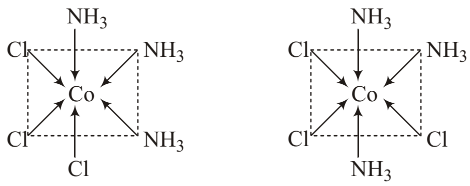
$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are given below:



trans-$[Co(NH_3)_4Cl_2]Cl$ (optically inactive)

cis-$[Co(NH_3)_4Cl_2]Cl$ (optically inactive)

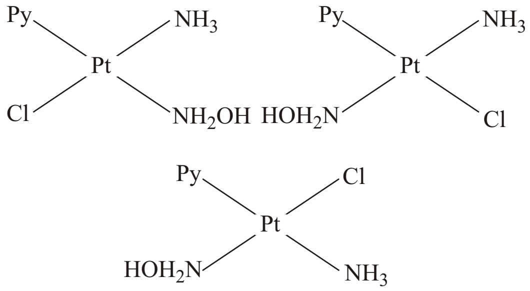
$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



fac-isomer (optically inactive)

mer-isomer (optically inactive)

10. $[Pt(Cl)(py)(NH_3)(NH_2OH)]$ is square planar complex. The structures are formed by fixing a group and then arranging all the groups.



Hence, this complex shows three geometrical isomers.

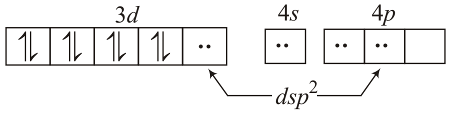
11. Optical isomerism is exhibited by only those complexes which lacks elements of symmetry. $[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

12. First of all, the compound has complex positive part "$[Co(H_2O)_4(NH_3)_2]^{3+}$ therefore, according to IUPAC conventions, positive part will be named first. Secondly, in writing name of complex, ligands are named first in alphabetical order, irrespective of its charge, hence "ammine" will be written prior to "aqua". Therefore, name of the complex is $[Co(H_2O)_4(NH_3)_2]Cl_3$. Diamminetetraaqua cobalt (III) chloride.

NOTE In alphabetical order, original name of ligands are considered not the initials of prefixes. Also, special precaution should be taken in spelling name of NH_3 ligand as it is ammine.

13. Ni^{2+} $4CN^-$ $[Ni(CN)_4]^{2-}$

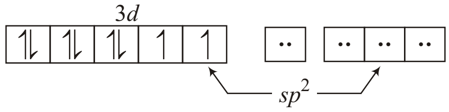
Here, Ni^2 has d^8-configuration with CN^- as strong ligand.



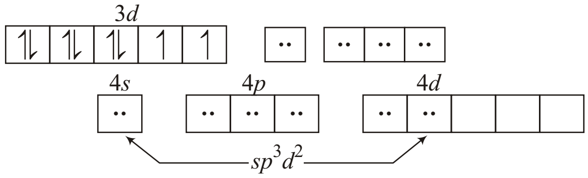
d^8-configuration in strong ligand field gives dsp^2-hybridisation, hence square planar geometry.

$Ni^{2+} + 4Cl^-$ $[NiCl_4]^{2-}$

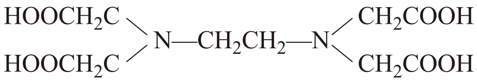
Here, Ni^2 has d^8-configuration with Cl^- as weak ligand.



d^8-configuration in weak ligand field gives sp^3-hybridisation, hence tetrahedral geometry. Ni^2 with H_2O forms $[Ni(H_2O)_6]^2$ complex and H_2O is a weak ligand.



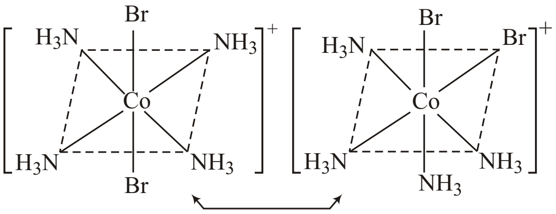
Therefore, $[Ni(H_2O)_6]^2$ has octahedral geometry.

14. 

15. Ionisation isomers are the complexes that produces different ions in solution, i.e. they have ions interchanged inside and outside the coordination sphere.
$[Cr(H_2O)_4Cl(NO_2)]Cl$ and $[Cr(H_2O)_4Cl_2](NO_2)$ have different ions inside and outside the coordinate sphere and they are isomers.
Therefore, they are ionisation isomers.

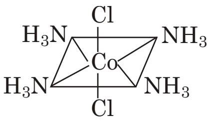
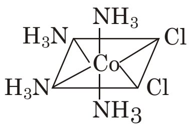
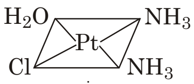
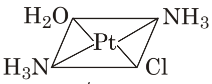
16. $[Ni(NH_3)_4]^{2+}$ tetraamminenickel (II)
$[NiCl_4]^{2}$ tetrachloronickelate (II)
Cationic part is named first, hence :
tetraamminenickel (II)-tetrachloronickelate(II)

17. $[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4BrCl]Br$ are ionisation isomers.

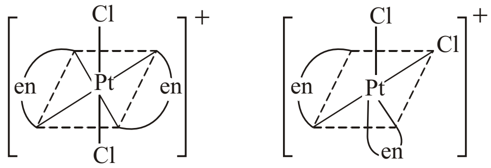


Geometrical isomers

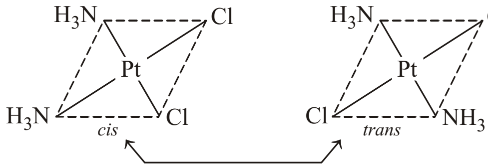
18. PLAN Depending on the structure of the complex,different types of isomerism are shown.

	Complex	Isomerism
A.	$[Cr(NH_3)_5Cl]Cl_2$ $[Cr(NH_3)_4Cl_2]Cl$	Neither of structural nor stereoisomerism
B.	$[Co(NH_3)_4Cl_2]$	 *trans w.r.t.* Cl  *cis w.r.t.* Cl
	$[Pt(H_2O)(NH_3)_2Cl]$	 *cis*  *trans*
C.	$[CoBr_2Cl_2]^{2}$ $[PtBr_2Cl_2]^{2}$	sp^3 tetrahedral dsp^2 square planar
D.	$[Pt(NH_3)_3(NO_3)]Cl$	$[Pt(NH_3)_3(NO_3)Cl]$ $[Pt(NH_3)_3Cl]NO_3]$ ionisation
	$[Pt(NH_3)_3Cl]Br$	$[Pt(NH_3)_3Cl]Br$ $[Pt(NH_3)_3Br]$ ionisation

19. Both $[Pt(en)_2Cl_2]Cl_2$ and $[Pt(NH_3)_2Cl_2]$ are capable of showing geometrical isomerism.

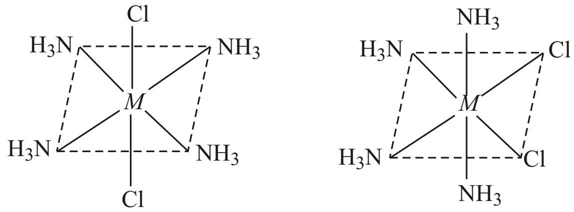


trans *cis*



Square planar complex

20. Both statements are true. However, axis of symmetry is not a criteria of optical isomerism. Optical inactivity of the two geometrical isomers of $[M(NH_3)_4Cl_2]$ is due to the presence of plane of symmetry.

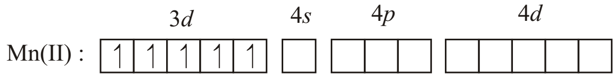


Trans *Cis*

Both have several planes of symmetry

21. A $K_2[Ni(CN)_4]$; B $K_2[NiCl_4]$
A : Potassium tetracyanonickelate (II)
B : Potassium tetrachloronickelate (II)

22. Paramagnetism : In $[Mn(H_2O)_6]^{2+}$, Mn(II) has $3d^5$ configuration. Since, H_2O is a weak ligand, all five d-electrons are unpaired :

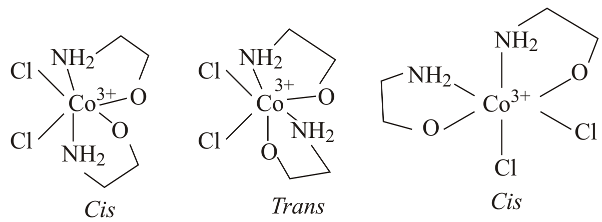


(weak ligand field)

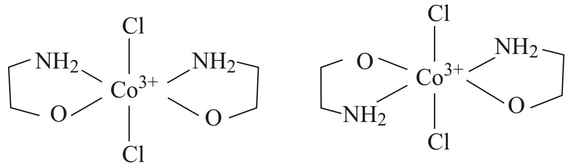
23. Ligand is $CH_2 — NH_2$

$CH_2\overline{O}$

Geometrical isomers are

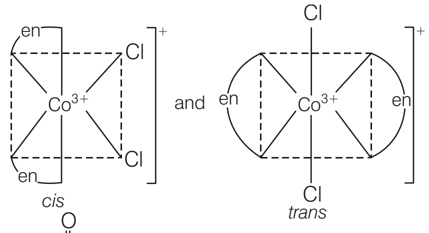


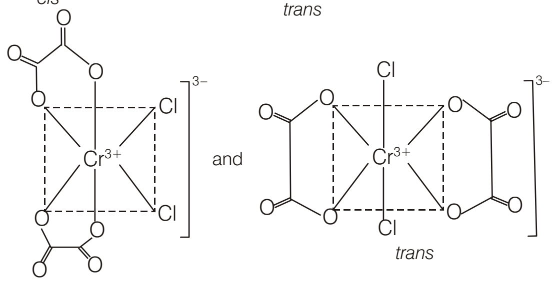
Cis *Trans* *Cis*

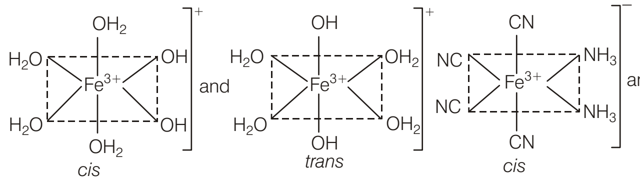


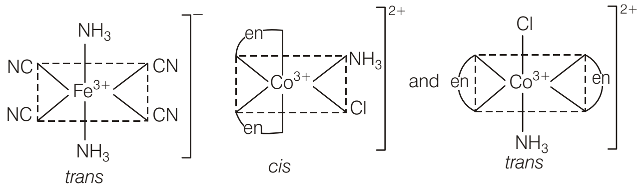
Cis *Trans*

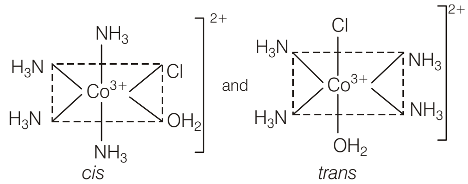
24. All six complex will show *cis-trans* isomerism











25. mmol of complex = 30 ×0.01 = 0.3

Also, 1 mole of complex $[Cr(H_2O)_5Cl]Cl_2$ gives only two moles of chloride ion when dissolved in solution

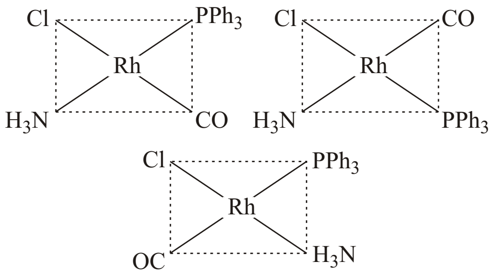
$$[Cr(H_2O)_5Cl]Cl_2 \qquad [Cr(H_2O)_5Cl]^{2+} + 2Cl^-$$

mmol of Cl^- ion produced from its 0.3 mmol = 0.6

Hence, 0.6 mmol of Ag^+ would be required for precipitation.

0.60 mmol of Ag^+ = 0.1M × V(in mL) $\qquad V$ = 6 mL

26.



27. (i) $[Co(NH_3)_5Cl]^{2+}$ (ii) $Li[AlH_4]$

28. $[Cr(NH_3)_5CO_3]Cl$

: pentaamminecarbonatochromium (III) chloride.

29. (i) $[Co(NH_3)_5ONO]Cl_2$

: pentaamminenitritocobalt (III) chloride.

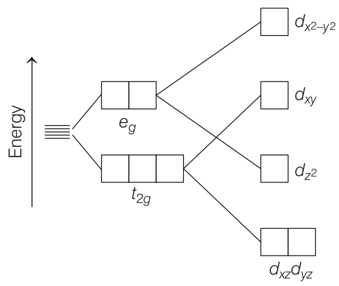
(ii) $K_3[Cr(CN)_6]$: potassium hexacyanochromate (III)

Topic 2 Bonding and Important Property of Coordination Compounds

1. The compound used in the treatment of lead poisoning is EDTA. Medication occurs through chelation therapy. Calcium disodium ethylenediamine tetraacetic acid chelates divalent metal ion such as Pb^2 from plasma and interstitial body fluids.

The metal displaces Ca and is chelated, mobilised and usually excreted. Less then 5% $CaNa_2EDTA$ is absorbed in the gastrointestinal tract and it possibly increases the absorption of Pb present in the tract. Therefore, it is not recommended for oral use. It is usually given intravenously.

2. Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to the following splitting pattern.



The single electron in the $d_{x^2\ y^2}$ orbital is being repelled by four ligands, while the electron in the d_{z^2} orbital is only being repelled by two ligands. Thus, the energy of the $d_{x^2\ y^2}$ increases relative to that of d_{z^2}. A more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_{z^2} orbital. This leaves the $d_{x^2\ y^2}$ orbital empty.

Thus, four ligands can now approach along x, x, y and y directions without any difficulty as $d_{x^2\ y^2}$ orbital is empty. However, ligands approaching along z and z directions meet very strong repulsive forces from filled d_{z^2} orbitals. Thus, only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

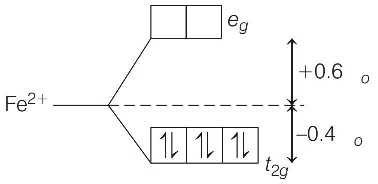
3.

> **Key Idea** Crystal field splitting occurs due to the presence of ligands in a definite geometry. In octahedral complexes the energy of two, e_g orbitals will increase by (0.6) $_o$ and that of three t_{2g} will decrease by (0.4) $_o$.

The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is $[Fe(phen)_3]^2$.

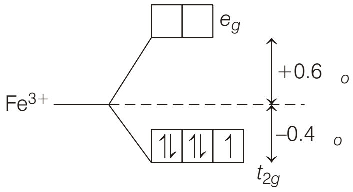
$$[Fe(phen)_3]^2 \quad {}^{e} \quad [Fe(phen)_3]^3$$

In $[Fe(phen)_3]^2$, electronic configuration of Fe^2 is $3d^6 4s^0$. Phenanthrene is a strong field symmetrical bidentate ligand. The splitting of orbital in Fe^2 is as follows:



CFSE 6 0.4 $_o$ 2.4 $_o$.

The splitting of orbital and arrangement of electrons in Fe^3 is as follows :



CFSE 5 0.4 $_o$ 2.0 $_o$

Fe^2 upon oxidation of its metal to 3 state lose its CFSE from 2.4 $_o$ to 2.0 $_o$.

4. **Key Idea** Crystal field stabilisation energy (CFSE) for octahedral complexes ($0.4x$ $0.6y$) $_o$

where, x number of electrons occupying t_{2g} orbital.

y number of electrons occupying e_g orbital.

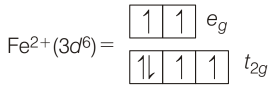
CFSE for tetrahedral complexes

($0.6x$ $0.4y$) $_t$

where, x number of electrons occupying e orbital.

y number of electrons occupying t orbital.

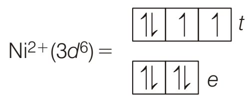
In $[Fe(H_2O)_6]Cl_2$, H_2O is a weak field ligand, so it is a high spin (outer orbital) octahedral complex of Fe^2 .



CFSE ($0.4x$ $0.6y$) $_o$

[0.4 4 0.6 2] $_o$ 0.4 $_o$

In $K_2[NiCl_4]$, Cl is a weak field ligand, so it is a high spin tetrahedral complex of Ni^2 .



CFSE (0.6 4 0.4 4) $_t$ 0.8 $_t$

5. The explanation of given statements are as follows :

(a) Ruby, a pink or blood-red coloured gemstone belongs to corundum (Al_2O_3, alumina) system which has trigonal crystalline lattice containing the repeating unit of $Al_2O_3 - Cr^{3+}$. So, ruby does not belong to beryl lattice ($Be_3Al_2Si_6O_{18}$).
Thus, statement (a) is incorrect.

(b) $[Co(Cl)(NH_3)_5]^{2+}$ is a low spin octahedral complex of Co^3 . It absorbs low energy yellow light and high energy complementary violet light will be shown off. Thus, statement (b) is correct.

(c) $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are the high-spin octahedral complexes of Fe^2 ($3d^6$, n 4) and Cr^2 ($3d^5$, n 5) ions and weak field ligand, H_2O respectively. So, spin-only magnetic moment $\sqrt{n(n \quad 2)}$ of the complexes.

$[Fe(H_2O)_6]^{2+}$, $_1$ $\sqrt{4(4 \quad 2)}$
(n 4), $\sqrt{24}$ 4.89 BM

$[Cr(H_2O)_6]^{2+}$, $_2$ $\sqrt{5(5 \quad 2)}$
(n 5), $\sqrt{35}$ 5.92 BM

So, $_1$ $_2$.Thus, statement (c) is correct.

(d) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is also a high-spin octahedral complex of Ni^2 ($3d^8$, n 2)

$\sqrt{2(2 \quad 2)}$ $\sqrt{8}$ 2.83 BM

Thus, statement (d) is correct.

6. **Key Idea** The wavelength ( ) of light absorbed by the complexes is inversely proportional to its $_0$ CFSE (magnitude). $_0$(CFSE) 1/

The complexes can be written as:

I. $[CoCl(NH_3)_5]^2$ $[Co(NH_3)_5(Cl)]^2$]

II. $[Co[NH_3]_5H_2O]^3$ $[Co(NH_3)_5(H_2O)]^3$

III. $[Co(NH_3)_5]^3$ $[Co(NH_3)_5(NH_3)]^3$

So, the differentiating ligands in the octahedral complexes of Co (III) in I, II and III are $Cl^{\ominus}$, H_2O and NH_3 respectively. In the spectrochemical series, the order of this power for crystal field splitting is Cl H_2O NH_3.

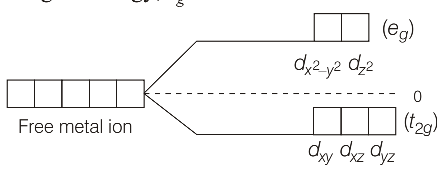
So, the crystal field splitting energy (magnitude) order will be

$^{CFSE}_0$ (I) $^{CFSE}_0$ (II) $^{CFSE}_0$ (III)

and the order of wavelength ( ) of light absorbed by the complexes will be

(I) (II) (III) $\because$ Energy ($^{CFSE}_0$) $\frac{1}{}$

7. The degenerate orbitals of $[Cr(H_2O)_6]^3$ are d_{xz} and d_{yz}. Electronic configuration of Cr^{3+} is $3d^5 4s^1$. The five d-orbitals in an isolated gaseous atom or ion have same energy, i.e. they are degenerate. This degeneracy has been removed due to the ligand electron–metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.



8. $[Fe(H_2O)_6]_2$ It will form 2 cationic species. i.e.

I. (i) As $[\overset{II}{Fe}(H_2O)_6]^2$ High spin octahedral complex of Fe^2 .

Fe^2 : $3d^6$, x 4 (unpaired electrons)

$\sqrt{4(4 \quad 2)}$ BM 4.9 BM

or (ii) as $[\overset{\text{III}}{\text{Fe}}(H_2O)_6]^{3}$ High spin octahedral complex of Fe^{3} .

$Fe^{3+}: 3d^5$, x 5, $\sqrt{5(5\quad 2)}$ 5.92 BM

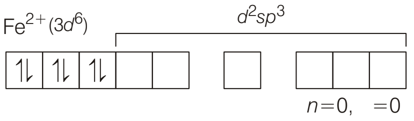
[H_2O is a neutral weak field ligand]

So, $[Fe(H_2O)_6]^{2}$ will be the cationic specie, 4.9 BM.

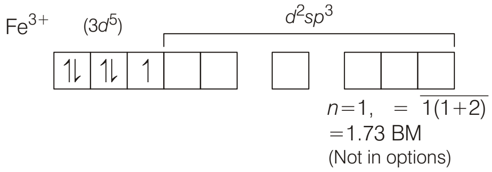
$[Fe(CN)_6]$ will have two anionic complexes

II. (i) $[\overset{\text{II}}{\text{Fe}}(CN)_6]^{4-}$ Low spin, octahedral complex of Fe^{2} .

As CN is a strong ligand it will pair up the electrons.



or, (ii) $[\overset{\text{III}}{\text{Fe}}(CN)_6]^{3-}$ Low spin octahedral complex of Fe^{3} .

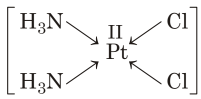


[CN is an anionic strong field ligand]

So,the anionic species is $[Fe(CN)_6]^{4}$, 0

Thus, the calculated spin only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$ respectively are 4.9 and 0.

9. *cis*-$[Pt(Cl)_2(NH_3)_2]$ is known as *cis*-platin. It is a -bonded organo-metallic compound and is used as an anti-tumor agent in the treatment of cancer.



10. **Key Idea** In presence of strong field ligands, $_0$ p, for fourth electron it is more energetically favourable to occupy t_{2g} orbital with configuration $t_{2g}^4e_g^0$ and form low spin complexes.

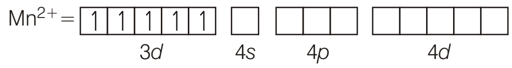
The correct order of the spin only magnetic moment of metal ions in the given low-spin complexes is V^2 Cr^2 Ru^3 Fe^2 .

All the given complexes possess strong field ligands (CN, NH_3). Hence, readily form low spin complexes.

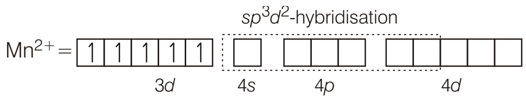
Complex	Oxidation state	Configuration	Orbital splitting	No. of unpaired electrons
$[V(CN)_6]^{4-}$	V^{2+}	$t_{2g}^3\ e_g^0$	e_g / t_{2g}	3
$[Cr(NH_3)_6]^{2+}$	Cr^{2+}	$t_{2g}^4 e_g^0$	e_g / t_{2g}	2
$[Ru(NH_3)_6]^{3+}$	Ru^{3+}	$t_{2g}^5 e_g^0$	e_g / t_{2g}	1
$[Fe(CN)_6]^{4-}$	Fe^{2+}	$t_{2g}^6 e_g^0$	e_g / t_{2g}	0

11. The magnetic moment of the magnitude 5.9 BM suggest the presence of 5 unpaired electrons in Mn(II). This can be cross verified by putting the value (5) of unpaired electrons in the formula, $\sqrt{n(n\quad 2)}$ BM

Thus, the valence electronic configuration of Mn(II) in the complex is



The octahedral homoleptic complex suggests sp^3d^2-hybridisation in the complex, i.e.



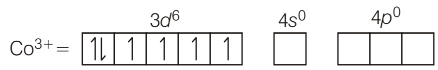
Thus, 5 unpaired electrons are present in the complex which suggest the presence of a weak ligand like NCS .

12. As H_2O is a weak field ligand. It readily forms high spin complexes. In $[M(H_2O)_6]Cl_2$, M exist in 2 oxidation state. The arrangement of electrons in the given metal ions are as follows:

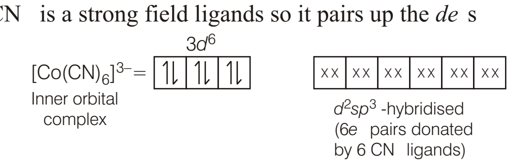
Metal ions	Configuration	Number of unpaired electrons	Spin only Magnetic moment (in BM) $\sqrt{n(n\quad 2)}$
Co^{2+}	$(d^7) = t_{2g}^5e_g^2$	3	3.9
Fe^{2+}	$(d^6) = t_{2g}^4e_g^2$	4	4.9
Cr^{2+}	$(d^4) = t_{2g}^3e_g^1$	4	4.9
Mn^{2+}	$(d^5) = t_{2g}^3e_g^2$	5	5.9
V^{2+}	$(d^3) = t_{2g}^3e_g^0$	3	3.9

Therefore, Co^{2} and V^{2} contains same value of magnetic moment (3.9 BM).

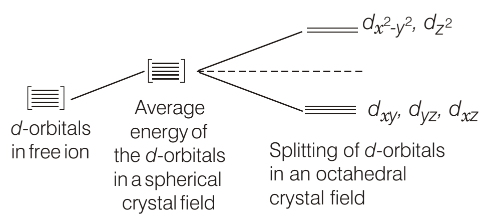
13. In $K_3[Co(CN)_6]$, Co have 3 oxidation state and electronic configuration of Co^{3+} is $[Ar]_{18}\ 3d^6$.



As, CN is a strong field ligands so it pairs up the *de* s



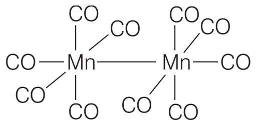
In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The lobes of the e_g orbitals ($d_{x^2\quad y^2}$ and d_{z^2}) point along the axes x, y and z under the influence of an octahedral field, the d- orbitals split as follow.



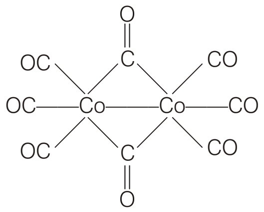
As the d-orbitals, i.e. $d_{x^2 \quad y^2}$ and d_{z^2} are vacant. Hence, these both orbitals are directly facing the ligands in $K_3[Co(CN)_6]$.

14. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of Mn C bond. The metal-carbon bond in organometallic compounds possess both and- character. The M C bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M C -bond is formed by the donation of pair of electrons from a filled d-orbital of metal into vacant antibonding * orbital of CO. The M L bonding creates a synergic effect which strengthens the bond between CO and the metal.

The structure of $Mn_2(CO)_{10}$ is shown below :



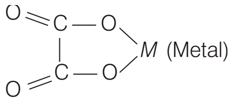
15. The structure of $Co_2(CO)_8$ (a polynuclear metal carbonyl) can be written as:



Total number of bridging CO ligands 2
and the Co Co bond 1

16. Coordination number is defined as the total number of ligands to which the metal is directly attached.

Here, $C_2O_4^{2}$ is a bidentate ligand,



and H_2O is a monodentate ligand, $H_2\ddot{O}: \longrightarrow M$

So, total number of sites offered by $C_2O_4^{2}$ and H_2O ligands around Th(IV) Coordination number of Th (IV)

4 2(by $C_2O_4^{2}$) 2 1(by H_2O) 10

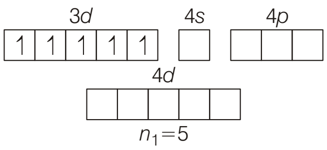
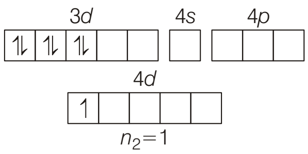
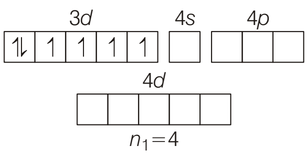
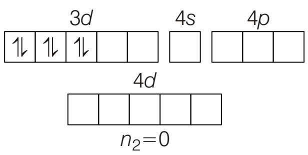
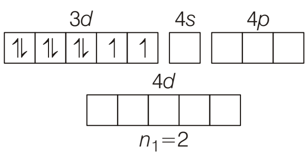
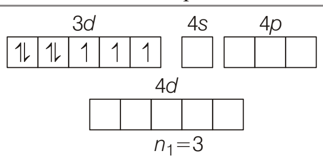
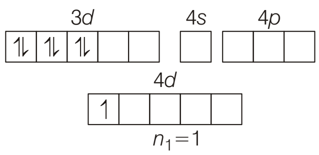
17. (A) Co is present in vitamin B_{12} (iii) having molecular formula, $C_{63}H_{88}\overset{II}{Co}N_{14}O_{14}P$.

(B) Zn is present in carbonic anhydrase (iv) in which three histidine units and the —OH group coordinate with one Zn (II) ion.

(C) Rh is present in Wilkinson catalyst (i) having molecular formula $[(Ph_3P)_3RhCl]$.

(D) Mg is present in chlorophyll (ii) having molecular formula $C_{55}H_{70}O_6N_4\overset{II}{Mg}$ (chlorophyll-b).

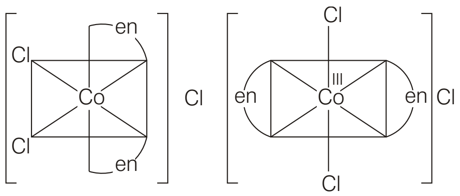
18. The difference in the number of unpaired electrons of different metal ions in their high spin and low spin octahedral complexes are given in the table below :

Metal ion	Number of e in high spin complex (n_1)	Number of e in low spin complax (n_2)	n_2 n_1
Mn^{2}			5 1 4
Fe^{2}			4 0 4
Ni^{2}	 Ni^{2} does not form low spin octahedral complexes.		
Co^{2}			3 1 2

19. According to the situation given in question, reactions are as follows:

$$\overset{\text{III}}{CoCl_3} + 2en \qquad \overset{\text{III}}{[Co(en)_2Cl_2]Cl}$$

$$en \quad \text{ethylene-1, 2-diamine,} \quad \begin{matrix} CH_2 — NH_2 \\ \\ CH_2 — NH_2 \end{matrix}$$



'*A*' Optically active (*cis*-form) (Violet) 'B' Optically inactive (*trans*-form) (Green)

20. Wilkinson's catalyst is a -bonded organometallic compound $[(Ph_3P)_3RhCl]$. It is commercially used for hydrogenation of alkenes and vegetable oils (unsaturated).

IUPAC name Chloridotris (triphenylphosphene) rhodium (I).

21. In homoleptic complexes, the metal atom/ion is linked to only one type of ligand. Assuming, ligands are neutral, the octahedral complexes of M^3 can be,

$$\underset{\text{(I)}}{[M(L_1)_6]^3}, \underset{\text{(II)}}{[M(L_2)_6]^3} \text{ and } \underset{\text{(III)}}{[M(L_3)_6]^3}$$

So, $\text{Absorption} \quad \underset{\text{III}}{L_3} \quad \underset{\text{I}}{L_1} \quad \underset{\text{II}}{L_2}$ (Green, Blue, Red (wavelength))

$\text{absorption}: \underset{\text{II}}{L_2} \quad \underset{\text{I}}{L_1} \quad \underset{\text{III}}{L_3}$ $[\because \text{Energy} (\quad \text{CFSE}) \quad \frac{1}{\ }]$

We know, ligand strength $\quad_{\text{absorption}}$

So, the increasing order of the ligand strength will be, $L_3 \quad L_1 \quad L_2$

22. All of the complex given are the octahedral complexes of Co (III) except $K_2[CoCl_4]$, which is a tetrahedral complex of Co (II) (sp^3-hybridised).

We know, $\quad _t \quad _o \qquad \because \quad _t \quad \frac{4}{9} \quad _o$

So, the octahedral complexes (*a, b, c*) have higher $_o$ values than that of tetrahedral, $K_2[CoCl_4]$.

Now, for the complexes, *a, b* and *c*,

the magnitude of $_o$ ligand strength, which is based on their positions in the spectrochemical series.

$Cl \ < H_2O < NH_3 < CN$

Hence, $K_3[Co(CN)_6]$ will have the highest value.

23. The spin only magnetic moment ((in BM) is given by

$$\text{(in BM)} \quad \sqrt{n(n \quad 2)}$$

where, n number of unpaired electrons

The highest value of n in transition metal complex is 5 in its d^5-configuration.

$$\sqrt{5(5 \quad 2)}\,\text{BM} \quad 5.916\,\text{BM}$$

24. '*A*' absorbs yellow light of less energy and emits violet light of high energy (complementary colour) because H_2O is a weak field ligand. But in case of '*B*', due to presence of strong field ligand (NH_3), it absorbs high energy violet light and emits low energy complementary yellow colour.

(CFSE) is measured with help of wavelength of the colour absorbed by the given coordination compound, as

$$_o \quad h \quad h \frac{c}{\ }$$

Both the complexes contain three unpaired electrons. Therefore, both are paramagnetic.

25. Fluoride ions help in making teeth enamel harder by converting $[3Ca_3(PO_4)_2 \ Ca(OH)_2]$ i.e. Hydroxy apatite to $[3Ca_3(PO_4)_2 \ CaF_2]$ i.e., Fluorapatite (Harder teeth enamel) *via* following reaction:

$$[3Ca_3(PO_4)_2 \ Ca(OH)_2] \quad \underset{\substack{\text{From} \\ \text{drinking} \\ \text{water}}}{2F} \qquad [3Ca_3(PO_4)_2 \ CaF_2] + 2OH$$

26. Molarity (M) $\dfrac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

Number of moles of complex

$$\frac{\text{Molarity} \quad \text{volume (in mL)}}{1000}$$

$$\frac{0.1 \quad 100}{1000} \quad 0.01\,\text{mole}$$

Number of moles of ions precipitate

$$\frac{1.2 \quad 10^{22}}{6.02 \quad 10^{23}} \quad 0.02\,\text{moles}$$

Number of Cl present in ionisation sphere

$$\frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} \quad \frac{0.02}{0.01} \quad 2$$

2 Cl are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is

$$[Co(H_2O)_5Cl]Cl_2 \ H_2O.$$

27.

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)
$[Cr(H_2O)_6]^2$	Cr^2 ; [Ar] 3 d^4	↑ ↑ ↑ ↑ ☐ ; 4
$[Fe(H_2O)_6]^{2+}$	Fe^2 ; [Ar] 3 d^6	⇅ ↑ ↑ ↑ ↑ ; 4
$[Mn(H_2O)_6]^{2+}$	Mn^2 ; [Ar] 3 d^5	↑ ↑ ↑ ↑ ↑ ; 5
$[CoCl_4]^2$	Co^2 ; [Ar] 3 d^7	⇅ ⇅ ↑ ↑ ↑ ; 3

28.

Compounds	Hybridisation	Unpaired electron(s)	Magnetic character
$Ni(CO)_4$	sp^3	No	Diamagnetic
$[NiCl_4]^2$	sp^3	two	Paramagnetic
$[Co(NH_3)_4Cl_2]Cl$	sp^3d^2	No	Diamagnetic
$Na_3[CoF_6]$	sp^3d^2	three	Paramagnetic
Na_2O_2	—	No	Diamagnetic (O_2^2)
CsO_2	—	One	Paramagnetic
			O_2 (superoxide ion is paramagnetic)

29. $KMnO_4$ $K^+ + MnO_4$

In MnO_4, Mn has + 7 oxidation state having no electron in *d*-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur *L* *M* charge transfer, because ligand is able to donate the electron into the vacant *d*-orbital of metal.

Since, charge transfer is laporate as well as spin allowed, therefore, it shows colour.

Time saving Technique There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.

30. This problem is based on conceptual mixing of properties of lithium oxide and preparation, properties of coordination compounds. To answer this question, keep in mind that on adding acid, ammine complexes get destroyed.

(a) $Li_2O + KCl$ $2LiCl + K_2O$

This is wrong equation, since a stronger base K_2O cannot be generated by a weaker base Li_2O.

(b) $[CoCl(NH_3)_5]$ $+ 5H^+$ Co^2 (aq) $5\ NH_4$ $+ Cl$

This is correct. All ammine complexes can be destroyed by adding H . Hence, on adding acid to $[CoCl(NH_3)_5]$, it gets converted to Co^2 $(aq)^+$ NH_4 and Cl .

(c) $[Mg(H_2O)_6]^2$ $EDTA^4$ $\xrightarrow[\text{Excess}]{OH}$ $[Mg(EDTA)]^2$ $6H_2O$

This is wrong, since the formula of complex must be $[Mg(EDTA)]^{2+}$ as EDT.

(d) The 4th reaction is incorrect. It can be correctly represented as

$$2CuSO_4 + 10KCN \quad 2K_3[Cu(CN)_4] + 2K_2SO_4 \quad (CN)_2$$

31. Arrange the complex formed by different ligands L_1, L_2, L_3 and L_4, according to wavelength of their absorbed light, then use of the following relation to answer the question.

Ligand field strength Energy of light absorbed $\dfrac{1}{\text{Wavelength of light absorbed}}$

	L_1	L_2	L_3	L_4
Absorbed light	Red	Green	Yellow	Blue

Wavelength of absorbed light decreases.

Increasing order of energy of wavelengths absorbed reflect greater extent of crystal field splitting, hence, higher field strength of the ligand.

Energy blue (L_4) green (L_2) yellow (L_3) red (L_1)

L_4 L_2 L_3 L_1 in field strength of ligands.

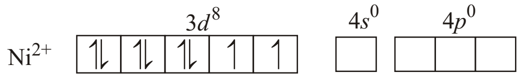
32. **PLAN** Spin only magnetic moment have the formula $\sqrt{n(n\quad 2)}$ BM, where *N* is the number of unpaired electrons. In the presence of weak ligand (as H_2O, Cl , F) there is no pairing of electrons, and electrons donated by ligands are filled in outer vacant orbitals.

In the presence of strong ligand (as CN , CO, NH_3, en) electrons are paired and electrons from ligands are filled in available inner orbitals

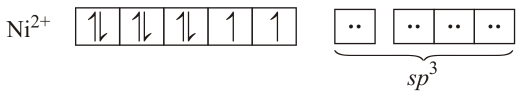
Complex	Atomic number of	O.N.	E.C.	Unpaired electrons	Magnetic moment
P : $[FeF_6]^3$ weak ligand	26	3	$[Ar]3d^5$	5	$\sqrt{35}$ BM
Q : $[V(H_2O)_6]^2$ weak ligand	23	2	[Ar]	3	$\sqrt{15}$ BM
R : $[Fe(H_2O)_6]^2$	26	2	$[Ar]3d^6$	4	$\sqrt{24}$ BM

Thus, order of spin-only magnetic moment $Q < R < P$

33. In the given complex, $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ nickel is in 2 oxidation state and the ground state electronic configuration of Ni^{2+} ions in free gaseous state is

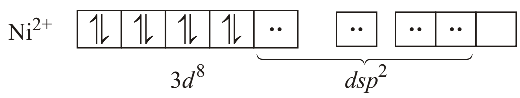


For the given four coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. To satisfy this condition, four lone pairs from the four ligands occupies the four sp^3-hybrid orbitals as :



Therefore, geometry of paramagnetic complex must be **tetrahedral**. On the otherhand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell.

This condition can be fulfilled by pairing electrons of 3*d*-orbitals against Hund's rule as



The above electronic arrangement gives dsp^2-hybridisation and therefore, **square planar** geometry to the complex.

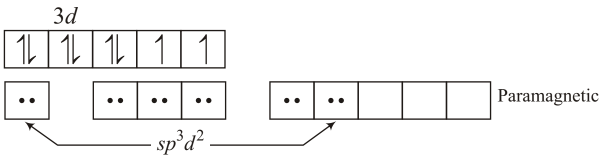
34. For a diamagnetic complex, there should not be any unpaired electron in the valence shell of central metal.

In $K_3[Fe(CN)_6]$, Fe (III) has d^5-configuration (odd electrons), hence it is paramagnetic.

In $[Co(NH_3)_6]Cl_3$, Co (III) has d^6-configuration in a strong ligand field, hence all the electrons are paired and the complex is diamagnetic.

In $Na_3[Co(ox)_3]$, Co (III) has d^6-configuration and oxalate being a chelating ligand, very strong ligand and all the six electrons remains paired in lower t_{2g} level, diamagnetic.

In $[Ni(H_2O)_6]Cl_2$, Ni (II) has $3d^8$-configuration and H_2O is a weak ligand, hence



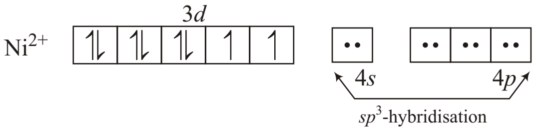
In $K_2[Pt(CN)_4]$, Pt(II) has d^8-configuration and CN^- is a strong ligand, hence all the eight electrons are spin paired . Therefore, complex is diamagnetic.

In $[Zn(H_2O)_6](NO_3)_2$, Zn (II) has $3d^{10}$configuration with all the ten electrons spin paired, hence diamagnetic.

35. Magnetic moment 2.83 BM indicates that there is two unpaired electrons.

$$u \quad \sqrt{n(n \quad 2)} \text{ BM} \quad \sqrt{8} \text{ BM} \quad 2.82 \text{ BM}$$

In $[NiCl_4]^2$, Ni has d^8 configuration and Cl is a weak ligand :



36. In $Cr(CO)_6$: $3d^6$, has no unpaired electrons, zero magnetic moment.

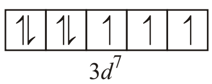
37. CuF_2 : Cu^{2+} has $3d^9$-configuration, allowed *d-d* transition, hence, coloured.

38. In $Ni(CO)_4$, Ni is sp^3-hybridised while in $[Ni(CN)_4]^2$, Ni^{2+} is dsp^2-hybridised.

39. Greater the extent of $d \quad - p$ back bonding, smaller will be the bond order of CO bond in metal carbonyls. In $Fe(CO)_5$, there is maximum number of valence shell electrons (*d*-electrons), greatest chances of $p \quad - d$ back bonding, lowest bond order of CO bond.

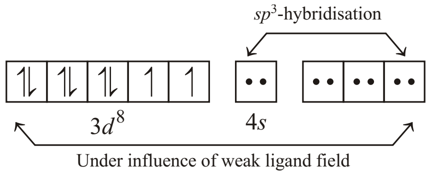
40. In CO, bond order = 3. In metal carbonyls like $Fe(CO)_5$, due to $d \quad - p$ back-bonding, bond order of CO decreases slightly therefore, bond length increases slightly.

41. In $Hg[Co(SCN)_4]$, Co^{2+} has $3d^7$ configuration. SCN produces weak ligand field, no pairing of electrons in *d*-orbitals occurs against Hund's rule, hence :

Co^{2+} :  $\sqrt{3(3 \quad 2)}$ BM $\sqrt{15}$ BM

$3d^7$

42. $[NiCl_4]^2$: $Ni^{2+}(3d^8)$
Tetrahedral



In all other complexes, hybridisation at central metal is dsp^2 and complexes have square planar geometries.

43. In 1 L solution, there will be 0.01 mole of each $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$. Addition of excess of $AgNO_3$ will give 0.01 mole of AgBr. Addition of excess of $BaCl_2$ will give 0.01 mole of $BaSO_4$.

44. In MnO_4, Mn^{+7} has $3d^0$ configuration.

45. In $Ni(CO)_4$, Ni is in $3d^{10}$ state due to strong ligand field produced by CO. Hence, Ni is sp^3-hybridised and complex is tetrahedral. In $NiCl_2(PPh_3)_2$, Ni^2 has $3d^8$-configuration. Due to weak ligand field, Ni is sp^3-hybridised and complex is tetrahedral.

46. $Cu^{2+} + CN \quad CuCN$

$CuCN + 3CN \quad [Cu(CN)_4]^3$

47. Fe in $[Fe(H_2O)_6]^{2+}$ has maximum (four) unpaired electrons, has highest paramagnetism.

48. In $Ni(CO)_4$, Ni has $3d^{10}$-configuration, diamagnetic. In $Ni(CN)_4]^2$, Ni has $3d^8$-configuration but due to strong ligand field, all the *d*-electrons are spin paired giving dsp^2-hybridisation, diamagnetic.

In $[NiCl_4]^2$, Ni has $3d^8$-configuration and there is two unpaired electrons (weak chloride ligand do not pair up *d* - electrons), hence paramagnetic.

49. Salt with least number of unpaired electrons in *d*- orbital of central metal will show lowest degree of paramagnetism

Mn^2 ($3d^5$, 5 unpaired electrons)

Cu^2 ($3d^9$, 1 unpaired electrons)

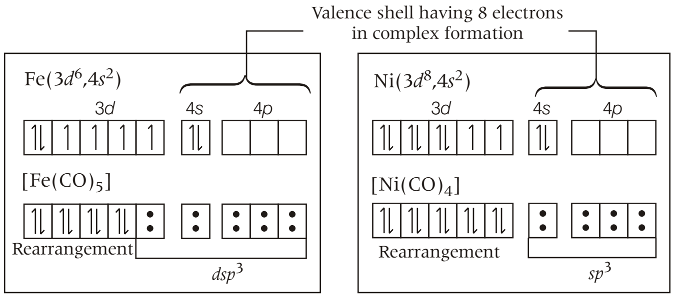
Fe^2 ($3d^6$, 4 unpaired electrons)

Ni^2 ($3d^8$, 2 unpaired electrons)

Hence, $CuSO_4 \; 5H_2O$ has lowest degree of paramagnetism.

50. Statement wise explanation is

(i) **Statement (a)** The total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 8 instead of 16 as shown below



Hence, this statement is incorrect.

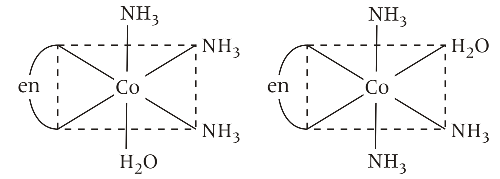
(ii) **Statement (b)** Carbonyl complexes are predominantly low spin complexes due to strong ligand fields. Hence, this statement is correct.

(iii) **Statement (c)** For central metal lowering of oxidation state results to increase in electron density on it. This in turn results to increase in extent of synergic bonding. Thus, we can say ''metal carbonyl bond strengthens, when oxidation state of metal is lowered''.
Hence, it is a correct statement.

(iv) **Statement (d)** Increase in positive charge on metal (i.e., increase in oxidation state) results to decrease in synergic bonding strength.
This in turn makes C—O bond stronger instead of weaker. Hence this statement is also incorrect.

51. Statement wise explanation is

Statement (a) $[Co(en)(NH_3)_3H_2O]^3$ have following 2 geometrical isomers.



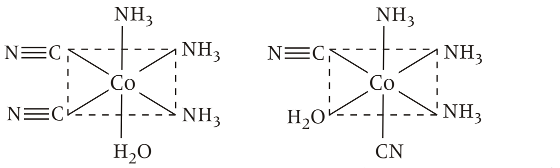
Fac *Mer*

$[M(AA)b_3c]$ type complex

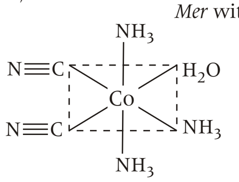
Hence, this is correct statement.

Statement (b) If bidentate ligand 'en' is replaced by two cyanide ligands then $[Co(NH_3)_3(H_2O)(CN)_2]$ is formed.

It is $[Ma_3b_2c]$ type complex which has following 3 geometrical isomers.



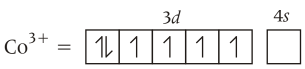
(*Fac*) *Fac* with respect to NH_3 and *Mer* with respect to —CN



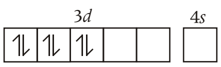
(*Mer*)

Hence, this statement is also correct.

Statement (c) Co metal has $[Ar]3d^7 4s^2$ configuration while in $[Co(en)(NH_3)_3(H_2O)]^3$ it is in +3 oxidation state. Thus, Co^{3+} has $[Ar]3d^6$ configuration.



As *en* is a strong ligand, so pairing will occur



Due to the presence of all paired electrons it show diamagnetic behaviour rather than paramagnetic.
Hence, this statement is incorrect.

Statement (d) According to CFT, absorption of light by coordination complexes depends upon CFSE i.e., crystal field splitting energy ( )as

$$_{0} \quad \frac{1}{\ }$$

Among the complexes given $[Co(en)(NH_3)_4]^3$ has more $_0$ value as compared to complex $[Co(en)(NH_3)_3(H_2O)]^3$. Thus, $[Co(en)(NH_3)_3(H_2O)]^3$ absorbs the light at longer wavelength for *d*-*d* transition.
Hence, this statement is also correct.

Note : For any complex, the value of $_0$ can be calculated via the difference or gap between e_g and t_{2g} values.

52. $\underset{\text{Pink }(X)}{[Co(H_2O)_6]Cl_2} \xrightarrow[O_2\,(Air)]{\text{Excess } NH_4OH/NH_4Cl} \underset{Y}{Co(NH_3)_6]Cl_3}$

$\underset{X}{[Co(H_2O)_6]^{2+}} \quad \underset{(Excess)}{4Cl} \quad \underset{\text{blue Z}}{[CoCl_4]^2}$

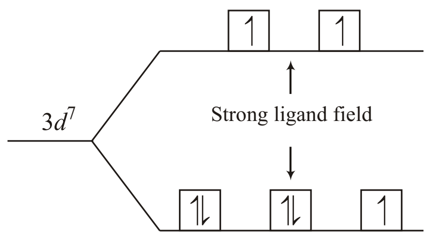
(a) Since NH_3 is moderately strong ligand, hybridisation of cobalt in *Y* is d^2sp^3.

(b) Cobalt is sp^3-hybridised in $[CoCl_4]^2$.

(c) $\underset{Y}{[Co(NH_3)_6]Cl_3} + 3AgNO_3(aq) \qquad 3AgCl$

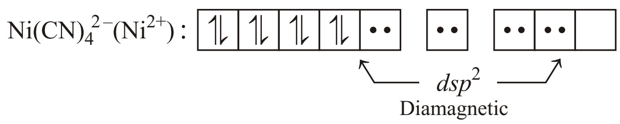
(d) $\underset{\text{Blue}}{[CoCl_4]^2} + 6H_2O \rightleftharpoons \underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4Cl\ ; \quad H \quad 0$

53. In the complex $[Fe(H_2O)_5NO]SO_4$, Fe is in +1 oxidation state because NO is in +1 state. Also NO is a strong ligand, complex has $3d^7$-configuration at Fe(I) as :

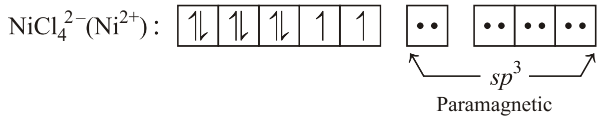


Three unpaired electrons

54. *A* is diamagnetic, square planar complex because of strong ligand field of CN .



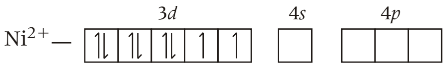
B is paramagnetic, tetrahedral complex because of weak ligand field of Cl .



55. Described in 2, *A* has dsp^2 hybridisation while *B* has sp^3-hybridisation of Ni.

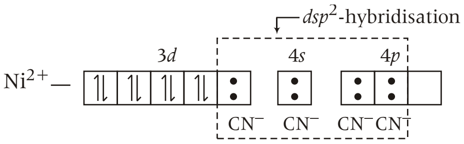
56. **For, *P* i.e. dsp^2,** It is seen in $[Ni(CN)_4]^2$

$$Ni \quad [Ar]3d^8 4s^2$$
$$Ni^{2+} \quad [Ar]3d^8$$



as CN is a strong ligand so when it approaches towards central metal pairing of unpaired electrons takes place.

Thus, in $[Ni(CN)_4]^2$



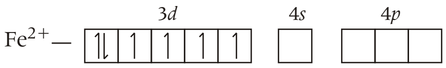
Structure : Square planar

So correct match for P is 6.

For *Q* i.e., *sp*^{3}

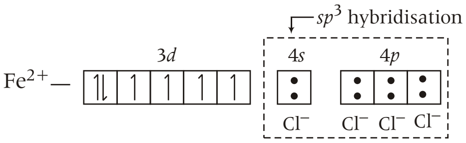
It is seen in $[FeCl_4]^2$ and $Ni(CO)_4$

$$Fe \quad [Ar]3d^6 4s^2$$
$$Fe^{2+} \quad [Ar]3d^6$$



As Cl is a weak ligand so when it approaches towards central metal pairing of unpaired electrons does not take place.

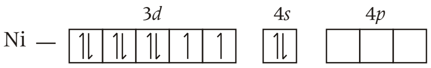
Thus, in $[FeCl_4]^2$



Structure-Tetrahedral

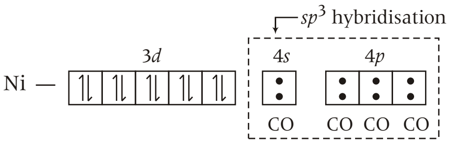
Likewise in $Ni(CO)_4$

$$Ni \quad [Ar]3d^8 4s^2$$



As CO is a strong ligand, hence when it approaches towards central metal atom pairing of unpaired electron of central atom takes place.

Thus, in $Ni(CO)_4$



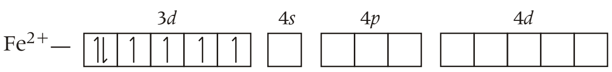
Structure Tetrahedral

So, for *Q*-4 and 5 are correct match.

For *R* i.e., *sp*^{3}*d*^{2}

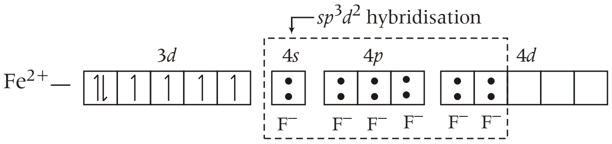
It is seen in $[FeF_6]^4$

$$Fe \quad [Ar]3d^6 4s^2$$
$$Fe^{2+} \quad [Ar]3d^6$$



As F is a weak field ligand hence, when it approaches towards central metal atom, pairing of its electrons does not take place.

Thus, in $[FeF_6]^4$



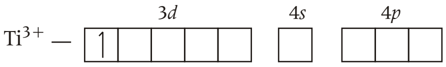
Structure : Octahedral

So, 1 is the correct match for *R*.

For *S* i.e., *d*^{2}*sp*^{3}

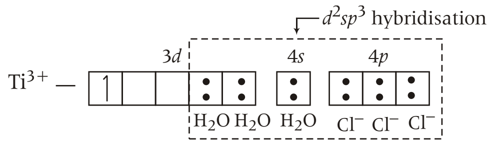
It is seen in $[Ti(H_2O)_3Cl_3]$ and $[Cr(NH_3)_6]^{3+}$

$$Ti \quad [Ar]3d^2 4s^2$$
$$Ti^{3+} \quad [Ar]3d^1$$



Here, both H_2O and Cl are weak ligands

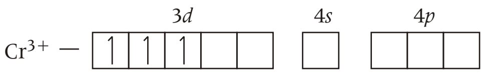
So, in $[Ti(H_2O)_3Cl_3]$



Structure Octahedral

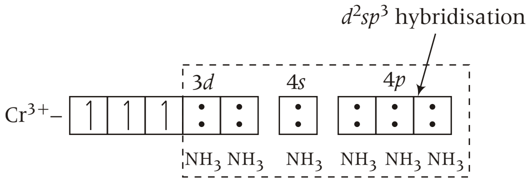
Likewise in $[Cr(NH_3)_6]^{3+}$

$$Cr \quad [Ar]3d^5 4s^1$$
$$Cr^{3+} \quad [Ar]3d^3 4s^0$$



Here, NH_3 is also a weak field ligand so due to its approach no pairing takes place in Cr.

Thus, In $[Cr(NH_3)_6]^{3+}$



So for, S-2 and 3 are the correct match.

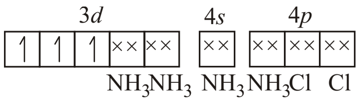
57. **PLAN** This problem is based on concept of VBT and magnetic properties of coordination compound.

Draw VBT for each coordination compound.

If unpaired electron is present then coordination compound will be paramagnetic otherwise diamagnetic.

Coordination compounds of $[MA_4B_2]$ type show geometrical isomerism. Molecular orbital electronic configuration (MOEC) for various coordination compound can be drawn using VBT as

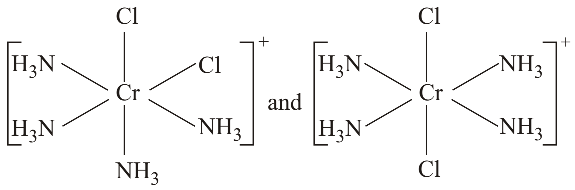
A. MO EC for $[Cr(NH_3)_4Cl_2]Cl$ is



Number of unpaired electrons (n) 3

Magnetic properties paramagnetic

Geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$ are



Cis *Trans*

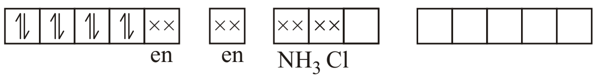
B. n 1

Magnetic properties paramagnetic

Ionisation isomers of $[Ti(H_2O)_5Cl](NO_3)_2$ are

$[Ti(H_2O)_5Cl](NO_3)_2$ and $[Ti(H_2O)_5(NO_3)]Cl(NO_3)$

C. MOEC of $[Pt(en)(NH_3)Cl]NO_3$ is



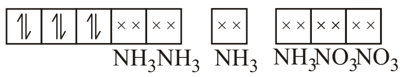
n 0

Magnetic property diamagnetic

Ionisation isomers are $[Pt(en)_2(NH_3)Cl]NO_3$

and $[Pt(en)_2NH_3(NO_3)]Cl$

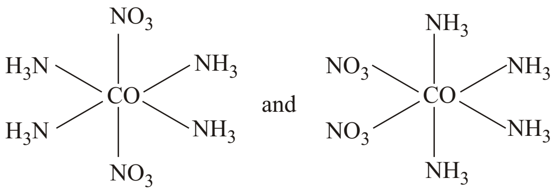
D. MOEC of $[Co(NH_3)_4(NO_3)_2]NO_3$



n 0

Magnetic property Diamagnetic

Geometrical isomers are



Trans *Cis*

Thus, magnetic property and isomerism in given coordination compound can be summarised as

(P) $[Cr(NH_3)_4Cl_2]Cl$ Paramagnetic and exhibits *cis-trans* isomerism (3)

(Q) $[Ti(H_2O)_5Cl](NO_3)_2$ Paramagnetic and exhibits ionisation isomerism (1)

(R) $[Pt(en)(NH_3)Cl]NO_3$ Diamagnetic and exhibits ionisation isomerism (4)

(S) $[Co(NH_3)_4(NO_3)_2]NO_3$ Diamagnetic and exhibits *cis-trans* isomerism (2)

P 3, Q 1, R 4, S 2

Hence, (b) is the correct choice.

58. (A) $[Co(NH_3)_4(H_2O)_2]Cl_2$:Co^{2} , $3d^7$

show geometrical isomerism, paramagnetic.

(B) $Pt(NH_3)_2Cl_2$:Pt^{2} has d^8-configuration with all paired electrons. Show geometrical isomerism, diamagnetic.

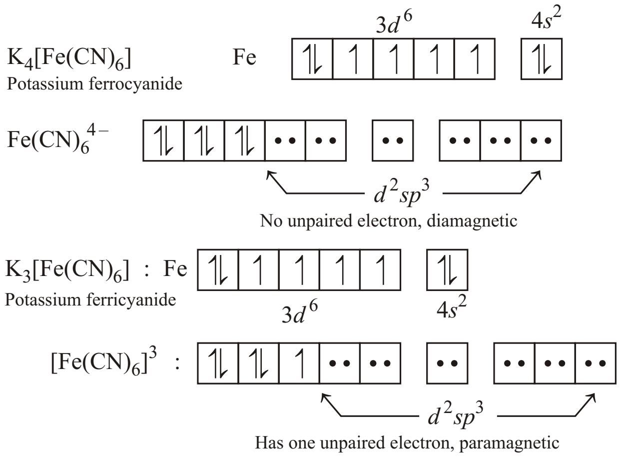
(C) $[Co(H_2O)_5Cl]Cl$: Co^{2} , $3d^7$

Cannot show geometrical isomerism, paramagnetic.

(D) $[Ni(H_2O)_6]Cl_2$: Ni^{2} , $3d^8$, weak ligand, has two unpaired electrons. Paramagnetic but cannot show geometrical isomerism.

59. Complex part is cationic, named first : $[Co(NH_3)_6]Cl_3$: hexaammine cobalt (III) chloride.

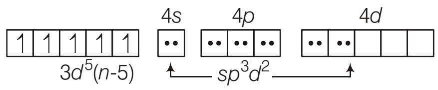
60. False : Cyanide (CN) is a strong ligand, brings about pairing of $3d$ electrons.



61. False : Lobes of $3d_{x^2\ \ y^2}$ orbitals lies in XY plane on the X and Y coordinate axes, therefore electron density of $d_{x^2\ \ y^2}$ orbital in XY plane is non-zero.

62. When S is donor atom of SCN , it produces weak ligand field and forms high spin complex as

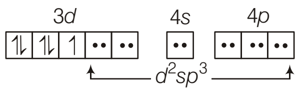
$[Fe(SCN)_6]^3$: Fe^{3+} $(3d^5)$



Spin only magnetic moment ($_s$) $\sqrt{5\ (5\quad 2)}$ BM $\sqrt{35}$ BM

In case of CN ligand, carbon is the donor atom , it produces strong ligand field and forms low spin complex as

$[Fe(CN)_6]^3$: Fe^{3+} $(3d^5)$

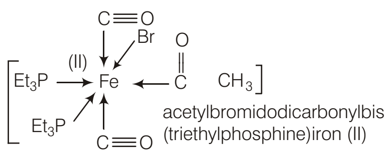


Spin only magnetic moment ($_s$) $\sqrt{1\ (1\quad 2)}$ BM $\sqrt{3}$ BM

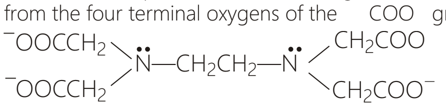
Hence, difference in spin only magnetic moment

$\sqrt{35}$ $\sqrt{3}$ 4 BM

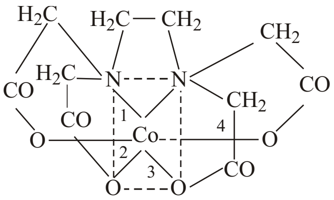
63.



64. **PLAN** EDTA is a multidentate ligand as it can donate six pairs of electrons – two pair from the two nitrogen atoms and four pair from the four terminal oxygens of the COO groups.

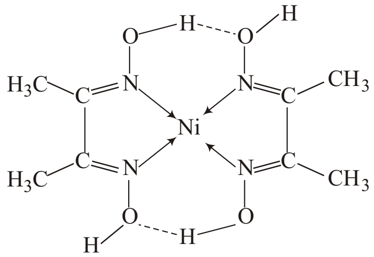


The structure of a chelate of a divalent Co^{2} with EDTA is shown as



Each N has four N Co O bonds thus total eight N Co O bonds.

65.



Ni-DMG complex

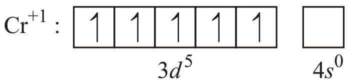
Oxidation state of Ni is +2 and hybridisation is dsp^2.

0 (no unpaired electron) hence, diamagnetic.

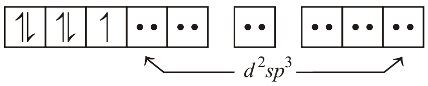
66. The spin-only magnetic moment ( ) of the complex is 1.73 BM. It indicates that nucleus of complex, chromium ion has one unpaired electron. So, the ligand NO is unit positively charged.

$K_2[Cr(NO)(CN)_4(NH_3)]$

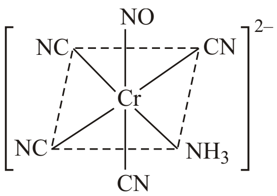
potassium amminetetracyanonitrosoniumchromate (I)



Cr(I) "under influence of strong ligand field".

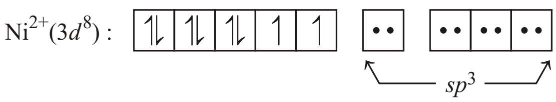


Octahedral



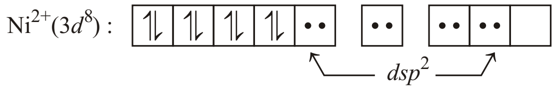
Octahedral geometry

67. $[NiCl_4]^{2}$: $Ni^{2+}(3d^8)$, weak ligand field.



$\sqrt{n(n \quad 2)}$ $\sqrt{8}$ M

$[Ni(CN)_4]^{2}$: Ni^{2+} $(3d^8)$, strong ligand field.



Square planar

0 (no unpaired electron)

68. In complexes A and B, one halide (Cl or Br) is outside coordination sphere, i.e. complexes are :

$[Cr(NH_3)_4Br_2]Cl$ and $[Cr(NH_3)_4BrCl]Br$

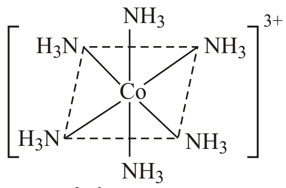
A gives white precipitate AgCl with excess of $AgNO_3$ which dissolve in excess ammonia. Therefore, A must be $[Cr(NH_3)_4Br_2]Cl$.

B gives a pale yellow precipitate with excess of $AgNO_3$, which dissolve in concentrated ammonia solution. Therefore, precipitate is AgBr and complex B is $[Cr(NH_3)_4ClBr]Br$.

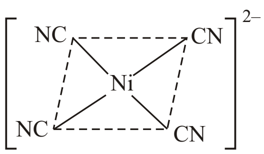
In both A and B, hybridisation of chromium is d^2sp^3 and magnetic moment : $\sqrt{n(n \quad 2)}$ BM 0

($3d^6$, strong ligand, no unpaired electron)

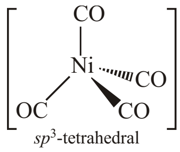
69.



d^2sp^3-octahedral



dsp^2-square planar



sp^3-tetrahedral

70. A has no water molecules of crystallisation.

Hence, A is $[Cr(H_2O)_6]Cl_3$.

Both B and C loses weight with concentrated H_2SO_4, therefore, both B and C have some water molecules of crystallisation.

Moreover, weight loss with C is just double of the same with B indicates that number of water molecules of crystallisation of C is double of the same for B. Therefore, B has one and C has two water molecules of crystallisation.

B = $[Cr(H_2O)_5Cl]Cl_2$ H_2O, C = $[Cr(H_2O)_4Cl_2]Cl$ $2H_2O$

71. (i) $[Ti(NO_3)_4]$: Ti^{4+} $(3d^0)$ No d-electron, no d-d transition possible, colourless.

(ii) $[Cu(NCCH_3)]BF_4$: Cu^+ $(3d^{10})$ All d-orbitals are completely filled, no d-d transition possible, colourless.

(iii) $[Cr(NH_3)_6]Cl_3$: Cr^{3+} $(3d^3)$ Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.

(iv) $K_3[VF_6]$: V^{3+} $(3d^2)$ Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.

72. I is a strong reducing agent, reduces Cu^{2+} to Cu^+ and precipitate out as stable CuI.

19

Extraction of Metals

Objective Questions I (Only one correct option)

1. The correct statement is
(a) leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate. **(2019 Main, 12 April II)**
(b) the hall-heroult process is used for the production of aluminium and iron.
(c) pig iron is obtained from cast iron.
(d) the blistered appearance of copper during the metallurgical process is due to the evolution of CO_2.

2. The idea of froth floatation method came from a person X and this method is related to the process Y of ores. X and Y, respectively, are **(2019 Main, 12 April I)**
(a) fisher woman and concentration
(b) washer woman and concentration
(c) fisher man and reduction
(d) washer man and reduction

3. The correct statement is **(2019 Main, 10 April II)**
(a) zone refining process is used for the refining of titanium.
(b) zincite is a carbonate ore.
(c) sodium cyanide cannot be used in the metallurgy of silver.
(d) aniline is a froth stabiliser.

4. Match the refining methods Column I with metals Column II.

	Column I (Refining Methods)		Column II (Metals)
I.	Liquation	(A)	Zr
II.	Zone refining	(B)	Ni
III.	Mond process	(C)	Sn
IV.	van Arkel method	(D)	Ga

(2019 Main, 10 April I)

(a) I- (C) ; II-(D); III-(B) ; IV-(A)
(b) I- (B) ; II-(C); III-(D) ; IV-(A)
(c) I- (C) ; II-(A); III-(B) ; IV-(D)
(d) I- (B) ; II-(D); III-(A) ; IV-(C)

5. The one that is not a carbonate ore is **(2019 Main, 9 April II)**
(a) siderite (b) calamine (c) malachite (d) bauxite

6. **Assertion** For the extraction of iron, haematite ore is used.

Reason Heamatite is a carbonate ore of iron. **(2019 Main, 9 April II)**

(a) Only the reason is correct.
(b) Both the assertion and reason are correct explanation for the assertion.
(c) Both the assertion and reason are correct and the reason is the correct explanation for the assertion.
(d) Only the assertion is correct.

7. The ore that contains the metal in the form of fluoride is **(2019 Main, 9 April I)**
(a) magnetite (b) sphalerite (c) malachite (d) cryolite

8. The Mond process is used for the **(2019 Main, 8 April II)**
(a) purification of Ni (b) extraction of Mo
(c) purification of Zr and Ti (d) extraction of Zn

9. With respect to an ore, Ellingham diagram helps to predict the feasibility of its **(2019 Main, 8 April I)**
(a) electrolysis (b) zone refining
(c) vapour phase refining (d) thermal reduction

10. The pair that does not require calcination is **(2019 Main, 12 Jan II)**
(a) ZnO and MgO (b) ZnO and $Fe_2O_3 \cdot xH_2O$
(c) $ZnCO_3$ and CaO (d) Fe_2O_3 and $CaCO_3 \cdot MgCO_3$

11. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of **(2019 Main, 12 Jan I)**
(a) platinum (b) carbon
(c) pure aluminium (d) copper

12. The reaction that does not define calcination is **(2019 Main, 11 Jan II)**
(a) $Fe_2O_3 \cdot XH_2O \xrightarrow{\Delta} Fe_2O_3 + XH_2O$
(b) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
(c) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$
(d) $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$

13. Match the ores (Column A) with the metals (Column B).

	Column A Ores		Column B Metals
A.	Siderite	P.	Zinc
B.	Kaolinite	Q.	Copper
C.	Malachite	R.	Iron
D.	Calamine	S.	Aluminium

(2019 Main, 11 Jan I)

(a) A - P; B- Q; C - R; D- S
(b) A - R; B- S; C - P; D- Q
(c) A - Q; B- R; C - S; D- P
(d) A - R; B- S; C - Q; D- P

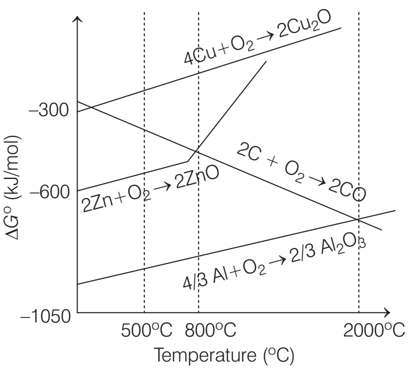
14. The electrolytes usually used in the electroplating of gold and silver, respectively, are **(2019 Main, 10 Jan II)**

(a) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$
(b) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$
(c) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$
(d) $[Au(CN)_2]^-$ and $[AgCl_2]^-$

15. Hall-Heroult's process is given by **(2019 Main, 10 Jan I)**

(a) $ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$
(b) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
(c) $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
(d) $Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$

16. The correct statement regarding the given Ellingham diagram is **(2019 Main, 9 Jan II)**



(a) At 800°C, Cu can be used for the extraction of Zn from ZnO
(b) At 1400°C, Al can be used for the extraction of Zn from ZnO
(c) At 500°C, coke can be used for the extraction of Zn from ZnO
(d) Coke cannot be used for the extraction of Cu from Cu_2O

17. The ore that contains both iron and copper is **(2019 Main, 9 Jan I)**

(a) malachite (b) azurite
(c) dolomite (d) copper pyrites

18. Which one of the following ores is best concentrated by froth floatation method? **(2016 Main)**

(a) Siderite (b) Galena
(c) Malachite (d) Magnetite

19. From the following statements regarding H_2O_2 choose the incorrect statement. **(2015 Main)**

(a) It can act only as an oxidising agent
(b) It decomposed on exposure to light
(c) It has to be stored in plastic or wax lined glass bottles in dark
(d) It has to be kept away from dust

20. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false? **(2015 Main)**

(a) CO and CO_2 are produced in this process
(b) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
(c) Al^{3+} is reduced at the cathode to form Al
(d) Na_3AlF_6 serves as the electrolyte

21. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is **(2014 Main)**

(a) Ag (b) Ca
(c) Cu (d) Cr

22. Sulphide ores are common for the metals **(2013 Adv.)**

(a) Ag, Cu and Pb (b) Ag, Cu and Sn
(c) Ag, Mg and Pb (d) Al, Cu and Pb

23. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are **(2012)**

(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively

24. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are **(2011)**

(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

25. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of **(2008, 3M)**

(a) nitrogen (b) oxygen
(c) carbon dioxide (d) argon

26. Extraction of zinc from zinc blende is achieved by **(2007, 3M)**

(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self-reduction

27. Which ore contains both iron and copper? **(2005, 1M)**

(a) Cuprite (b) Chalcocite
(c) Chalcopyrite (d) Malachite

28. The methods chiefly used for the extraction of lead and tin from their ores are respectively **(2004, 1M)**

(a) self-reduction and carbon reduction
(b) self-reduction and electrolytic reduction
(c) carbon reduction and self-reduction
(d) cyanide process and carbon reduction

29. In the process of extraction of gold,

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + HO$$
$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes $[X]$ and $[Y]$. **(2003, 1M)**

(a) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$
(b) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$
(c) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$
(d) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

30. Anhydrous ferric chloride is prepared by **(2002)**
(a) heating hydrated ferric chloride at a high temperature in a stream of air
(b) heating metallic iron in a stream of dry chlorine gas
(c) reaction of ferric oxide with hydrochloric acid
(d) reaction of metallic iron with hydrochloric acid

31. Which of the following process is used in extractive metallurgy of magnesium? **(2002, 3M)**
(a) Fused salt electrolysis
(b) Self-reduction
(c) Aqueous solution electrolysis
(d) Thermite reduction

32. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is **(2001, 1M)**
(a) $Cu_2O + FeS$ (b) $FeSiO_3$
(c) $CuFeS_2$ (d) $Cu_2S + FeO$

33. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out **(2000, 1M)**
(a) in the presence of NaCl
(b) in the presence of fluorite
(c) in the presence of cryolite which forms a melt with lower melting temperature
(d) in the presence of cryolite which forms a melt with higher melting temperature

34. The chemical process in the production of steel from haematite ore involve **(2000, 1M)**
(a) reduction
(b) oxidation
(c) reduction followed by oxidation
(d) oxidation followed by reduction

35. In the commercial electrochemical process for aluminium extraction, the electrolyte used is **(1999, 2M)**
(a) $Al(OH)_3$ in NaOH solution
(b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of Al_2O_3 and Na_3AlF_6
(d) a molten mixture of $AlO(OH)$ and $Al(OH)_3$

36. The major role of fluorspar (CaF_2) which is added in small amount in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is **(1993, 1M)**
(a) as a catalyst
(b) to make the fused mixture very conducting
(c) to increase the temperature of the melt
(d) to decrease the rate of oxidation of carbon at the anode

37. Hydrogen gas will not reduce **(1985, 1M)**
(a) heated cupric oxide
(b) heated ferric oxide
(c) heated stannic oxide
(d) heated aluminium oxide

38. In the alumino-thermite process, aluminium acts as **(1983, 1M)**
(a) an oxidising agent (b) a flux
(c) a reducing agent (d) a solder

39. Type of bonds present in $CuSO_4 \cdot 5H_2O$ are only **(1983)**
(a) electrovalent and covalent
(b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent

40. In metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in **(1982)**
(a) slag
(b) gangue
(c) metallic calcium
(d) calcium carbonate

41. Iron is rendered passive by treatment with concentrated **(1982)**
(a) H_2SO_4 (b) H_3PO_4
(c) HCl (d) HNO_3

Objective Questions II
(One or more than one correct option)

42. Extraction of copper from copper pyrite ($CuFeS_2$) involves **(2016 Adv.)**
(a) crushing followed by concentration of the ore by froth-floatation
(b) removal of iron as slag
(c) self reduction step to produce 'blister copper' following evolution of SO_2
(d) refining of 'blister copper' by carbon reduction

43. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is/are **(2015 Adv.)**
(a) impure Cu strip is used as cathode
(b) acidified aqueous $CuSO_4$ is used as electrolyte
(c) pure Cu deposits at cathode
(d) impurities settle as anode-mud

44. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are **(2014 Adv.)**
(a) $CuFeS_2$ (b) CuO
(c) Cu_2O (d) $CuSO_4$

45. The carbon-based reduction method is not used for the extraction of **(2013 Adv.)**
(a) tin from SnO_2
(b) iron from Fe_2O_3
(c) aluminium from Al_2O_3
(d) magnesium from $MgCO_3$, $CaCO_3$

46. Extraction of metal from the ore cassiterite involves **(2011)**
(a) carbon reduction of an oxide ore
(b) self-reduction of a sulphide ore
(c) removal of copper impurity
(d) removal of iron impurity

47. Addition of high proportions of manganese makes steel useful in making rails **(1998)**
(a) gives hardness to steel
(b) helps the formation of oxides of iron
(c) can remove oxygen and sulphur
(d) can show highest oxidation state of + 7

48. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are **(1990, 1M)**
(a) Ag (b) Mg (c) Cu
(d) Al (e) Cr

49. In the electrolysis of alumina, cryolite is added to **(1986, 1M)**
(a) lower the melting point of alumina
(b) increase the electrical conductivity
(c) minimise the anode effect
(d) remove impurities from alumina

Assertion and Reason

Read the following questions and answer as per the direction given below :
(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
(c) Statement I is correct; Statement II is incorrect.
(d) Statement I is incorrect; Statement II is true.

50. **Statement I** $Al(OH)_3$ is amphoteric in nature.
Statement II Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$. **(1998)**

Passage Based Questions

Passage

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 \cdot 5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. **(2010)**

51. Partial roasting of chalcopyrite produces
(a) Cu_2S and FeO (b) Cu_2O and FeO
(c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3

52. Iron is removed from chalcopyrite as
(a) FeO (b) FeS (c) Fe_2O_3 (d) $FeSiO_3$

53. In self-reduction, the reducing species is
(a) S (b) O^{2-} (c) S^{2-} (d) SO_2

Match the Columns

54. Match the anionic species given in Column I that are present in the ore (s) given in Column II. **(2015 Adv.)**

	Column I		Column II
A.	Carbonate	p.	Siderite
B.	Sulphide	q.	Malachite
C.	Hydroxide	r.	Bauxite
D.	Oxide	s.	Calamine
		t.	Argentite

55. Match each of the reactions given in Column I with the corresponding product(s) given in Column II. **(2009)**

	Column I		Column II
A.	Cu + dil. HNO_3	p.	NO
B.	Cu + conc. HNO_3	q.	NO_2
C.	Zn + dil. HNO_3	r.	N_2O
D.	Zn + conc. HNO_3	s.	$Cu(NO_3)_2$
		t.	$Zn(NO_3)_2$

56. Match the conversions in Column I with the type(s) of reaction(s) given in Column II. **(2008, 6M)**

	Column I		Column II
A.	$PbS \longrightarrow PbO$	p.	Roasting
B.	$CaCO_3 \longrightarrow CaO$	q.	Calcination
C.	$ZnS \longrightarrow Zn$	r.	Carbon reduction
D.	$Cu_2S \longrightarrow Cu$	s.	Self-reduction

57. Match the extraction processes listed in Column I with metals listed in Column II. **(2006, 6M)**

	Column I		Column II
A.	Self-reduction	p.	Lead
B.	Carbon reduction	q.	Silver
C.	Complex formation and displacement by metal	r.	Copper
D.	Decomposition of iodide	s.	Boron

58. Each entry in Column *X* is in some way related to the entries in Columns *Y* and *Z*. Match the appropriate entries. **(1988, 3M)**

	Column *X*		Column *Y*		Column *Z*
A.	Invar	p.	Co, Ni	m.	Cutlery
B.	Nichrome	q.	Fe, Ni	n.	Heating element
C.	Stainless steel	r.	Fe, Cr, Ni	o.	Watch spring

59. Match the following choosing one item from Column *X* and the appropriate item from Column *Y*. **(1983, 2M)**

	Column *X*		Column *Y*
A.	Al	p.	Calamine
B.	Cu	q.	Cryolite
C.	Mg	r.	Malachite
D.	Zn	s.	Carnalite

60. Match the following metals listed in Column I with extraction processes listed in Column II. **(1979, 2M)**

	Column I		Column II
A.	Silver	p.	Fused salt electrolysis
B.	Calcium	q.	Carbon reduction
C.	Zinc	r.	Carbon monoxide reduction
D.	Iron	s.	Amalgamation
E.	Copper	t.	Self-reduction

Fill in the Blanks

61. Silver jewellery items tarnish slowly in the air due to their reaction with………… **(1997)**

62. In the extractive metallurgy of zinc, partial fusion of ZnO with coke is called …… and reduction of the ore to the molten metal is called …… (smelting, calcining, roasting, sintering). **(1988, 1M)**

63. Silver chloride is sparingly soluble in water because its lattice energy greater than ……….. energy. **(1987)**

64. Galvanisation of iron denote coating with …… **(1983)**

65. Cassiterite is an ore of …… **(1980, 1M)**

66. In the thermite process …… is used as a reducing agent. **(1980, 1M)**

67. In the basic Bessemer process for the manufacture of steel, the lining of the converter is made up of … . The slag formed consists of …… **(1980, 1M)**

68. AgCl dissolve in excess of KCN solution to give ………… complex compound. **(1980)**

True/False

69 Cu^{+} disproportionate to Cu^{2+} and elemental copper in solution. **(1991)**

70. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. **(1984, 1M)**

71. Dilute HCl oxidises metallic Fe to Fe^{2+}. **(1983, 1M)**

72. Silver fluoride is fairly soluble in water. **(1982)**

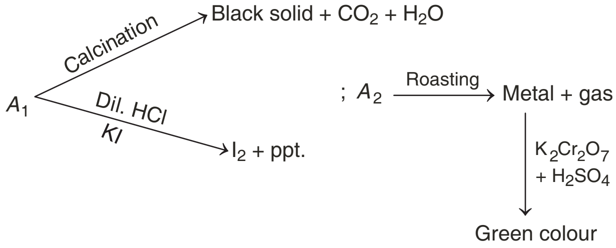
Subjective Questions

73. Give the coordination number of Al in the crystalline state of $AlCl_3$. **(2009, 2M)**

74. Give the number of water molecule (s) directly bonded to the metal centre in $CuSO_4 \cdot 5H_2O$. **(2009, 2M)**

75. Write balanced chemical equation for developing a black and white photographic film. Also give reason, why the solution of sodium thiosulphate on acidification turns milky white and give balance equation of this reaction. **(2005, 2M)**

76. A_1 and A_2 are two ores of metal M. A_1 on calcination gives black precipitate, CO_2 and water.



Identify A_1 and A_2. **(2004, 4M)**

77. Which of the two, anhydrous or hydrated $AlCl_3$ is more soluble in diethyl ether? Justify using the concepts of bonding in not more than 2 or 3 sentences. **(2003)**

78. Write the balanced chemical reactions involved in the extraction of lead from galena. Mention oxidation state of lead in litharge. **(2003, 2M)**

79. Write the balanced chemical equation for developing photographic films. **(2000)**

80. Write the chemical reactions involved in the extraction of silver from argentite. **(2000, 2M)**

81. Work out the following using chemical equations.
In moist air, copper corrodes to produce a green layer on the surface. **(1998)**

82. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag, that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. **(1998, 4M)**

83. Give balance equation for the reaction of aluminium with aqueous sodium hydroxide. **(1997)**

84. Write a balanced equation for the reaction of argentite with KCN and name the products in the solution. **(1996)**

85. Give reasons for the following

"Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water." **(1994, 1M)**

86. Complete the following reaction :

$$Sn + 2KOH + 4H_2O \longrightarrow ...... + ...$$ **(1994)**

87. Give briefly the isolation of magnesium from sea water by the Dow's process.
Give equations for the steps involved. **(1993, 3M)**

88. Complete and balance the following reaction :
Copper reacts with HNO_3 to give NO and NO_2 in the molar ratio of 2:1

$$Cu + HNO_3 \longrightarrow …… + NO + NO_2 + ……$$ **(1992)**

89. Write balanced equation for the extraction of "Copper from copper pyrites by self reduction." **(1990, 2M)**

90. Give balanced equations for the extraction of "Silver from silver glance by cyanide process." **(1988, 1M)**

91. Answer the following questions briefly

(i) What is the actual reducing agent of haematite in blast furnace?

(ii) Give the equation for the recovery of lead from galena by air reduction.

(iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride?

(iv) Zinc, not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$, explain.

(v) Why is chalcocite roasted and not calcinated during recovery of copper? **(1987, 5M)**

92. Write balanced chemical equation for the following "Gold is dissolved in aqua regia." **(1987)**

93. Each of the following statement is true, only under some specific conditions. Write the condition for each subquestion in not more than 2 sentences.

(i) Metals can be recovered from their ores by chemical methods

(ii) High purity metals can be obtained by zone refining method. **(1984, 2M)**

94. Give reason for the following in one or two sentences : "Silver bromide is used in photography." **(1983)**

95. State the conditions under which the preparation of alumina from aluminium is carried out. Give the necessary equations which need not be balanced. **(1983, 2M)**

96. Write the chemical equations involved in the extraction of lead from galena by self reduction process. **(1979, 2M)**

97. Write balanced equation involved in the preparation of tin metal from cassiterite. **(1979)**

Answers

1. (a)	**2.** (b)	**3.** (d)	**4.** (a)
5. (d)	**6.** (d)	**7.** (d)	**8.** (a)
9. (d)	**10.** (a)	**11.** (b)	**12.** (d)
13. (d)	**14.** (c)	**15.** (c)	**16.** (b)
17. (d)	**18.** (b)	**19.** (a)	**20.** (d)
21. (b)	**22.** (a)	**23.** (b)	**24.** (d)
25. (b)	**26.** (b)	**27.** (c)	**28.** (a)
29. (a)	**30.** (b)	**31.** (a)	**32.** (b)
33. (c)	**34.** (a)	**35.** (c)	**36.** (b)
37. (d)	**38.** (c)	**39.** (c)	**40.** (a)
41. (d)	**42.** (a,b,c)	**43.** (b,c,d)	**44.** (b,c,d)
45. (c,d)	**46.** (a,d)	**47.** (a,c)	**48.** (b,d)
49. (a,b)	**50.** (b)	**51.** (b)	**52.** (d)

53. (c) **54.** $A \to p, q, s;\ B \to t;\ C \to q;\ D \to r$

55. $A \to p, s;\ B \to q, s;\ C \to r, t;\ D \to q, t$

56. $A \to p; B \to q; C \to r, s;\ D \to p, s$

57. $A \to p, r; B \to p;\ C \to q;\ D \to s$

58. $A \to q, o; B \to p, n; C \to r, m$

59. $A \to q; B \to r;\ C \to s;\ D \to p$

60. $A \to s; B \to p; C \to q; D \to q, r; E \to t$

61. H_2S **62.** Sintering, Smelting

63. Hydration **64.** Zn **65.** Sn **66.** Al

67. Lime, calcium phosphate **68.** $K[Ag(CN)_2]$

69. T **70.** T **71.** T **72.** T

73. (6) **74.** (4) **78.** (2)

Hints & Solutions

1. The correct statement is ''leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate''. Bauxite usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. Here, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces precipitation.

$$2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3 \cdot xH_2O(s) + 2NaHCO_3(aq)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470\text{ K}} Al_2O_3(s) + xH_2O(g)$$

2. The idea of froth floatation method came from a person 'washer woman' (X) and this method is related to the process concentration (Y) of ores.

This method is based upon the preferential wetting properties with the frothing agent (collector) and water.

3. The explanation of given statements are as follows:

(a) Zone refining process is used for the refining of B, Ga, In, Si and Ge.
Ti is refined by van Arkel method.
Thus, statement (a) is incorrect.

(b) Zincite (ZnO) is an oxide ore of Zn.
Thus, statement (b) is incorrect.

(c) NaCN is used in the hydrometallurgy of silver. It is known as Mc. Arthur Forrest process.
The reactions occuring during the process are as follows:

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$
$$4Na_2S + 2H_2O + 5O_2 \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$
$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

Thus, statement (c) is incorrect.

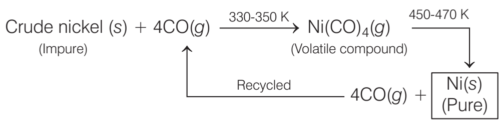
(d) Aniline and cresol help in stabilising the froth in froth floatation process.
Thus, statement (d) is correct.

4. Refining of crude metals results pure metals and its impurities get separated out.

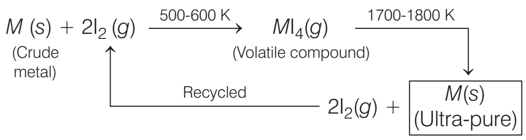
I. **Liquation** In this method low melting metals like Sn, Pb, Bi and Hg can be made to flow down through a sloping surface leaving behind the higher melting impurities on the hearth.

II. **Zone refining** The basic principle of the method is, impurities are more soluble in the molten metal than in the solid state of the metal. This method is useful to produce semiconductors and ultra-pure metals like B, Ga, In, Si and Ge.

III. **Mond process**



IV. van Arkel method



Here, M = Zr, Hf, Ti

Hence, the correct matching is

$$\mathrm{I} \to (\mathrm{C}),\ \mathrm{II} \to (\mathrm{D}),\ \mathrm{III} \to (\mathrm{B}),\ \mathrm{IV} \to (\mathrm{A}).$$

5. Bauxite is not a carbonate ore. Its chemical formula is Al_2O_3 or $AlO_x(OH)_{3-2x}$, where $0 < x < 1$. Chemical formula of other ores given in options are as follows:

Siderite-$FeCO_3$

Calamine-$ZnCO_3$

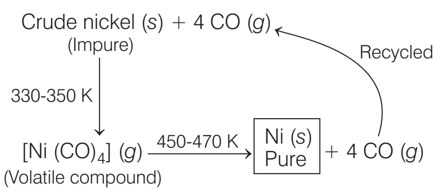
Malachite-$CuCO_3 \cdot Cu(OH)_2$

6. Only assertion is correct and reason is incorrect. Haematite is not a carbonate ore. It is an oxide ore, i.e. Fe_2O_3. Cast iron is extracted chiefly from its oxide ore (haematite) by heating in the presence of coke and limestone in a blast furnace.

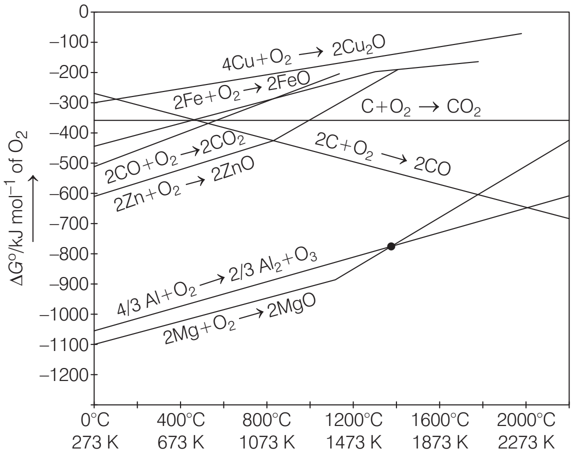
7. Cryolite ore (Na_3AlF_6, sodium hexafluoroaluminate) contain fluorine while other given options such as malachite ($Cu_2(CO)_3(OH)_2$), sphalerite ((Zn, Fe)S) and bauxite (Al_2O_3) does not contain fluorine.

8. Mond process is used in the purification of Ni. It is a vapour phase refining process.

It is based on the principle that Ni is heated in the presence of carbon monoxide to form nickel tetracarbonyl, which is a volatile complex. This complex is then decomposed by subjecting it to a higher temperature (450-470 K) to obtain pure nickel metal.



9. With respect to an ore, Ellingham diagram helps to predict the feasibility of its thermal reduction. It is a graph representation of Gibbs energy change *versus* absolute temperature.



Gibbs energy (ΔG°) *versus* T plots (schematic) for the formation of some oxides (Ellingham diagram)

Generally, the diagram consists of plots of ΔG° *versus* T for the formation of oxides of elements

$$2xM(s) + O_2(g) \longrightarrow \underset{\text{Thermal reduction product}}{2M_xO(s)}$$

In this reaction, amount of gas decreases thus, randomness decreases. Hence, ΔS becomes negative. Therefore, the value of free energy increases with increase in temperature. There is a point in a curve below which ΔG is negative. So, M_xO is stable. Above this point, M_xO will decompose on its own.

10. The hydroxide, hydrated oxides and carbonate ores, after concentration, are subjected to calcination. In the process, the ore is heated below its melting point in the limited supply or absence of air. As the result, these are converted into their oxides.

So, among the given options, the options having either carbonates (e.g. $ZnCO_3$ and $CaCO_3 \cdot MgCO_3$) or hydrated oxide (e.g. $Fe_2O_3 \cdot xH_2O$), require calcination while pair of option (a), i.e. ZnO and MgO does not require calcination.

11. In the Hall - Heroult's process, aluminium in formed at the cathode. The cathode is made out of carbon. In this method, Al_2O_3 is melted with cryolite, $Na_3[AlF_6]$ and electrolysed in a graphite lined steel tank, which serves as the cathode. The anode is also made of graphite.

The cell runs continuously and at intervals molten aluminium is drained from the bottom of the cell and more bauxite is added. The electrolytic reactions are as follows:

At cathode $\quad Al^{3+} + 3e^- \longrightarrow Al$

At anode $\quad C(s) + O^{2-}\text{(melt)} \longrightarrow CO(g) + 2e^-$

$\quad C(s) + 2O^{2-}\text{(melt)} \longrightarrow CO_2(g) + 4e^-$

12. Calcination is one of the pyrometallurgical process, like roasting by which a concentrated ore gets converted into its oxide.

In calcination, a hydrated carbonate or bicarbonate ore or a hydrated ore is heated at lower temperature (compared to roasting) in absence of air to give its oxide as in options (a), (b) and (c). Here, volatile non-metallic oxides like H_2O, CO_2, are also produced.

Roasting is valid mainly for sulphide ores like option (d), where SO_2 gets liberated. In this reaction, calcination cannot be used.

13. The correct match is: $A \rightarrow R$; $B \rightarrow S$; $C \rightarrow Q$; $D \rightarrow P$.

(A) Siderite is an ore of iron with molecular formula $FeCO_3$(R).

(B) Kaolinite is an ore of aluminium with molecular formula $Al_2Si_2(OH)_2O_5$ (S).

(C) Malachite is an ore of copper with molecular formula $CuCO_3 \cdot Cu(OH)_2$ (Q).

(D) Calamine is an ore of zinc with molecular formula $ZnCO_3$(P).

14. Electroplating is a process of coating one metal or metal object with a very thin layer of another metal typically applying a direct electric current.

Electrolytes used in the electroplating of gold and silver are given in the table below:

	Process	Article to be plated out acts as cathode	Pure metal block acts an anode by which electroplating will be done	Electrolyte (aqueous solution)
(a)	Gold plating	Article	Au(*s*)	$Na[\overset{I}{A}u(CN)_2]$ (Sodium auro-cyanide)
(b)	Silver plating	Article	Ag(*s*)	$Na[\overset{I}{A}g(CN)_2]$ (Sodium argento cyanide)

15. Hall-Heroult's process is an electro-reduction process by which pure alumina (Al_2O_3) is reduced to crude Al.

In this process, electrolysis of a fused mixture of Al_2O_3, $Na_3[AlF_6]$(cryolite) and CaF_2 (fluorspar) is carried out at carbon cathode and graphite anode.

The overall reaction is represented as:

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

16. From the Ellingham diagram, we can say that any oxide with lower value of $\Delta G°$ is more stable than a oxide with higher value of $\Delta G°$. We can also predict that the oxide placed higher in the diagram can be reduced by the element involved in the formation of its oxide placed lower at that temperature in the diagram.

It is happening in case of ZnO for its reduction by Al at 1400°C.

17. The formulae of the given ores are as follows:

Malachite	: $CuCO_3 \cdot Cu(OH)_2$
Copper pyrites	: $CuFeS_2$
Dolomite	: $CaMg(CO_3)_2$
Azurite	: $Cu_3(CO)_3(OH)_2$

18. Sulphide ores are concentrated by froth floatation method e.g. Galena (PbS)

19. H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is –1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state –2.

H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax linked glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

20. (a) In Hall-Heroult process for extraction Al, carbon anode is oxidised to CO and CO_2.

(b) When Al_2O_3 is mixed with CaF_2, it lowers the melting point of the mixture and brings conductivity.

(c) Al^{3+} is reduced at cathode to form Al.

(d) Here, Al_2O_3 is an electrolyte, undergoing the redox process. Na_3AlF_6 although is an electrolyte but serves as a solvent, not electrolyte.

21. Higher the position of element in the electrochemical series more difficult is the reduction of its cations.

If $Ca^{2+}(aq)$ is electrolysed, water is reduced in preference to it. Hence, it cannot be reduced electrolytically from their aqueous solution.

$$Ca^{2+}(aq) + H_2O \longrightarrow Ca^{2+} + OH^- + H_2\uparrow$$

22.

Element	Ores	Name
Ag	Ag_2S	Argentite
Cu	$CuFeS_2$	Copper pyrites
Pb	PbS	Galena
Sn	SnO_2	Cassiterite
Mg	$MgCO_3 \cdot CaCO_3$	Dolomite
Al	$Al_2O_3 \cdot xH_2O$	Bauxite

23. The reactions involved in extraction of silver by cyanide process are

$$Ag_2S + CN^- + O_2 \longrightarrow [Ag(CN)_2]^- + SO_2 \quad \text{...(i)}$$
$$[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + Ag \quad \text{...(ii)}$$

In reaction (i), sulphide is oxidised to SO_2 by oxygen. In the reaction (ii), silver ion (Ag^+) is reduced to Ag by Zn. Therefore, O_2 is oxidising agent and Zn is reducing agent.

24. Haematite is Fe_2O_3, in which oxidation number of iron is III. Magnetite is Fe_3O_4 which is infact a mixed oxide ($FeO \cdot Fe_2O_3$), hence iron is present in both II and III oxidation state.

25. A water soluble complex with silver and dilute aqueous solution of NaCN is $Na[Ag(CN)_2]$. In the cyanide process, the native silver is crushed and treated with aqueous NaCN solution and aerated.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

26. Zinc blende contain ZnS which is first roasted partially and then subjected to reduction with carbon

$$ZnS + O_2 \longrightarrow ZnO + SO_2 \text{ Roasting}$$
$$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow \text{Carbon reduction}$$

27. Chalcopyrite contain both iron and copper.

28. Lead is mainly extracted by self-reduction process while tin is extracted by carbon reduction method.

29.
$$\underset{}{Au} + 2CN^- \longrightarrow \underset{X}{[Au(CN)_2]^-}$$
$$2Au(CN)_2^- + Zn \longrightarrow \underset{Y}{[Zn(CN)_4]^{2-}} + 2Au$$

30. Heating iron in stream of dry chlorine gas gives $FeCl_3$ in anhydrous form. In all other cases (*a* and *c*) hydrated $FeCl_3$ is obtained while in (*d*), $FeCl_2$ is formed.

31. Mg is extracted by electrolysis of molten $MgCl_2$.

32. Iron present in copper pyrite is removed by forming $FeSiO_3$ as slag.

33. Cryolite is added to alumina in order to lower the melting point.

34. Haematite ore contain Fe_2O_3 which is reduced by CO in the blast furnace as
$$Fe_2O_3 + CO \longrightarrow Fe + CO_2$$

35. Al_2O_3 mixed with cryolite $Na_3[AlF_6]$ is fused and electrolysed in the extraction of Al.

36. Fluorspar (CaF_2) improve the electrical conductivity during electrolytic reduction of alumina.

37. Al itself is a very strong reducing agent.

38. In thermite welding, Al acts as a reducing agent
$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe + Heat$$

39. The actual representation of $CuSO_4 \cdot 5H_2O$ (blue vitriol) is $[Cu(H_2O)_4]SO_4 \cdot H_2O$ and it has covalent, ionic and coordinate covalent bonds.

40. Ca^{2+} end up in $CaSiO_3$ (slag).

41. Iron is rendered passive by concentrated HNO_3 due to formation of a thick protective layer of Fe_3O_4.

42. $CuFeS_2$ (copper pyrite) is converted into copper into following steps:

Step I Crushing (grinding) followed by concentration by froth-floatation process.

Step II Roasting of ore in the presence of SiO_2 which removes iron as slag ($FeSiO_3$).
$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \longrightarrow 2SO_2 + 2FeO$$
$$FeO + SiO_2 \longrightarrow FeSiO_3(\text{Slag})$$

Step III Self-reduction in Bessemer converter
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$
Copper obtained is blister copper (98% pure).

Step IV Refining of blister copper is done by electrolysis

Impure copper—Anode

Pure copper— Cathode

At anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

Carbon-reduction method is not used. Thus, (d) is incorrect.

43. (a) is wrong statement. Impure copper is set as anode where copper is oxidised to Cu^{2+} and goes into electrolytic solutions.

(b) $CuSO_4$ is used as an electrolyte in purification process.

(c) Pure copper is deposited at cathode as:

$Cu^{2+} + 2e^- \longrightarrow Cu$: (At cathode)

(d) Less active metals like Ag, Au etc settle down as anode mud.

44. (b) $4CuO \xrightarrow{1100°C} 2Cu_2O + O_2$
$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$$

(c) $Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2$

(d) $CuSO_4 \xrightarrow{720°C} CuO + SO_2 + \frac{1}{2}O_2$
$$4CuO \xrightarrow{1100°C} 2Cu_2O + O_2$$
$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$$

Reaction is believed to proceed as
$$Cu_2S \rightleftharpoons 2Cu^+ + S^{2-}$$
$$2Cu_2O \rightleftharpoons 4Cu^+ + 2O^{2-}$$
$$S^{2-} + 2O^{2-} \longrightarrow SO_2 + 6e^-$$
$$6Cu^+ + 6e^- \longrightarrow 6Cu; \; E^\circ_{cell} = 0.52$$

Here, copper sulphide is reduced to copper metal. Solidified copper has blistered appearance due to evolution of SO_2 and thus obtained copper is known as blister copper.

Other compounds which give Cu are

(i) CuO as $4CuO \xrightarrow{1100°C} 2Cu_2O + O_2$
$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$$

(ii) $CuSO_4$ as $CuSO_4 \xrightarrow{720°C} CuO + SO_2 + \frac{1}{2}O_2$
$$4CuO \xrightarrow{\Delta} 2Cu_2O + O_2$$
$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$$

While $CuFeS_2$ will not give Cu on heating. The heating in the presence of O_2 gives Cu_2S and FeS with the evolution of SO_2.

45. Al has greater affinity for oxygen, hence oxide is not reduced by carbon. MgO and CaO (formed in the calcination from carbonates) are stable species and not reduced by carbon.

During Smelting $SnO_2 + C \xrightarrow{1300°C} Sn + CO$
$$2Fe_2O_3 + 3C \xrightarrow{\Delta} 4Fe + 3CO_2$$

46. The important ore of tin is cassiterite (SnO_2). Tin is extracted from cassiterite ore by carbon reduction method in a blast furnace.
$$SnO_2 + 2C \longrightarrow Sn + 2CO$$
The product often contain traces of iron which is removed by blowing air through the melt to oxidise to FeO which then floats to the surface.
$$2Fe + O_2 \longrightarrow 2FeO$$

47. Addition of manganese to iron improve hardness of steel as well as remove oxygen and sulphur.

48. Magnesium and aluminium are both highly electropositive, more electropositive than water cannot be obtained by electrolysis of aqueous solution of their salts.

49. Alumina (Al_2O_3) has very high melting point and it is poor conductor of electricity. Both these factors posses difficulty in electrolysis of molten alumina.

Cryolite, Na_3AlF_6, when mixed with alumina, lowers melting point as well as improve electrical conductivity, hence helps in electrolysis of Al_2O_3.

50. $Al(OH)_3$ is amphoteric

$$\underset{\text{Base}}{Al(OH)_3} + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$\underset{\text{Acid}}{Al(OH)_3} + NaOH \longrightarrow Na[Al(OH)_4]$$

High charge and small size of Al^{3+} makes Al—O and O—H bonds equally ionisable.

51. $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$

52. $FeO + SiO_2 \longrightarrow FeSiO_3$ (Slag)

53. $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

In Cu_2S, sulphur is S^{2-} and in SO_2, sulphur is in +4 state. Hence, S^{2-} is acting as reducing agent.

54. Siderite $= FeCO_3$, Malachite $= CuCO_3 \cdot Cu(OH)_2$

Bauxite $= Al_2O_3 \cdot 2H_2O_2$ consisting some $Al(OH)_3$

Calamine $= ZnCO_3$, Argentite $= Ag_2S$

55. A. $3Cu + \underset{\text{Dil.}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

B. $Cu + \underset{\text{Conc.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

C. $4Zn + \underset{\text{Dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

D. $Zn + \underset{\text{Conc.}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

56. A. $PbS \xrightarrow{O_2} PbO + SO_2$, roasting

B. $CaCO_3 \longrightarrow CaO + CO_2\uparrow$; calcination

C. $ZnS \longrightarrow Zn$, can be done by carbon reduction or self reduction

D. $Cu_2S \longrightarrow Cu$, roasting followed by self reduction

57.

	Extraction methods		Metals extracted
A.	Self reduction	r.	Copper, (P) Lead
B.	Carbon reduction	p.	Lead
C.	Complex formation and displacement by metal	q.	Silver : $Ag_2S + NaCN \longrightarrow Na[Ag(CN)_2]$ $Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Ag$
D.	Decomposition of iodide	s.	Boron : $BI_3 \xrightarrow{\Delta} B + \frac{3}{2} I_2$

58.

Column *X*	Column *Y*	Column *Z*
Invar	Fe, Ni	Watch spring
Nichrome	Co, Ni	Heating element
Stainless steel	Fe, Cr, Ni	Cutlery

59.

	Column *X* (Metals)		Column *Y* (Ores)
A.	Al	q.	Cryolite
B.	Cu	r.	Malachite
C.	Mg	s.	Carnalite
D.	Zn	p.	Calamine

60. A. Silver is extracted by amalgamation process

$$Ag + Hg \longrightarrow \underset{\text{Amalgam}}{Ag(Hg)} \xrightarrow{\text{Distillation}} Ag(s) + Hg(v)\uparrow$$

B. Calcium is extracted by electrolysis of fused $CaCl_2$.

C. Zinc is extracted by carbon reduction method

$$ZnO + C \longrightarrow Zn + CO$$

D. Iron is extracted by both carbon reduction method and CO reduction methods

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

E. Copper is extracted by self reduction methods

$$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$$
$$Cu_2O + Cu_2S \longrightarrow Cu + SO_2$$

61. **H_2S** Ag_2S (black) is formed on the surface.

62. $ZnO + C \xrightarrow[\text{sintering}]{\Delta} Zn + CO$ = Smelting

63. Hydration energy Energy required to break the crystal lattice during dissolving process comes from hydration. If lattice energy is very high and hydration energy is low, salt becomes sparingly soluble.

64. Zn Galvanisation involves coating of iron with zinc metal in order to prevent if from rusting.

65. Sn Cassiterite is an ore of tin.

66. Al Aluminium reduces Fe_2O_3 to Fe.

67. Lime, calcium phosphate In basic Bessemer process, the Bessemer converter is lined with lime but in acid Bessemer process, it is lined with silica. In basic Bessemer process, phosphorus is slagged off as calcium phosphate :

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
$$6CaO + P_4O_{10} \longrightarrow \underset{\text{Thomas slag}}{2Ca_3(PO_4)_2}$$

68. $K[Ag(CN)_2]$: $AgCl + 2KCN \longrightarrow K[Ag(CN)_2] + KCl$

69. True: Cu^+ is unstable

$$2Cu^+ \xrightarrow{H^+} Cu^{2+} + Cu$$

70. True Complex ($Na[AgCl_2]$) formation increases solubility of otherwise sparingly soluble AgCl.

71. True Iron is more electropositive than hydrogen

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

72. True : Solubility of silver halides decreases down in the group

Solubility : $AgF > AgCl > AgBr > AgI$

73. In crystalline state, $AlCl_3$ has rock-salt like structure with coordination number of Al = 6.

74. Four, the complex has formula $[Cu(H_2O)_4]SO_4 \cdot H_2O$

75. (a) $2AgBr + \underset{\substack{\text{Hydroquinone}\\\text{(developer)}}}{C_6H_4(OH)_2} \longrightarrow 2Ag + 2HBr + \underset{\text{Quinone}}{C_6H_4O_2}$

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

(b) $Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2SO_3 + \underset{\substack{\text{Colloidal}\\\text{sulphur}}}{S\downarrow}$

76. A_1 is basic copper carbonate ($Cu(OH)_2 \cdot CuCO_3$) while A_2 is Cu_2S. The confirmatory reactions are :

(i) $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} \underset{\text{Black}}{CuO} + CO_2\uparrow + H_2O$

(ii) $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{HCl} CuCl_2 + CO_2\uparrow + H_2O$

$$CuCl_2 \xrightarrow{KI} \underset{D}{Cu_2I_2}\downarrow + KCl + I_2$$

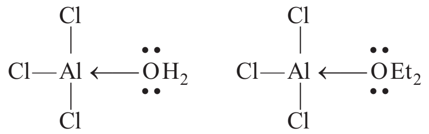
$$A_2 \xrightarrow{\text{Roasting}} Cu_2O + SO_2\uparrow$$

$$Cu_2S + Cu_2O \longrightarrow Cu + SO_2\uparrow$$

SO_2 is a reducing gas that gives green colour with acidified $K_2Cr_2O_7$ as

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 4H_2O$$

77. Anhydrous $AlCl_3$ is more soluble in diethyl ether as the oxygen atom of ether donate its lone-pair of electrons to the vacant orbital of Al in electron deficient $AlCl_3$. In case of hydrated $AlCl_3$, Al is not electron deficient as oxygen of water molecule has already donated its lone-pair of electrons to compensate electron deficiency of Al.



hydrated anhydrous

78. The reactions involved in the extraction of lead from galena (PbS) by self reduction are

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$
$$PbS + 2O_2 \longrightarrow PbSO_4 \text{ (side reaction)}$$
$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

In litharge (PbO), the oxidation state of Pb is +2

79. The common photographic film is coated with AgBr and during developing of photographic film, the unreacted AgBr is removed by $Na_2S_2O_3$ as

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

80. $4NaCN + Ag_2S \longrightarrow 2Na[Ag(CN)_2] + Na_2S$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

81. $2Cu + H_2O + CO_2 + O_2 \longrightarrow \underset{\substack{\text{Green}\\\text{(basic copper carbonate)}}}{Cu(OH)_2 \cdot CuCO_3}$

82. $C + O_2 \xrightarrow{2000°C} CO$

$$3CO + Fe_2O_3 \longrightarrow 2Fe + 3CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

83. $Al + NaOH \xrightarrow{H_2O} NaAlO_2 + \frac{3}{2}H_2$

84. $4KCN + Ag_2S \longrightarrow \underset{\substack{\text{Potassium}\\\text{dicyanoargentate (I)}}}{2K[Ag(CN)_2]} + K_2S$

85. Due to formation of protective, inert layer of Al_2O_3 on surface.

86. $Sn + 2KOH + 4H_2O \longrightarrow K_2[Sn(OH)_6] + 2H_2$

87. Sea water (contain $MgCl_2$) + $Ca(OH)_2$

$$\longrightarrow Mg(OH)_2\downarrow + CaCl_2(aq)$$

(i) $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

$$\xrightarrow[\text{Dryness}]{\text{Heat to}} MgCl_2(s)$$

(ii) $MgCl_2(s) \xrightarrow[\text{NaCl}]{\text{Fusion}} Mg^{2+} + 2Cl^- \xrightarrow{\text{electrolysis}} Mg$

(At cathode)

88. $7Cu + 20HNO_3 \longrightarrow 7Cu(NO_3)_2 + 4NO + 2NO_2 + 10H_2O$

89.
$$\left.\begin{array}{l} \underset{\text{Copper pyrite}}{2CuFeS_2} + O_2 \longrightarrow Cu_2S + 2FeS + SO_2 \\ 2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \\ 2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \\ FeS + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3} \end{array}\right\} \text{Roasting}$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \quad \text{Bessemerisation}$$

90.
$$Ag_2S + 2NaCN \longrightarrow 2AgCN + Na_2S$$
$$AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$$
$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

91. (i) Carbon monoxide :
$$C + O_2 \longrightarrow CO$$
$$CO + Fe_2O_3 \longrightarrow CO_2 + Fe$$

(ii)
$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

(iii) To improve electrical conductivity of melt.

(iv) A metal which is much more electropositive than Ag can only replace Ag^+ completely from $[Ag(CN)_2]^-$ as
$$Zn + 2[Ag(CN)_2]^- \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$$

(v) Chalcocite is a sulphide ore of copper, during roasting, SO_2 is liberated, which is not possible in calcination.

92. $2Au + 3HNO_3 + 11HCl \longrightarrow 2HAuCl_4 + 6H_2O + 3NOCl$

93. (i) If the metal is moderately electropositive, e.g. Fe, Sn, Pb or Cu, they can be obtained from their ore by chemical reduction methods.

However, if the metal is highly electropositive, e.g. Al, Mg etc., no reducing agent exist for reduction of their ions (Al^{3+}, Mg^{2+}) and they are obtained by electrolytic reduction of their molten salt.

(ii) Metals like Ge is required in high purity, can be readily melted and can easily crystallise out from the melt form.

94. AgBr is sensitive to visible light.
$$AgBr \xrightarrow{h\nu} Ag + \frac{1}{2}Br_2$$
A photographic plate coated with AgBr, when exposed to light, gets blackened due to the above reaction.

95. $Al + NaOH(aq) \longrightarrow NaAlO_2 + H_2$
$$NaAlO_2 + CO_2(aq) \longrightarrow Na_2CO_3 + Al(OH)_3 \downarrow$$
$$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + H_2O$$

96. In the first step, galena is heated in presence of O_2 (limited quantity) in a reverberatory furnace, where PbS is partially oxidised to PbO :
$$PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2$$
In the second step, more PbS is added and heated in absence of O_2, where the following self reduction takes place
$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$

97. $SnO_2 + 2C \longrightarrow Sn + 2CO(g)$, Carbon reduction method.

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20
Qualitative Analysis

Objective Questions I (Only one correct option)

1. An organic compound X showing the following solubility profile is **(2019 Main, 8 April I)**

$$X \begin{cases} \xrightarrow{\text{Water}} \text{Insoluble} \\ \xrightarrow{\text{5\% HCl}} \text{Insoluble} \\ \xrightarrow{\text{10\% NaOH}} \text{Soluble} \\ \xrightarrow{\text{10\% NaHCO}_3} \text{Insoluble} \end{cases}$$

(a) o-toluidine (b) oleic acid
(c) m-cresol (d) benzamide

2. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is **(2018 Main)**

(a) Zn (b) Ca (c) Al (d) Fe

3. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are **(2016 Adv.)**

$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\text{(Clear solution)}}{X} \xrightarrow{Ag^+} \underset{\text{(White ppt.)}}{Y} \xrightarrow{\text{With time}} \underset{\text{(Black ppt.)}}{Z}$$

(a) $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S
(b) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3, Ag_2S
(c) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag
(d) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4, Ag

4. In Carius method of estimation of halogens 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (atomic mass Ag $= 108$, Br $= 80$) **(2015 Main)**

(a) 24 (b) 36 (c) 48 (d) 60

5. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is **(2013 Adv.)**

(a) Fe (III) (b) Al (III)
(c) Mg (II) (d) Zn(II)

6. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates

(a) CuS and HgS (b) MnS and CuS **(2011)**
(c) MnS and NiS (d) NiS and HgS

7. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is **(2007, 3M)**

(a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+}

8. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula? **(2006)**

(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$
(c) $MgCl_2 \cdot MgSO_4$ (d) $MgSO_4$

9. $CuSO_4$ decolourises on addition of KCN, the product is

(a) $[Cu(CN)_4]^{2-}$ **(2006, 3M)**
(b) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$
(c) $Cu(CN)_2$
(d) CuCN

10. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl / NH_4OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4OH / NH_4Cl. **(2006, 3M)**

(a) $Zn(OH)_2$ (b) $Al(OH)_3$
(c) $Mg(OH)_2$ (d) $Ca(OH)_2$

11. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is **(2005, 1M)**

(a) Hg^{2+} (b) Bi^{3+} (c) Sn^{2+} (d) Pb^{2+}

12. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by **(2004, 1M)**

(a) Heating NH_4NO_2 (b) Heating NH_4NO_3
(c) $Mg_3N_2 + H_2O$ (d) $Na(\text{comp.}) + H_2O_2$

13. A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is **(2004, 1M)**

(a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-} (d) NO_3^-

14. $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell

$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution

$[X]$ and $[Y]$ are **(2003, 1M)**

(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

15. A gas X is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas Y. Identify X and Y. **(2002, 3M)**
(a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
(c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$

16. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a **(2000, 1M)**
(a) Hg_2^{2+} salt (b) Cr^{2+} salt (c) Ag^+ salt (d) Pb^{2+} salt

17. In nitroprusside ion the iron and NO exist as Fe (II) and NO^+ rather than Fe (III) and NO. These forms can be differentiated by **(1998, 2M)**
(a) estimating the concentration of iron
(b) measuring the concentration of CN
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound

18. An aqueous solution $FeSO_4 \cdot Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are **(1996, 1M)**
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and brown residue

19. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)^+]SO_4$. The oxidation state of iron is **(1987, 1M)**
(a) 1 (b) 2 (c) 3 (d) 0

20. Which one amongst the following pairs of ions cannot be separated by H_2S in dilute HCl? **(1986, 1M)**
(a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+}
(c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+}

21. The compound insoluble in acetic acid is **(1986, 1M)**
(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

22. The ion that cannot be precipitated by both HCl and H_2S is **(1982, 1M)**
(a) Pb^{2-} (b) Cu^+
(c) Ag^+ (d) Sn^{2+}

23. For the equilibrium, $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately **(2019 Main 11 Jan II)**
(a) -80 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 80 kJ mol^{-1} (d) -100 kJ mol^{-1}

Objective Questions II
(One or more than one correct option)

24. The correct option(s) to distinguish nitrate salts to Mn^{2+} and Cu^{2+} taken separately is (are) **(2018 Adv.)**
(a) Mn^{2+} shows the characteristic green colour in the flame test
(b) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium
(c) Only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium
(d) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions)

25. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is (are) **(2016 Adv.)**
(a) $CuCl_2$ (b) $BaCl_2$
(c) $Pb(OOCCH_3)_2$ (d) $Na_2[Fe(CN)_5NO]$

26. The pair(s) of ions where both the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are) **(2015 Adv.)**
(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}
(c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

27. For the given aqueous reaction which of the statement(s) is (are) true? Excess KI + $K_3[Fe(CN)_6] \xrightarrow{\text{Dilute } H_2SO_4}$

$$\text{Brownish-yellow solution} \xrightarrow{ZnSO_4} (\text{White precipitate + Brownish-yellow filtrate}) \xrightarrow{Na_2S_2O_3} \text{Colourless solution}$$

(2012)
(a) The first reaction is a redox reaction
(b) White precipitate is $Zn_3[Fe(CN)_6]_2$
(c) Addition of filtrate to starch solution gives blue colour
(d) White precipitate is soluble in NaOH solution

28. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are) **(2008, 4M)**
(a) NH_4NO_3 (b) NH_4NO_2
(c) NH_4Cl (d) $(NH_4)_2SO_4$

29. Which of the following statement(s) is(are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4? **(1998, 2M)**
(a) A deep red vapour is evolved
(b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(c) Chlorine gas is evolved
(d) Chromyl chloride is formed

30. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions ? **(1998, 2M)**
(a) Fe^{3+} gives brown colour with potassium ferricyanide
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives red colour with potassium thiocyanate
(d) Fe^{2+} gives brown colour with ammonium thiocyanate

31. The reagents, NH_4Cl and aqueous NH_3 will precipitate **(1991, 1M)**

(a) Ca^{2+} (b) Al^{3+} (c) Bi^{3+} (d) Mg^{2+}
(e) Zn^{2+}

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct Statement II is correct Statement II is a correct; explanation of Statement I
(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I.
(c) Statement I is correct; Statement II is incorrect.
(d) Statement I is incorrect; Statement II is correct.

32. **Statement I** Sulphate is estimated as $BaSO_4$, not as $MgSO_4$.

Statement II Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}. **(1998, 2M)**

33. **Statement I** A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing H_2S.

Statement II Solubility product of CdS is more than that of NiS. **(1989, 2M)**

Passage Based Questions

Passage 1

An aqueous solution of metal ion M_1 reacts separately with reagents Q and R in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion M_2 always forms tetrahedral complexes with these reagents. Aqueous solution of M_2 on reaction with reagent S gives white precipitate which dissolves in excess of S. The reactions are summarised in the scheme given below

$$\text{Tetrahedral} \xleftarrow[\text{excess}]{Q} M_1 \xrightarrow[\text{excess}]{R} \text{Square planar}$$

$$\text{Tetrahedral} \xleftarrow[\text{excess}]{Q} M_2 \xrightarrow[\text{excess}]{R} \text{Tetrahedral}$$

$$M_2 \xrightarrow{S\text{, stoichiometric amount}} \text{White precipitate} \xrightarrow[\text{excess}]{S} \text{Precipitate dissolves}$$

34. M_1, Q and R, respectively are

(a) Zn^{2+}, KCN and HCl (b) Ni^{2+}, HCl and KCN
(c) Cd^{2+}, KCN and HCl (d) Co^{2+}, HCl and KCN

35. Reagent S is

(a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4
(c) K_2CrO_4 (d) KOH

Passage 2

An aqueous solution of a mixture of two inorganic salts,when treated with dilute HCl, gave a precipitate (P) and filtrate (Q). The precipitate (P) was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

36. The precipitate P contains **(2013 Adv.)**

(a) Pb^{2+} (b) Hg_2^{2+} (c) Ag^+ (d) Hg^{2+}

37. The coloured solution S contains

(a) $Fe_2(SO_4)_3$ (b) $CuSO_4$ (c) $ZnSO_4$ (d) Na_2CrO_4

Passage 3

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH_3 dissolves O and gives an intense blue solution. **(2011)**

38. The metal rod M is

(a) Fe (b) Cu (c) Ni (d) Co

39. The compound N is

(a) $AgNO_3$ (b) $Zn(NO_3)_2$
(c) $Al(NO_3)_3$ (d) $Pb(NO_3)_2$

40. The final solution contains

(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$
(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$
(c) $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$
(d) $[Ag(NH_3)_2]^+$ and $[Ni(NH_3)_6]^{2+}$

Passage 4

p-amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown colouration due to the formation of Z.

41. The compound X, is **(2009, 1M)**

(a) $NaNO_3$ (b) NaCl
(c) Na_2SO_4 (d) Na_2S

42. The compound Y, is **(2009, 1M)**

(a) $MgCl_2$ (b) $FeCl_2$
(c) $FeCl_3$ (d) $ZnCl_2$

43. The compound Z, is **(2009, 1M)**

(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$
(c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

Fill in the Blanks

44. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is... **(1993, 1M)**

45. If metal ions of group III are precipitated by NH_4Cl and NH_4OH without prior oxidation by conc. HNO_3....... is not completely precipitated. **(1984, 1M)**

True/False

46. From the solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. **(1987, 1M)**

47. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. **(1985, 1/2M)**

Integer Answer Type Question

48. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2 the total number of black coloured sulphides is **(2014 Adv.)**

Subjective Questions

49. $$\underset{\text{(White fumes having smell)}}{B} \xleftarrow{\text{moist air}} \underset{M\,=\,\text{(Transition element colourless)}}{M\text{Cl}_4} \xrightarrow{\text{Zn}} \underset{\text{(Purple colour)}}{A}$$

Identify the metal M and hence $M\text{Cl}_4$. Explain the difference in colours of $M\text{Cl}_4$ and A. **(2005, 4M)**

50. $$Fe^{3+} \xrightarrow{\text{SCN}^- \text{ (excess)}} \text{Blood red } (A) \xrightarrow{\text{F}^- \text{ (excess)}} \text{Colourless } (B)$$

Identify A and B.

(i) Write IUPAC name of A and B.

(ii) Find out spin only magnetic moment of B. **(2005)**

51. A_1 and A_2 are two ores of metal M. A_1 on calcination gives black precipitate, CO_2 and water.

$$A_1 \xrightarrow{\text{Calcination}} \text{Black solid} + CO_2 + OH_2$$

$$A_1 \xrightarrow[\text{KI}]{\text{dil. HCl}} I_2 + \text{ppt}$$

$$A_2 \xrightarrow{\text{Roasting}} \text{Metal} + \text{Gas}$$

$$\text{Gas} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Green colour}$$

Identify A_1 and A_2. **(2004)**

52. A salt mixture consists of a yellow solid (A) and a colourless solid (B). The aqueous solution of the mixture

(i) On passing H_2S, we get a black precipitate of (C), which dissolves only in aqua-regia. On extraction and reaction with $SnCl_2$ a greyish white precipitate is obtained.

(ii) On treatment with ammonium hydroxide a reddish brown precipitate (D) is obtained.

The sodium extract of the solution gives the following tests:

(i) On reaction with $AgNO_3$ it gives a yellow precipitate which is insoluble in NH_3.

(ii) On shaking with $FeCl_3$ and CCl_4 a violet colouration in CCl_4 layer is obtained.

Mixture on performing flame test gives lilac colour. Identify the compounds (A), (B), (C) and (D). **(2003)**

53. When a white crystalline compound X is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate a yellow precipitate C is obtained.

When X is heated with NaOH solution, colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X. Write the equations of reactions involved. **(2002)**

54. A white substance A reacts with dilute H_2SO_4 to produce a colourless gas B and a colourless solution C. The reaction between B and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate D. The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify A, B, C, D and E. Write the equations of the reactions involved. **(2001, 10M)**

55. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. **(2000, 3M)**

56. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate A, which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate B. Identify the transition metal ion. Write the chemical reactions involved in the formation of A and B. **(2000, 4M)**

57. Write the chemical reactions associated with the 'brown ring test'. **(2000, 1M)**

58. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. **(1999, 3M)**

59. During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passed through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly. **(1998, 2M)**

60. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. **(1997)**

61. A soluble compound of a poisonous element M, when heated with Zn/H_2SO_4 gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. **(1997)**

62. A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper, while the gas (B) is a neutral oxide.

White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. **(1996, 3M)**

63. Gradual addition of KI solution of $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. **(1996, 2M)**

64. A scarlet compound A is treated with conc. HNO_3 to give a chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow ppt C. The brown ppt B on warming with conc. HNO_3 in the presence of $Mn(NO_3)_2$ produces a pink coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. **(1995, 4M)**

65. An orange solid A on heating gave a green residue B, a colourless gas C and water vapour. The dry gas C on passing over heated Mg gave a white solid D. D on reaction with water gave a gas E which formed dense white fumes with HCl. Identify A to E and give the reaction involved. **(1993, 3M)**

66. The acidic aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^-, by the following two steps :

$$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow \ldots + [Fe(H_2O)_6]^{3+}$$

$$[Fe(H_2O)_6]^{2+} + \ldots \longrightarrow \ldots\ldots + H_2O$$

Complete and balance the equation. **(1993, 2M)**

67. A light bluish green crystalline compound responds to the following tests

(i) Its aqueous solution gives a brown precipitate or colouration with $K_2[HgI_4]$.

(ii) Its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$.

(iii) Its solution in hydrochloric acid gives a white precipitate with $BaCl_2$.

Identify the ions present and suggest the formula of the compound. **(1992, 4M)**

68. In the following reaction, identify the compounds/reaction conditions represented by the alphabets A and B.

$$PbS \xrightarrow[\text{air}]{\text{Heat in}} A + PbS \xrightarrow{B} Pb + SO_2$$ **(1991, 1M)**

69. Give reason in one or two sentences for the following

"The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from other. **(1991, 2M)**

70. The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl.

On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of A and B. **(1991, 4M)**

71. Write the balanced chemical equations for the following

(i) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium.

(ii) Cobalt (II) solution reacts with KNO_2 in acetic acid medium. **(1989, 2M)**

72. Give reasons for, "The colour of mercurous chloride, Hg_2Cl_2, changes from white to black when treated with ammonia." **(1988, 1M)**

73. A mixture of two salts was treated as follows :

(i) The mixture was heated with maganese dioxide and concentrated sulphuric acid, when yellowish green gas was liberated.

(ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.

(iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.

(iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.

Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii). **(1987, 5M)**

74. Write balanced equation for the following "potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid." **(1987, 1M)**

75. Mention the products formed in the following:

(i) Zinc oxide is treated with excess of sodium hydroxide solution.

(ii) Iodine is added to a solution of stannous chloride.

(iii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. **(1986, 3M)**

76. What happen when

(i) hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.

(ii) aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess.

(iii) tin is treated with concentrated nitric acid.

(iv) $CrCl_3$ solution is treated with sodium hydroxide and then with hydrogen peroxide.

(v) Pb_3O_4 is treated with nitric acid. **(1985, 5M)**

77. Write down the balanced equations for the reactions, when, 'a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. **(1985, 1M)**

78. When 16.8 g of white solid, *X* were heated, 4.4 g of acid gas *A*, that turned lime water milky was driven off together with 1.8 g of a gas *B* which condensed to a colourless liquid.

The solid that remained, *Y*, dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate *Z*. The precipitate effervesces with acid giving of carbon dioxide. Identify *A, B* and *Y* and write down the equation for the thermal decomposition of *X*. **(1984, 4M)**

79. Compound *A* is a light green crystalline solid. It gives the following tests

(i) It dissolves in dilute sulphuric acid. No gas is produced.

(ii) A drop of $KMnO_4$ is added to the above solution. The pink colour disappears.

(iii) Compound *A* is heated strongly. Gases *B* and *C*, with pungent smell, come out. A brown residue *D* is left behind.

(iv) The gas mixture (*B* and *C*) is passed into a dichromate solution. The solution turns green.

(v) The green solution from step (iv) gives a white precipitate *E* with a solution of barium nitrate.

(vi) Residue *D* from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance.

Name the compound *A, B, C, D* and *E*. **(1980, 4M)**

80. Explain the following in not more than two sentences.
A solution of $FeCl_3$ in water gives a brown precipitate on standing. **(1980, 1M)**

81. The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in the presence of hydrochloric acid but not in nitric acid. Explain. **(1979, 2M)**

82. A white amorphous powder *A* on heating yields a colourless, non-combustible gas *B* and a solid *C*. The later compound assumes a yellow colour on heating and changes to white on cooling. *C* dissolves in dilute hydrochloric acid and the resulting solution gives a white precipitate with $K_4Fe(CN)_6$ solution. *A* dissolves in dil. HCl with the evolution of gas, which is identical in all respect with *B*.

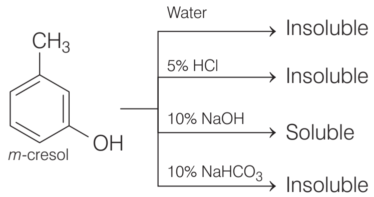
The gas *B* turns lime water milky, but the milkiness disappears with the continuous passage of gas. The solution of *A* as obtained above, gives a white ppt *E* on addition of NaOH solution, which dissolves on further addition of base. Identify the compounds *A*, *B*, *C, D* and *E*. **(1979, 4M)**

Answers

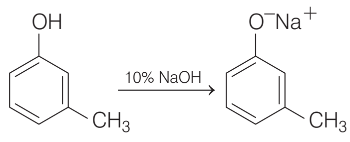
1. (c)	**2.** (c)	**3.** (a)	**4.** (a)	**29.** (a, b, c, d)	**30.** (b, c)	**31.** (b, c)	**32.** (b)
5. (d)	**6.** (a)	**7.** (b)	**8.** (a)	**33.** (c)	**34.** (b)	**35.** (d)	**36.** (d)
9. (b)	**10.** (a)	**11.** (b)	**12.** (a)	**37.** (d)	**38.** (b)	**39.** (a)	**40.** (c)
13. (b)	**14.** (a)	**15.** (c)	**16.** (d)	**41.** (d)	**42.** (c)	**43.** (b)	**44.** CrO_2Cl_2
17. (c)	**18.** (c)	**19.** (a)	**20.** (a)	**45.** Fe^{3+}	**46.** True	**47.** True	**48.** (6 or 7)
21. (c)	**22.** (c)	**23.** (c)	**24.** (b,d)	**50.** (5.92 BM)			
25. (a)	**26.** (c, d)	**27.** (a, c, d)	**28.** (a, b)				

Hints & Solutions

1. *m*-cresol is the organic compound that shows the following solubility profile.



m-cresol on reaction with 10% NaOH forms 3-methyl sodiumphenoxide ion.



It does not react with H_2O, 5% HCl and 10% $NaHCO_3$.

Oleic acid ($C_{18}H_{34}O_2$) is soluble in 10% NaOH and 10% $NaHCO_3$ due to the presence of COOH group.

Benzamide ($C_6H_5\overset{\overset{O}{||}}{C}NH_2$) is insoluble in 5% HCl, 10% NaOH and 10% $NaHCO_3$ due to the presence —$CONH_2$ group. ***o*-toluidine** is soluble in 5%. HCl due to presence of basic group (—NH_2) attached to ring.

2. Among the given metals Al forms white gelatinous ppt. with NaOH.

Hence, the probable metal can be Al. This ppt. is dissolved in excess of NaOH due to the formation of sodium metal Aluminate. Both the reactions are shown below.

$$Al^{3+} \xrightarrow{NaOH} \underset{\substack{\text{White gelatinous} \\ \text{ppt. } (X) \text{ of} \\ \text{aluminium} \\ \text{hydroxide}}}{Al(OH)_3} \xrightarrow{\text{Excess of NaOH}} \underset{\substack{\text{Sodium} \\ \text{metaaluminate)} \\ \text{soluble}}}{NaAlO_2}$$

Aluminium hydroxide on strong heating gives alumina (Al_2O_3) which is used as an adsorbent in chromatography. This reaction can be seen as :

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Thus, metal M is Al.

Ca, being below sodium in electrochemical reactivity series, cannot displaces Na from its aqueous solution.

Zn reacts with NaOH to form sodium zincate which is a soluble compound.

Fe reacts with sodium hydroxide to form tetrahydroferrate (II) sodium which is again a soluble complex.

3. $2S_2O_3^{2-} + Ag^+ \longrightarrow \underset{\text{(Clear solution)}}{[Ag(S_2O_3)_2]^{3-}}$

$[Ag(S_2O_3)_2]^{3-} + 3Ag^+ \longrightarrow \underset{\text{(White ppt.)}}{2Ag_2S_2O_3}$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{(Black ppt.)}}{Ag_2S} + H_2SO_4$

4. Given, Weight of organic compound = 250 mg

Weight of AgBr = 141 mg

$\therefore$ According to formula of % of bromine by Carius method

$$\% \text{ of Br} = \frac{\text{Atomic weight of Br}}{\text{Molecular weight of AgBr}} \times \frac{\text{Weight of AgBr}}{\text{Weight of organic bromide}} \times 100$$

$$\therefore \% \text{ of Br} = \frac{80}{188} \times \frac{141}{250} \times 100 = \frac{1128000}{47000} = 24\%$$

5. PLAN K_{sp}(ZnS) is very high and Zn^{2+} is precipitated as ZnS by high concentration of S^{2-} formed when H_2S is passed in ammoniacal solution.

$$H_2S \rightleftharpoons Zn^+ + S^{2-} \quad \text{(I)}$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad \text{(II)}$$

Reaction (I) is favoured in forward side if H^+ is removed immediately by OH^- (NH_4OH).

$$Zn^{2+} + S^{2-} \longrightarrow \underset{\text{White ppt}}{ZnS\downarrow}$$

Fe^{3+} and Al^{3+} are precipitated as hydroxide.

6. In acidic medium, H_2S is very feebly ionised giving very small concentration of sulphide ion for precipitation. Therefore, the most insoluble salts CuS and HgS are precipitated only.

7. $Hg^{2+} + 2I^- \longrightarrow HgI_2$ (red)

$HgI_2 + 2KI \longrightarrow \underset{\text{Soluble}}{K_2[HgI_4]}$

$Hg^{2+} + Co(SCN)_2 \longrightarrow \underset{\text{Blue}}{Co[Hg(SCN)_4]}$

8. $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow \underset{\text{White}}{Mg(NH_4)PO_4\downarrow} + Na_2SO_4 + H_2O$

9. $CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$

$\underset{\text{Unstable}}{2Cu(CN)_2} \longrightarrow 2Cu(CN) + \begin{array}{c} CN \\ | \\ CN \end{array}$ (Cyanogen)

$CuCN + 3KCN \longrightarrow 3K^+ + [Cu(CN)_4]^{3-}$

10. $Zn^{2+} + 2H_2O \longrightarrow \underset{\text{White}}{Zn(OH)_2\downarrow} + 2H^+$

11. $Bi^{3+} + 3I^- \longrightarrow \underset{\text{Black}}{BiI_3\downarrow} \xrightarrow[\text{excess}]{I^-} \underset{\text{Orange solution}}{[BiI_4]^-}$

12. Both $(NH_4)_2Cr_2O_7$ and NH_4NO_2 on heating gives nitrogen gas.

13. A sodium salt of an unknown anion when treated with MgCl gives white precipitate ($MgCO_3$) only on boiling. Hence, the action must be HCO_3^- ion.

$$MgCl_2 + 2NaHCO_3 \xrightarrow{\Delta} MgCO_3 + 2NaCl + H_2O + CO_2$$

14. $\underset{X}{SO_3^{2-}} + H_2SO_4 \longrightarrow \underset{Y}{SO_2\uparrow} + H_2O + SO_4^{2-}$

SO_2 is a colourless gas with irritating odour.

$$\underset{Y}{3SO_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{Green solution}}{Cr_2(SO_4)_3} + H_2O$$

15. $\underset{X}{Cl_2} + H_2O \longrightarrow HCl + HOCl$

$HCl + AgNO_3 \longrightarrow AgCl\downarrow \text{(white)} + HNO_3$

$2HCl + Mg \longrightarrow MgCl_2 + H_2(g)\uparrow$

16. $PbCl_2$ is soluble in hot water and PbS (black) is formed on passing $H_2S(g)$ through acidic solution.

17. Fe(II) and Fe(III) will have different values of magnetic moment due to different number of unpaired electrons in their d-orbitals.

18. Yellow filtrate contains CrO_5 and brown residue contain Fe_2O_3.

19. The total positive valency is +2 (because the only anion is SO_4^{2-}). Therefore, oxidation state of Fe must be +1.

20. Both Bi^{3+} and Sn^{4+} belongs to same analytical group II.

21. CaC_2O_4 is insoluble in acetic acid. This distinguishes Ca^{2+} from Ba^{2+} ion.

22. Ag^+ is precipitated by HCl only while all others are precipitated by passing H_2S in the presence of HCl.

23. We know that,

$$\Delta G^\circ = -2.303\,RT \log K$$

Also, given equilibrium is

$$2H_2O \rightleftharpoons H_3O^+ + \bar{O}H$$

$$[H^+][OH^-] = 10^{-14} \quad \text{or} \quad K = 10^{-14}$$

$$\therefore \quad \Delta G^\circ = -2.303 \times 8.314\,JK^{-1}mol^{-1} \times 298K \times \log 10^{-14}$$

$$= 79881.8\,J\,mol^{-1} = 79.8\,kJ \approx 80\,kJ\,mol^{-1}$$

24. Statement wise explanation is

Statement (a) Mn^{2+} produces yellow-green colour in flame test while Cu^{2+} produces bluish-green colour in flame test. Thus, due to the presence of green colour in both the cases, flame test is not the suitable method to distinguish between nitrate salts of Cu^{2+} and Mn^{2+}. Hence this statement is wrong.

Statement (b) Cu^{2+} belong to group II of cationic or basic radicals. It gives black ppt. of CuS if H_2S is passed through it in the presence of acid (e.g HCl). Mn^{2+} does not show this property hence this can be considered as a suitable method to distinguish between Mn^{2+} and Cu^{2+}.

Hence, this statement is correct.

Statement (c) In faintly basic medium when H_2S is passed both Cu^{2+} and Mn^{2+} forms precipitates. Thus, it is not suitable method to distinguish between them.

Hence, this statement is incorrect

Statement (d) The standard reduction potential of Cu^{2+}/Cu is +0.34 V while that of Mn^{2+}/Mn is –1.18V. This can be used to distinguish between Cu^{2+} and Mn^{2+}. In general less electropositive metals have higher SRP.

Hence, this statement is correct.

25. $S^{2-} + CuCl_2 \longrightarrow CuS\downarrow$ (black ppt.)

$SO_4^{2-} + CuCl_2 \longrightarrow$ Soluble, Thus

(a) $CuCl_2$ selectively precipitates S^{2-}.

(b) $S^{2-} + BaCl_2 \longrightarrow BaS\downarrow$ (soluble)

$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4\downarrow$ (white ppt.)

(b) precipitates SO_4^{2-} and not S^{2-}.

(c) $S^{2-} + Pb^{2+} \longrightarrow PbS\downarrow$ (black ppt.)

$SO_4^{2-} + Pb^{2+} \longrightarrow PbSO_4\downarrow$ (white ppt.)

S^{2-} and SO_4^{2-}, both are precipitated.

(d) $S^{2-} + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)]_5NO} \longrightarrow \underset{\text{(Purple colour)}}{Na_4[Fe(CN)]_5NOS]}$

But no colour with SO_4^{2-}.

26. Only radicals of I and II group of qualitative analysis get precipitated with H_2S in the presence of dilute HCl.

(*c*) $Cu^{2+} + H_2S \xrightarrow{H^+} \underset{\text{Black}}{CuS\downarrow}$

$Pb^{2+} + H_2S \xrightarrow{H^+} \underset{\text{Black}}{PbS\downarrow}$

(*d*) $Hg^{2+} + H_2S \xrightarrow{H^+} \underset{\text{Black}}{HgS\downarrow}$

$Bi^{3+} + H_2S \xrightarrow{H^+} \underset{\text{Brown ppt}}{Bi_2S_3\downarrow}$

Ba^{2+}, Zn^{2+} and Fe^{3+} are not precipitated as sulphide.

27. $K_3[\overset{+3}{Fe}(CN)_6] + KI\text{ (excess)} \longrightarrow$

$K_4[\overset{+2}{Fe}(CN)_6] + \underset{\substack{\text{Brownish yellow}\\\text{solution}}}{KI_3}\text{(redox)}$

$K_4[Fe(CN)_6] + ZnSO_4 \rightarrow K_2Zn_3[Fe(CN)_6]_2$

or $\underset{\text{White ppt}}{K_2Zn[Fe(CN)_6]}$

$\underset{\substack{\text{Brownish}\\\text{yellow}\\\text{filtrate}}}{I_3^-} + 2Na_2S_2O_3 \longrightarrow \underset{\substack{\text{Clear}\\\text{solution}}}{Na_2S_4O_6} + 2NaI + \underset{\substack{\text{(Turns starch}\\\text{solution}\\\text{blue)}}}{I_2}$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as

$K_2Zn[Fe(CN)_6] + NaOH \longrightarrow [Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-}$

28. $NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$

$NH_4NO_2 + NaOH \longrightarrow NaNO_2 + NH_3 + H_2O$

29. When mixture of NaCl is heated with $K_2Cr_2O_7$ in concentrated H_2SO_4, red vapour of chromyl chloride (CrO_2Cl_2) is produced. Vapours of chromyl chloride when passed through NaOH, solution turns yellow due to formation of Na_2CrO_4. Some chlorine gas is also evolved owing to the following side reaction :

$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2(g)\uparrow + 2Cr^{3+} + 7H_2O$

30. The blue precipitate of Fe^{2+} ion with potassium ferricyanide is due to formation of Turnbull's blue $KFe[Fe(CN)_6]$.

$Fe^{2+} + K_3[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + 2K^+$

The red colour of Fe^{3+} ion with potassium thiocyanate is due to formation of $[Fe(SCN)_3]$.

$Fe^{3+} + 3KSCN \longrightarrow \underset{\text{Red coloured}}{[Fe(SCN)_3]} + 3K^+$

31. Both Al^{3+} and Bi^{3+} are precipitated as their hydroxides.

32. As $MgSO_4$ is soluble in water, so not used for estimation of SO_4^{2-} ion.

33. Cation Cd^{2+} belongs to group II while Ni^{2+} belongs to group III of analytical group. Group II radicals are precipitated by passing $H_2S(g)$ through acidic solution of salt but radicals of group III are precipitated by passing $H_2S(g)$ in NH_3/NH_4Cl buffer solution of salt due to greater solubility products of later salts.

34. **PLAN** This problem can be solved by using concept of chemical reactions of transition metal ions (,) colour and structure of transition metal compounds.

Here, among given four option Ni^{2+} and Zn^{2+} has ability to form tetrahedral as well as square planar complex depending upon types of reagent used.

Ni^{2+} on reaction with KCN forms square planar complex $[Ni(CN)_4]^{2-}$ due to strong field strength of CN.

$Ni^{2+} + KCN \longrightarrow \underset{\text{Square planar}}{[Ni(CN)_4]^{2-}}$

While on reaction with HCl, Ni^{2+} forms stable tetrahedral complex $[Ni(Cl)_4]^{2-}$.

Zn^{2+}, on the other hand, on reaction with KCN as well as HCl produces tetrahedral complex because of its d^{10} electronic configuration.

$Zn^{2+} \xrightarrow{HCl} [ZnCl_4]^{2-}$

$Zn^{2+} \xrightarrow{KCN} [Zn(CN)_4]^{2-}$

$Zn^{2+} \xrightarrow[\text{excess}]{KOH} \underset{\text{White ppt}}{[Zn(OH)_4]^{2-}}$

Complete reaction sequence can be shown as

$$\underset{\text{Tetrahedral}}{[NiCl_4]^{2-}} \xleftarrow[\text{excess}]{HCl(Q)} \underset{(M_1)}{Ni^{2+}} \xrightarrow[\text{excess}]{KCN(R)} \underset{\text{Square planar}}{[Ni(CN)_4]^{2-}}$$

$$\underset{\text{Tetrahedral}}{[ZnCl_4]^{2-}} \xleftarrow[\text{excess}]{HCl(Q)} \underset{(M_2)}{Zn^{2+}} \xrightarrow[\text{excess}]{KCN(R)} \underset{\text{Tetrahedral}}{[Zn(CN)_4]^{2-}}$$

$$Zn^{2+} \xrightarrow{KOH\,(s)} \underset{\text{White ppt}}{Zn(OH)_2} \xrightarrow[\text{excess}]{KOH} \underset{\text{Soluble}}{[Zn(OH)_4]^{2-}}$$

35. Zn^{2+} on treatment with excess of KOH produces $[Zn(OH)_4]^{2-}$.

36, 37. PLAN $PbCl_2$ is soluble in hot water.

In ammoniacal medium, cations of group III and IV may be precipitated as hydroxide or sulphide and dissolved in H_2O_2 due to oxidation.

$$\text{Mixture of two inorganic salts} \xrightarrow[\text{(ii) Filter}]{\text{(i) HCl}} \text{Filtrate} + \text{ppt}$$

$$\underset{\underset{(S)}{\text{Yellow}}}{CrO_4^{2-}} \xleftarrow[NaOH]{H_2O_2} \underset{\text{ppt}}{Cr(OH)_3} \xleftarrow{NH_4OH/H_2S} \text{Filtrate}$$

Thus, **Q. 35.** P is Pb^{2+}. **Q. 36.** S is Na_2CrO_4.

38. Appearance of blue colour on addition of the metal rod M to the solution of N is an indication that metal may be Cu. Later formation of white precipitate on addition of NaCl and dissolution of this precipitate in aqueous ammonia confirm that while precipitate is of AgCl. This implies that the solution N is of $AgNO_3$. This confirm that the metal M is only Cu.

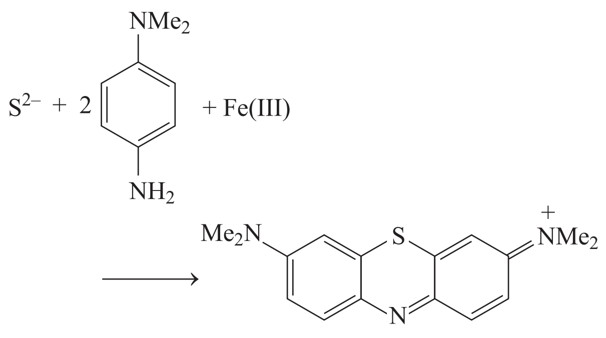
39. The compound N is $AgNO_3$, explained above.

40. Since, in the beginning, concentrated $AgNO_3$ solution was taken, some $AgNO_3$ remain in solution which gives white precipitate of AgCl on addition of NaCl. The precipitate finally dissolve in ammonia and Cu^{2+} present in solution also forms complex with ammonia as

$$Cu(NO_3)_2 + 4NH_3(aq) \rightarrow \underset{\text{Blue}}{[Cu(NH_3)_4]^{2+}} + 2NO_3^-$$

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

The comprehension describing methylene-blue test.



Blue solution

Therefore,

41. X is Na_2S.

42. Y is $FeCl_3$.

43. Compound Z is $Fe[Fe(CN)_6]$.

44. Heating chloride salt with $K_2Cr_2O_7$ in conc. H_2SO_4 gives off a deep vapour of chromyl chloride (CrO_2Cl_2).

45. Because $Fe(OH)_2$ is soluble.

46. ZnS is soluble in dil. HCl but CuS does not dissolve in dil. HCl.

47. In absence of NH_4Cl, both $Fe(OH)_3$ and $Mg(OH)_2$ will be precipitated.

48. From qualitative analysis of the different metal ions it is found that PbS, CuS, HgS, Ag_2S, NiS, CoS are black coloured.

MnS — dirty pink/buff coloured, SnS_2—yellow coloured.

Bi_2S_3 — brown/black (brownish black) coloured.

Hence, correct integer is (6 or 7).

49. $$\underset{\text{Colourless}}{MCl_4} \xrightarrow{Zn} \text{Purple coloured compound } (A)$$

$$\underset{\text{Transition metal}}{M} \xrightarrow[\text{Air}]{\text{Moist}} B \text{ (white fumes)}$$

$\Rightarrow$ $M = Ti$, $A = [Ti(H_2O)_6]^{3+}$; $B = TiO_2$

Ti (IV) contains no d-electron, while d-d transition of single electron of Ti (III) will cause colour change.

50. (i) $$Fe^{3+} + 3SCN^- \longrightarrow \underset{\underset{A}{\text{Iron (III) thiocyanate}}}{Fe(SCN)_3} \text{ (blood red colouration)}$$

$$Fe(SCN)_3 + F^- \text{ (excess)} \longrightarrow \underset{\underset{B}{\text{(Hexafluoroferrate)}}}{[FeF_6]^{3-}} + 3SCN^-$$

(ii) Magnetic moment $(\mu_S) = \sqrt{n(n+2)}$ BM

$= \sqrt{35}$ BM $= 5.92$ BM

51. $A_1 = Cu(OH)_2 \cdot CuCO_3$ and $A_2 = Cu_2S$

$$A_1 \xrightarrow{\text{Calcination}} \underset{\text{Black}}{2CuO} + CO_2 + H_2O$$

$$A_1 \xrightarrow{\text{Dil. HCl}} CuCl_2 + CO_2 + H_2O$$

$$2CuCl_2 + 4KI \longrightarrow 2CuI + I_2 + 4KCl$$

$$2Cu_2S\,(A_2) + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2$$

52. $$\underbrace{A + B}_{\text{Mixture}} \longrightarrow \text{lilac colour in flame}$$

(i) $$\underbrace{A + B}_{\text{Mixture}} \xrightarrow{H_2S} \underset{\text{Black}}{C\downarrow}$$

$$C \xrightarrow[\text{in } aqua\text{-}regia]{\text{Soluble}} \text{Soluble} \xrightarrow{\text{Evaporation}} \text{Residue} \xrightarrow{SnCl_2} \text{Greyish black} \downarrow (D)$$

$\Rightarrow$ C is HgS.

(ii) $\underbrace{A + B}_{\text{Solution of mixture}} \xrightarrow{NH_4OH}$ Brown ppt.

Sodium extract $\xrightarrow{AgNO_3}$ Yellow ppt. $\xrightarrow{NH_3}$ Insoluble

Sodium extract of salt $\xrightarrow{CCl_4/FeCl_3}$ Violet layer

$\Rightarrow \quad A = KI$ and $B = HgI_2$.

53. $X = NH_4Cl$; $A = CrO_2Cl_2$; $B = Na_2CrO_4$; $C = PbCrO_4$;

$D = H_2N(HgO)HgI$.

Reactions involved :

(i) $4NH_4Cl(X) + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2\ (A) + 4NH_4HSO_4 + 2KHSO_4 + 3H_2O$

(ii) $CrO_2Cl_2\,(A) + 2NaOH \longrightarrow Na_2CrO_4\ (B) + 2HCl$

(iii) $Na_2CrO_4\ (B) + (CH_3COO)_2Pb \longrightarrow PbCrO_4\downarrow (C) + 2CH_3COONa$

(iv) $NH_4Cl\ (X) + NaOH \longrightarrow NaCl + H_2O + NH_3$

(v) $2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2N(HgO)HgI\ (D) + 7KI + 2H_2O$

54. Since, the white substance A gives a colourless gas B with dil. H_2SO_4, such gas may be H_2S. So, the substance A may be a metal sulphide (Na/K/Zn, etc.)

When H_2S gas reacts with acidified $K_2Cr_2O_7$, it gives green coloured solution of $Cr_2(SO_4)_3$ alongwith slightly yellow ppt of D as sulphur.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + \underset{D}{3S} + 7H_2$$

S on burning in air gives SO_2 (E). Substance E on reaction with B (H_2S) produces D (s) :

$$\underset{B}{2H_2S} + \underset{E}{SO_2} \longrightarrow 2H_2O\ (l) + \underset{D}{3S\downarrow}$$

Anhydrous $CuSO_4$ produces blue colour in water.

Solution C produces ppt first with $NH_3/NaOH$ which dissolve in excess $NH_3/NaOH$. Hence, A must be ZnS.

$$\underset{A}{ZnS} + \text{dil. } H_2SO_4 \longrightarrow \underset{C}{ZnSO_4(aq)} + H_2S(g)$$

$$\underset{C}{ZnSO_4} + 2NaOH \longrightarrow \underset{\text{White}}{Zn(OH)_2\downarrow} + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \longrightarrow [Zn(OH)_4]^{2-} + 2Na^+$$

55. $$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

$$CoO + B_2O_3 \xrightarrow{\Delta} \underset{\text{Blue}}{Co(BO_2)_2}$$

56. The transition metal is Cu^{2+}. The compound is $CuSO_4 \cdot 5H_2O$. It dissolves in water to give blue coloured solution due to presence of Cu^{2+}. On passing $H_2S(g)$ in acid medium of salt solution black precipitate of CuS is obtained which is not soluble in aqueous KOH solution.

$$CuSO_4 + H_2S \xrightarrow{H^+} \underset{\text{black}}{CuS\downarrow} + H_2SO_4$$

On adding KI solution to aqueous solution of $CuSO_4$, yellow solution of CuI_2 is formed in the beginning which decompose into white ppt of CuI.

$$CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$$

$$2CuI_2 \longrightarrow \underset{\text{White}}{2CuI\downarrow} + I_2$$

57. $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$FeSO_4 + NO \longrightarrow \underset{\substack{\text{Brown ring}\\ \text{(nitrosoferrous sulphate)}}}{[Fe(NO)SO_4]}$$

58. NaI on reaction with HgI_2 gives a complex salt :

$$2NaI + HgI_2 \rightleftharpoons Na_2[HgI_4]$$

The orange colour is due to residual HgI_2. On addition of excess NaI, whole HgI_2 is converted to complex $Na_2[HgI_4]$ as colour disappear. The orange colour of HgI_2 reappear due to conversion of $Na_2[HgI_4]$ into HgI_2 on treatment with NaOCl.

$$3Na_2[HgI_4] + 2NaOCl + 2H_2O \longrightarrow 3HgI_2 + 2NaCl + 4NaOH + 2NaI$$

59. K_{sp} (solubility product) of CuS is less than K_{sp} of ZnS. On passing $H_2S(g)$ in acidic solution, dissociation of H_2S is suppressed due to common ion effect and it provide small concentration of S^{2-}, sufficient for precipitation of CuS but insufficient for precipitation of ZnS.

60. $$Al_2S_3 + 6H_2O \longrightarrow 2Al(OH)_3\downarrow + \underset{\text{Foul odour}}{3H_2S\uparrow}$$

61. The poisonous element M may be As. On the basis of given information :

$$AsCl_3 + 6H \xrightarrow[H_2SO_4]{Zn} \underset{N}{AsH_3} + 3HCl$$

$$2AsH_3 \xrightarrow{\Delta} \underset{M}{2As} + 3H_2\uparrow$$

62. $$\underset{\text{Inorganic salt}}{A} \xrightarrow{250°C} \underset{\text{Neutral oxide}}{B} + \underset{\substack{\text{Neutral oxide}\\ \text{(liquid)}}}{C}$$

Oxide C is liquid and neutral to litmus, so it is H_2O. White phosphorus burns in excess of B to give P_4O_{10}.

Therefore, B is N_2O.

$$NH_4NO_3\ (A) \xrightarrow{\Delta} \underset{B}{N_2O} + 2H_2O(l)$$

$$P_4 + 10N_2O \longrightarrow P_4O_{10} + 10N_2$$

63. On addition of KI solution to a $Bi(NO_3)_3$ solution, firstly a dark brown precipitate of BiI_3 is formed that dissolve in excess of KI forming a clear yellow solution of BiI_4^- :

$$\underset{}{Bi^{3+}} + 3I^- \longrightarrow \underset{\text{Dark brown}}{BiI_3\downarrow} \xrightarrow{I^-} \underset{\text{Clear yellow solution}}{BiI_4^-}$$

64. $$\underset{\text{Scarlet}}{A\,(Pb_3O_4)} \xrightarrow{C{\cdot}HNO_3} \underset{\text{Chocolate}}{B\,(PbO_2)} \xrightarrow{\text{Filtered}} \underset{\text{Filtrate}}{Pb(NO_3)_2}$$

Filtrate is neutralised with NaOH and on reaction with KI, gives yellow ppt of PbI_2.

$$Pb(NO_3)_2 + 2KI \longrightarrow \underset{\text{Yellow}}{PbI_2\downarrow} + 2KNO_3$$

PbO_2 on warming with conc. HNO_3 in presence of $Mn(NO_3)_2$ produced pink solution due to formation of $Pb(MnO_4)_2$ (I).

$$5PbO_2 + 2Mn(NO_3)_2 + 4HNO_3 \longrightarrow Pb(MnO_4)_2 + 4Pb(NO_3)_2 + 2H_2O$$

$\Rightarrow$ $A = Pb_3O_4$, $B = PbO_2$, $C = PbI_2$ and $D = Pb(MnO_4)_2$.

65. $$\underset{\text{Orange solid}}{A} \xrightarrow{\Delta} \underset{\text{Green}}{B\downarrow} + \underset{\text{Colourless}}{C\uparrow} + H_2O(v)\uparrow$$

$$C + Mg \longrightarrow D \text{ (white solid)}$$

$$D + H_2O \longrightarrow E\,(g) \xrightarrow{HCl} \text{White fumes.}$$

Hence, E must be ammonia gas so D must be Mg_3N_2 and C is $N_2(g)$. This N_2 is obtained on strong heating of $(NH_4)_2Cr_2O_7$ because $(NH_4)_2Cr_2O_7$ is orange solid and produces green Cr_2O_3 residue on heating.

$$\underset{\text{Orange }(A)}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{Green }(B)}{Cr_2O_3} + \underset{C}{N_2} + 4H_2O$$

$$N_2 + Mg \xrightarrow{\Delta} \underset{D}{Mg_3N_2} \xrightarrow{H_2O} \underset{E}{NH_3} + Mg(OH)_2$$

$$\underset{E}{NH_3} + HCl \longrightarrow NH_4Cl \text{ (white fumes)}$$

66. $$3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \longrightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$$

67. (i) Brown precipitate or colour with K_2HgI_4, indicates the presence of NH_4^+ ion.

(ii) Aqueous Fe(II) solution gives a blue colour with $K_3[Fe(CN)_6]$ due to formation of $Fe[Fe(CN)_6]^-$ ion :

$$Fe^{2+} + Fe(CN)_6^{3-} \longrightarrow \underset{\text{Blue colouration}}{Fe[Fe(CN)_6]^-}$$

(iii) Aqueous solution of SO_4^{2-} ion in HCl gives white ppt with $BaCl_2$ solution.

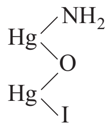
$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4\downarrow + 2Cl^-$$

68. $$PbS \xrightarrow[\text{air}]{\text{Heat in}} \underset{A}{PbO} + PbS \xrightarrow[\text{absence of air}]{\text{Heat in}} Pb + SO_2$$

69. In excess of NaOH, $Al(OH)_3$ dissolves forming $NaAlO_2$ while $Fe(OH)_3$ remains insoluble.

70. Formation of a reddish-brown precipitate with alkaline K_2HgI_4 solution indicates the presence of NH_4^+ ion and the gas liberated is ammonia :

$$NH_4^+ + OH^- \longrightarrow H_2O + NH_3(g)$$

$2K_2HgI_4 + 3NaOH + NH_4^+ \longrightarrow$  $\downarrow$

$$+ 4KI + 3NaI + 3OH^-$$

On treatment with $BaCl_2$, a white precipitate is formed which indicates the presence of SO_4^{2-} anion :

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\text{White}}{BaSO_4}\downarrow + 2Cl^-$$

With $K_2Cr_2O_7$ and conc. H_2SO_4, red vapour of CrO_2Cl_2 is evolved. This indicates presence of Cl^- ion.

On treatment with potassium ferricyanide, formation of deep blue solution indicates presence of Fe (II) ion :

$$Fe^{2+} + Fe(CN)_6^{3-} \longrightarrow \underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3}$$

71. (i) $AgCl + 2NaCN \longrightarrow NaCl + Na[Ag(CN)_2]$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

(ii) $Co^{2+} + 3KNO_3 + 4NO_2^- + 2H^+ \longrightarrow K_3[Co(NO_2)_6] + H_2O + NO$

72. Mercurous chloride changes from white to black when treated with ammonia due to formation of metallic Hg.

73. (i) $\text{Mixture} + MnO_2 + \underset{\text{conc.}}{H_2SO_4} \longrightarrow \text{Yellowish green gas.}$

The above reaction suggest that the mixture contain Cl^-.

$$2Cl^- + MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + Cl_2\uparrow + H_2O$$

(ii) $\text{Mixture} + NaOH \longrightarrow \text{Gas turning red litmus blue.}$

The above reaction indicates that the gas is ammonia.

$$NH_4^+ + NaOH \longrightarrow NH_3 + H_2O + Na^+$$

(iii) Solution of mixture + $K_3[Fe(CN)_6] \longrightarrow$ blue ppt.

The above reaction suggest that mixture contain a Fe(II) salt. Fe(II) salt react with $K_3[Fe(CN)_6]$ to give blue ppt of Prussian blue complex

$$3Fe^{2+} + 2Fe(CN)_6^{3-} \longrightarrow \underset{\text{Blue}}{Fe_3[Fe(CN)_6]_2}\downarrow$$

Red colouration with NH_4SCN suggests that some Fe(III) is also present. It is likely that a part of Fe(II) is oxidised to Fe(III) by air :

$$Fe^{3+} + 3NH_4SCN \longrightarrow \underset{\text{Red colouration}}{Fe(SCN)_3} + 3NH_4^+$$

(iv) $\text{Mixture} + KOH \longrightarrow \text{gas}\uparrow \xrightarrow{K_2HgI_4} \text{brown ppt.}$

The above reaction indicates that the gas is NH_3, i.e. mixture contain NH_4^+ ion. Hence, the mixture contains Fe^{2+}, NH_4^+ and Cl^- ions with some impurity of Fe^{3+} ion.

The two salts are $FeCl_2$ and NH_4Cl.

74. $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

75. (i) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

(ii) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

(iii) $SO_2 + H_2O + \frac{1}{2}O_2 + 2NaCl \longrightarrow Na_2SO_4 + 2HCl$

76. (i) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$

(ii) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

(iii) $\underset{\text{Conc.}}{Sn + 3HNO_3} \longrightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

(iv) $H_2O_2 + CrCl_3 + NaOH \longrightarrow \underset{\text{Yellow}}{Na_2CrO_4} + NaCl + H_2O$

(v) $Pb_3O_4 \longrightarrow 2PbO + PbO_2$

$2PbO + PbO_2 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2\downarrow$

77. $3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

$(COOH)_2 + C\cdot H_2SO_4 \longrightarrow CO + CO_2 + H_2O$

78. (X) is $NaHCO_3$ ($M = 84$). The reactions involved are :

$$\underset{X}{2NaHCO_3} \longrightarrow \underset{Y}{Na_2CO_3(s)} + \underset{A}{CO_2(g)} + \underset{B}{H_2O(g)}$$

$$\begin{array}{lcccc} & 168\text{ g} & 106\text{ g} & 44\text{ g} & 18\text{ g} \\ \Rightarrow & 16.8\text{ g} & 10.6\text{ g} & 4.4\text{ g} & 1.8\text{ g} \end{array}$$

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$

$H_2O(g)$ is condensed to liquid water.

$$\underset{Y}{Na_2CO_3} + BaCl_2 \longrightarrow \underset{Z}{BaCO_3} + 2NaCl$$

$$\underset{Z}{BaCO_3} + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2$$

79. Compound A is a light green crystalline solid, so it may be $FeSO_4$.

(i) $FeSO_4$ is a salt of strong acid and weak base, so it hydrolyses in dil. H_2SO_4 but no gas is evolved.

(ii) $FeSO_4$ is a strong reducing agent, thus decolourises $KMnO_4$ solution :

$$5Fe^{2+} + \underset{\text{Purple}}{MnO_4^-} + 8H^+ \longrightarrow 5Fe^{3+} + \underset{\text{Colourless}}{Mn^{2+}} + 4H_2O$$

(iii) $FeSO_4$ on strong heating gives both SO_2 (B) and SO_3 (C) gases alongwith a residue of Fe_2O_3 (D).

$$2FeSO_4 \xrightarrow{\Delta} \underset{D}{Fe_2O_3} + \underset{B}{SO_2} + \underset{C}{SO_3}$$

(iv) The gaseous mixture reduced dichromate solution to green solution and also gives H_2SO_4 in solution :

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 3SO_4^{2-} + H_2O + \underset{\text{Green}}{2Cr^{3+}}$$

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

(v) The sulphuric acid (formed in previous step) gives white ppt. with $Ba(NO_3)_2$ due to formation of $BaSO_4$ (E) :

$$H_2SO_4 + Ba(NO_3)_2 \longrightarrow \underset{\text{White }(E)}{BaSO_4\downarrow} + 2HNO_3$$

(vi) The residue D when heated on charcoal in a reducing flame reduces to iron (Fe) which is a magnetic substance.

Hence, $A = FeSO_4$, $B = SO_2$, $C = SO_3$, $D = Fe_2O_3$ and $E = BaSO_4$.

80. $FeCl_3$ is a salt of strong acid and weak base. In water, it hydrolyses slowly producing brown ppt of $Fe(OH)_3$.

$$FeCl_3 + 3H_2O \longrightarrow 3HCl + \underset{\text{Brown}}{Fe(OH)_3\downarrow}$$

81. Nitric acid is a strong oxidising agent, oxidises H_2S to S.

82. (i) The compound C produced by heating A is white in colour and changes to yellow on heating, thus compound C may be ZnO. C with dil. HCl and $K_4[Fe(CN)_6]$ gives white ppt. This confirms that the compound C must be ZnO.

$$A \xrightarrow{\Delta} \underset{\text{'}C\text{'}}{ZnO} + B\text{ (gas)}$$

$$\underset{C}{ZnO} + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow 4KCl + \underset{\text{White ppt}}{Zn_2[Fe(CN)_6]\downarrow}$$

(ii) The gas B turns lime water milky and milkiness disappear with continuous passage of gas. Hence, the gas is CO_2 and compound A in $ZnCO_3$.

$$\underset{B}{CO_2} + Ca(OH)_2 \longrightarrow H_2O + CaCO_3\downarrow$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

$$\underset{A}{ZnCO_3} \xrightarrow{\Delta} \underset{C}{ZnO} + \underset{B}{CO_2}$$

(iii) The solution of A gives white ppt of ZnS D with NH_4OH and excess of H_2S.

$$ZnCO_3 + HCl \longrightarrow \underset{B}{CO_2\uparrow} + ZnCl_2$$

$$ZnCl_2 + H_2S \xrightarrow{NH_4OH} 2HCl + \underset{D}{ZnS\downarrow}\text{ (white)}$$

(iv) The solution of A also gives initially a white ppt E with NaOH, which dissolve in excess of reagent.

$$ZnCl_2 + 2NaOH \longrightarrow \underset{E\text{ (white)}}{Zn(OH)_2\downarrow} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2[Zn(OH)_4]}$$

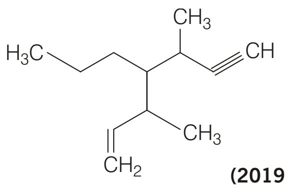
21

Organic Chemistry Basics

Topic 1 Nomenclature and Isomerism

Objective Questions I (Only one correct option)

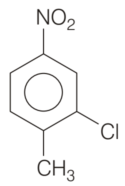
1. The IUPAC name for the following compound is



(2019 Main, 12 April II)

(a) 3-methyl-4-(3-methylprop-1-enyl)-1-heptyne
(b) 3, 5-dimethyl-4-propylhept-6-en-1-yne
(c) 3-methyl-4-(1-methylprop-2-ynyl)-1-heptene
(d) 3, 5-dimethyl-4-propylhept-1-en-6-yne

2. The correct IUPAC name of the following compound is



(2019 Main, 9 April I)

(a) 2-methyl-5-nitro-1-chlorobenzene
(b) 3-chloro-1-methyl-1-nitrobenzene
(c) 2-chloro-1-methyl 1-4-nitrobenzene
(d) 5-chloro-4-methyl 1-1-nitrobenzene

3. Which of the following compounds will show the maximum 'enol' content? **(2019 Main, 8 April II)**

(a) CH_3COCH_3
(b) $CH_3COCH_2COCH_3$
(c) $CH_3COCH_2COOC_2H_5$
(d) $CH_3COCH_2CONH_2$

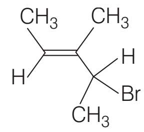
4. The IUPAC name of the following compound is

CH_3 OH

H_3C CH CH CH_2 COOH **(2019 Main, 8 April I)**

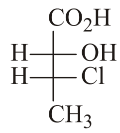
(a) 4,4 - dimethyl -3-hydroxybutanoic acid
(b) 2-methyl-3-hydroxypentan-5-oic acid
(c) 3- hydroxy -4- methylpentanoic acid
(d) 4-methyl-3-hydroxypentanoic acid

5. What is the IUPAC name of the following compound?



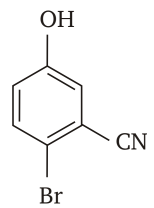
(2019 Main, 10 Jan II)

(a) 3-bromo-3-methyl-1,2-dimethylprop-1-ene
(b) 3-bromo-1,2-dimethylbut-1-ene
(c) 2-bromo-3-methylpent-3-ene
(d) 4-bromo-3-methylpent-2-ene

6. The absolute configuration of  is **(2016 Main)**

(a) (2S, 3R) (b) (2S, 3S)
(c) (2R, 3R) (d) (2R, 3S)

7. The IUPAC name of the following compound is



(2009)

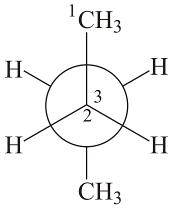
(a) 4-bromo-3-cyanophenol
(b) 2-bromo-5-hydroxybenzonitrile
(c) 2-cyano-4-hydroxybromobenzene
(d) 6-bromo-3hydroxybenzonitrile

8. The number of stereoisomers obtained by bromination of *trans*-2-butene is **(2007, 3M)**

(a) 1 (b) 2 (c) 3 (d) 4

9. The IUPAC name of C_6H_5COCl is **(2006, 3M)**

(a) benzoyl chloride
(b) benzene chloro ketone
(c) benzene carbonyl chloride
(d) chloro phenyl ketone

10. 

C_2 is rotated anti-clockwise 120° about C_2-C_3 bond. The resulting conformer is **(2004, 1M)**
(a) partially eclipsed (b) eclipsed
(c) gauche (d) staggered

11. Which of the following compounds exhibits, stereoisomerism? **(2002, 3M)**
(a) 2-methylbutene-1 (b) 3-methylbutyne-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

12. The number of isomers for the compound with molecular formula $C_2BrClFI$ is **(2001, 1M)**
(a) 3 (b) 4 (c) 5 (d) 6

13. Which of the following compounds will exhibit geometrical isomerism ? **(2000, 1M)**
(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene (d) 1,1-diphenyl-1-propene

14. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive **(1999, 2M)**
(a) optical rotation and is derived from D-glucose
(b) pH in organic solvent
(c) optical rotation and is derived from D-(+)-glyceraldehydes
(d) optical rotation when substituted by deuterium

15. How many optically active stereoisomers are possible for butane-2, 3-diol ? **(1997, 1M)**
(a) 1 (b) 2 (c) 3 (d) 4

16. Isomers which can be interconverted through rotation around a single bond are **(1992, 1M)**
(a) conformers (b) diastereomers
(c) enantiomers (d) positional isomers

17. The enolic form of acetone contains **(1990, 1M)**
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(c) 10 sigma bonds, 1 pi bond and 1 lone pair
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair

18. The number of isomers of C_6H_{14} is **(1987, 2007, 3M)**
(a) 4 (b) 5 (c) 6 (d) 7

19. If two compounds have the same empirical formula but different molecular formulae, they must have **(1987, 1M)**
(a) different percentage composition
(b) different molecular weight
(c) same velocity
(d) same vapour density

20. Which of the following will have least hindered rotation about carbon-carbon bond ? **(1987, 1M)**
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane

21. The IUPAC name of the compound
$CH_2{=}CH \quad CH(CH_3)_2$ is **(1987, 1M)**
(a) 1,1-dimethyl-2-butene (b) 3-methyl-1-butene
(c) 2-vinyl propane (d) None of these

22. An isomer of ethanol is **(1986, 1M)**
(a) methanol (b) diethyl ether
(c) acetone (d) dimethyl ether

23. The IUPAC name of the compound having the formula is

$$\begin{array}{c} CH_3 \\ H_3C \quad C \quad CH{=}CH_2 \\ CH_3 \end{array}$$

(1984, 1M)
(a) 3, 3, 3-trimethyl-1-propene
(b) 1, 1, 1-trimethyl-2-propene
(c) 3, 3-dimethyl-1-butene
(d) 2, 2-dimethyl-3-butene

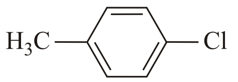
24. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism ? **(1983, 1M)**
(a) 2-butene (b) 2-butyne
(c) 2-butanol (d) butanal

25. The compound which is not isomeric with diethyl ether is **(1981, 1M)**
(a) *n*-propyl methyl ether (b) butane-1-ol
(c) 2-methyl propane-2-ol (d) butanone

Objective Questions II

(One or more than one correct option)

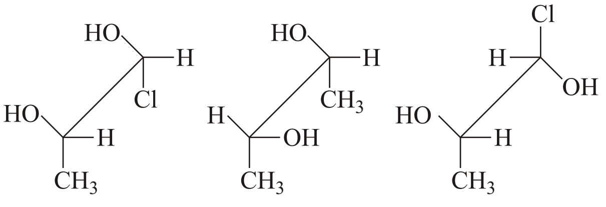
26. The IUPAC name(s) of the following compound is (are) **(2017 Adv.)**



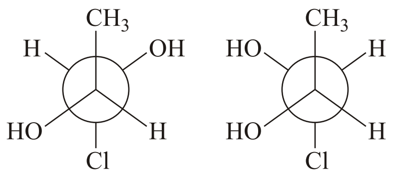
(a) 4-methylchlorobenzene
(b) 4-chlorotoluene
(c) 1-chloro-4-methylbenzene
(d) 1-methyl-4-chlorobenzene

27. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are **(2014 Adv.)**
(a) *tert*-butanol and 2-methylpropan-2-ol
(b) *tert*-butanol and 1,1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol
(d) *iso*-butyl alcohol and 2-methylpropan-1-ol

28. Which of the given statement(s) about *N*, *O*, *P* and *Q* with respect to *M* is/are correct? **(2012)**



M *N* *O*

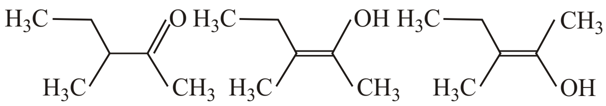


P *Q*

(a) *M* and *N* are non-mirror image stereoisomers
(b) *M* and *O* are identical
(c) *M* and *P* are enantiomers
(d) *M* and *Q* are identical

29. The correct statement(s) about the compound (2009)
$H_3C(HO)\,HC \quad CH \quad CH \quad CH(OH)CH_3$ (X) is/are
(a) The total number of stereoisomers possible for X is 6
(b) The total number of diastereomers possible for X is 3
(c) If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4
(d) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2

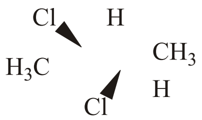
30. The correct statement(s) concerning the structures E, F and G is/are



(E) (F) (G)

(a) E, F and G are resonance structures (2008, 4M)
(b) E, F and E, G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomers

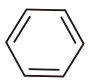
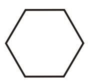
31. The correct statement(s) about the compound given below is/are

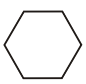


(2008, 4M)

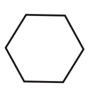
(a) the compound is optically active
(b) the compound possesses centre of symmetry
(c) the compound possesses plane of symmetry
(d) the compound possesses axis of symmetry

32. Tautomerism is exhibited by (1998, 2M)

(a)  CH═CH OH (b) O  O

(c)  O

O

(d)  O

O

33. Which of the following compounds will show geometrical isomerism ? (1998, 2M)
(a) 2-butene (b) propene
(c) 1-phenyl propene (d) 2-methyl-2-butene

34. Which of the following have asymmetric carbon atom? (1989, 1M)

(a) H C(Cl)(H) C(Br)(H) H
(b) H C(H)(H) C(Cl)(H) Cl
(c) H C(H)(H) C(Cl)(H) D
(d) H C(H)(Br) C(H)(OH) CH_3

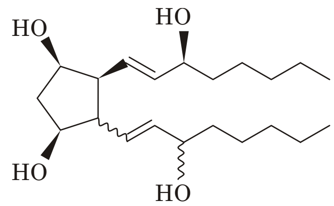
35. Keto-enol tautomerism is observed in (1988, 2M)

(a) C_6H_5 C(O) H (b) C_6H_5 C(O) CH_3
(c) C_6H_5 C(O) C_6H_5 (d) C_6H_5 C(O) CH_2 C(O) CH_3

36. Only two isomeric monochloro derivatives are possible for (1986, 1M)
(a) *n*-butane (b) 2, 4-dimethyl pentane
(c) benzene (d) 2-methyl propane

Numerical Value Based Question

37. For the given compound X, the total number of optically active stereoisomers is ……… .



This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed
This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is not fixed

(2018 Adv.)

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

38. **Statement I** Molecules that are non-superimposable on their mirror images are chiral.
Statement II All chiral molecules have chiral centres. (2007, 3M)

Fill in the Blanks

39. Isomers which are ……… mirror images are known as ……… (superimposable, non-superimposable, enantiomers, diastereomers, epimers) (1988, 1M)

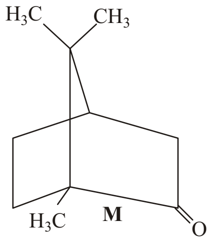
True/False

40. 2, 3, 4-trichloropentane has three asymmetric carbon atoms. **(1990, 1M)**

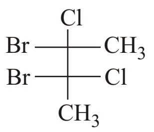
41. *m*-chlorobromobenzene is an isomer of *m*-bromochloro benzene. **(1985, $\frac{1}{2}$M)**

Integer Answer Type Questions

42. The total number of stereoisomers that can exist for *M* is **(2015 Adv.)**



43. The total number(s) of stable conformers with non-zero dipole moment for the following compound is/are



(2014 Adv.)

Subjective Questions

44. Give the total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula C_5H_{10}. **(2009)**

45. $_{obs}$ $_i x_i$

where $_i$ is the dipole moment of stable conformer and x_i is the mole fraction of that conformer.

(a) Write stable conformer for Z CH_2 CH_2 Z in Newman's projection.

If $_{solution}$ 1.0 D and mole fraction of *anti* form 0.82, find $_{gauche}$

(b) Write most stable *meso* conformer of $(CHDY)_2$. If

(i) Y CH_3 about C_2-C_3 rotation and

(ii) Y OH about C_1-C_2 rotation. **(2005, 6M)**

46. (a) Draw Newman's projection for the less stable staggered form of butane.

(b) Relatively less stability of the staggered form is due to

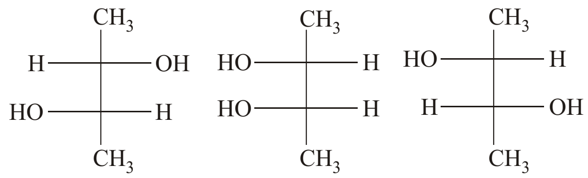
(i) Torsional strain

(ii) van der Waals' strain

(iii) Combination of the above two **(2004, 5M)**

47. Glycerine contain one ……… hydroxy group. **(2004)**

48. Identify the pairs of enantiomers and diastereomers from the following **(2000, 2M)**



I II III

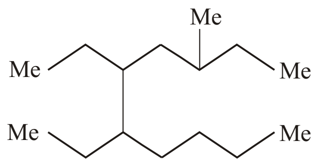
49. Write tautomeric forms of phenol. **(1992, 1M)**

50. Write the IUPAC name of the following compound:

$$\begin{array}{c} CH_3 \\ H_3C \quad N \quad -C \quad CH_2 \quad CH_3 \\ CH_3 \quad C_2H_5 \end{array}$$

(1991, 1M)

51. Give the IUPAC name of the following compound :



(Me = methyl)

(1990, 1M)

52. Write the IUPAC name of $CH_3CH_2CH{=}CH$ COOH . **(1986, 1M)**

53. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment ? **(1985, 2M)**

54. Write structural formulae for the isomeric alcohols having the molecular formula $C_4H_{10}O$. **(1984, 2M)**

Topic 2 General Organic Chemistry

Objective Questions I (Only one correct option)

1. 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O. This unknown hydrocarbon contains **(2019 Main, 12 April II)**

(a) 20 g of carbon and 5 g of hydrogen
(b) 22 g of carbon and 3 g of hydrogen
(c) 24 g of carbon and 1 g of hydrogen
(d) 18 g of carbon and 7 g of hydrogen

2. An organic compound *A* is oxidised with Na_2O_2 followed by boiling with HNO_3. The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate.

Based on above observation, the element present in the given compound is **(2019 Main, 12 April I)**

(a) nitrogen
(b) phosphorus
(c) fluorine
(d) sulphur

3. The increasing order of nucleophilicity of the following nucleophiles is **(2019 Main, 10 April II)**

(1) $CH_3CO_2^{\ominus}$ (2) H_2O (3) $CH_3SO_3^{\ominus}$ (4) $\overset{\ominus}{O}H$

(a) (1) < (4) < (3) < (2) (b) (2) < (3) < (1) < (4)
(c) (4) < (1) < (3) < (2) (d) (2) < (3) < (4) < (1)

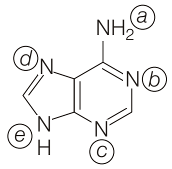
4. In chromatography, which of the following statements is incorrect for R_f? **(2019 Main, 10 April II)**

(a) R_f value depends on the type of chromatography
(b) Higher R_f value means higher adsorption
(c) R_f value is dependent on the mobile phase
(d) The value of R_f can not be more than one

5. The principle of column chromatography is **(2019 Main, 10 April I)**

(a) differential absorption of the substances on the solid phase
(b) differential adsorption of the substances on the solid phase
(c) gravitational force
(d) capillary action

6. In the following compound,



the favourable site/s for protonation is/are **(2019 Main, 11 Jan II)**

(a) (*a*) and (*e*) (b) (*b*), (*c*) and (*d*)
(c) (*a*) and (*d*) (d) (*a*)

7. The correct match between items I and II is

	Item - I (Mixture)		Item II (Separation method)
A.	H_2O : Sugar	P.	Sublimation
B.	H_2O : Aniline	Q.	Recrystallisation
C.	H_2O : Toluene	R.	Steam distillation
		S.	Differential extraction

(2019 Main, 11 Jan I)

(a) (A) (Q); (B) (R); (C) (S)
(b) (A) (Q); (B) (R); (C) (P)
(c) (A) (S); (B) (R); (C) (P)
(d) (A) (R); (B) (P); (C) (S)

8. An organic compound is estimated through Dumas method and was found to evolved 6 moles of CO_2, 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is **(2019 Main, 11 Jan I)**

(a) C_6H_8N (b) $C_{12}H_8N$ (c) $C_{12}H_8N_2$ (d) $C_6H_8N_2$

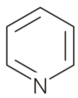
9. If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct? **(2019 Main, 10 Jan I)**

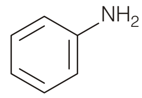
(a) DCM and H_2O would stay as lower and upper layer respectively in the S.F.
(b) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (S.F.)
(c) DCM and H_2O will be miscible clearly
(d) DCM and H_2O will make turbid/colloidal mixture

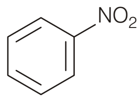
10. Which amongst the following is the strongest acid? **(2019 Main, 9 Jan I)**

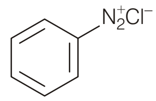
(a) $CHBr_3$ (b) CHI_3
(c) $CHCl_3$ (d) $CH(CN)_3$

11. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation? **(2018 Main)**

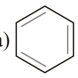
(a) 

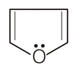
(b) 

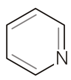
(c) 

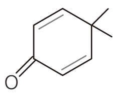
(d) 

12. Which of the following molecules is least resonance stabilised? **(2017 Main)**

(a) 

(b) 

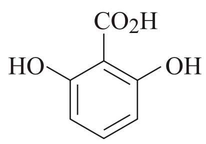
(c) 

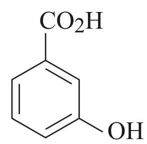
(d) 

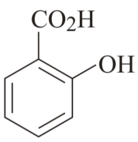
13. The distillation technique most suited for separating glycerol from spent lye in the soap industry is **(2016 Main)**

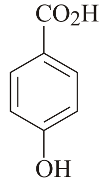
(a) fractional distillation
(b) steam distillation
(c) distillation under reduced pressure
(d) simple distillation

14. The correct order of acidity for the following compounds is **(2016 Adv.)**

I 

II 

III 

IV 

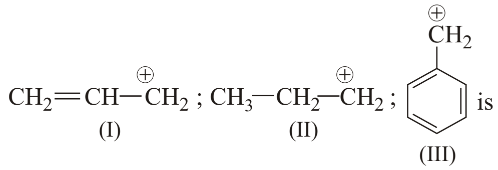
(a) I > II > III > IV
(b) III > I > II > IV
(c) III > IV > II > I
(d) I > III > IV > II

15. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of $M/10$ sulphuric acid. The unreacted acid required 20 mL of $M/10$ sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is **(2014 Main)**

(a) 6% (b) 10%
(c) 3% (d) 5%

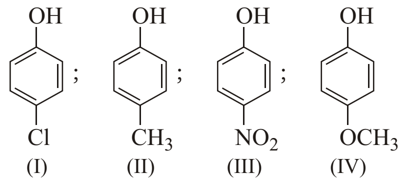
16. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is **(2013 Main)**
(a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8

17. The order of stability of the following carbocations



(2013 Main)
(a) III > II > I (b) II > III > I
(c) I > II > III (d) III > I > II

18. Arrange the following compounds in the order of decreasing acidity **(2013 Main)**



(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

19. A solution of (l) 1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of **(2013 Main)**
(a) carbanion (b) carbene
(c) carbocation (d) free radical

20. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms, is (are) **(2012)**
(a) sp and sp^3 (b) sp and sp^2
(c) only sp^3 (d) sp^2 and sp^3

21. Among the following compounds, the most acidic is **(2011)**
(a) p-nitrophenol (b) p-hydroxybenzoic acid
(c) o-hydroxybenzoic acid (d) p-toluic acid

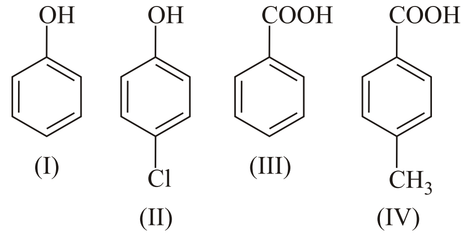
22. The correct stability order of the following resonance structure is
(I) $H_2C\ \overset{+}{N}\ \overset{-}{N}$ (II) $H_2\overset{+}{C}\ N\ \overset{-}{N}$
(III) $H_2\overset{-}{C}\ \overset{+}{N}\ N$ (IV) $H_2\overset{-}{C}\ N\ N$ **(2009)**
(a) (I) > (II) > (IV) > (III)
(b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV)
(d) (III) > (I) > (IV) > (II)

23. In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is **(2009)**

$$\begin{array}{ccccc} & H & & H & \\ \overset{1}{H_3C} & C^2 & C^3 & C^4 & \overset{5}{CH_3} \\ & OH & H & CH_3 & \end{array}$$

(a) CH_3 at C-4 (b) H at C-4
(c) CH_3 at C-2 (d) H at C-2

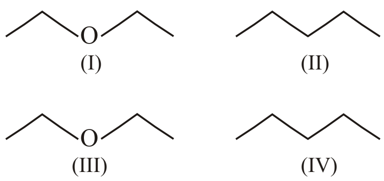
24. The correct acidity order of the following is **(2009)**



(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

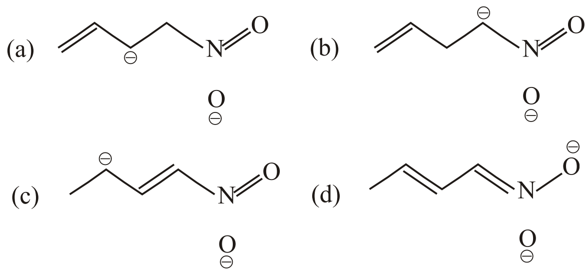
25. Hyperconjugation involves overlap of the following orbitals **(2008, 3M)**
(a) - (b) -p (c) p-p (d) -

26. The correct stability order for the following species is



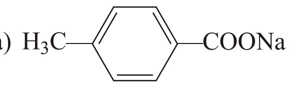
(2008, 3M)
(a) (II) (IV) (I) (III) (b) (I) (II) (III) (IV)
(c) (II) (I) (IV) (III) (d) (I) (III) (II) (IV)

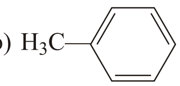
27. Among the following, the least stable resonance structure is **(2007, 3M)**

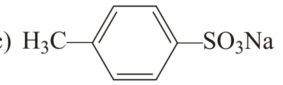


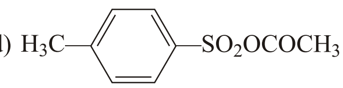
28. When benzene sulphonic acid and p-nitrophenol are treated with $NaHCO_3$, the gases released respectively are **(2006)**
(a) SO_2, NO_2 (b) SO_2, NO
(c) SO_2, CO_2 (d) CO_2, CO_2

29. Which of the following is obtained when 4-methylbenzene sulphonic acid is hydrolysed with excess of sodium acetate? **(2005, 1M)**

(a) 

(b)  + SO_3

(c)  + CH_3COOH

(d)  + NaOH

30. For 1-methoxy-1, 3-butadiene, which of the following resonating structure is least stable? **(2005, 1M)**

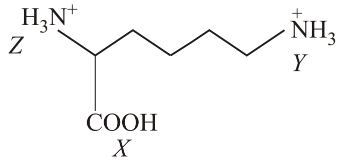
(a) $\overset{\ominus}{C}H_2$ CH CH$=$CH O CH_3

(b) $\overset{\ominus}{C}H_2$ CH$=$CH CH$=$O CH_3

(c) $CH_2=$CH CH—$\overset{\ominus}{C}$H O CH_3

(d) $CH_2=$CH $\overset{\ominus}{C}$H CH$=$O CH_3

31.



Arrange in order of increasing acidic strength **(2004, 1M)**

(a) X Z Y (b) Z X Y

(c) X Y Z (d) Z X Y

32. Among the following, the molecule with the highest dipole moment is **(2003, 1M)**

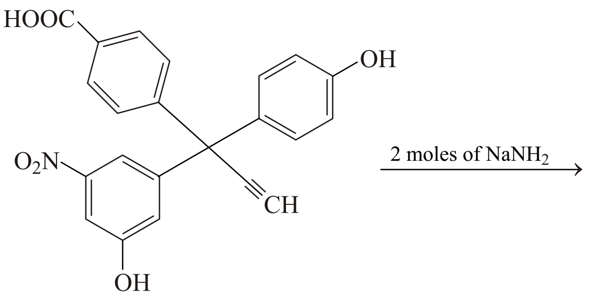
(a) CH_3Cl (b) CH_2Cl_2 (c) CH_2Cl_2 (d) CCl_4

33. Which of the following represent the given mode of hybridisation sp^2 sp^2 sp sp from left to right? **(2003, 1M)**

(a) $H_2C=$CH C N (b) HC C C CH

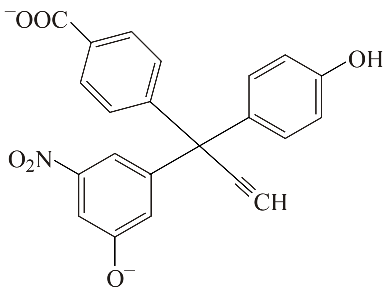
(c) $H_2C=C=C=CH_2$ (d)

34.

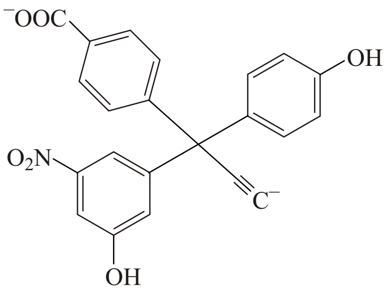


The product A will be **(2003)**

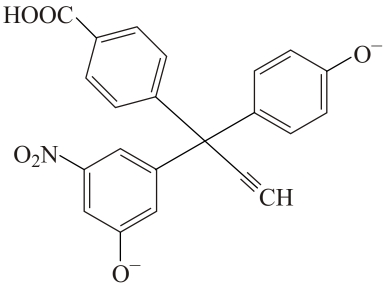
(a)



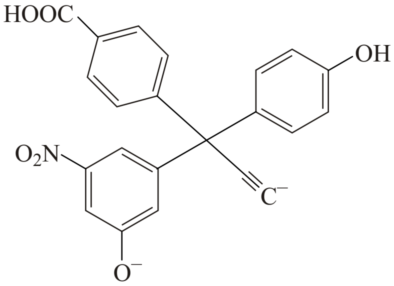
(b)



(c)



(d)



35. Which of the following acids has the smallest dissociation constant? **(2002)**

(a) $CH_3CHFCOOH$

(b) FCH_2CH_2COOH

(c) $BrCH_2CH_2COOH$

d) $CH_3CHBrCOOH$

36. Identify the correct order of boiling points of the following compounds:

$CH_3CH_2CH_2CH_2OH$ (1) $CH_3CH_2CH_2CHO$ (2)

$CH_3CH_2CH_2COOH$ (3) **(2002)**

(a) 1 > 2 > 3 (b) 3 > 1 > 2

(c) 1 > 3 > 2 (d) 3 > 2 > 1

37. Which of the following hydrocarbons has the lowest dipole moment? **(2002)**

(a) *cis*-2-butene (b) 2-butyne

(c) 1-butyne (d) H_2C CH—C CH

38. The correct order of basicities of the following compounds is **(2001)**

H_3C C(=NH)NH_2 (1) $CH_3CH_2NH_2$ (2)

$(CH_3)_2NH$ (3) CH_3CONH_2 (4)

(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

39. Among the following, the strongest base is **(2000)**

(a) $C_6H_5NH_2$

(b) p-$NO_2C_6H_4NH_2$

(c) m-NO_2—$C_6H_4NH_2$

(d) $C_6H_5CH_2NH_2$

40. Which of the following, has the most acidic hydrogen? **(2000)**

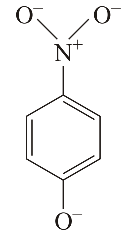
(a) 3-hexanone

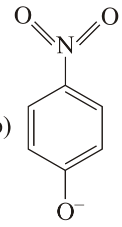
(b) 2, 4-hexanedione

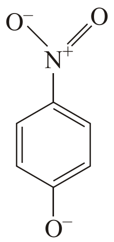
(c) 2, 5-hexanedione

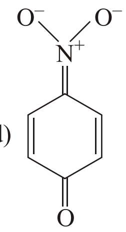
(d) 2, 3-hexanedione

41. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is **(1999)**

(a) 

(b) 

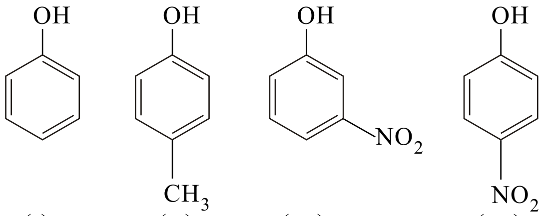
(c) 

(d) 

42. Among the following compounds, the strongest acid is **(1998)**

(a) HC CH (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

43. In the following compounds **(1997)**



(I) (II) (III) (IV)

The order of acidity is

(a) III > IV > I > II
(b) I > IV > III > II
(c) II > I > III > IV
(d) IV > III > I > II

44. What is the decreasing order of strength of the bases?
OH , NH_2 , H C C and CH_3 CH_2 **(1997)**

(a) CH_3 CH_2 > NH_2 H C C OH
(b) H C C CH_3 CH_2 > NH_2 OH
(c) OH > NH_2 H C C CH_3 CH_2
(d) NH_2 H C C OH > CH_3 CH_2

45. The hybridisation of carbon atoms in C C single bond H C C CH=CH_2 is **(1991, 1M)**

(a) sp^3 sp^3 (b) sp^2 sp^3
(c) sp sp^2 (d) sp^3 sp

46. Amongst the following, the most basic compound is **(1990, 1M)**

(a) benzylamine (b) aniline
(c) acetanilide (d) *p*-nitroaniline

47. The number of sigma and pi-bonds in 1-butene 3-yne are **(1989, 1M)**

(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi (d) 6 sigma and 4 pi

48. The compound which gives the most stable carbonium ion on dehydration is **(1989, 1M)**

(a) CH_3 CH CH_2OH (with CH_3 below CH)

(b) CH_3 C OH (with CH_3 above and CH_3 below C)

(c) CH_3CH_2 CH_2 CH_2OH

(d) CH_3 CH CH_2CH_3 (with OH above CH)

49. Polarisation of electrons in acrolein may be written as **(1988, 1M)**

(a) H_2C=CH C H (O above C)

(b) H_2C=CH C H (O above C)

(c) H_2C=CH C H (O above C)

(d) H_2C=CH C H (O above C)

50. The bond between carbon atom (1) and carbon atom (2) in compound

N C CH=CH_2
   1   2

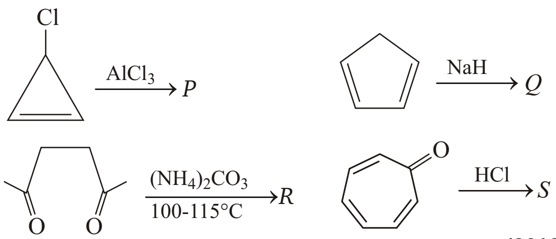
involves the hybridisation as **(1987, 1M)**

(a) sp^2 and sp^2 (b) sp^3 and sp
(c) sp and sp^2 (d) sp and sp

Objective Questions II

(One or more than one correct option)

51. Among *P, Q, R* and *S*, the aromatic compounds(s) is/are



(2013 Adv.)

(a) *P* (b) *Q* (c) *R* (d) *S*

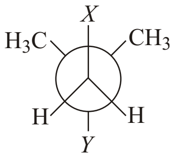
52. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to **(2013 Adv.)**

(a) *p* (empty) and * electron delocalisations
(b) * and electron delocalisations
(c) *p* (filled) and electron delocalisations
(d) *p* (filled) * and * electrons delocalisations

53. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is/are **(2011)**

(a) H_2C=C(H) C(H)=CH_2 (b) H C C C(H)=CH_2
(c) H_2C C O (d) H_2C C CH_2

54. In the Newman's projection for 2,2-dimethylbutane



X and Y can respectively be **(2010)**

(a) H and H
(b) H and C_2H_5
(c) C_2H_5 and H
(d) CH_3 and CH_3

55. The molecules that will have dipole moment are **(1992, 1M)**

(a) 2, 2-dimethyl propane
(b) *trans*-2-pentene
(c) *cis*-3-hexene
(d) 2,2,3,3-tetramethyl butane

56. The compound in which C uses its sp^3-hybrid orbitals for bond formation is **(2000, 1M)**

(a) HCOOH (b) $(H_2N)_2CO$
(c) $(CH_3)_3COH$ (d) CH_3CHO

57. Phenol is less acidic than **(1986)**

(a) acetic acid (b) *p*-methoxy phenol
(c) *p*-nitrophenol (d) ethanol

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

58. **Statement I** *p*-hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.

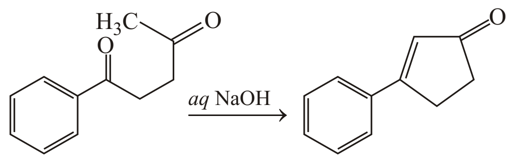
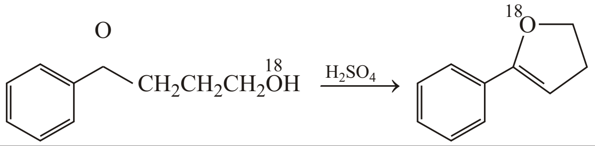
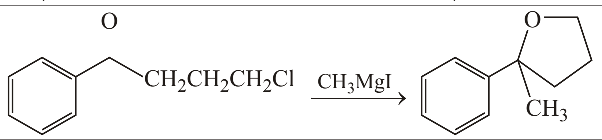
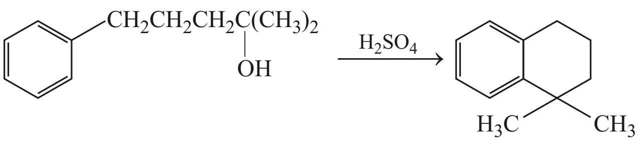
Statement II *o*-hydroxybenzoic acid has intramolecular hydrogen bonding.

59. **Statement I** *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

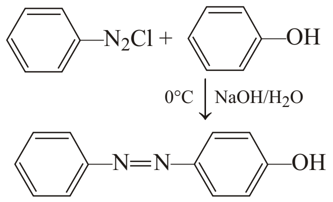
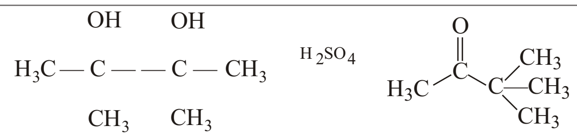
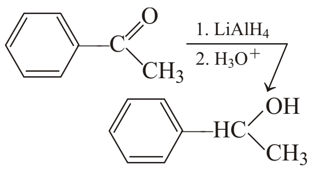
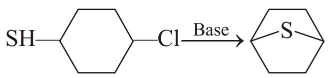
Statement II Intramolecular hydrogen bonding make the *o*-isomer weaker acid than *p*-isomer.

Match the Columns

60. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II. **(2011)**

	Column I		Column II
A.		p.	Nucleophilic substitution
B.		q.	Electrophilic substitution
C.		r.	Dehydration
D.		s.	Nucleophilic addition
		t.	Carbanion

61. Match the reaction in Column I with appropriate options in Column II. **(2010)**

	Column I	Column II
A.		p. Racemic mixture
B.		q. Addition reaction
C.		r. Substitution reaction
D.		s. Coupling reaction
		t. Carbocation intermediate

Fill in the Blanks

62. The kind of delocalisation involving sigma bond orbitals is called…… **(1994, 1M)**

63. The bond dissociation energy needed to form the benzyl radical from toluene is ……… than the formation of the methyl radical from methane. **(1994, 1M)**

64. The structure of the enol form of

$CH_3 \quad CO \quad CH_2 \quad CO \quad CH_3$

with intermolecular hydrogen bonding is ……… **(1993, 1M)**

65. The IUPAC name of succinic acid is ……… **(1990, 1M)**

66. The shape of (CH_3) is ……… **(1990, 1M)**

67. A…… diol has two hydroxyl groups on ……carbon atoms. **(1985, 1M)**

68. The terminal carbon atom in butane is …… hybridised. **(1985, 1M)**

69. ………ring is most strained. (cyclopropane, cyclobutane, cyclopentane) **(1981, 1M)**

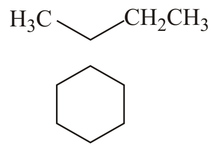
70. The compound having both *sp* and *sp*^{2}-hybridised carbon atoms is ……. (propane, propene, propadiene). **(1981, 1M)**

71. In acidic medium, ……….. behaves as the strongest base. (nitrobenzene, aniline, phenol) **(1981, 1M)**

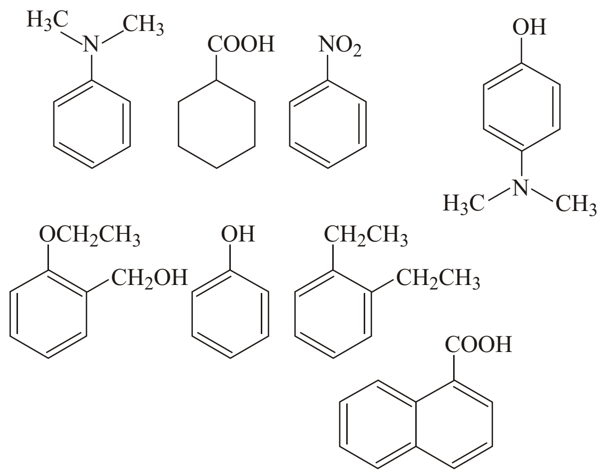
72. Among the given cations, ……… is most stable. (*sec*-butyl carbonium ion, *tert*-butyl carbonium ion, *n*-butyl carbonium ion) **(1981, 1M)**

Integer Answer Type Questions

73. The total number of contributing structures showing hyperconjugation (involving C — H bonds) for the following carbocation is **(2011)**

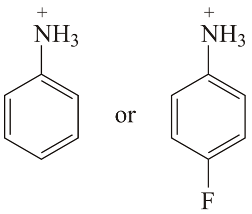


74. Amongst the following, the total number of compounds soluble in aqueous NaOH is **(2010)**

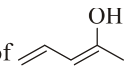


Subjective Questions

75. Which of the following is more acidic and why?



(2003)

76. Draw the resonating structures of  . (2003)

77. You have an ether solution containing 4-hydroxybenzoic acid and 4-aminobenzoic acid. Explain, how will you separate the two in not more than 3 steps? Give confirmatory tests with reagents and conditions for functional groups of each. (2003)

78. Match the following with their K_a values

Benzoic acid	$4.2 \quad 10^{5}$
p-nitrobenzoic acid	$3.3 \quad 10^{5}$
p-chlorobenzoic acid	$6.4 \quad 10^{5}$
p-methylbenzoic acid	$36.2 \quad 10^{5}$
p-methoxybenzoic acid	$10.2 \quad 10^{5}$

(2003)

79. Give reasons for the following:
$CH_2 \quad CH$ is more basic than $HC \quad C$. (2000)

80. Explain, why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid? (1999)

81. Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the -orbital overlaps. (1999, 3M)

82. Give reasons for the following in one or two sentences.
The central carbon-carbon bond in 1, 3-butadiene is shorter than that of *n*-butane. (1998)

83. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? (1997)

84. Arrange the following in the order of their increasing basicity.
p-toluidine, N,N-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline. (1985, 1M)

Answers

Topic 1

1. (d)	**2.** (c)	**3.** (b)	**4.** (c)
5. (d)	**6.** (a)	**7.** (b)	**8.** (a)
9. (c)	**10.** (c)	**11.** (d)	**12.** (d)
13. (a)	**14.** (c)	**15.** (b)	**16.** (a)
17. (a)	**18.** (b)	**19.** (b)	**20.** (a)
21. (b)	**22.** (d)	**23.** (c)	**24.** (a)
25. (d)	**26.** (b,c)	**27.** (a,c,d)	**28.** (a,b,c)
29. (a,d)	**30.** (b,c,d)	**31.** (a,d)	**32.** (a,c,d)
33. (a,c)	**34.** (c,d)	**35.** (b,d)	**36.** (d)
37. (7)	**38.** (c)		
39. Non-superimposable, Enantiomers			**40.** False
41. False	**42.** (2)	**43.** (3)	**44.** (7)

Topic 2

1. (c)	**2.** (b)	**3.** (c)	**4.** (b)
5. (b)	**6.** (b)	**7.** (a)	**8.** (d)
9. (a)	**10.** (d)	**11.** (b)	**12.** (d)
13. (c)	**14.** (a)	**15.** (b)	**16.** (d)
17. (d)	**18.** (c)	**19.** (c)	**20.** (b)
21. (c)	**22.** (b)	**23.** (d)	**24.** (a)
25. (b)	**26.** (d)	**27.** (a)	**28.** (d)
29. (c)	**30.** (c)	**31.** (a)	**32.** (a)
33. (a)	**34.** (a)	**35.** (c)	**36.** (b)
37. (b)	**38.** (b)	**39.** (d)	**40.** (b)
41. (b)	**42.** (d)	**43.** (d)	**44.** (a)
45. (d)	**46.** (a)	**47.** (b)	**48.** (b)
49. (d)	**50.** (c)	**51.** (a,b,c,d)	**52.** (a)
53. (b,c)	**54.** (b,d)	**55.** (b,c)	**56.** (c,d)
57. (a,c)	**58.** (d)	**59.** (a)	

60. A r, s, t; B p, s; C r, s; D q, r

61. A r, s; B t; C p, q; D r

62. hyperconjugation

63. less **64.** cyclic **65.** butanedioic acid

66. triangular planar **67.** *geminal*, same

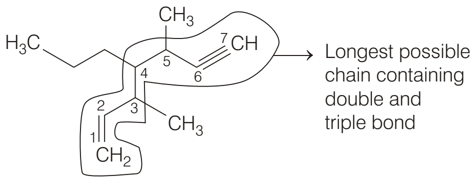
68. sp^3 **69.** cylopropane **70.** propene **71.** aniline

72. *tert*-butyl carbonium ion, **73.** (6) **74.** (4)

Hints & Solutions

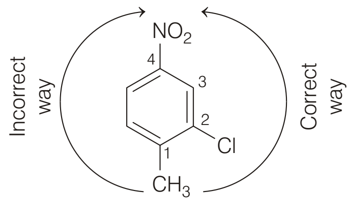
Topic 1 Nomenclature and Isomerism

1. The IUPAC name for the given compound is 3, 5-dimethyl-4-propylhept-1-en-6-yne.



If both double and triple bonds are present in the compound, the endings like-en-yne, a (numeral) dien-(numeral)-yne etc., are used. Numbers as low as possible are given to double and triple bonds as a set.

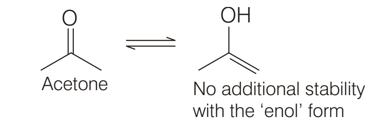
2. The IUPAC name of the given compound is

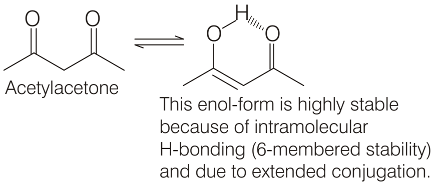


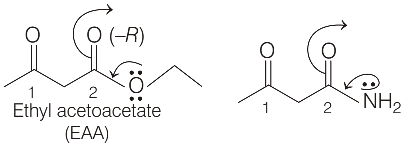
2- chloro-1-methy l- 4-nitrobenzene

Here, the given compound contains two or more functional groups. So, the numbering is done in such a way that the sum of the locants is the lowest.

3.







In both of the compounds, C-2 of $\overset{\displaystyle O}{\overset{\|}{-C-}}$ group is a part of the acid derivative (ester, $-\overset{O}{\overset{\|}{C}}-OEt$ and acid amide, $-\overset{O}{\overset{\|}{C}}-NH_2$). So, $>C^2=O$ does not take part in enolisation, because it is already in resonance (–*R*) with the derivative group itself.

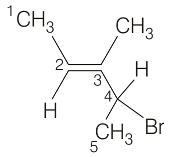
4. The IUPAC name of the given compound is 3-hydroxy-4-methylpentanoic acid.

$$\boxed{\overset{5}{H_3C}-\underset{}{\overset{4}{CH}}(CH_3)-\overset{3}{CH}(OH)-\overset{2}{CH_2}-\overset{1}{COOH}}$$

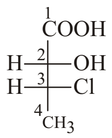
Principal chain

While naming the compound, the longest chain that have principal functional group –COOH is choosen and numbered in such a manner that the principal functional group gets the lowest possible number. –OH act as substituent and used as prefix in nomenclature.

5. While naming the compound, alkene gets priority over functional group (–Br) and numbering starts from alkene side. Hence, **IUPAC** name: 4-bromo-3-methyl pent-2-ene



6.



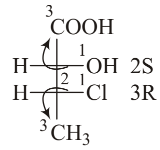
For C-2, order of priority of substituents is

$OH > CH(Cl)(CH_3) > COOH$

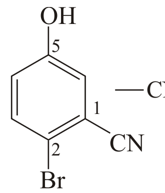
For C-3, order of priority of substituents is

$Cl > CH(OH)COOH > CH_3$

Hence, according to CIP rules,



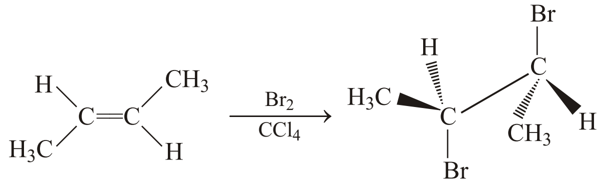
7.

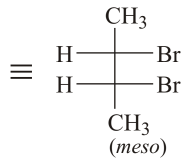


—CN has the highest priority.

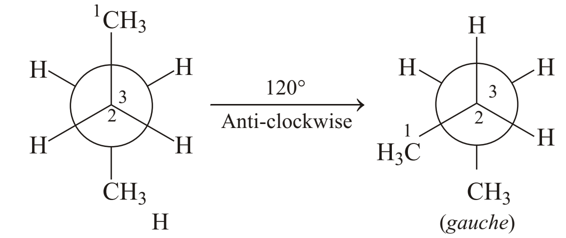
(2-bromo-5-hydroxybenzonitrile)

8.



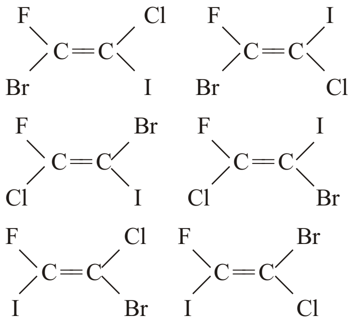


9. $C_6H_5-\overset{O}{\overset{\|}{C}}-Cl$: Benzene carbonyl chloride

10. 

11. $CH_3—CH_2—\overset{*}{C}$ COOH : Has a chiral carbon, optically active.

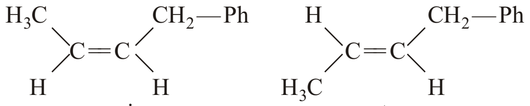
CH_3
(2-methylbutanoic acid)

12. 

Geometrical isomers

Geometrical isomers

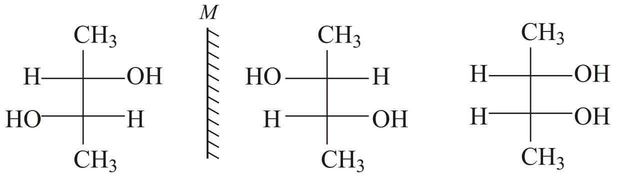
Geometrical isomers

13. 

cis *trans*

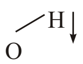
1-phenyl-2-butene

14. The 'D' term in name is derived from D-glyceraldehyde.

15. 

I II III

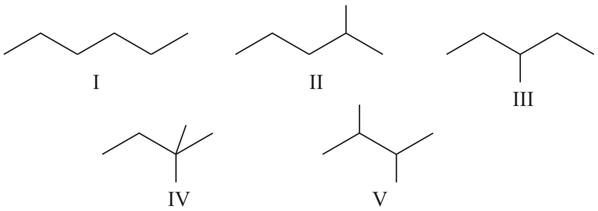
I and II are optically active while III is optically inactive (*meso* form).

16. Conformers can be interconverted through rotation about C—C bond. 

17. H—C C CH_3 :

H
Enol of acetone

It has 9 (6 with H, two C—C and one C O), one -bond and two lone-pairs.

18. 

I II III IV V

19. Compounds with same empirical formula but different molecular formula have same percentage composition of elements but different molecular weight.

20. H H
H—C—C—H ; Ethane has the smallest sized group (H)
H H

bonded to carbons, hence there will be least hindered rotation about C—C bond.

21. $\overset{1}{C}H_2{=}\overset{2}{C}H—\overset{3}{C}H—\overset{4}{C}H_3$: 3-methyl-1-butene

CH_3

22. Ethers and alcohols (saturated, acyclic) with same number of carbons are always isomeric.

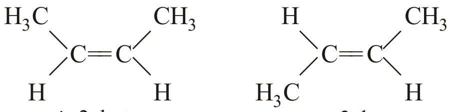
$CH_3—O—CH_3$ and $CH_3—CH_2—OH$ are functional isomers.

23. Double bond has preference over alkyl group hence :

CH_3

$H_3\overset{4}{C}—\overset{3}{C}$ $\overset{2}{C}H{=}\overset{1}{C}H_2$: 3,3-dimethyl-l-butene

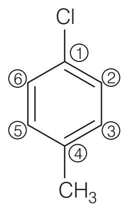
CH_3

24. 

cis-2-butene *trans*-2-butene

25. Diethyl ether ($C_2H_5OC_2H_5$) will be isomeric with all 4-carbon saturated alcohols. Butanone ($CH_3CH_2COCH_3$) is unsaturated, has two hydrogen less than the diethylether.

26. Since, there is no principal functional groups, numbering of disubstituted benzene is done in alphabetical order as



Hence IUPAC name of this compound is 1-chloro-4-methyl benzene.

Also, toluene is an acceptable name in IUPAC, hence this compound can also be named as 4-chloro toluene.

27. **PLAN** This problem is based on structure and nomenclature of organic compound.

Draw structure of each compound and write IUPAC name of the given compound.

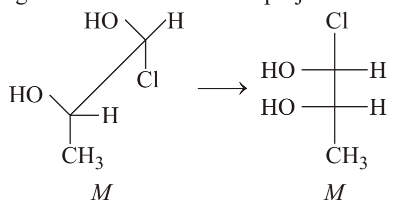
Match the molecular formula of given compound with molecular formula of compound given in choices.

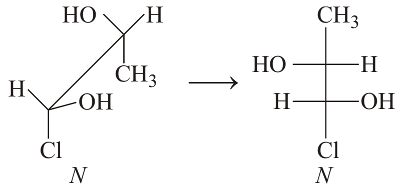
The combination of names for possible isomeric alcohols with molecular formula $C_4H_{10}O$ is/are

Formula	Names
$CH_3CH_2CH_2CH_2OH$	*n*-butyl alcohol / *n*-butanol / butan-1-ol
CH_3 CH CH_2 OH with CH_3 on CH	*Iso*-butyl alcohol / 2-methyl propan-1-ol
CH_3 CH_2 CH OH with CH_3 on CH	Secondary butyl alcohol / butan-2-ol
CH_3 C OH with two CH_3 on C	Tertiary butyl alcohol / *tert* butanol / 2-methyl propan-2-ol

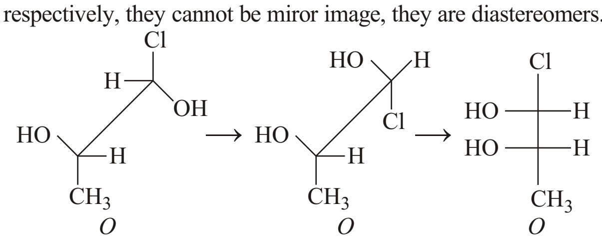
Hence, choices (a), (c) and (d) are correct.

28. Converting all of them into Fischer projection.





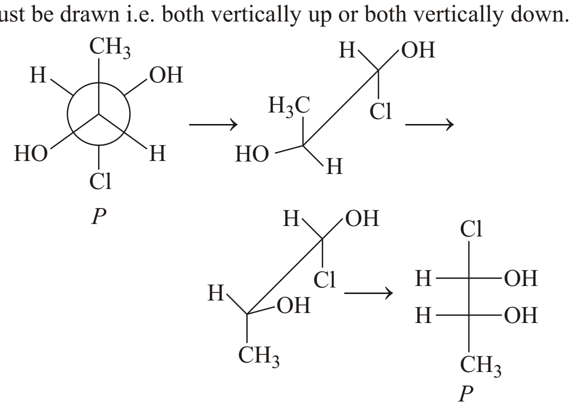
Since, *M* and *N* have OH on same side and opposite side respectively, they cannot be miror image, they are diastereomers.



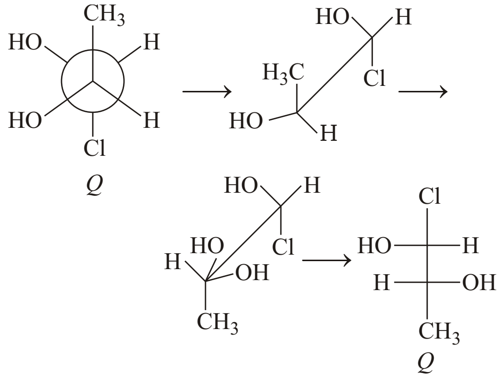
M and *O* are identical.

NOTE Fischer projection represents eclipse form of Sawhorse projection.

For comparision purpose, similar types of eclipse conformers must be drawn i.e. both vertically up or both vertically down.

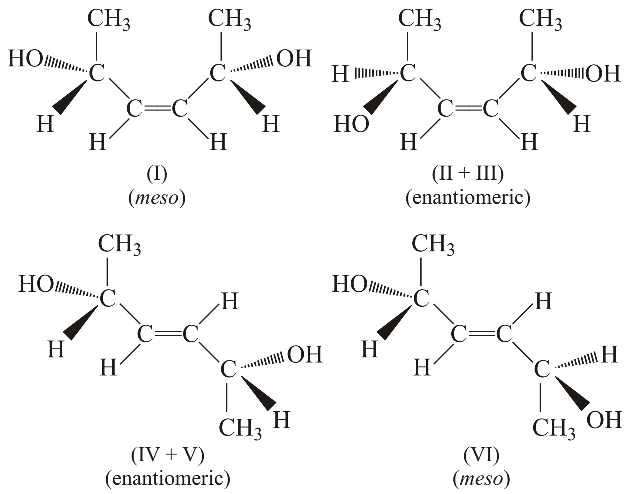


M and *P* are non-superimposable mirror images, hence, enantiomers.



M and *Q* are non-identical they are distereomers.

29.



Total six isomers. In both *cis* and *trans* forms, there are two enantiomers each.

30. *E*, *F* and *G* are not resonance structures because movement of hydrogen between *E* and *F* are involved.

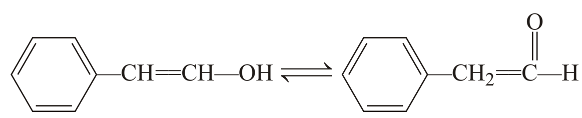
E, *F* and *E*, *G* are tautomers in which *E* is keto form and both *F* and *G* are enol form of the same *E*.

F and *G* are geometrical isomers.

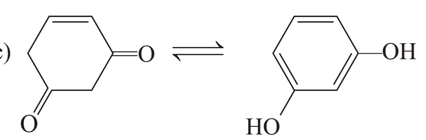
F and *G* are distereomers as they are stereo isomers but not related by mirror image relationship.

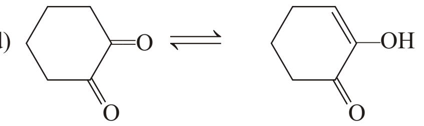
31. The compound is optically active as well as it possesses a two-fold axis of symmetry.

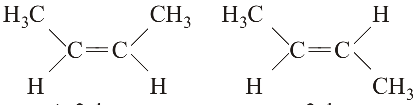
32. (a)



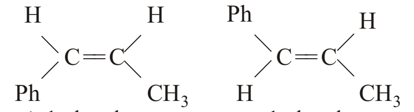
(c)



(d) 

33. (a) 

cis-2-butene *trans*-2-butene

(c) 

cis-1-phenylpropene *trans*-1-phenylpropene

34. A carbon bonded to four different atoms or groups is called asymmetric carbon :

(c) $CH_3—\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C^*}}—D$ (d) $BrCH_2—\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C^*}}—CH_3$

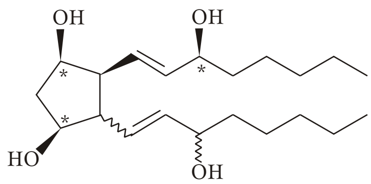
35. Carbonyl compounds containing -H show keto-enol tautomerism.

(b) $C_6H_5 \quad \overset{O}{C} \quad CH_3 \rightleftharpoons C_6H_5—\overset{OH}{C}=CH_2$

(d) $C_6H_5 \quad \overset{O}{C} \quad CH_2 \quad \overset{O}{C} \quad CH_3 \rightleftharpoons C_6H_5 \quad \overset{O}{C} \quad CH=\overset{OH}{C}—CH_3$

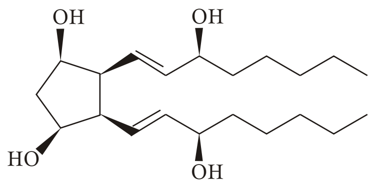
36. $CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}—CH_3 \quad \overset{Cl_2}{h} \quad CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}—CH_2Cl + CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}—CH_3$

37. (7) As given in the question 3 stereocentres are visible, i.e.



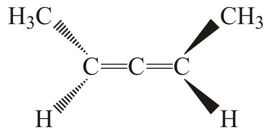
Hence, the total number of stereoisomers $2^3 \quad 8$

But out of these the following one is optically inactive due to symmetry



Hence, total number of optically active stereoisomers=7

38. Molecules that are non-superimposable on its mirror image are optically active and known as chiral molecule. However, for chirality of molecule, presence of chiral centre is not essential, e.g.



Molecule is chiral but does not possesses any chiral carbon.

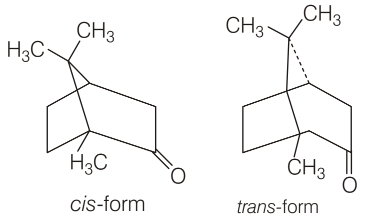
39. Non-superimposable, Enantiomers.

True / False

40. It has only two asymmetric carbon, carbon no.3 is not asymmetric.

41. They are identical.

42. Although the compound has two chiral carbons (indicated by stars), it does not has four optically active isomers as expected. It is due to its existence in *cis*-form only.

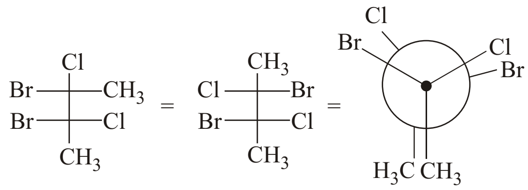


cis-form *trans*-form (only hypothetical)

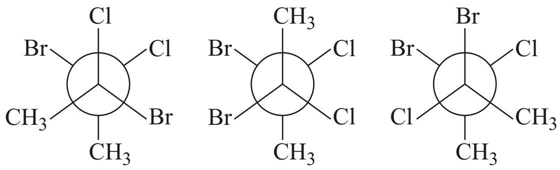
The above shown transformation does not exist due to restricted rotation about the bridge head carbons, hence only *cis*-form and its mirror image exist.

43. **PLAN** This problem can be solved by using concept of conformational analysis of given organic compound. To solve the question draw the stable conformational structures of organic compound and determine the net resultant dipole moment.

The conformations of the given compound are as follows



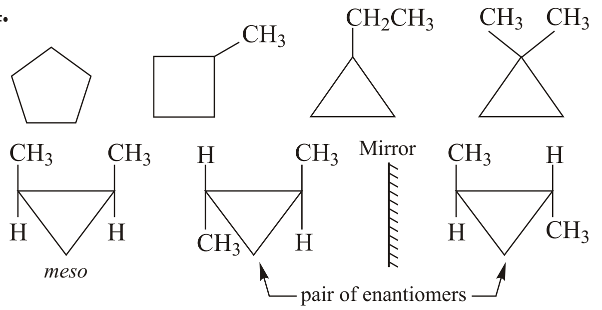
$\overset{1}{C}H_3 \quad \overset{H}{\underset{Cl}{C_2^*}} \quad \overset{H}{\underset{Cl}{C_3^*}} \quad \overset{H}{\underset{Cl}{C_4^*}} \quad \overset{5}{C}H_3$



(Me-Me)*gauche* (Br-Me)*gauche* (Cl-Me)*gauche*

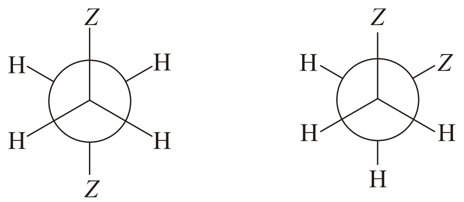
These three have non-zero dipole moment due to non-cancellation of all dipole moment created by C—Cl and C—Br bond.

44.



Total seven isomers

45. (a)



anti *gauche*

Mole fraction of *anti* form 0.82

Mole fraction of *gauche* form = 0.18

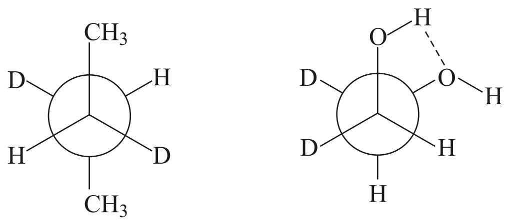
$_{obs} = 1$ D

$1 = {}_{anti} \; 0.82 + {}_{gauche} \; 0.18$

$\because \quad {}_{anti} = 0 \qquad 1 = {}_{gauche} \; 0.18$

${}_{gauche} \quad \dfrac{1}{0.18} \quad 5.55$ D

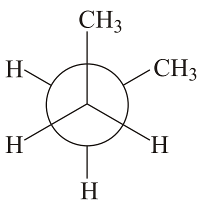
(b)



(i) (ii)

Structure (ii) is more stable than its *anti* conformer because of intramolecular H-bonding.

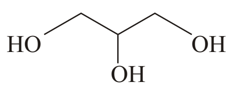
46. (a)



less stable staggered form of butane

(b) The less stability of above mentioned conformer is due to van der Waals' repulsion between the adjacent methyl groups.

47.



glycerine

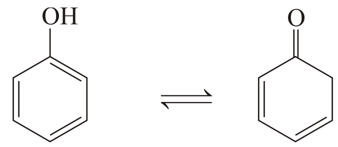
It contains a secondary (2°) hydroxy group.

48. I and III are mirror images of one another as well as they are non-superimposable while II is a *meso* form.

(I + III) = Enantiomers

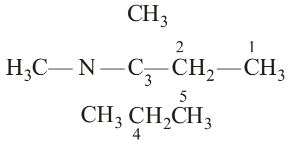
I + II and II + III = Diastereomers

49.



enol keto

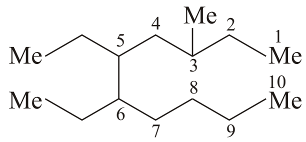
50.



3-(N, N-dimethyl)-3-methyl pentanamine

or 3-methyl-3-(N, N-dimethyl) pentanamine

51.

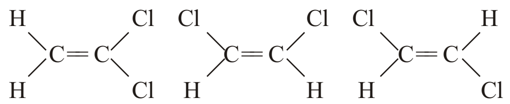


5,6-diethyl-3-methyl decane

52. $\overset{5}{CH_3}\overset{4}{CH_2}—\overset{3}{CH}{=}\overset{2}{CH}—\overset{1}{COOH}$

2-pentenoic acid or pent-2-enoic acid

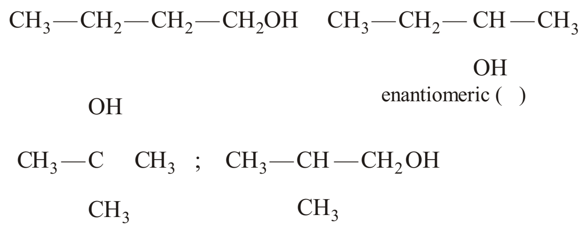
53.



I II III

III is non-polar, has zero dipole moment.

54.



Total number of isomers (including stereoisomers) = 5

Topic 2 General Organic Chemistry

1. Hydrocarbon containing C and H upon burning produces CO_2 and water vapour respectively. The equation is represented as

$$C_xH_y \quad (x \quad y/4)O_2 \qquad xCO_2 \quad (y/2)H_2O$$

Mass of carbon $\dfrac{12}{44}$ mass of CO_2

$\dfrac{12}{44}$ 88 g 24 g

Mass of hydrogen $\dfrac{2}{18}$ mass of H_2O

$\dfrac{2}{18}$ 9 1 g

So, the unknown hydrocarbon contains 24 g of carbon and 1g of hydrogen.

2. Organic compound '*A*' contain phosphorus as it gives positive test with ammonium molybdate. Phosphorus present in organic compound '*A*' get oxidised with Na_2O_2 and form Na_3PO_4.

$2P \quad 5Na_2O_2 \qquad 2Na_3PO_4 \quad 2Na_2O$
Compound Sodium phosphate

Na_3PO_4 in presence of HNO_3 form H_3PO_4 and $NaNO_3$.

$Na_3PO_4 \quad 3HNO_3 \qquad H_3PO_4 \quad 3NaNO_3$

Upon cooling, a few drops of ammonium molybdate solution are added. A yellow ppt. confirms the presence of phosphorus in the organic compound.

$H_3PO_4 \quad 12\,(NH_4)_2MoO_4 \quad 21HNO_3$
$(NH_4)_3PO_4.12MoO_3 \quad 21NH_4NO_3 \quad 12H_2O$
Yellow ppt.

3. Higher the basicity of a base, stronger will be its nucleophilic power.
Again we know, a weaker acid produces a stronger base (conjugate), i.e. a stronger nucleophile.

H

Acid	Conjugate base
H_3O^+	H_2O
CH_3SO_3H	$CH_3SO_3^{\ominus}$
CH_3CO_2H	$CH_3CO_2^{\ominus}$
H_2O	$^{\ominus}OH$
↑ Acid strength	↓ Base strength Nucleophilicity

Thus, the correct order of nucleophilicity of given nucleophiles are as follows :

$H_2O(2) < CH_3SO_3\,(3) < CH_3CO_2\,(1) < OH(4)$

4. In chromatography, the expression of retention factor (R_f) is

$$R_f \quad \frac{\text{Distance travelled by the compound from origin}}{\text{Distance travelled by the solvent from origin}} \quad 1$$

The value of R_f signifies the relative ratio of migration of each component of the mixture with respect to the developing solvent used. R_f value depends on the type of adsorption chromatography like TLC (Thin-Layer Chromatography), paper chromatography etc. The R_f value is also the characteristic of a compound (sample) for a given developing solvent at a given temperature.
When the compound in the sample (usually less polar) is weakly adsorbed the spot will travel a shorter distance from the origin and hence the R_f value will be decreased.

5. In column chromatography, separation of mixture of compounds (adsorbate) takes place over a column of solid adsorbent (silica gel and Al_2O_3) packed in a glass tube.
When an appropriate eluant (liquid) is allowed to flow down the column, the compounds present in the mixture get adsorbed to different extent on the adsorbent column and thus complete separation takes place.
Thus, column chromatography is based on the differential adsorption of the substance on the solid phase.

6. All sites (*a*, *b*, *c*, *d*, *e*) of the given molecule have lone pair on N-atoms. Higher the ease of donation of *lp* of electrons of N, more favourable will be the site for protonation. Ease of donation of *lp* of $\bar{e}s$, i.e. Lewis basicity inversely depend on the percentage of *s*-character in hybridisation of 'N' which will decide the electronegativity of 'N'.

At '*a*' and '*e*', N-atoms are sp^3 ($s\%$ 25) hybridised, whereas at '*b*', '*c*' and '*d*', N-atoms are sp^2 ($s\%$ 33) hybridised. So, '*b*', '*c*' and '*d*' are the favourable sites for protonation
(H is a Lewis acid, i.e. electrons acceptor).

7. The correct option is :
(A) (Q); (B) (R); (C) (S)

(A) **H_2O and sugar mixture** They do not react chemically. On heating, solubility of sugar in H_2O increases and on rapid cooling of saturated solution, sugar recrystallises (*Q*).

(B) **H_2O and aniline mixture** Aniline is steam volatile but insoluble in H_2O. So, steam distillation (*R*) is employed for their separation.

(C) **H_2O and toluene mixture** Toluene is steam non-volatile and also insoluble in H_2O. So, differential extraction method (S) can be used to separate them.

8. In Dumas method, organic compound is heated with dry cupric oxide in a combustion tube in the atmosphere of CO_2. Upon heating, C and H present are oxidised to CO_2 and water vapours while N_2 is set free. Let, the molecular formula of the organic compound (1 mol) be $C_xH_yN_z$. In Dumas method,

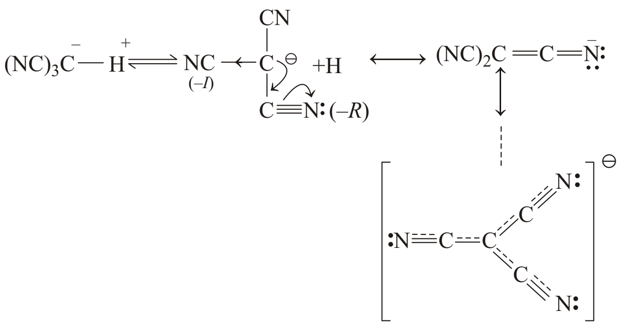
$$\underset{1\text{ mol}}{C_xH_yN_z} \quad 2x \quad \frac{y}{2}\ CuO \quad \underset{x\text{ mol}}{xCO_2} \quad \underset{\frac{y}{2}\text{ mol}}{\frac{y}{2}H_2O} \quad \underset{\frac{z}{2}\text{ mol}}{\frac{z}{2}N_2} \quad 2x \quad \frac{y}{2}\ Cu$$

Now, $x \quad 6, \frac{y}{2} \quad 4 \qquad y \quad 8$ and $\frac{z}{2} \quad 1 \quad z \quad 2$

Molecular formula of the compound is $C_6H_8N_2$.

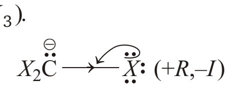
9. Dichloromethane, DCM (CH_2Cl_2) is heavier (density $1.3266\ g\,cm^{\ 3}$) than water (density $1\ g\,cm^{\ 3}$). So, DCM and H_2O will stay as lower and upper layer respectively in the separating funnel (SF).

10. We know, a stronger acid produces its stable or weaker conjugate base. Here, $CH(CN)_3$ produces the most stable conjugate base $(NC)_3C$. Stronger *R* and *I* effects of the CN group, make the carbanion (conjugate base) very stable. The resonance hybrid structure of $[(NC)_3C]$ is as follows:



Resonance hybrid structure of $[NC)_3C]^-$

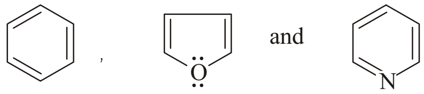
However, halogen (X Cl, Br, I) show *I* effect but *R* effect of halogens, destabilises the carbanion, X_3C^- (conjugate base of the haloform, HX_3).



Thus, $CH(CN)_3$ is the strongest acid among the given options.

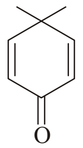
11. Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. It is because of the fact that nitrogen of these compounds does not show conversion to Ammonium sulphate ($(NH_4)_2SO_4$) during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

12. Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or $4n$ 2 rule), "For a planar, cyclic compound to be aromatic, its cloud must contain ($4n$ 2) electrons, where, n is any whole number." Thus,



(6 e^- system) (4 $e^- + 2e^-$ system) and (6 e^- system)

are aromatic and stabilised by resonance.
They follow Huckel's rule.

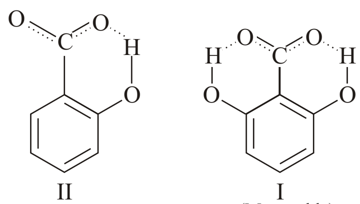


is non-aromatic, hence, least stabilised by resonance.

13. Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

14. OH group displays both kinds of effect; an electron withdrawing acid-strengthening inductive effect from the *meta*-position and an electron-releasing acid weakening resonance effect from the *para*-position (at this position, resonance effect overweighs the inductive effect).
Thus, III > IV.
o-hydroxybenzoic acid (II) is far stronger than the corresponding *meta* and *para* isomers as the carboxylate ion is stabilised by intramolecular H-bonding.
2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramolecular H-bonding, Thus, correct order is

I II III IV



II I (Most stable)

15. **THINKING PROCESS** This problem is based on the estimation of percentage of N in organic compound using Kjeldahl's method. Use the concept of stoichiometry and follow the steps given below to solve the problem.

(a) Write the balanced chemical reaction for the conversion of N present in organic compound to ammonia, ammonia to ammonium sulphate and ammonium sulphate to sodium sulphate.

(b) Calculate millimoles (m moles) of N present in organic compound followed by mass of N present in organic compound using the concept of stoichiometry.

(c) At last, calculate % of N present in organic compound using formula

$$\%\text{ of N} \quad \frac{\text{Mass of N} \quad 100}{\text{Mass of organic compound}}$$

Mass of organic compound 1.4 g

Let it contain x m mole of N atom.

Organic compound NH_3 (x m mole)

$2NH_3 + H_2SO_4$ (6 m mole initially taken) $(NH_4)_2SO_4$ …(i)

H_2SO_4 2 NaOH Na_2SO_4 2 H_2O ...(ii)

2 m mole NaOH reacted.

Hence, m moles of H_2SO_4 reacted in Eq. (ii) 1

m moles of H_2SO_4 reacted from Eq. (i) 6 1

5 m moles

m moles of NH_3 in Eq. (i) 2 5 10 m moles

m moles of N atom in the organic compound

10 m moles

Mass of N 10 10^{3} 14 0.14 g

$$\%\text{ of N} \quad \frac{\text{Mass of N present in organic compound}}{\text{Mass of organic compound}} \quad 100$$

$$\%\text{ of N} \quad \frac{0.14}{1.4} \quad 100$$

10%

16. 18 g H_2O contains 2g H

0.72 g H_2O contains 0.08 g H

44 g CO_2 contains 12 g C

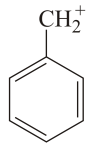
3.08 g CO_2 contains 0.84 g C

$$C : H \quad \frac{0.84}{12} : \frac{0.08}{1}$$

0.07 : 0.08 7 : 8

Empirical formula C_7H_8

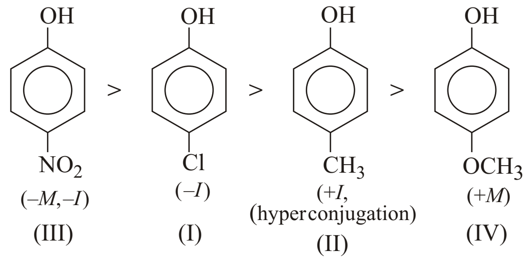
17. The order of stability of carbocation will be



$> CH_2{=}CH{-}\overset{+}{C}H_2 > CH_3{-}CH_2{-}\overset{+}{C}H_2$

Benzyl (resonance stabilised with more canonical forms) (III) | Allyl (resonance stabilised) (I) | Propyl (stabilised by $+I$ effect) (II)

18.



Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

19. Cl CH CH_3 $\xrightarrow[\text{Toluene}]{SbCl_5}$ Ph CH CH_3 $SbCl_6$

Ph ( ) (Carbocation) (planar)

Ph CH CH_3

Cl

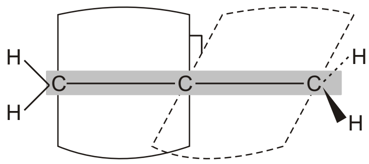
(*d* and *l*) mixture

$SbCl_5$

20. Allene is the name given to propdiene, H_2C C CH_2.
Allene

Hybridisation of an atom is determined by determining the number of hybrid orbitals at that atom which is equal to the number of sigma ( ) bonds plus number of lone pairs at the concerned atom.

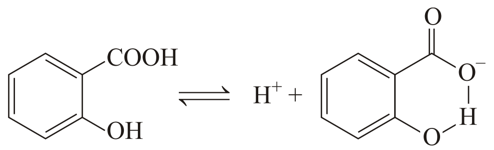
Pi( ) bonds are not formed by hybrid orbitals, therefore, not counted for hybridisation.



Here, the terminal carbons have only three sigma bonds associated with them, therefore, hybridisation of terminal carbons is sp^3. The central carbon has only two sigma bonds associated, hence hybridisation at central carbon is *sp*.

21. A mono-substituted benzoic acid is stronger than a mono-substituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, *ortho*-hydroxy acid is strongest acid although —OH causes electron donation by resonance effect which tends to decrease acid strength.

It is due to a very high stabilisation of conjugate base by intramolecular H-bond which outweigh the electron donating resonance effect of —OH.



The overall order of acid-strength of given four acids is *ortho*-hydroxybenzoic acid ($pK_a = 2.98$) > Toluic acid $pK_a = 4.37$) > *p*-hydroxybenzoic acid ($pK_a = 4.58$) > *p*-nitrophenol ($pK_a = 7.15$)

22. I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen. III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is

I > III > II > IV

23. H at C_2 will migrate giving resonance stabilised carbocation.

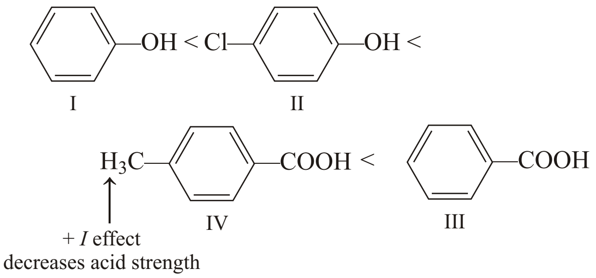
H_3C C $\overset{+}{C}$ C CH_3 $\xrightarrow[\text{shift}]{H}$ H_3C $\overset{+}{C}$ $CH_2CH(CH_3)_2$

(H above first and third C; OH H CH_3 below) (OH below)

H_3C C CH_2 $CH(CH_3)_2$

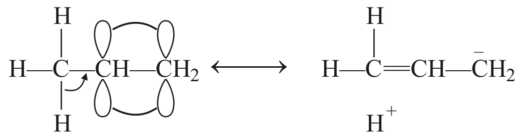
OH

24.

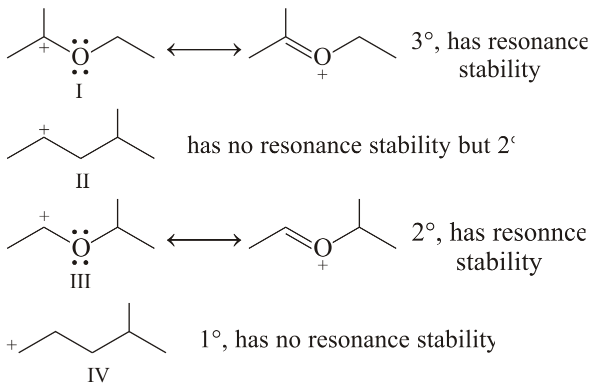


Cl has overall electron withdrawing effect, increases acid strength.

25.

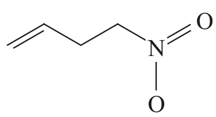


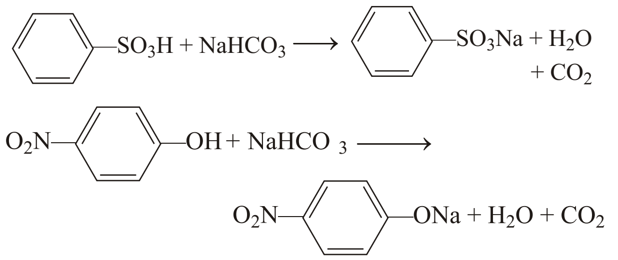
26. The -electron of C H bond is delocalised with *p*-orbitals of -bond.



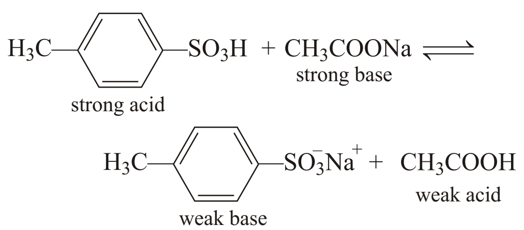
Therefore, overall stability order is : I > III > II > IV

27. The following structure has like charge on adjacent atoms, therefore, least stable



28. 

29. A spontaneous neutralisation will occur between strong acid and strong base as



30. $H_2C{=}CH \quad CH \quad CH \quad O \quad CH_3$

Lone pair of oxygen is not the part of this mode of delocalisation.

31. Carboxylic acid is stronger acid than ammonium ion, hence —COOH(X) is most acidic. $Z\,(\overset{+}{N}H_3)$ is more acidic than $Y\,(\overset{+}{N}H_3)$ due to $-I$ effect of —COOH on Z. Hence, overall acid strength order is

$$X > Z > Y$$

32. CH_3Cl has highest dipole moment.

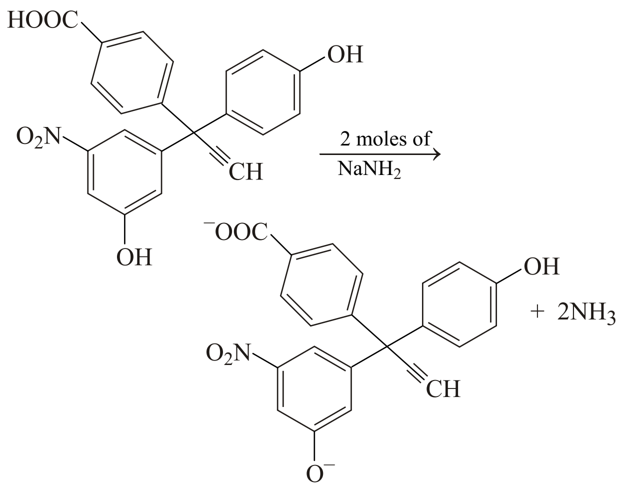
33. $\underset{sp^2}{H_2C}{=}\underset{sp^2}{CH} \quad \underset{sp}{C} \quad \underset{sp}{N}$

34. In general, the order of acid strength is

C CH < ROH < H_2O < PhOH < R COOH

Therefore, during stepwise neutralisation of given acid, —COOH will be neutralised first.

In the second step, the phenolic —OH, assisted by $-I$ effect of NO_2 at *meta* position will be neutralised.

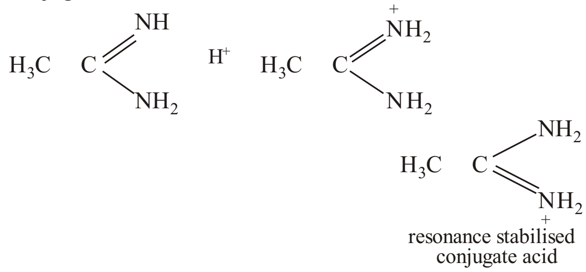


35. Weakest acid $BrCH_2CH_2COOH$ has smallest dissociation constant.

36. Butanoic acid forms more exhaustive H-bonds than butanol and butanal do not form intermolecular H-bonds. Hence, boiling point order will be 3 > 1 > 2.

37. $CH_3 \quad C \quad C \quad CH_3$
symmetric

38. I is most basic due to formation of resonance stabilised conjugate acid.



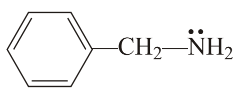
IV is amide, least basic.

$$\overset{O}{CH_3 \quad C} \quad NH_2 \qquad \overset{O}{CH_3 \quad C} \quad NH_2$$

lone pair is part of delocalisation

Also, among alkyl amines, 2° is more basic than 1° amine. Hence, overall order of basic strength is

1 > 3 > 2 > 4

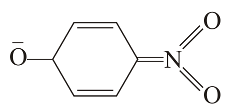
39. 

Lone pair is not taking part in resonance, most basic. In other cases, lone pair of nitrogen is part of delocalisation which decreases Lewis base strength.

40. A methylene (CH_2) with carbonyl on both side is highly acidic.

$$CH_3 \quad \overset{O}{C} \quad \underset{*}{CH_2} \quad \overset{O}{C} \quad CH_2 \quad CH_3$$

has very acidic H.

41. 

octet of nitrogen is violated.

42. Although alcohols are weaker acid than water, it is stronger than ammonia and terminal alkynes.

43. Nitro group from *para* position exert electron withdrawing resonance effect, increases acidity of phenol the most. This is followed by *meta* nitrophenol in which nitro group exert electron withdrawing effect on acidity. CH_3— is an electron donating group, decreases acid strength. Hence, the overall order is

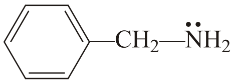
IV > III > I > II

44. CH_3CH_2 > NH_2 > H C C > HO

It is because the order of acid-strength of their conjugate acid is $CH_3CH_3 < NH_3 <$ H C C H $< H_2O$: Acid strength.

45. H C C CH$=$$CH_2$

sp sp^3

46. 

benzylamine

Lone pair is not involved in resonance, most basic. In all other cases, lone pair of nitrogen is involved in resonance, less basic.

47. $H_2C=C$ (H) C C H : It has 7 sigma and 3 pi bonds.

1-butene-3-yne

48. CH_3 $\overset{CH_3}{\underset{CH_3}{C}}$—OH $\xrightarrow[H_2O]{H^+}$ CH_3 $\overset{CH_3}{\underset{CH_3}{C^+}}$

(3°, most stable alkyl carbocation)

49. $CH_2$$=$CH $\overset{O}{CH}$ $CH_2CH$$=$$\overset{O}{CH}$ CH_2 CH $\overset{O}{C}$ H

50. N $\underset{1}{C}$ $\underset{2}{CH}$ CH_2

sp sp^2

51. **PLAN** A species is said to have aromatic character if

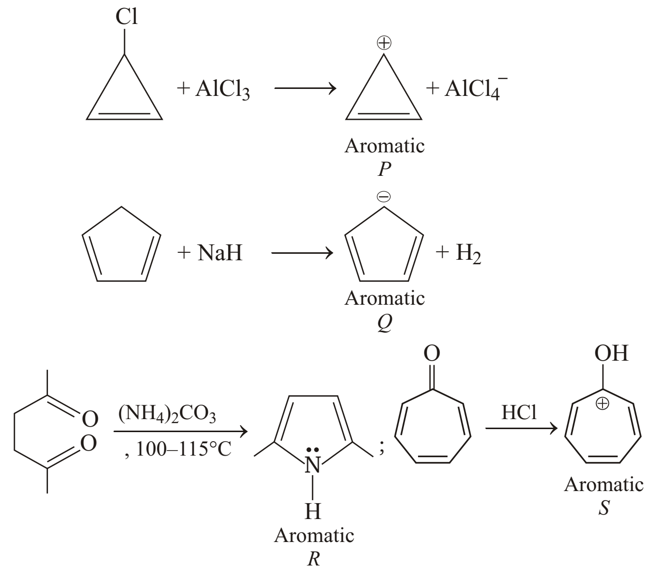
(a) ring is planar

(b) their is complete delocalisation of -electrons

(c) Huckel rule i.e. (4*n* 2) rule is followed.

where, *n* is the number of rings

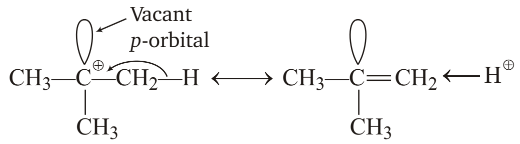
(4*n* 2) electron delocalised.



		n	(4*n* 2)	electrons
P	–	0	2	2
Q	–	1	6	6 (including lone pair)
R	–	1	6	6 (including lone pair on N)
S	–	1	6	6

In all cases there is complete delocalisation of -electrons.

52. **PLAN** Spreading out charge by the overlap of an empty *p*-orbital with an adjacent -bond is called hyperconjugation. This overlap (the hyperconjugation) delocalises the positive charge on the carbocation, spreading it over a larger volume, and this stabilises the carbocation.

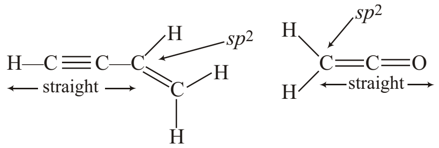


tertiary butyl carbocation has one vacant *p*-orbital, hence, it is stabilised by -*p* (empty) hyperconjugation.

H—CH_2—CH$=$CH—CH_3 ⟷ H $CH_2$$=$CH—$\overset{\ominus}{C}$H—$CH_3$

In 2-butene, stabilisation is due to hyperconjugation between - * electron delocalisation.

53. In both (b) and (c), all the atoms are present in one single plane



In (a) 1, 3-butadiene, conformational change is possible between C_2 — C_3 bond in which atoms will be present in more than one single plane.

In (d) allene, the terminals H—C—H planes are perpendicular to one another.

54. $\underset{4}{H_3C}$—$\underset{3}{CH_2}$—$\overset{CH_3}{\underset{2\;CH_3}{C}}$—$\underset{1}{CH_3}$

On C_2 — C_3 axis, *X* CH_3 , *Y* CH_3

On C_1 — C_2 axis, *X* H, *Y* C_2H_5

55. H_3C $\overset{CH_3}{\underset{CH_3}{C}}$—$CH_3$ = 0

$\begin{matrix} H_3C & & H \\ & C=C & \\ H & & C_2H_5 \end{matrix}$ 0

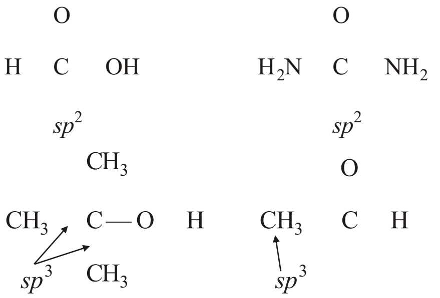
unsymmetrical

$\begin{matrix} H_5C_2 & & C_2H_5 \\ & C=C & \\ H & & H \end{matrix}$ 0

CH_3 $\overset{CH_3}{\underset{CH_3}{C}}$—$\overset{CH_3}{\underset{CH_3}{C}}$—$CH_3$ = 0

symmetrical

56.



57. Phenol is less acidic than a carboxylic acid (acetic acid). Nitro group from *para* position exert electron withdrawing resonance effect, increases acid strength. Therefore, phenol is less acidic than *p*-nitro phenol.

On the other hand, methoxy group from *para* position, donate electrons by resonance effect, decreases acid strength of phenol. Also ethanol is weaker acid than phenol due to resonance stabilisation in phenoxide ion.

Hence,

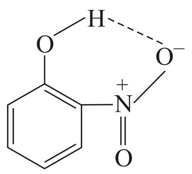
ethanol < *p*-methoxyphenol < phenol < *p*-nitrophenol < acetic acid

increasing acid strength

58. Statement I is incorrect; Statement II is correct. Intramolecular H-bonding in *ortho*-hydroxy benzoic acid lowers the boiling point.

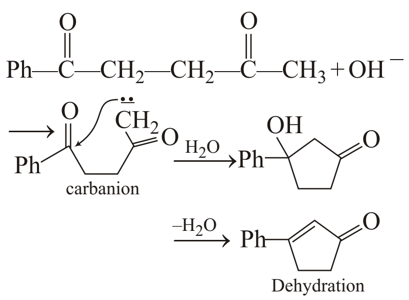
59. Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.

Intramolecular H-bonding discourage release of H to some extent, hence weaker acid than its *para* isomer.

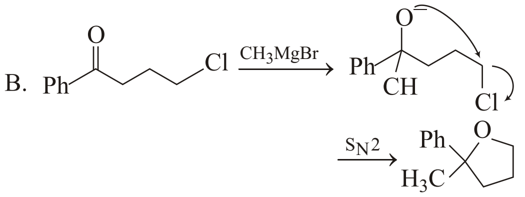


60.

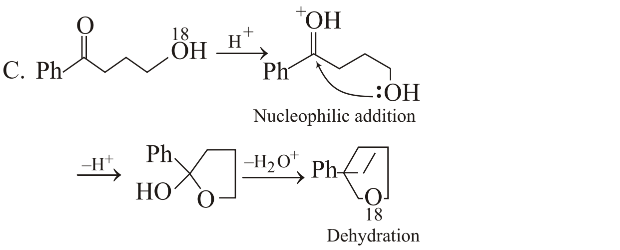
A.



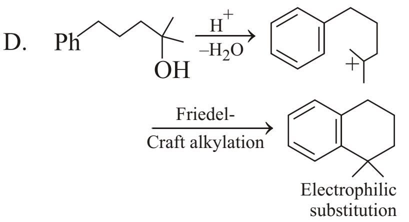
B.



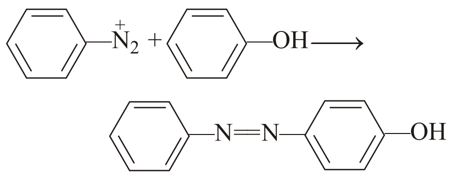
C.



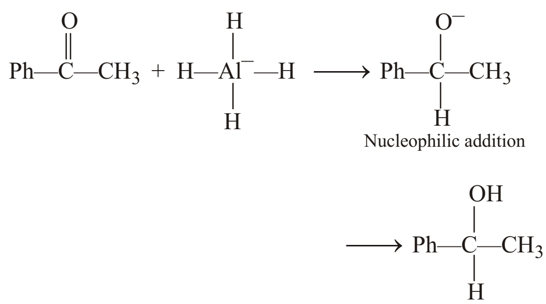
D.



61.

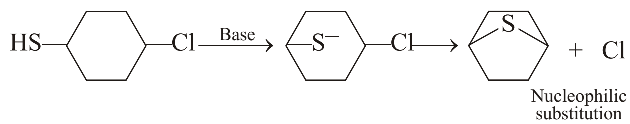


this is an example of electrophilic substitution at *para* position of phenol, giving a coupling product.



Pianacol-pinacolone rearrangement, occur through carbocation intermediate.

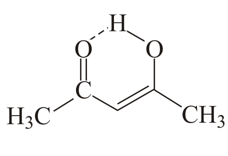
Nucleophilic addition occur at sp^2 (planar) carbon, generating a chiral centre, hence product will be a racemic mixture.



62. Hyperconjugation.

63. Less, stable free radical is formed.

64. Cyclic



65. $HO\ \ \overset{O}{C}\ \ CH_2\ \ CH_2\ \ \overset{O}{C}\ \ OH$
butanedioic acid

66. Triangular planar; carbon is sp^2-hybridised

67. *geminal*, same

68. sp^3-hybridised

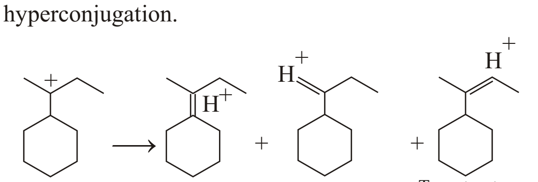
69. Cyclopropane: here the C—C—C bond angle is 60° while the requirement is 109°.

70. Propene : $\underset{sp^2}{CH_2{=}CH}\ \ \underset{sp^3}{CH_3}$

71. Aniline

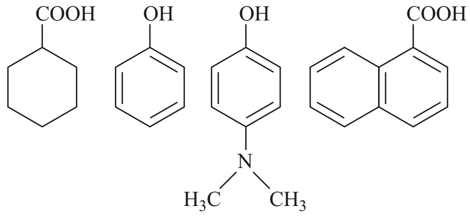
72. *Tert*-butyl carbonium ion because the three methyl group stabilises carbocation by + *I* effect.

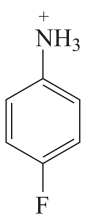
73. These are total 6 -H to sp^2 carbon and they all can participate in hyperconjugation.

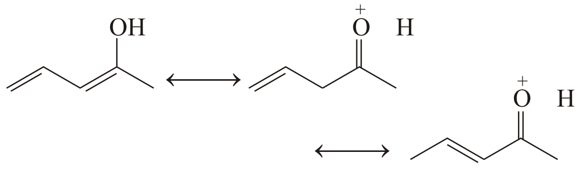


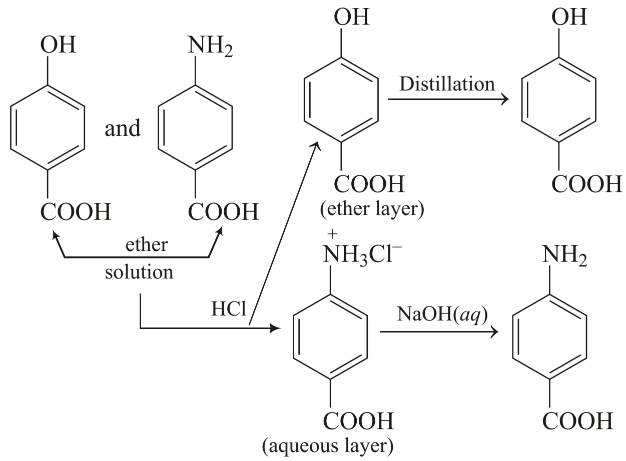
Three structures   Two structures

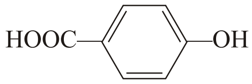
74. Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH :



75.  is more acidic due to – *I* effect of F.

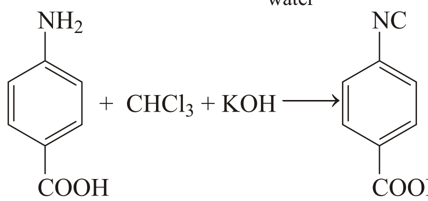
76. 

77. 

Tests of functional groups 

$FeCl_3$ violet colouration confirm phenolic group

$NaHCO_3$ CO_2 $\xrightarrow{\text{lime water}}$ milky —COOH



– NH_2 group confirmed.

characteristic foul smell of isocyanide

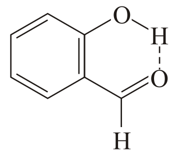
78. *p*-methoxy benzoic acid is the weakest and *p*-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acid strength of benzoic acid. Methyl group decreases acid strength of benzoic acid by + *I* effect. Therefore,

	K_a
p-methoxy benzoic acid	$3.3\ \ 10^{\ 5}$
p-methyl benzoic acid	$4.2\ \ 10^{\ 5}$
benzoic acid	$6.4\ \ 10^{\ 5}$
p-chlorobenzoic acid	$10.2\ \ 10^{\ 5}$
p-nitrobenzoic acid	$36.2\ \ 10^{\ 5}$

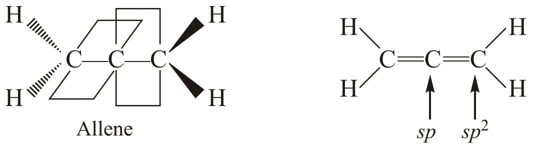
79. H C C H is more acidic than $CH_2{=}CH_2$.

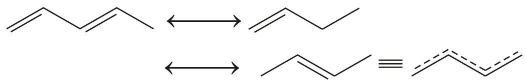
80. Intramolecular H-bonding in *ortho*-hydroxybenzaldehyde decreases its melting point as well as boiling point.

Molecules of p-hydroxybenzaldehyde is symmetrical, associated together by intermolecular H-bonds, has higher boiling point and melting point.



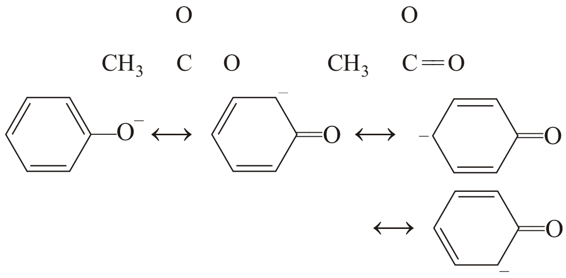
Intramolecular H-bonding

81. 

82. 

The above shown resonance introduces some double bond character to central C—C bond. Therefore, the central C—C bond in 1, 3-butadiene is shorter (stronger) than C—C bond in butane.

83. In case of acetate ion, both the resonance structures are equivalent and negative charge always remains on electronegative oxygen. These factors makes acetate ion more stable than phenoxide ion in which negative charge also moves on carbon atoms.



84. *p*-nitroaniline < aniline < *p*-toluidine < N,N-dimethyl-*p*-toluidine. Nitro group, by electron withdrawing resonance effect decreases the basic strength. Methyl group by electron donating inductive effect, increases basic strength.

Download Chapter Test
http://tinyurl.com/y6tyd62g *or*

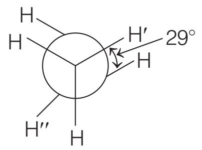
22

Hydrocarbons

Topic 1 Saturated Hydrocarbons

Objective Questions I (Only one correct option)

1. In the following skew conformation of ethane, $H'—C—C—H''$ dihedral angle is **(2019 Main, 12 April II)**

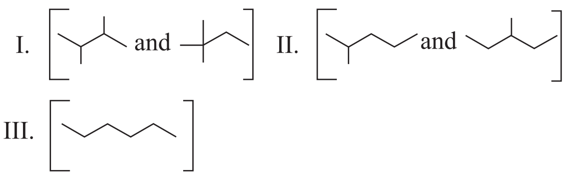


(a) 58° (b) 149° (c) 151° (d) 120°

2. Which of these factors does not govern the stability of a conformation in acyclic compounds? **(2019 Main, 10 April II)**

(a) Electrostatic forces of interaction
(b) Torsional strain
(c) Angle strain
(d) Steric interactions

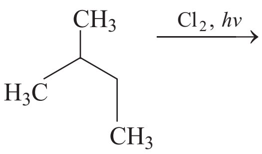
3. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. **(2014 Adv.)**



The correct order of their boiling point is

(a) I > II > III
(b) III > II > I
(c) II > III > I
(d) III > I > II

4.

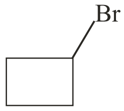


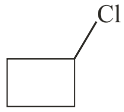
$\xrightarrow{Cl_2,\ h\nu} N$ (isomeric products) $C_5H_{11}Cl$ $\xrightarrow{\text{Fractional distillation}} M$ (isomeric products)

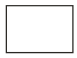
What are N and M? **(2006, 5M)**

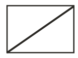
(a) 6, 6 (b) 6, 4
(c) 4, 4 (d) 3, 3

5. 1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? **(2005, 1M)**

(a) 

(b) 

(c) 

(d) 

6. How many chiral compounds are possible on mono chlorination of 2-methyl butane? **(2004, 1M)**

(a) 2 (b) 4
(c) 6 (d) 8

7. Consider the following reaction

$$\underset{\displaystyle D}{H_3C—\underset{|}{C}H}—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_3 + \dot{B}r \longrightarrow X + HBr$$

Identify the structure of the major product X **(2002, 3M)**

(a) $H_3C—\underset{D}{\underset{|}{C}H}—\underset{CH_3}{\underset{|}{C}H}—\dot{C}H_2$ (b) $H_3C—\underset{D}{\underset{|}{C}H}—\underset{CH_3}{\underset{|}{\dot{C}}}—CH_3$

(c) $H_3C—\underset{D}{\underset{|}{\dot{C}}}—\underset{CH_3}{\underset{|}{C}H}—CH_3$ (d) $H_3C—\dot{C}H—\underset{CH_3}{\underset{|}{C}H}—CH_3$

8. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with **(1998)**

(a) SO_2Cl_2 (b) $SOCl_2$
(c) Cl_2 (d) NaOCl

9. $(CH_3)_3CMgCl$ on reaction with D_2O produces **(1997)**

(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$

10. When cyclohexane is poured on water, it floats because **(1997, 1M)**

(a) cyclohexane is in 'boat' form
(b) cyclohexane is in 'chair' form
(c) cyclohexane is in 'crown' form
(d) cyclohexane is less dense than water

11. The C—H bond distance is the longest in **(1989, 1M)**

(a) C_2H_2 (b) C_2H_4
(c) C_2H_6 (d) $C_2H_2Br_2$

12. The compound which has one isopropyl group, is **(1989, 1M)**

(a) 2,2,3,3-tetramethyl pentane (b) 2,2-dimethyl pentane
(c) 2,2,3-trimethyl pentane (d) 2-methyl pentane

13. The highest boiling point is expected for **(1986, 1M)**

(a) *iso*-butane (b) *n*-octane
(c) 2, 2, 3, 3-tetramethyl butane (d) *n*-butane

14. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming ? **(1983, 1M)**

(a) Ethylene (b) Benzene
(c) Hexane (d) Aniline

15. The compound with highest boiling point is **(1982, 1M)**

(a) 2-methyl butane (b) *n*-pentane
(c) 2, 2-dimethyl propane (d) *n*-hexane

16. Marsh gas mainly contains **(1980, 1M)**

(a) C_2H_2 (b) CH_4
(c) H_2S (d) CO

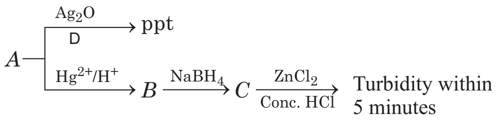
Integer Answer Type Question

17. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compound, is $CH_3CH_2CH(CH_3)CH_2CH_2$ **(2011)**

Topic 2 Unsaturated Hydrocarbons

Objective Questions I (Only one correct option)

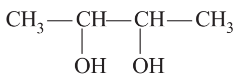
1. Consider the following reactions,



A is **(2019 Main, 12 April II)**

(a) $CH\equiv CH$ (b) $CH_3-C\equiv C-CH_3$
(c) $CH_3-C\equiv CH$ (d) $CH_2=CH_2$

2. But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give **(2019 Main, 12 April I)**

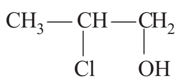
(a) 

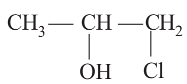
(b) one molecule of CH_3CHO and one molecule of CH_3COOH
(c) 2 molecules of CH_3COOH
(d) 2 molecules of CH_3CHO

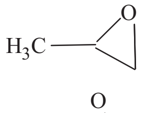
3. The major product of the following addition reaction is

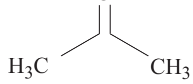
$$H_3C—CH=CH_2 \xrightarrow{Cl_2/H_2O}$$

(2019 Main, 12 April I)

(a) 

(b) 

(c) 

(d) 

4. The major product of the following reaction is

$$CH_3C\equiv CH \xrightarrow[\text{(ii) DI}]{\text{(i) DCl (1 equiv.)}}$$

(2019 Main, 9 April I)

(a) $CH_3CD(Cl)CHD(I)$ (b) $CH_3CD_2CH(Cl)(I)$
(c) $CH_3CD(I)CHD(Cl)$ (d) $CH_3C(I)(Cl)CHD_2$

5. Which one of the following alkenes when treated with HCl yields majorly an anti Markownikov product? **(2019 Main, 8 April II)**

(a) $Cl—CH=CH_2$ (b) $H_2N—CH=CH_2$
(c) $CH_3O—CH=CH_2$ (d) $F_3C—CH=CH_2$

6. The correct order for acid strength of compounds $CH\equiv CH, CH_3-C\equiv CH$ and $CH_2=CH_2$ is as follows : **(2019 Main, 12 Jan I)**

(a) $CH_3-C\equiv CH > CH_2=CH_2 > HC\equiv CH$
(b) $CH_3-C\equiv CH > CH\equiv CH > CH_2=CH_2$
(c) $HC\equiv CH > CH_3-C\equiv CH > CH_2=CH_2$
(d) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH$

7. The *trans*-alkenes are formed by the reduction of alkynes with **(2018 Main)**

(a) H_2-Pd/C, $BaSO_4$ (b) $NaBH_4$
(c) Na/liq. NH_3 (d) Sn-HCl

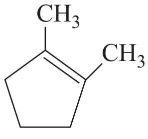
8. The reaction of propene with HOCl (Cl_2+H_2O) proceeds through the intermediate **(2016 Main)**

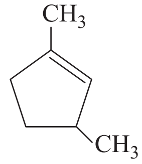
(a) $CH_3—\overset{+}{C}H—CH_2—Cl$ (b) $CH_3—CH(OH)—\overset{+}{C}H_2$
(c) $CH_3—CHCl—\overset{+}{C}H_2$ (d) $CH_3—\overset{+}{C}H—CH_2—OH$

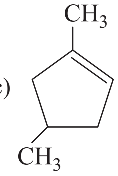
9. Which of the following compounds will exhibit geometrical isomerism? **(2015 Main)**

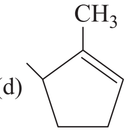
(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene (d) 1, 1-diphenyl-1-propane

10. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **(2015 Main)**

(a) 

(b) 

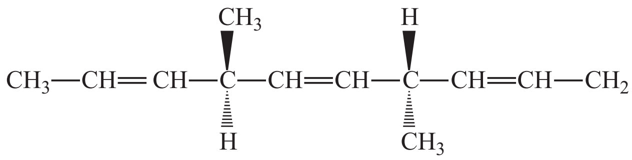
(c) 

(d) 

11. The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is **(2014 Main)**

(a) acetylene (b) ethene
(c) 2-butyne (d) 2-butene

12. The number of optically active products obtained from the complete ozonolysis of the given compound, is **(2012)**



(a) 0 (b) 1 (c) 2 (d) 4

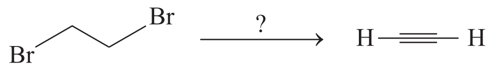
13. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are **(2010)**

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

14. The number of stereoisomers obtained by bromination of *trans*-2-butene is **(2007)**

(a) 1 (b) 2
(c) 3 (d) 4

15. The reagent(s) for the following conversion,



is/are **(2007, 3M)**

(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

16. $CH_3-CH=CH_2 + NOCl \longrightarrow P$; Identify the adduct. **(2006, 3M)**

(a) $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{NO}{\underset{|}{CH_2}}$ (b) $CH_3-\underset{NO}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(c) $CH_3-CH_2-\overset{Cl}{\overset{|}{\underset{NO}{\underset{|}{CH}}}}$ (d) $\underset{NO}{\underset{|}{CH_2}}-CH_2-\underset{Cl}{\underset{|}{CH_2}}$

17. Cyclohexene is best prepared from cyclohexanol by which of the following? **(2005)**

(a) conc. H_3PO_4 (b) conc. $HCl / ZnCl_2$
(c) conc. HCl (d) conc. HBr

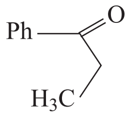
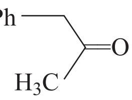
18. 2-hexyne gives *trans*-2-hexene on treatment with **(2004, 1M)**

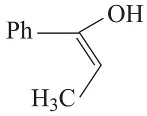
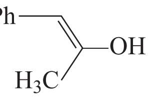
(a) Li/NH_3 (b) $Pd/BaSO_4$
(c) $LiAlH_4$ (d) Pt/H_2

19. 2-phenyl propene on acidic hydration, gives **(2004, 1M)**

(a) 2-phenyl-2-propanol
(b) 2-phenyl-1-propanol
(c) 3-phenyl-1-propanol
(d) 1-phenyl-2-propanol

20. $Ph-C\equiv C-CH_3 \xrightarrow[H^+]{Hg^{2+}} A$; A is **(2003, 3M)**

(a)  (b) 

(c)  (d) 

21. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. **(2002, 3M)**

(a) bromine, CCl_4 (b) H_2, Lindlar catalyst
(c) dilute H_2SO_4, $HgSO_4$ (d) ammoniacal $CuCl_2$ solution

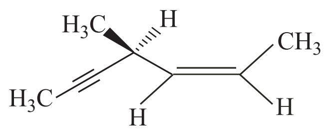
22. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because **(2001, 1M)**

(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

23. The reaction of propene with HOCl proceeds *via* the addition of **(2001)**

(a) H^+ in the first step (b) Cl^+ in the first step
(c) OH^- in the first step (d) Cl^+ and OH^- single step

24. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives **(2001, 1M)**

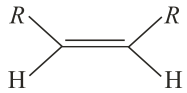
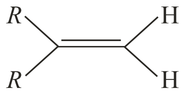


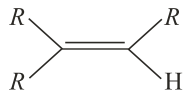
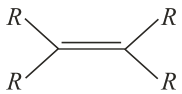
(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture

25. Propyne and propene can be distinguished by **(2000)**

(a) conc. H_2SO_4 (b) Br_2 in CCl_4
(c) dil. $KMnO_4$ (d) $AgNO_3$ in ammonia

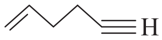
26. Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition ? **(2000, 1M)**

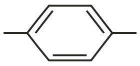
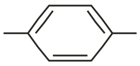
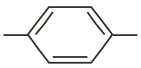
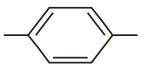
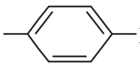
(a)  (b) 

(c)  (d) 

27. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be **(1999, 2M)**

(a) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
(b) $CH_3-CH_2-CH_2-CHO$
(c) $CH_3-CH_2-CHO + HCHO$
(d) $CH_3-CH_2-COOH + HCOOH$

28. In the compound,  , the C2-C3 bond is of the type **(1999, 2M)**
(a) $sp - sp^2$ (b) $sp^3 - sp^3$ (c) $sp - sp^3$ (d) $sp^2 - sp^3$

29. The reaction of $CH_3CH{=}CH$  OH with HBr gives **(1998, 2M)**
(a) $CH_3CHBrCH_2$  OH
(b) $CH_3CHBrCH_2$  Br
(c) CH_3CH_2CHBr  OH
(d) CH_3CH_2CHBr  Br

30. Which one of the following has the smallest heat of hydrogenation per mole ? **(1993, 1M)**
(a) 1-butene (b) *trans*-2-butene
(c) *cis*-2-butene (d) 1, 3-butadiene

31. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively, are **(1988, 1M)**
(a) 1 and 2 (b) 2 and 4 (c) 4 and 2 (d) 2 and 1

32. Acidic hydrogen is present in **(1985, 1M)**
(a) ethyne (b) ethene (c) benzene (d) ethane

33. Baeyer's reagent is **(1984, 1M)**
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution

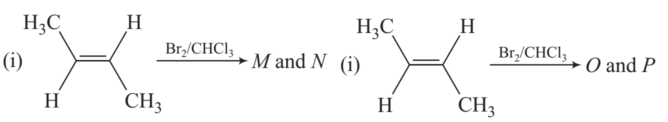
34. When propyne is treated with aqueous H_2SO_4 in the presence of $HgSO_4$, the major product is **(1983, 1M)**
(a) propanal (b) propyl hydrogen sulphate
(c) acetone (d) propanol

35. The compound 1, 2-butadiene has **(1983, 1M)**
(a) only *sp*-hybridised carbon atoms
(b) only sp^2-hybridised carbon atoms
(c) both *sp* and sp^2-hybridised carbon atoms
(d) *sp*, sp^2 and sp^3-hybridised carbon atoms

36. Which of the following will decolourise alkaline $KMnO_4$ solution? **(1980, 1M)**
(a) C_3H_8 (b) CH_4 (c) CCl_4 (d) C_2H_4

Objective Questions II
(One or more than one correct option)

37. The correct statement(s) for the following addition reactions is (are) **(2017 Adv.)**



(a) (M and O) and (N and P) are two pairs of enantiomers
(b) Bromination proceeds through *trans*-addition in both the reactions
(c) O and P are identical molecules
(d) (M and O) and (N and P) two pairs of diastereomers

Assertion and Reason

Read the following questions and answer as per the direction given below :
(a) Statement I is correct Statement II is correct Statement II is a correct explanation of Statement I.
(b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I.
(c) Statement I is correct Statement II is incorrect.
(d) Statement I is incorrect Statement II is correct.

38. **Statement I** Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.
Statement II Bromine addition to an alkene is an electrophilic addition. **(2001, 1M)**

39. **Statement I** Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.
Statement II It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. **(2001, 1M)**

40. **Statement I** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Statement II It involves the formation of a primary radical. **(2000, 1M)**

41. **Statement I** Addition of Br_2 to 1-butene gives two optical isomers.
Statement II The product contains one asymmetric carbon. **(1998 , 1M)**

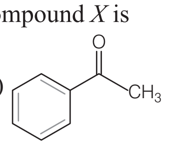
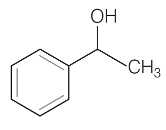
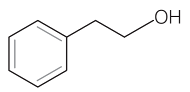
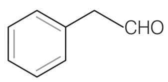
Passage Based Questions

Passage 1

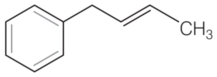
$$C_8H_6 \xrightarrow[H_2]{Pd\text{-}BaSO_4} C_8H_8 \xrightarrow[(ii)\ H_2O_2, NaOH, H_2O]{(i)\ B_2H_6} X$$

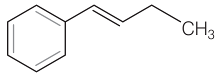
$$C_8H_6 \xrightarrow{H_2O,\ HgSO_4, H_2SO_4} C_8H_8 \xrightarrow[(ii)\ H^+,\ Heat]{(i)\ EtMgBr,\ H_2O} Y$$

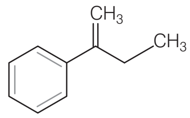
(2015 Adv.)

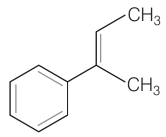
42. Compound X is
(a)  (b) 
(c)  (d) 

43. The major compound Y is

(a) 

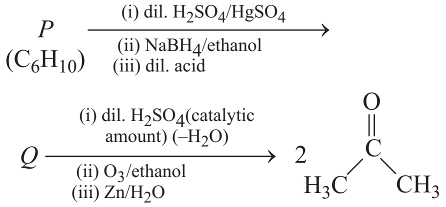
(b) 

(c) 

(d) 

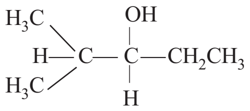
Passage 2

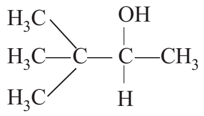
An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.

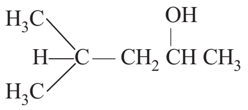


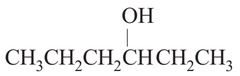
(2011)

44. The structure of the compound Q is

(a) 

(b) 

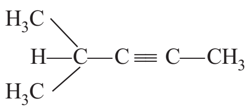
(c) 

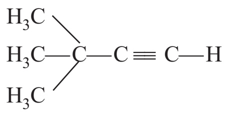
(d) 

45. The structure of compound P is

(a) $CH_3CH_2CH_2CH_2—C\equiv C—H$

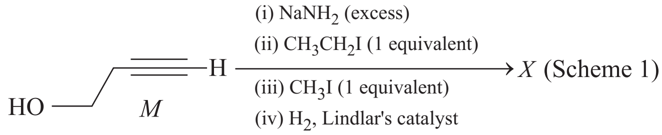
(b) $H_3CH_2C—C\equiv C—CH_2CH_3$

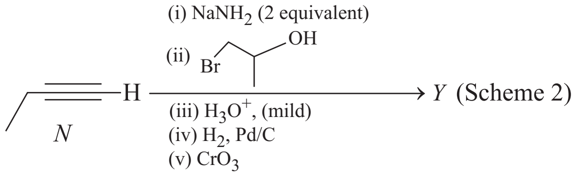
(c) 

(d) 

Passage 3

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.





46. The correct statement with respect to product Y is

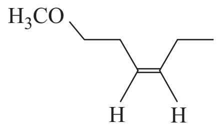
(a) it gives a positive Tollen's test and is a functional isomer of X

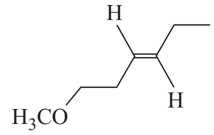
(b) it gives a positive Tollen's test and is a geometrical isomer of X

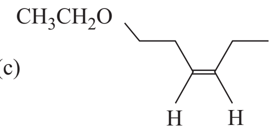
(c) it gives a positive iodoform test and is a functional isomer of X

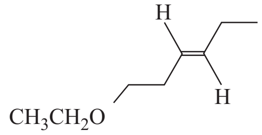
(d) it gives a positive iodoform test and is a geometrical isomer of X

47. The product X is

(a) 

(b) 

(c) 

(d) 

Fill in the Blanks

48. 1,3-butadiene with bromine in molar ratio of 1 : 1 generate predominantly .... **(1997, 1M)**

49. Addition of water to acetylene compounds is catalysed by ...... and ...... **(1993, 1M)**

50. Kolbe's electrolysis of potassium succinate gives CO_2 and .... **(1993, 1M)**

51. The terminal carbon atom in 2-butene is ...... hybridised. **(1985, 1M)**

52. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is .... **(1983, 1M)**

53. ...... is most acidic. (Ethane, Ethene, Ethyne) **(1981, 1M)**

True/False

54. Moist ethylene can be dried by passing it through concentrated sulphuric acid. **(1981)**

Integer Answer Type Question

55. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is **(2010)**

Subjective Questions

56. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH_3COCHO.

(a) Deduce the structure of A.

(b) Write the structure of all *cis* form of polymer of compound A. **(2005, 2M)**

57. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determine by the following reactions.

(a) On hydrogenation, Bombykol gives a compound A, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester.

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound A and Bombykol. How many geometrical isomers are possible for Bombykol?

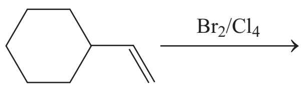
58. Identify X, Y and Z in the following synthetic scheme and write their structures.

$$CH_3CH_2—C\equiv C—H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2}$$

$$X \xrightarrow{H_2/Pd\ BaSO_4} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

Is the compound Z optically active? Justify your answer. **(2002)**

59. (a) Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures :



$$A \xrightarrow{NaNH_2} B \xrightarrow{HgSO_4/H_2SO_4} C$$

$$C \xrightarrow{H_2NHNCONH_2} D \xrightarrow{NaOD/D_2O\text{ (excess)}} E$$

(b) Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

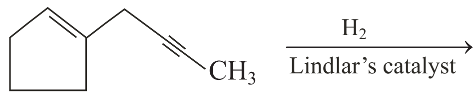
$BaC^*O_3 + H_2SO_4 \rightarrow (X)$ gas

[C* denotes C^{14}]

$$H_2C{=}CH—Br \xrightarrow[\text{(ii) } X \text{ (iii) } H_3O^+]{\text{(i) Mg/ether}} (Y) \xrightarrow{LiAlH_4} (Z)$$ **(2001)**

60. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd - C) gives a racemic mixture. **(2001)**

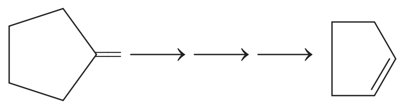
61. What would be the major product in the following reaction?



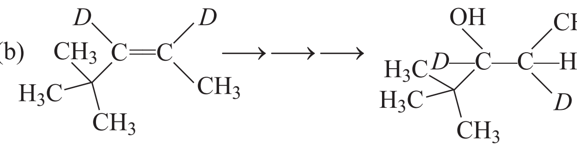
(2000, 1M)

62. Complete the following reactions with appropriate reagents :

(a)



(b)



(1999)

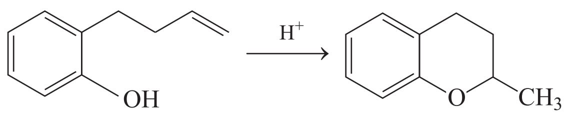
63. Complete the following reactions with appropriate structures of products/reagents :

$$C_6H_5CH{=}CH_2 \xrightarrow{Br_2} [A] \xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3 equivalent)}} [B]$$ **(1998, 2M)**

64. Write the intermediate steps for each of the following reactions :

(i) $C_6H_5CH(OH)C\equiv CH \xrightarrow{H_3O^+} C_6H_5—CH{=}CH—CHO$

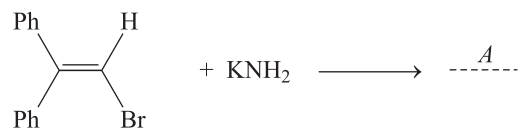
(ii)



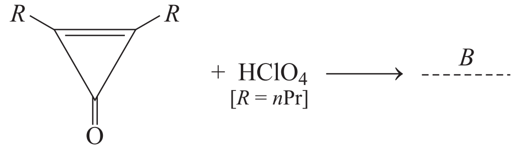
65. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidised vigorously with $KMnO_4$, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. **(1997, 2M)**

66. Complete the following, giving the structures of the principal organic products : **(1997, 1M)**

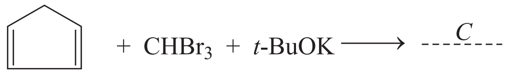
(i)



(ii)



(iii)



67. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Predict the structures of X, Y and Z. **(1996, 3M)**

68. Give the structure of the major organic products obtained from 3-ethyl-2-pentene under each of the following reaction conditions : **(1996)**

(a) HBr in the presence of peroxide

(b) Br_2 / H_2O

(c) $Hg(OAc)_2 / H_2O$, $NaBH_4$

69. Write down the structure of the stereoisomers formed when *cis*-2-butene is reacted with bromine. **(1995)**

70. An organic compound E (C_5H_8) on hydrogenation gives compound F (C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-keto propanal. Deduce the structure of compound E. **(1995)**

71. When gas A is passed through dry KOH at low temperature, a deep red coloured compound B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with Zn / H_2O yields acetaldehyde. Identify A, B and C. **(1994, 3M)**

72. Give the structures of A, B and C (explanation are not required)

(i) A (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give same product.

(ii) B (C_4H_8) which when treated with H_2O / H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.

(iii) C (C_6H_{12}), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound C_6H_{14}. **(1993, 1M × 3 = 3M)**

73. Write the balanced chemical equation for the following "Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate." **(1991, 1M)**

74. Give a chemical test and the reagents used to distinguish between cyclohexane and cyclohexene. **(1991, 1M)**

75. A white precipitate was formed slowly when silver nitrate was added to compound A with molecular formula $C_6H_{13}Cl$. Compound A on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes B and C, having formula C_6H_{12}. The mixture of B and C, on ozonolysis, furnished four compounds

(i) CH_3CHO (ii) C_2H_5CHO

(iii) CH_3COCH_3 (iv) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$

What are the structures of A, B and C ? **(1986, 4M)**

76. How would you convert acetylene to acetone? **(1985, 1M)**

77. Give the chemical test to distinguish between 2-butyne and 1-butyne. **(1985, 1M)**

78. Following statements are true, only under some specific conditions. Write the condition for each subquestion in not more than two sentences :

(i) 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide.

(ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. **(1984, 1M × 2 = 2M)**

79. Give reasons for the following in one or two sentences :

(i) Methane does not react with chlorine in the dark.

(ii) Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide. **(1983, 1M × 2 = 2M)**

80. State with balanced equation, what happens when "propene is bubbled through a hot aqueous solution of potassium permanganate."? **(1982, 1M)**

81. One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound, $C_5H_{10}Br_2$. Compound A on treatment with cold dilute alkaline potassium permanganate solution forms a compound, $C_5H_{12}O_2$. On ozonolysis A gives equimolar quantities of propanone and ethanal. Deduce the structural formula of A. **(1981, 1M)**

82. Write the structural formula of the major product in each of the following cases

(i) Ethene mixed with air is passed under pressure over a silver catalyst.

(ii) The compound obtained by hydration of ethyne is treated with dilute alkali. **(1981, 2 × 1/2 M = 1M)**

83. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). **(1981, 1M)**

84. Give one characteristic test which would distinguish CH_4 from C_2H_2. **(1979, 1M)**

Answers

Topic 1

1. (b)	**2.** (c)	**3.** (b)	**4.** (b)
5. (d)	**6.** (c)	**7.** (b)	**8.** (c)
9. (a)	**10.** (d)	**11.** (c)	**12.** (d)
13. (b)	**14.** (c)	**15.** (d)	**16.** (b)
17. (8)			

Topic 2

1. (c)	**2.** (c)	**3.** (b)	**4.** (d)
5. (d)	**6.** (c)	**7.** (c)	**8.** (a)
9. (a)	**10.** (b)	**11.** (c)	**12.** (a)
13. (d)	**14.** (a)	**15.** (b)	**16.** (a)
17. (a)	**18.** (a)	**19.** (a)	**20.** (a)
21. (d)	**22.** (c)	**23.** (b)	**24.** (b)
25. (d)	**26.** (a)	**27.** (a)	**28.** (d)
29. (c)	**30.** (b)	**31.** (b)	**32.** (a)
33. (a)	**34.** (c)	**35.** (d)	**36.** (d)
37. (a,b,d)	**38.** (b)	**39.** (a)	**40.** (c)
41. (a)	**42.** (c)	**43.** (d)	**44.** (b)
45. (d)	**46.** (c)	**47.** (a)	
48. 3,4-dibromo-1-butene		**49.** H_2SO_4, $HgSO_4$	
50. ethene	**51.** sp^3	**52.** 2-butyne	
53. Terminal alkyne (ethyne)		**54.** False	**55.** (5)

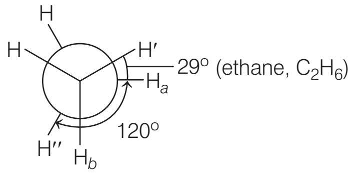
Hints & Solutions

Topic 1 Saturated Hydrocarbons

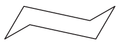
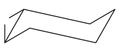
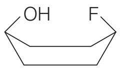
1. A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is

H′—C—C—H″

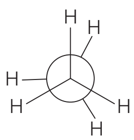
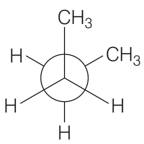
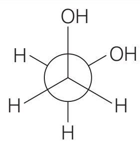
$$= (H'—C—C—H_a) + (H_a—C—C—H'')$$
$$= 29°+120° = 149°$$



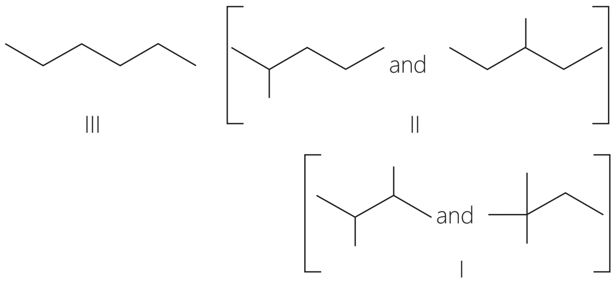
2. The four types of strains *viz* (a) electrostatic force of attraction, (b) torsional strain, (c) angle strain, (d) steric stain, are responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

Compound	Type of strains/forces
	*a* + *c*
	*a* + *b* + *c*
	*a* + *b* + *c* + *d*

In a cyclic or open-chain compounds, angle strain (c) is absent. e.g.

Compound	Types of strains/forces
	*a*
	*a* + *b*
	*a* + *b* + *d*

3. PLAN This problem is based on boiling point of isomeric alkanes. As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point

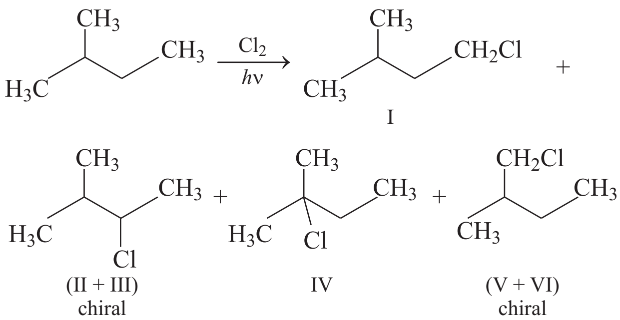


On moving left to right (III to I)

- branching increases
- surface area decreases
- boiling point decreases

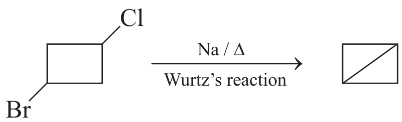
Hence, correct choice is (b).

4.



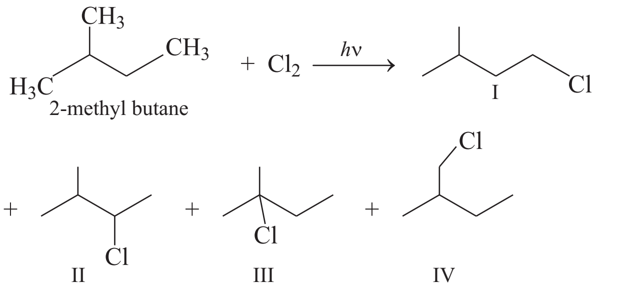
Since, fractional distillation cannot separate enantiomers (II + III and V + VI), $M = 4$ and $N = 6$.

5.



1-bromo-3-chlorocyclobutane

6.



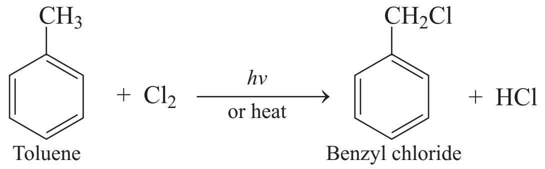
Out of the four products formed above, II and IV are chiral, produced in pairs, giving total of six mono-chlorination products.

7. Bromination is highly selective, occur at the carbon, where the most stable free radical is formed :

$$CH_3-CHD-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 + Br^{\bullet} \longrightarrow CH_3-CHD-\underset{\displaystyle CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_3 + HBr$$

(a tertiary free radical)

8. Toluene on treatment with Cl_2 in the presence of heat or light undergo free-radical chlorination at benzylic position, giving benzyl chloride

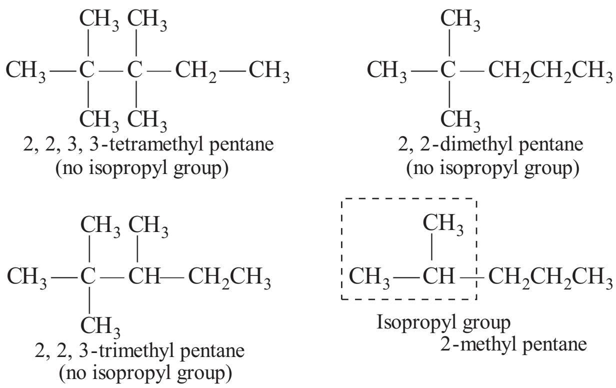


9. $(CH_3)_3CMgCl + D_2O \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-D + Mg(OD)Cl$

10. Alkanes are all less dense than water, floats over water.

11. C—H bond with sp^3-C will be longest in C_2H_6.

12.



13. Boiling point of alkane increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-octane has highest boiling point, higher than 2, 2, 3, 3-tetramethyl-butane (an isomer of *n*-octane).

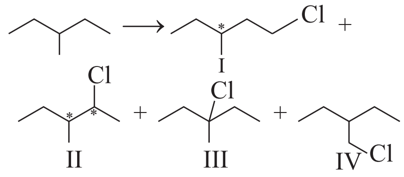
14. Ethylene absorb H_2SO_4 forming $CH_3-CH_2OSO_3H$ and dissolve. Benzene, with warm H_2SO_4, undergo sulphonation and dissolve.

Aniline, with H_2SO_4, forms anilinium sulphate salt and dissolve. Hexane, a hydrophobic molecule, does not react with H_2SO_4, remains insoluble.

15. Among alkanes, boiling point increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-hexane has highest boiling point among these.

16. Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria. Due to this method of formation, methane is also known as marsh gas.

17.



I has one chiral carbon = two isomers

II has two chiral carbons and no symmetry = four isomers.

III and IV have no chiral carbon, no stereoisomers.

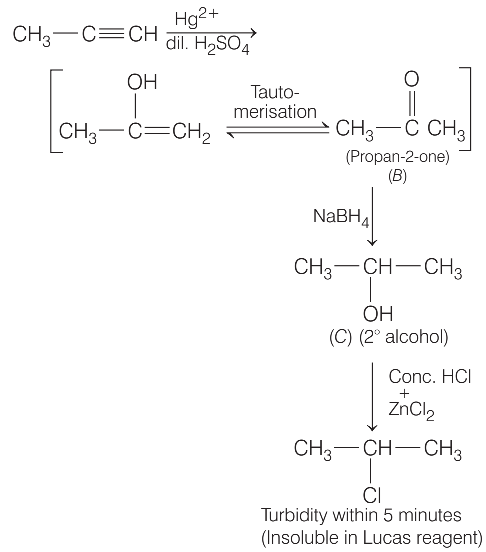
Topic 2 Unsaturated Hydrocarbons

1. According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows:

Step 1

$$\underset{\substack{\text{Prop-1-yne}\\(A)}}{CH_3-C\equiv CH} \xrightarrow{Ag_2O} \underset{\text{(Precipitates)}}{CH_3-C\equiv C-Ag\downarrow}$$

Step 2



In step-1, prop-1-yne reacts with Ag_2O to form $CH_3-C\equiv C-Ag$, that forms white precipitates.

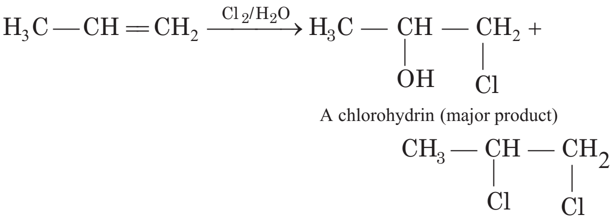
In step 2, prop-1-yne in presence of mercuric sulphate and dil $\cdot$ H_2SO_4 produces carbonyl compound $(CH_3)_2C=O$ which produces $(CH_3)_2CH-OH$ in presence of $NaBH_4$. 2°alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

2. But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give acetic acid (CH_3COOH). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes. The reaction proceed as follows :

$$\underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3} \xrightarrow[H_3O^+]{\text{Alk. } KMnO_4\text{, heat}} \underset{\text{Acetic acid}}{2CH_3COOH}$$

3. The major product of the given addition reaction is $H_3C - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{CH_2}}$.

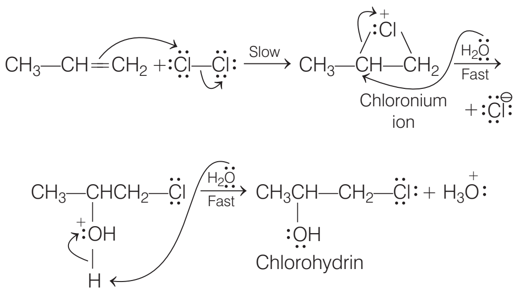
In this reaction, H_2O is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.



A chlorohydrin (major product)

(Minor product)

The reaction proceeds through following mechanism :

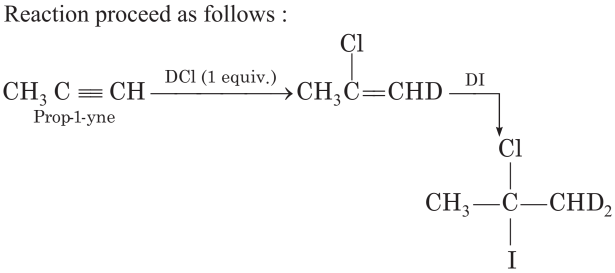


4. The major product obtained in the given reaction is $CH_3C\,(I)\,(Cl)\,CHD_2$.

$$CH_3C \equiv CH \xrightarrow[\text{2. DI}]{\text{1. DCl (1 equiv.)}} CH_3C\,(I)(Cl)CHD_2$$

Addition in unsymmetrical alkynes takes place according to Markovnikov's rule.

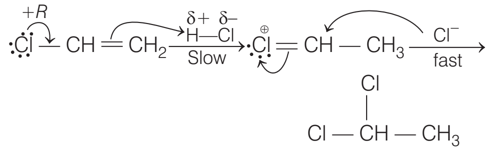
Reaction proceed as follows :



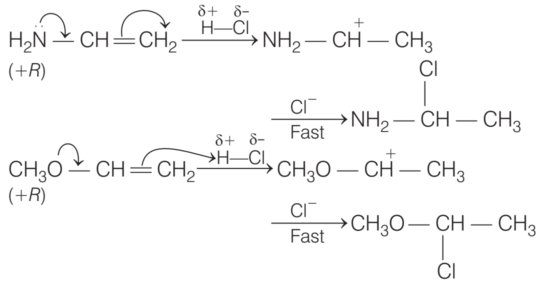
5. Attachment of electron donating group ($+R$ or $+I$) with sp^2-carbon of an unsymmetrical alkene supports Markovnikov's addition rule through electrophilic-addition-pathway.

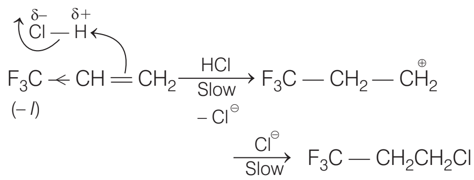
But, attachment of electron-withdrawing group ($-R$ or $-I$) for the same will follow anti-Markovnikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

The product formed by given alkenes when treated with HCl.



Similarly,





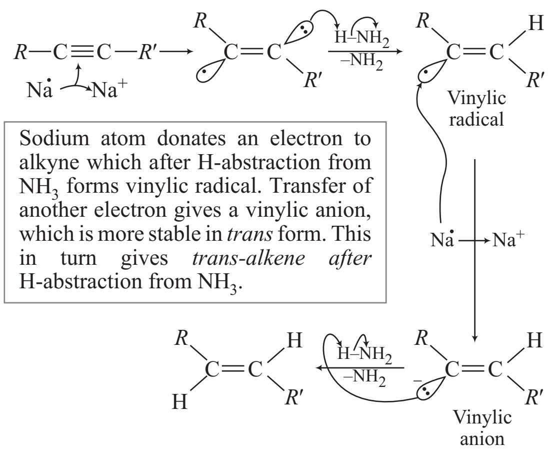
6. Ethene ($H_2C = CH_2$) is sp^2-hybridised and ethyne ($HC \equiv CH$) is sp-hybridised. In ethyne, the sp-hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity. Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

Presence of electron donating group in alkyne ($H_3C—C \equiv CH$) decreases the acidic strength of compound. Hence, the correct order of acidic strength is:

$$HC \equiv CH > H_3C - C \equiv CH > CH_2 = CH_2$$

7. Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

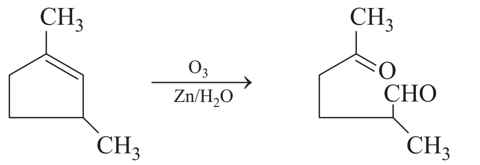
Mechanism



8. $$CH_3-CH=CH_2 \xrightarrow[\text{(Electrophilic addition)}]{\overset{\delta^-}{HO}-\overset{\delta^+}{Cl}} \underset{\text{(Intermediate)}}{CH_3-\overset{+}{C}H-CH_2-Cl} \xrightarrow{\bar{O}H} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-Cl$$

9. 

cis form　　*trans* form

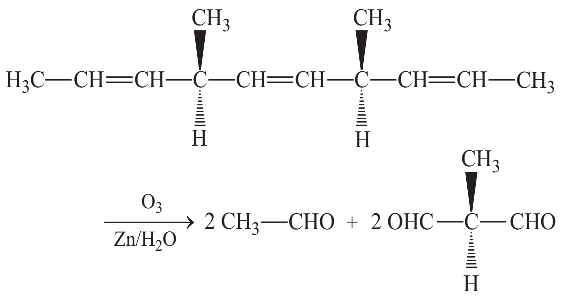
10. 

5-keto-2-methyl hexanal

11. The reaction is

$$2CH_3-CCl_3 \xrightarrow[\Delta]{6Ag} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + 6\,AgCl$$

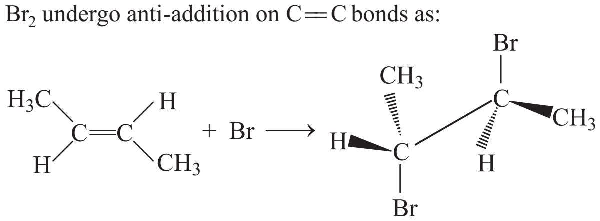
12. Ozonolysis of the given triene occur as follows :



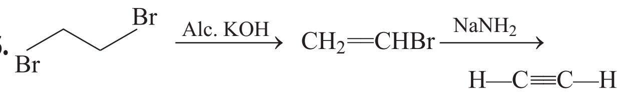
Since, none of the above dial is chiral, no optically active product is obtained.

13. $$CH_3CH_2C\equiv CH + Br-CH_2CH_2CH_2CH_3 \xrightarrow[-HBr]{} \underset{\text{3-octyne}}{CH_3CH_2-C\equiv C-CH_2CH_2CH_2CH_3}$$

14. Br_2 undergo anti-addition on C=C bonds as:



(*meso* isomer)

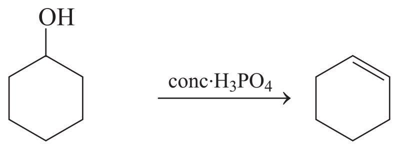
15. 

16. NOCl undergo electrophilic addition on alkene as:

$$NOCl \longrightarrow {}^{+}N=O + Cl^-$$

$$CH_3-CH=CH_2 + {}^{+}NO \longrightarrow CH_3-\underset{NO}{\underset{|}{\overset{+}{C}H}}-CH_2 \xrightarrow{Cl^-} CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{NO}{\underset{|}{CH_2}}$$

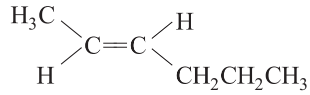
17. Cyclohexanol on treatment with concentrated H_3PO_4 undergo acid catalysed dehydration giving cyclohexene.



cyclohexanol　　cyclohexene

18. Alkynes on treatment with alkali metals in liquid ammonia gives *trans* hydrogenation product:

$$\underset{\text{2-hexyne}}{CH_3-C\equiv C-CH_2-CH_2-CH_3} \xrightarrow{Li/NH_3}$$



trans-2-hexene

19. Reaction proceeds through carbocation intermediate:

$$\underset{\text{2-phenyl propene}}{CH_3-\underset{Ph}{\underset{|}{C}}=CH_2} \xrightarrow{H^+} \underset{3°\text{, resonance stabilised}}{CH_3-\underset{Ph}{\underset{|}{\overset{+}{C}}}-CH_3} \xrightarrow{H_2O} \underset{\text{2-phenyl-2-propanol}}{CH_3-\underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3}$$

20. Reaction proceeds through carbocation intermediate :

$$Ph-C\equiv C-CH_3 + H^+ \longrightarrow \underset{\text{Resonance stabilised}}{Ph-\overset{+}{C}=CH-CH_3} \xrightarrow{H_2O}$$

$$\underset{\text{Unstable enol}}{Ph-\overset{OH}{\overset{|}{C}}=CH-CH_3} \underset{\text{(Tautomerisation)}}{\rightleftharpoons} Ph-\overset{O}{\overset{||}{C}}-CH_2-CH_3$$

21. Ammoniacal $CuCl_2$ forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:

$$CH_3-CH_2-C\equiv C-H + CuCl_2 \xrightarrow{NH_3(aq)} \underset{\text{red ppt.}}{CH_3-CH_2-C\equiv C^-Cu^+\downarrow}$$

22. In addition of HBr to an alkene, in the presence of peroxide, both the propagation steps are exothermic :

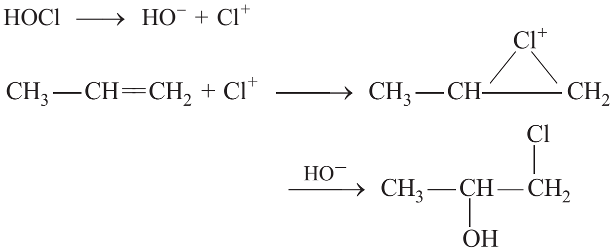
$$HBr + HO^{\bullet} \longrightarrow H_2O + Br^{\bullet}$$

Propagation

$$\begin{cases} CH_3-CH=CH_2 + Br^{\bullet} \longrightarrow CH_3-\dot{C}H-CH_2Br; \ \Delta H < 0 \\ CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3-CH_2-CH_2Br + Br^{\bullet}; \ \Delta H < 0 \end{cases}$$

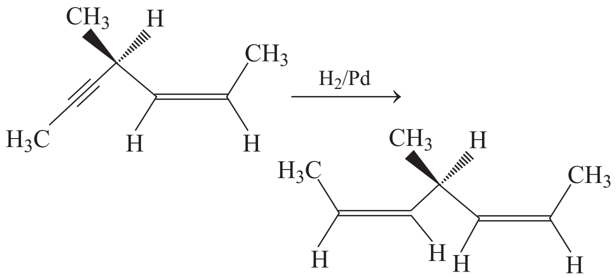
In case of addition of HCl and HI, one of the propagation step is endothermic, reaction fail to occur.

23. $HOCl \longrightarrow HO^- + Cl^+$



i.e. reaction is initiated by Cl^+ (chloronium ion electrophile)

24. Hydrogenation with poisoned palladium brings about *cis* hydrogenation of alkyne and does not affect double bonds :



meso-compound
(optically inactive)

25. Terminal alkynes forms silver salt with Tollen's reagent while alkene does not react with Tollen's reagent.

$$CH_3-C\equiv C-H + AgNO_3 \xrightarrow{NH_3(aq)} \underset{\text{white ppt.}}{CH_3-C\equiv CAg\downarrow}$$

Therefore, Tollen's reagent can be used to distinguish a terminal alkyne like propyne from alkene as well as from internal alkynes.

26. Ease of catalytic hydrogenation depends upon the size of groups present at the doubly bonded carbon. Larger the size of groups, difficult the hydrogenation. Therefore, in the given situation, disubstituted reacts at faster rate than tri and tetra substituted alkenes. Among disubstituted, the stability order is :

cis < *geminal* < *trans*.

27. Oxymercuration-demercuration brings about Markownikoff's addition of water as :

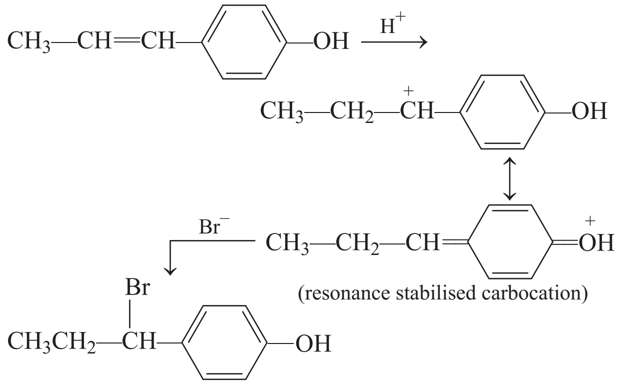
$$CH_3-CH_2-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4} \underset{\text{unstable enol}}{\left[CH_3-CH_2-\overset{\overset{OH}{|}}{C}=CH_2\right]} \longleftrightarrow \underset{\text{butanone}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

28. According to the IUPAC conventions, compound can be numbered as:

$$\overset{1}{H_2C}=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}-H$$

Here, C-2 is sp^2 and C-3 is sp^3-hybridised.

29. Electrophilic addition on C=C is governed by stability of carbocation:



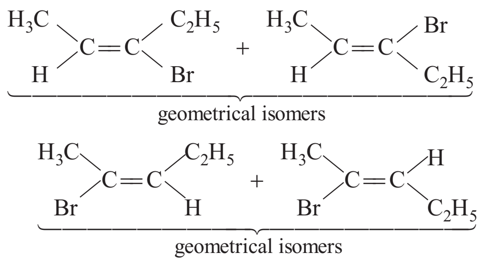
30. Among alkenes-heat of hydrogenation depends on :

(a) The number of double bonds-greater, greater the amount of heat evolved in hydrogenation.

Hence, 1, 3-butadiene has highest heat of hydrogenation among these.

(b) Relative stability of alkenes-greater the stability, smaller the heat evolved in hydrogenation. *trans*-2-butene is most stable among three given butenes, has least heat of hydrogenation.

31. $CH_3-C\equiv C-CH_2CH_3 + HBr \longrightarrow$



Therefore, two structural and four configurational isomers.

32. Terminal alkynes are slightly acidic, forms salt with very strong base like Na, $NaNH_2$ etc.

$$\underset{\text{ethyne}}{H-C\equiv C-H} + Na \xrightarrow{\Delta} H-C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$$

33. Baeyer's reagent is cold, dilute, alkaline permanganate solution, used to detect presence of olefinic bonds.

34. Alkynes undergo Markownikoff's addition of water in the presence of H_2SO_4 / $HgSO_4$:

$$CH_3-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4} \underset{\text{Unstable enol}}{\left[CH_3-\overset{\overset{OH}{|}}{C}=CH_2\right]} \underset{\text{(Tautomerisation)}}{\rightleftharpoons} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

35. Structural formula of 1, 2-butadiene is :

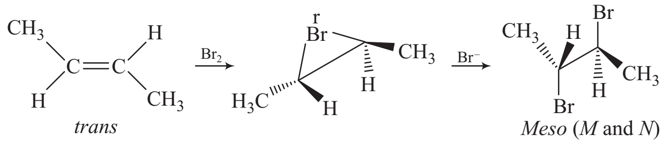
$$\underset{sp^2}{\underset{\uparrow}{H_2C}}=\underset{sp}{\underset{\uparrow}{C}}=\underset{sp^2}{\underset{\uparrow}{CH}}-\underset{sp^3}{\underset{\uparrow}{CH_3}}$$

36. Unsaturated compounds which contain C=C or C≡C, decolourises the purple colour of alkaline $KMnO_4$ solution.

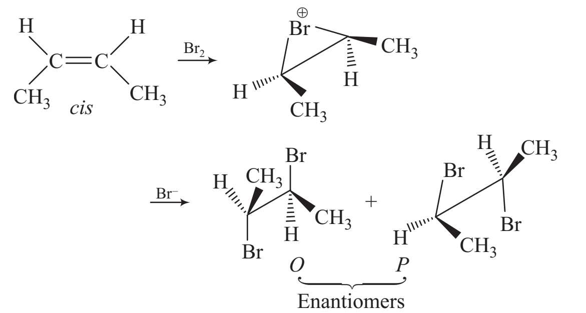
$$CH_2{=}CH_2 + \underset{\text{purple coloured}}{KMnO_4} \xrightarrow{HO^-} \begin{matrix} CH_2{-}OH \\ | \\ CH_2{-}OH \end{matrix} + MnO_2\downarrow$$

37. Addition of halogen at double bond occur in antiorientation *via* cyclic halonium ion intermediate.

(i)

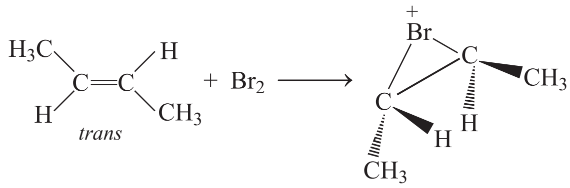


(ii)

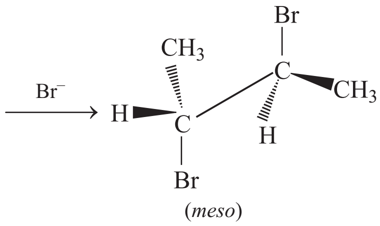


Here, ($M + O$) and ($N + P$) are pair of diastereomers.

38.

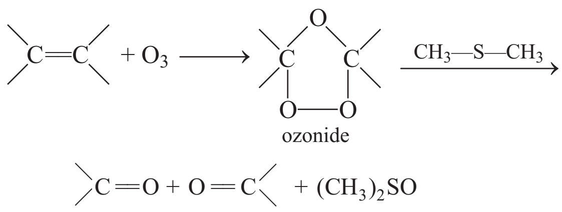


Statement I is correct. Statement II is also correct. *Meso* form of the product is due to *anti* addition of Br^- on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement I.



(*meso*)

39.



Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

40. $CH_3{-}CH_2{-}CH{=}CH_2 + Br^\bullet \longrightarrow$

$$CH_3{-}CH_2{-}\dot{C}H{-}CH_2Br$$

a secondary radical

Therefore, Statement I is correct but Statement II is incorrect.

41. $CH_3{-}CH_2{-}CH{=}CH_2 + Br_2 \longrightarrow$

$$CH_3{-}CH_2{-}\underset{Br}{\underset{|}{C}H}{-}CH_2Br$$

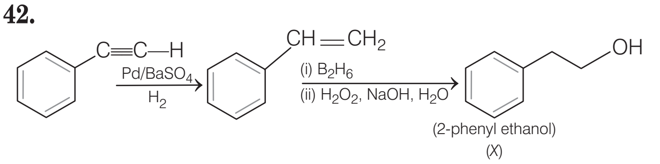
has one chiral carbon

Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

Passage 1

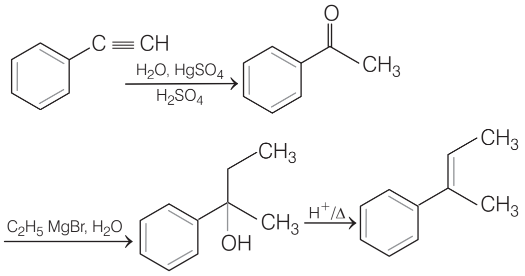
The reaction condition indicates that starting compound is phenyl acetylene.

42.



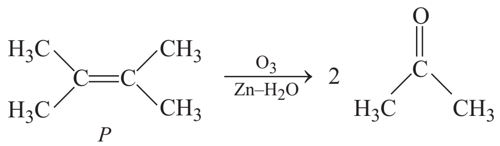
Hydroboration oxidation brings about anti-Markonikoff's hydration of alkene.

43.

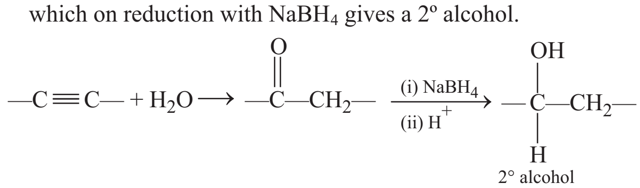


Passage 2

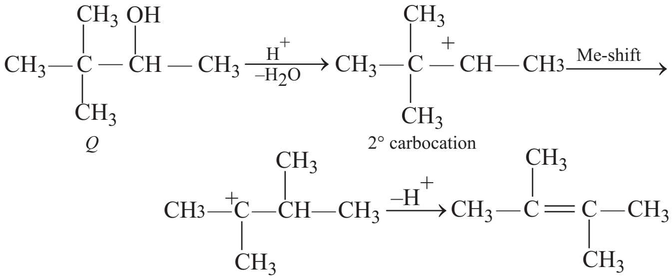
The final ozonolysis product indicates that the alkene before ozonolysis is



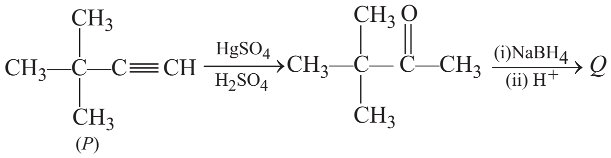
Also $P(C_6H_{10})$ has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with $NaBH_4$ gives a 2° alcohol.



The secondary alcohol that can give above shown alkene on acid catalysed dehydration is



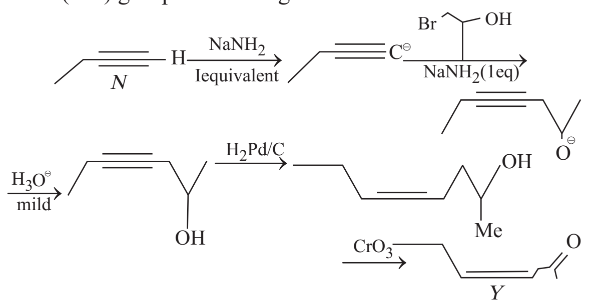
44. Explained in the beginning.

45. 

Passage 3

46. **PLAN** This problem can be solved by using the concept of iodoform test and functional isomerism.

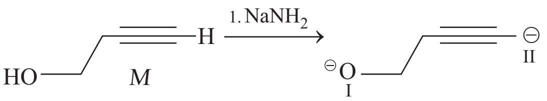
Iodoform test The compound containing —$COCH_3$ or —CH(OH) group will undergo iodoform test



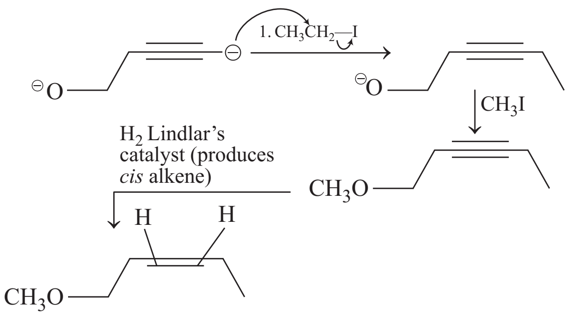
- Thus, *X* and *Y* are functional isomers of each other and *Y* gives iodoform test due to the presence of CH_3CO group as Indicated. Hence, correct choice is (c).

47. **PLAN** This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.

Reaction of Scheme 1 can be completed as

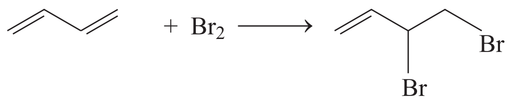


Among two nacked nucleophilic group I and II, II is more nucleophilica and then will react selectively as follows



Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (a).

48. 3, 4-dibromo-1-butene :



49. $CH\equiv CH + H_2SO_4 \xrightarrow{HgSO_4} CH_3CHO$

50. $\begin{matrix} CH_2—COOK \\ | \\ CH_2—COOK \end{matrix} \xrightarrow{\text{Electrolysis}} \underset{\text{ethene}}{CH_2{=}CH_2} + 2CO_2$

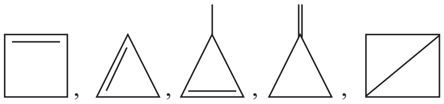
51. $CH_3—\overset{sp^3}{CH}{=}CH—CH_3$
2-butene

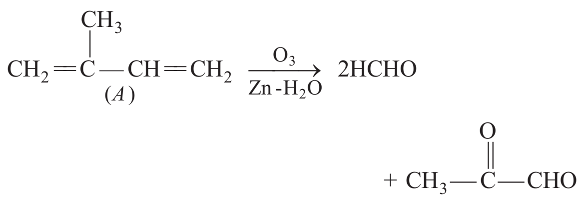
52. 2-butyne :

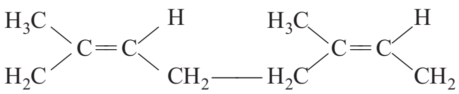
$H—C\equiv C—H + \underset{\text{excess}}{Na} \longrightarrow \overset{+}{Na}\overset{-}{C}\equiv C^{-}Na^{+} \xrightarrow[\text{excess}]{CH_3I} CH_3—C\equiv C—CH_3$

53. Terminal alkyne (ethyne) is most acidic among these.

54. Sulphuric acid undergo addition to alkene.

55. 

56. (a) 

(b) 

natural rubber

57. From oxidation products, structure of starting compound can be deduced as :

$\underset{\text{butanoic acid}}{C_3H_8—COOH} + \underset{\text{oxalic acid}}{HOOC—COOH}$

$+ \underset{\text{10-acetoxy decanoic acid}}{HOOC—(CH_2)_8—CH_2O—\overset{O}{\overset{\|}{C}}—CH_3}$

$\uparrow O_3 / H_2O_2$

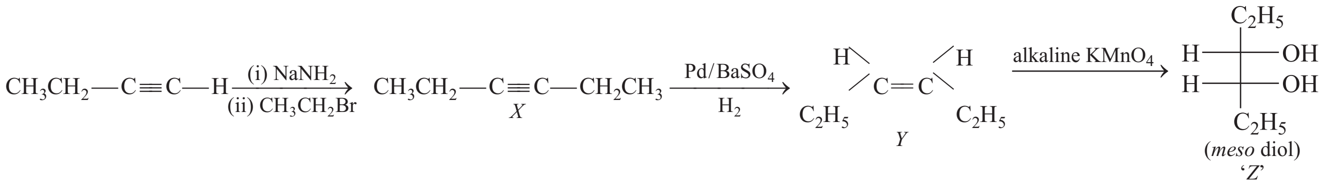
$CH_3CH_2CH_2CH{=}CH—CH{=}CH—(CH_2)_8—CH_2OCOCH_3$

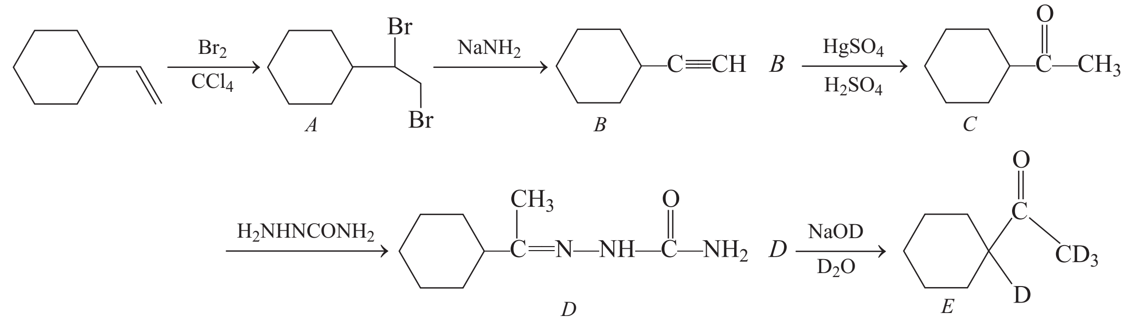
Therefore, Bombykol is :

$$\underset{\text{Bombykol}}{CH_3CH_2CH_2—CH{=}CH—CH{=}CH—(CH_2)_8—CH_2OH}$$

$$\downarrow H_2$$

$$\underset{(A)}{CH_3—(CH_2)_{14}—CH_2OH}$$

58. 

59. (a) 

(b) $Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow \underset{X}{\overset{*}{C}O_2} + BaSO_4$

$$CH_2{=}CH{-}Br \xrightarrow[\text{(ii) } X \text{ (iii) } H_3O^+]{\text{(i) Mg/ether}} \underset{Y}{CH_2{=}CH{-}\overset{\overset{O}{\|}}{\underset{*}{C}}{-}OH} \xrightarrow{LiAlH_4} \underset{Z}{CH_2{=}CH{-}\overset{*}{C}H_2{-}OH}$$

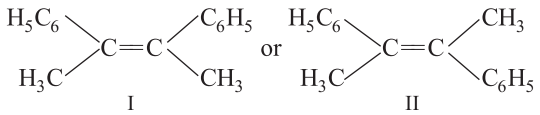
60. $B + NaOH + I_2 \longrightarrow C_6H_5{-}COONa$ (Iodoform reaction)

$\therefore$ B is $C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

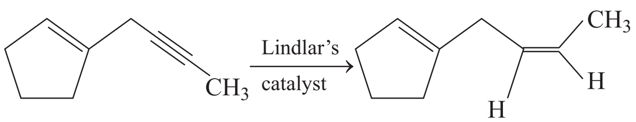
$B + N_2H_4 \xrightarrow{KOH}$ Hydrocarbon (C) $\underset{}{}$ "Wolff-Kishner Reduction"
C_8H_{10}

$\therefore C$ is $C_6H_5{-}CH_2{-}CH_3$

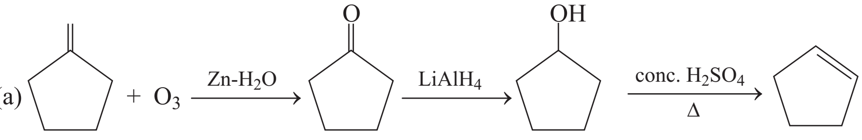
Hence, A can be one of the following :

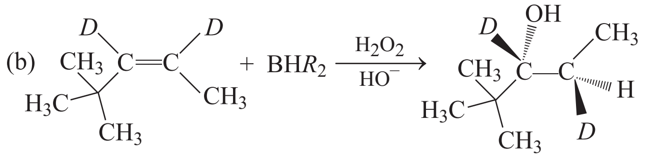


I on catalytic hydrogenation, would give meso compound while II on catalytic hydrogenation, would produce racemic mixtures.

61. 

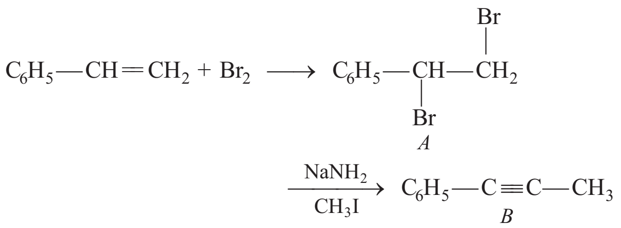
cis hydrogenation

62. (a) 

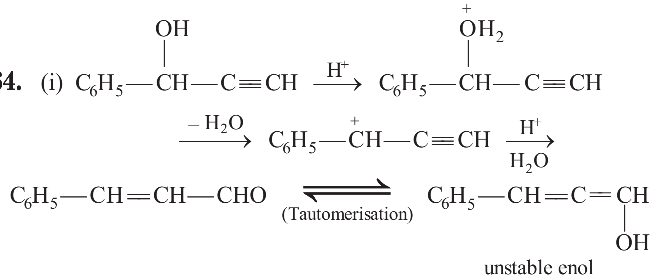
(b) 

$R = (CHl_3)_2CHCH_2$

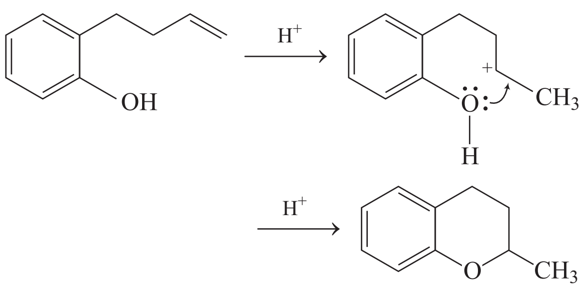
63.



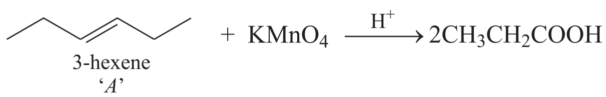
64. (i)



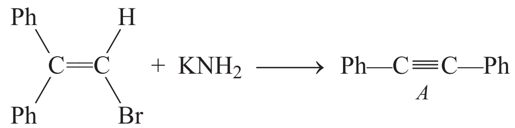
(ii)



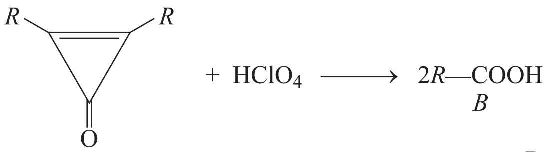
65. Oxidation product indicates that alkene is symmetrical :



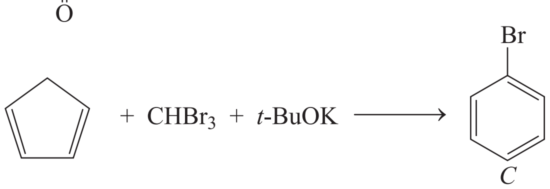
66. (i)



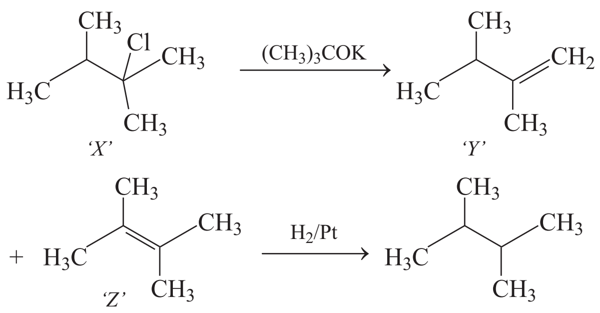
(ii)



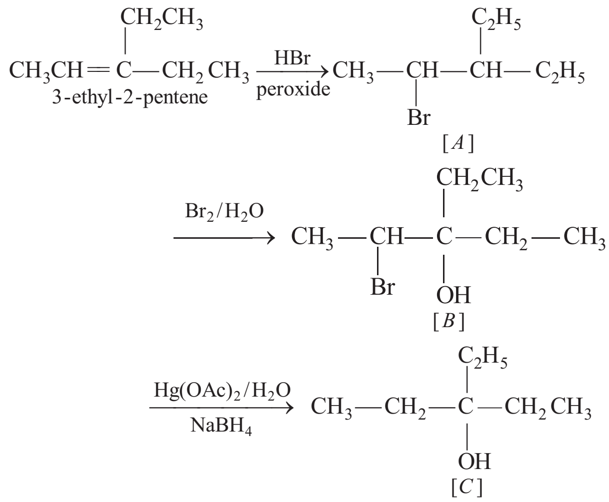
(iii)



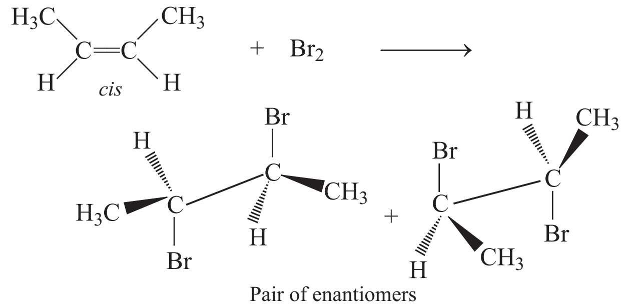
67.



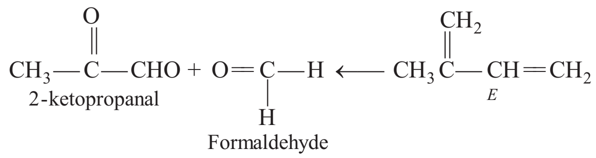
68.



69.



70.



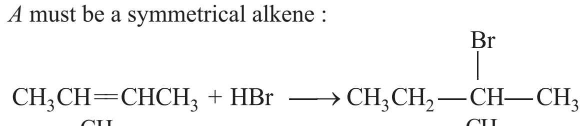
71. $CH_3-CH=CH-CH_3 \xrightarrow[Zn-H_2O]{\text{Gas } A} 2CH_3-CHO$

∴ Gas A is ozone (O_3)

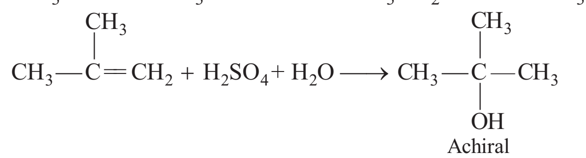
Also; Gas A + KOH (dry) $\longrightarrow$ $\underset{\text{deep red coloured}}{B}$ + Gas C

∴ $4O_3 + 4KOH \longrightarrow \underset{B}{4KO_3} + 2H_2O + \underset{C}{O_2}$

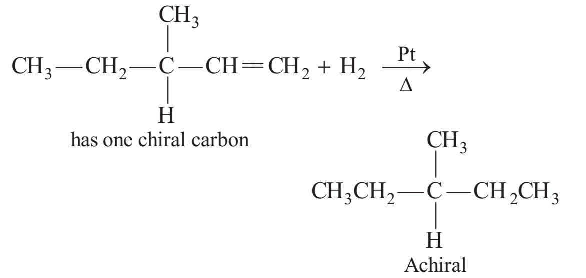
72. (i) A must be a symmetrical alkene :

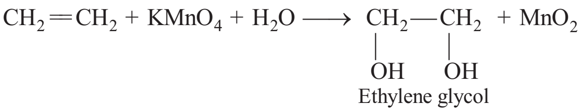


(ii)



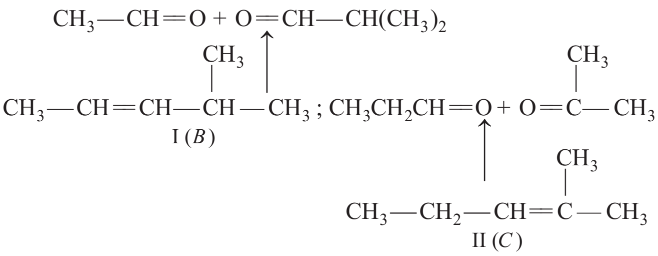
(iii)



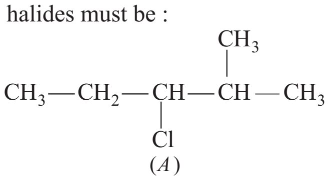
73. 

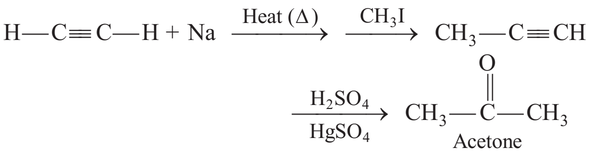
74. Baeyer's reagent (cold, dilute, alkaline permanganate) can be used to distinguish between alkanes and alkenes. Alkenes decolourises purple colour of Baeyer's reagent while alkanes do not.

75. The alkenes are :

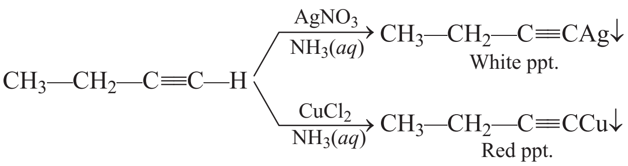


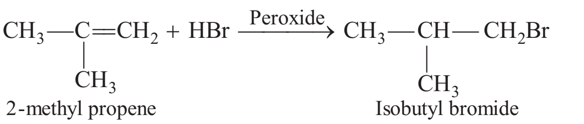
Since, both alkenes I and II are obtained by β-elimination of same halides, the halides must be :



76. 

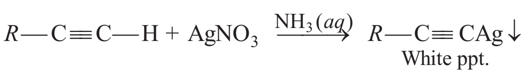
77. 1-butyne (terminal) can be distinguished from 2-butyne (internal) by either Tollen's test or through Fehling's test.



78. (i) 

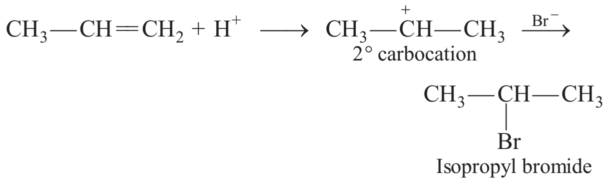
In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

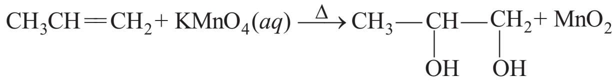
(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate :



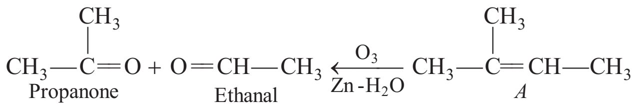
79. (i) Free radical chlorination of alkane require energy which is supplied either in the form of heat or radiation.

(ii) Addition of HBr proceeds through carbocation intermediates.

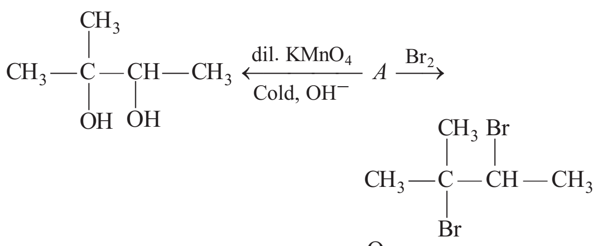


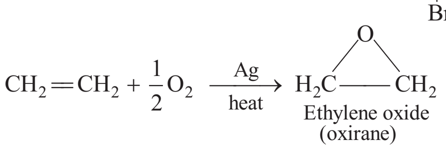
80. 

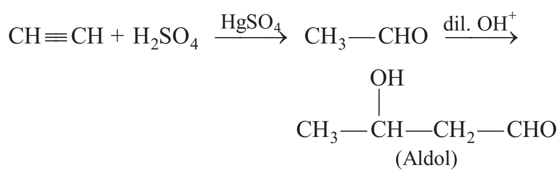
81. Ozonolysis products are the key of identification :

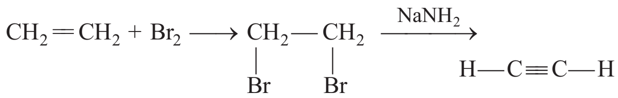


Other products are:

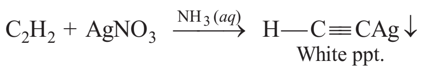


82. (i) 

(ii) 

83. 

84. Acetylene can be distinguished from methane using Tollen's reagent :

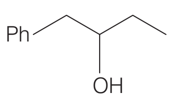
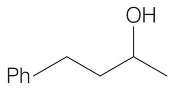
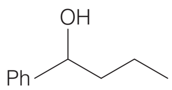
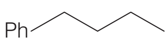


No such reaction occur with methane.

23

Alkyl Halides

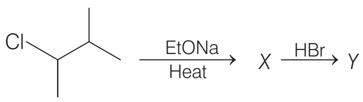
1. Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives X as the major product. Reaction of X with $Hg(OAc)_2 / H_2O$ followed by $NaBH_4$ gives Y as the major product. Y is **(2019 Main, 12 April II)**

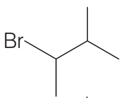
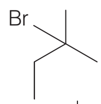
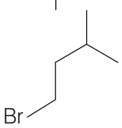
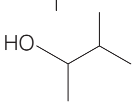
(a) 
(b) 
(c) 
(d) 

2. Which one of the following is likely to give a precipitate with $AgNO_3$ solution? **(2019 Main, 12 April II)**

(a) $CH_2{=}CH{-}Cl$
(b) CCl_4
(c) $CHCl_3$
(d) $(CH_3)_3CCl$

3. The major product Y in the following reaction is **(2019 Main, 10 April II)**



(a) 
(b) 
(c) 
(d) 

4. The major product of the following reaction is

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{CH_3OH}$$

(2019 Main, 10 April I)

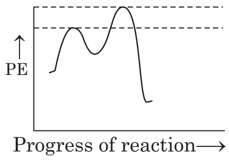
(a) $CH_3-\overset{\overset{CH_3}{|}}{C}=CHCH_3$

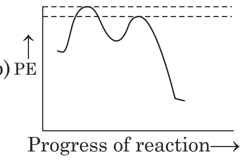
(b) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$

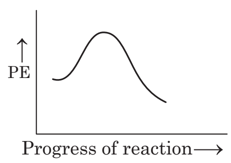
(c) $CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

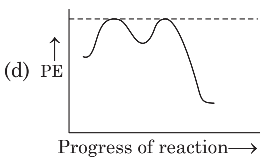
(d) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OCH_3}{|}}{C}HCH_3$

5. Which of the following potential energy (PE) diagrams represents the S_N1 reaction? **(2019 Main, 9 April II)**

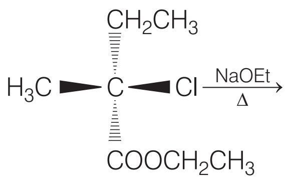
(a) 

(b) 

(c) 

(d) 

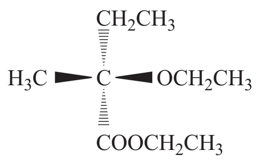
6. The major product of the following reaction is

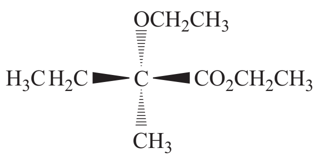


(2019 Main, 12 Jan II)

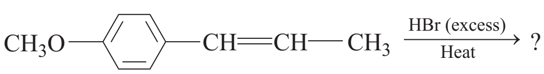
(a) $CH_3CH_2\underset{\underset{CO_2CH_2CH_3}{|}}{C}=CH_2$

(b) $CH_3\overset{\overset{CO_2CH_2CH_3}{|}}{C}=CHCH_3$

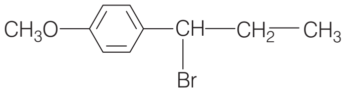
(c) 

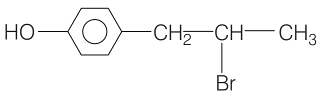
(d) 

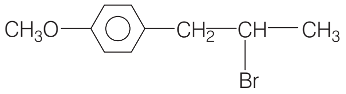
7. The major product in the following conversion is

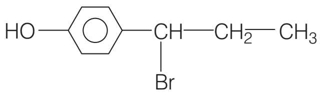


(2019 Main, 12 Jan II)

(a) 

(b) 

(c) 

(d) 

8. The major product of the following reaction is

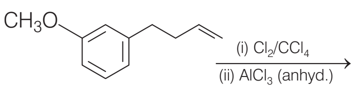
$$\underset{\qquad\ \ \ \ \ Br\ \ \ \ \ Br}{CH_3CH_2CH{-}CH_2} \xrightarrow[\text{(ii) } NaNH_2 \text{ in liq. } NH_3]{\text{(i) KOH alc.}}$$

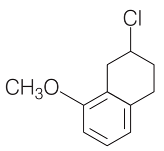
(2019 Main, 12 Jan II)

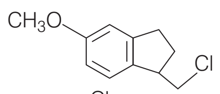
(a) $CH_3CH_2\underset{NH_2}{C}H{-}\underset{NH_2}{C}H_2$ (b) $CH_3CH{=}CHCH_2NH_2$

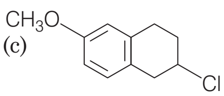
(c) $CH_3CH{=}C{=}CH_2$ (d) $CH_3CH_2C{\equiv}CH$

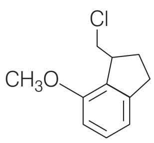
9. The major product of the following reaction is **(2019 Main, 12 Jan I)**



(a) 

(b) 

(c) 

(d) 

10. Which hydrogen in compound (*E*) is easily replaceable during bromination reaction in presence of light?

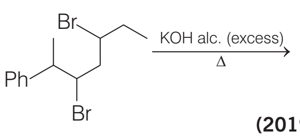
$$\underset{\delta}{CH_3}{-}\underset{\gamma}{CH_2}{-}\underset{\beta}{CH}{=}\underset{\alpha}{CH_2} \quad (E)$$

(2019 Main, 10 Jan I)

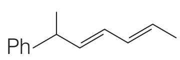
(a) β-hydrogen (b) δ-hydrogen

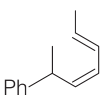
(c) γ-hydrogen (d) α-hydrogen

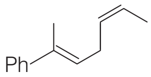
11. The major product of the following reaction is

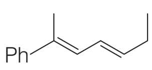


(2019 Main, 10 Jan I)

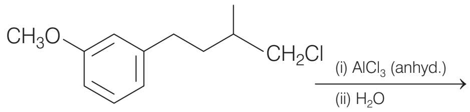
(a) 

(b) 

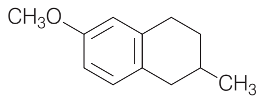
(c) 

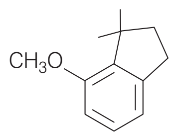
(d) 

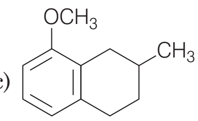
12. The major product of the following reaction is

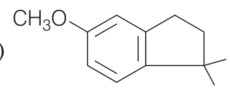


(2019 Main, 10 Jan I)

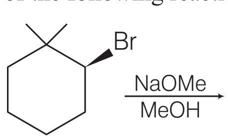
(a) 

(b) 

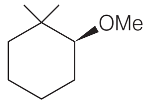
(c) 

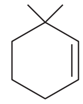
(d) 

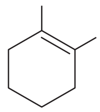
13. The major product of the following reaction is

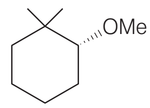


(2018 Main)

(a) 

(b) 

(c) 

(d) 

14. The increasing order of reactivity of the following halides for the S_N1 reaction is **(2017 Main)**

I. $CH_3CH(Cl)CH_2CH_3$

II. $CH_3CH_2CH_2Cl$

III. p-$H_3CO{-}C_6H_4{-}CH_2Cl$

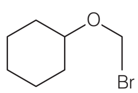
(a) (III) < (II) < (I)

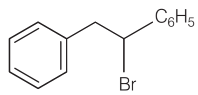
(b) (II) < (I) < (III)

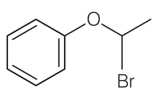
(c) (I) < (III) < (II)

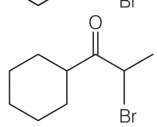
(d) (II) < (III) < (I)

15. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ? **(2017 Main)**

(a) 

(b) 

(c) 

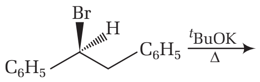
(d) 

16. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is **(2017 Main)**

(a) six (b) zero

(c) two (d) four

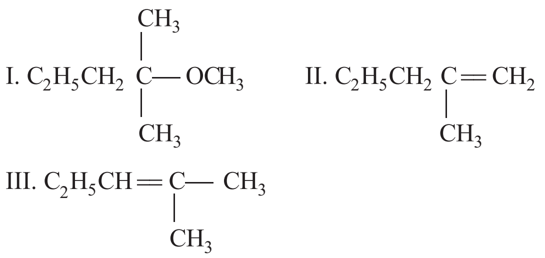
17. The major product obtained in the following reaction is



(2017 Main)

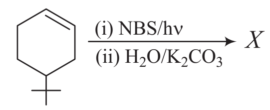
(a) $(\pm)\ C_6H_5CH(O^tBu)CH_2C_6H_5$
(b) $C_6H_5CH=CHC_6H_5$
(c) $(+)\ C_6H_5CH(O^tBu)CH_2C_6H_5$
(d) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$

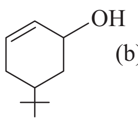
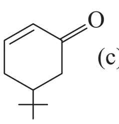
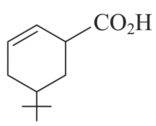
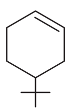
18. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields **(2016 Main)**



(a) Both I and III
(b) Only III
(c) Both I and II
(d) All of these

19. The product of the reaction given below is **(2015 Adv.)**



(a)  (b)  (c)  (d) 

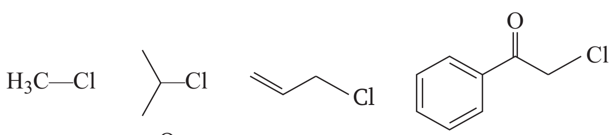
20. The synthesis of alkyl fluorides is best accomplished by **(2015 Main)**

(a) free radical fluorination
(b) Sandmeyer's reaction
(c) Finkelstein reaction
(d) Swarts reaction

21. In S_N2 reactions, the correct order of reactivity for the following compounds $CH_3Cl, CH_3CH_2Cl, (CH_3)_2CHCl$ and $(CH_3)_3CCl$ is **(2014 Main)**

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

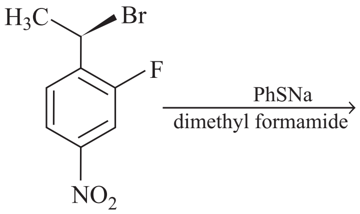
22. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as **(2013 Adv.)**

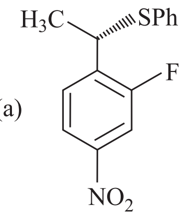


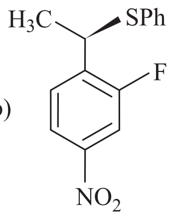
P Q R S

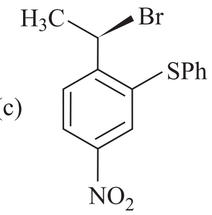
(a) $P > Q > R > S$
(b) $S > P > R > Q$
(c) $P > R > Q > S$
(d) $R > P > S > Q$

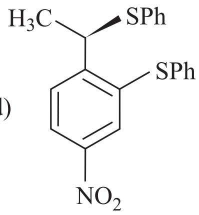
23. The major product of the following reaction is **(2008, 3M)**



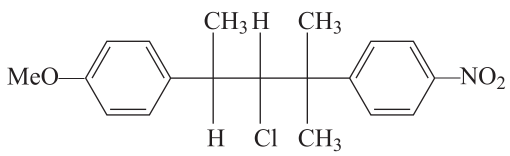
(a) 

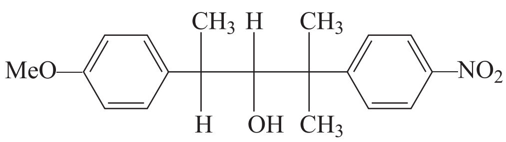
(b) 

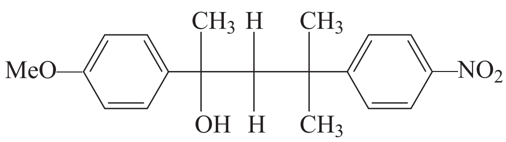
(c) 

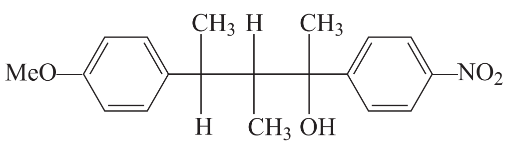
(d) 

24. The following compound on hydrolysis in aqueous acetone will give **(2005, 1M)**



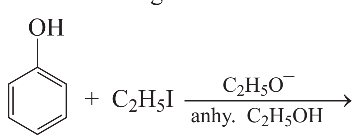
(K) 

(L) 

(M) 

It mainly gives
(a) K and L
(b) only K
(c) L and M
(d) only M

25. The product of following reaction is



(2003, 1M)

(a) $C_6H_5OC_2H_5$
(b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$
(d) C_6H_5I

26. Identify the set of reagents/reaction conditions X and Y in the following set of transformations– **(2002, 3M)**

$$CH_3—CH_2—CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3—\underset{\underset{Br}{|}}{CH}—CH_3$$

(a) X = dilute aqueous NaOH, 20°C, Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C, Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C, $Y = Br_2/CHCl_3$, 0°C
(d) X = concentrated aqueous NaOH, 80°C, $Y = Br_2/CHCl_3$, 0°C

27. The compound that will react most readily with NaOH to form methanol is **(2001, 1M)**

(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
(c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3Cl$

28. An S_N2 reaction at an asymmetric carbon of a compound always gives **(2001)**

(a) an enantiomer of the substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereomers
(d) a single stereoisomer

29. The order of reactivities of the following alkyl halides for a S_N2 reaction is– **(2000, 1M)**

(a) $RF > RCl > RBr > RI$ (b) $RF > RBr > RCl > RI$
(c) $RCl > RBr > RF > RI$ (d) $RI > RBr > RCl > RF$

30. Which of the following has the highest nucleophilicity? **(2000)**

(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^-

31. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of **(1999)**

(a) carbanion (b) carbene
(c) free-radical (d) carbocation

32. Which of the following is an organometallic compound? **(1997)**

(a) Lithium methoxide (b) Lithium acetate
(c) Lithium dimethylamide (d) Methyl lithium

33. $(CH_3)_3CMgCl$ on treatment with D_2O produces **(1997, 1M)**

(a) $(CH_3)_3CD$ (b) $(CH_3)_3COD$ (c) $(CD)_3CD$ (d) $(CD)_3COD$

34. 1-chlorobutane on reaction with alcoholic potash gives **(1991, 1M)**

(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

35. *n*-propyl bromide on treatment with ethanolic potassium hydroxide produces **(1987, 1M)**

(a) propane (b) propene (c) propyne (d) propanol

36. The reaction condition leading to the best yield of C_2H_5Cl are– **(1986, 1M)**

(a) $C_2H_6\text{(excess)} + Cl_2 \xrightarrow{\text{UV light}}$

(b) $C_2H_6 + Cl_2\text{ (excess)} \xrightarrow[\text{room temp.}]{\text{dark}}$

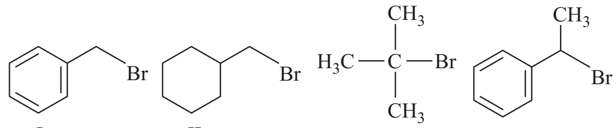
(c) $C_2H_6 + Cl_2\text{ (excess)} \xrightarrow{\text{UV light}}$

(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

Objective Questions II

(One or more than one correct option)

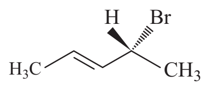
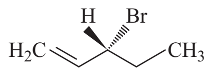
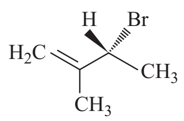
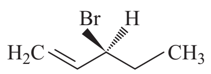
37. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are) **(2017 Adv.)**



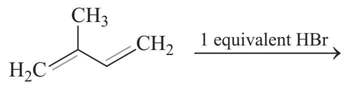
I II III IV

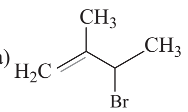
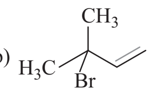
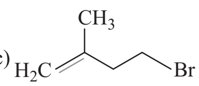
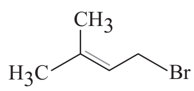
(a) Compound IV undergoes inversion of configuration
(b) The order of reactivity for I, III and IV is : IV > I > III
(c) I and III follow S_N1 mechanism
(d) I and II follow S_N1 mechanism

38. Compound(s) that on hydrogenation produce(s) optically inactive compound (s) is/are **(2015 Adv.)**

(a) 
(b) 
(c) 
(d) 

39. In the following reaction, the major product is **(2015 Adv.)**



(a) 
(b) 
(c) 
(d) 

40. The compounds used as refrigerant are **(1990, 1M)**

(a) NH_3 (b) CCl_4 (c) CF_4 (d) CF_2Cl_2
(e) CH_2F_2

Assertion and Reason

41. An **Assertion** and a **Reason** are given below. Choose the correct answer from the following options.

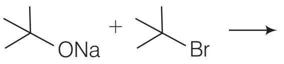
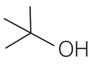
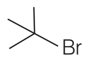
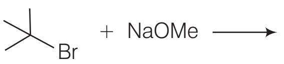
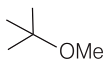
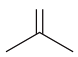
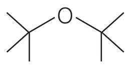
Assertion (A) Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R) Even though the intermediate carbocation is stabilised by loosely held π-electrons, the cleavage is difficult because of strong bonding. **(2019 Main, 12 April II)**

(a) Both (A) and (R) are wrong statements.
(b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).
(c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
(d) (A) is a correct statement but (R) is a wrong statement.

Match the Columns

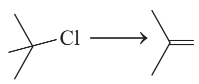
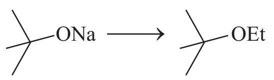
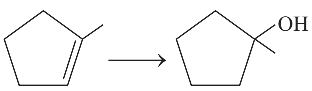
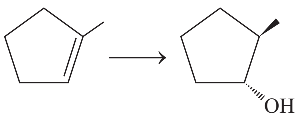
42. List-I contains reactions and List-II contains major products.

	List-I		List-II
P.		1.	
Q.		2.	
R.		3.	
S.		4.	
		5.	

Match each reaction in List-I with one or more products in List-II and choose the correct option. **(2018 Adv.)**

(a) P $\rightarrow$ 1, 5; Q $\rightarrow$ 2; R $\rightarrow$ 3; S $\rightarrow$ 4
(b) P $\rightarrow$ 1, 4; Q $\rightarrow$ 2; R $\rightarrow$ 4; S $\rightarrow$ 3
(c) P $\rightarrow$ 1, 4; Q $\rightarrow$ 1,2; R $\rightarrow$ 3,4; S $\rightarrow$ 4
(d) P $\rightarrow$ 4, 5; Q $\rightarrow$ 4; R $\rightarrow$ 4; S $\rightarrow$ 3,4

43. Match the chemical conversion in Column I with the appropriate reagents in Column II and select the correct answer using the code given below the lists. **(2013 Adv.)**

	Column I		Column II
P.		1.	(i) $Hg(OAc)_2$; (ii) $NaBH_4$
Q.		2.	NaOEt
R.		3.	Et-Br
S.		4.	(i) BH_3 ; (ii)H_2O_2 / NaOH

Codes

	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

44. Match the following : **(2006, 3M)**

	Column I		Column II
A.	CH_3 —CHBr—CD_3 on treatment with alc. KOH gives CH_2 =CH—CD_3 as a major product.	p.	E1 reaction
B.	Ph—CHBr—CH_3 reacts faster than Ph—CHBr—CD_3	q.	E2 reaction
C.	Ph—CH_2 —CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph—CD =CH_2 as the major product.	r.	E1CB reaction
D.	PhCH_2CH_2Br and PhCD_2CH_2Br react with same rate.	s.	First order reaction

Fill in the Blanks

45. Vinyl chloride on reaction with the dimethyl copper gives ………. **(1997)**

46. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with …… **(1983, 1M)**

47. The halogen which is most reactive in the halogenation of alkanes under sunlight is … **(1981 , 1M)**

True/False

48. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. **(1993, 1M)**

49. During S_N1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule. **(1990, 2M)**

50. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. **(1989, 2M)**

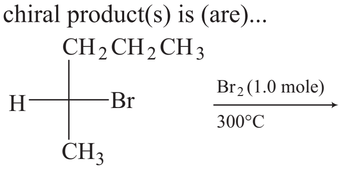
51. Iodide is better nucleophile than bromide. **(1985)**

52. Carbon tetrachloride is inflammable. **(1985, 1/2M)**

53. Carbon tetrachloride burns in air when lighted to give phosgene. **(1983, 1M)**

Integer Answer Type Question

54. In the following monobromination reaction, the number of possible chiral product(s) is (are)...



(1.0 mole) (Enantiomerically pure)

55. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **(2011)**

Subjective Questions

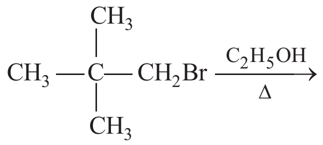
56. Identify X, Y and Z in the following synthetic scheme and write their structures

$$CH_3CH_2C \equiv CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} X$$

$$X \xrightarrow{H_2/Pd\text{-}BaSO_4} Y \xrightarrow[KMnO_4]{\text{alkaline}} Z$$

(2002, 5M)

57. What would be the major product in each of the following reactions?

(i) 

(2000, 2M)

58. Write the structures of the products :

$$C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alc. KOH}}$$

(1998, 2M)

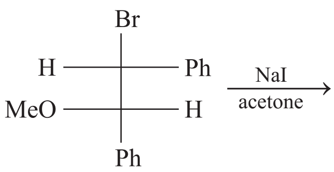
59. Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why?

$$(CH_3)_3CBr + NaOMe \longrightarrow$$

or $$CH_3Br + NaO\text{-}t\text{-}Bu \longrightarrow$$

(1997, 2M)

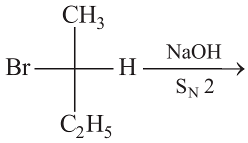
60. Predict the structure of the product in the following reaction



(1996, 1M)

61. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. **(1995, 2M)**

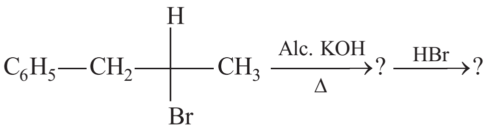
62. Draw the stereochemical structure of product in the following reaction



(1994)

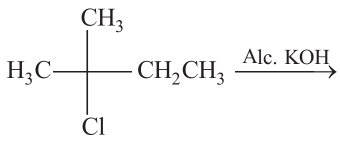
63. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. **(1994, 2M)**

64. Identify the major product in the following reaction.



(1993, 1M)

65. Write the structures of the major organic product expected from each of the following reactions :

(i) 

(ii) $CH_3CH_2CHCl_2 \xrightarrow[\text{boil}]{aq.\text{ alkali}}$ **(1992, 2M)**

66. Arrange the following in order of their

(i) Increasing basicity
H_2O, OH^-, CH_3OH, CH_3O^-

(ii) Increasing reactivity in nucleophilic substitution reactions
CH_3F, CH_3I, CH_3Br, CH_3Cl **(1992, 2M)**

67. Chloroform is stored in dark coloured bottles. Explain in not more than two sentences. **(1980 , 1M)**

68. Show by chemical equations only, how would you prepare the following from the indicated starting materials? Specify the reagents in each step of the synthesis. **(1979, 2M)**

(i) Chloroform from carbon disulphide.

(ii) Hexachloroethane (C_2Cl_6) from calcium carbide.

Answers

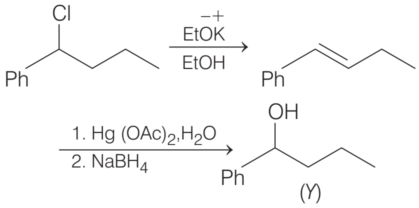
1. (c)	**2.** (d)	**3.** (b)	**4.** (c)
5. (b)	**6.** (b)	**7.** (d)	**8.** (d)
9. (c)	**10.** (c)	**11.** (d)	**12.** (d)
13. (b)	**14.** (b)	**15.** (a)	**16.** (d)
17. (b)	**18.** (d)	**19.** (a)	**20.** (d)
21. (b)	**22.** (b)	**23.** (a)	**24.** (a)
25. (a)	**26.** (b)	**27.** (a)	**28.** (d)
29. (d)	**30.** (c)	**31.** (d)	**32.** (d)
33. (a)	**34.** (a)	**35.** (b)	**36.** (a)
37. (a, d)	**38.** (b,d)	**39.** (d)	**40.** (a,d)
41. (c)	**42.** (b)	**43.** (a)	
44. $A \rightarrow q, B \rightarrow q, C \rightarrow r, D \rightarrow p, s$			
45. propene	**46.** ethyne	**47.** chlorine	**48.** False
49. True	**50.** True	**51.** True	**52.** False
53. False	**54.** (5)	**55.** (5)	

Hints & Solutions

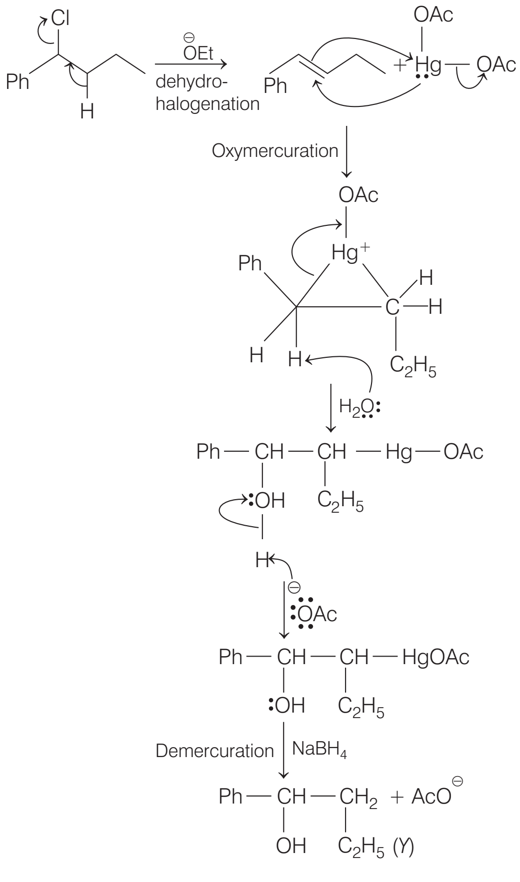
1. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene(X).

Reaction of X with $Hg(OAc)_2$ / H_2O followed by $NaBH_4$ gives 1-phenyl butan-1-ol (Y).

Reaction involved is as follows:



Mechanism



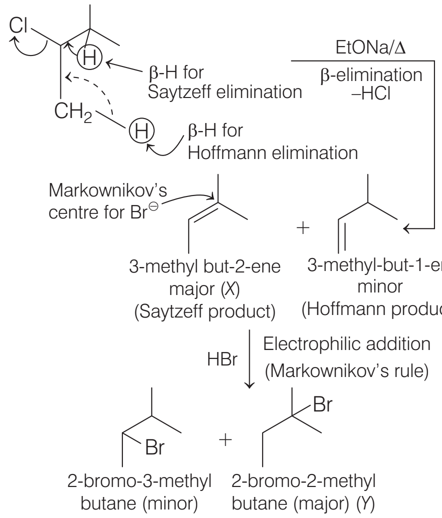
2. $(CH_3)_3CCl$ gives a precipitate with $AgNO_3$ solution because it forms stable carbocation. (i.e. tertiary) that readily combines with $AgNO_3$ to give precipitates of AgCl.

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + AgNO_3 \longrightarrow (CH_3)_3\overset{+}{C} + \underset{\text{(White ppts.)}}{AgCl}$$

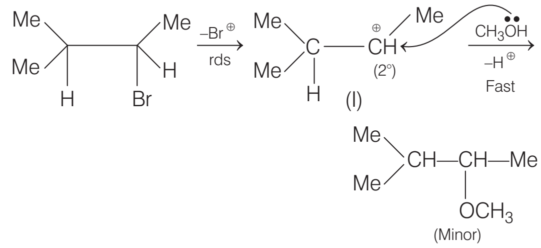
$CH_2=CH-Cl$ forms unstable carbocation.

Hence, it does not readily react with $AgNO_3$.

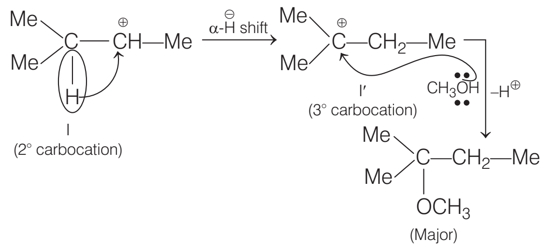
3. The given reaction takes place as follows :



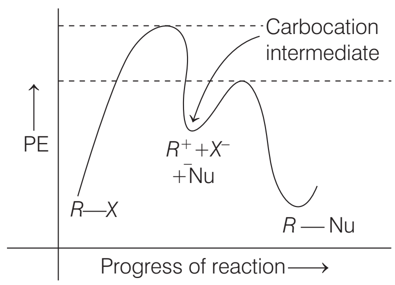
4. In the given question, the substrate is a 2º-halide (bromide) and the medium, CH_3OH (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly S_N1 pathways *via* the formation of a carbocation intermediate (I).



The intermediate, I can be rearranged into the more stable form I′ (3°) by α-hydride shift. I ′ will give the major product.



5. The potential energy (PE) diagram for S_N1 reaction is



S_N1 reaction has two steps. In the first step, the carbon halogen bond breaks heterolytically, with the halogen retaining the previously shared pair of electron. In the second step, the nucleophile reacts rapidly with the carbocation formed in the first step.

In the above graph, the alkyl halide is the only species that participates in the rate limiting step. Here, the rate of reaction depends on the concentration of the alkyl halide and does not depend on the concentration of nucleophile.

6. Presence of strong base (EtO^-) and heat indicates elimination. Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:

(i) $CH_3CH_2\underset{\underset{\displaystyle COOCH_2CH_3}{|}}{C}=CH_2$

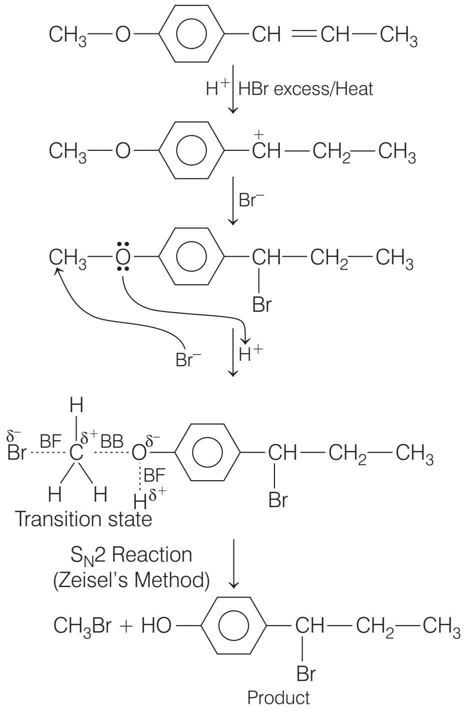
(ii) $CH_3CH=\underset{\underset{\displaystyle COOCH_2CH_3}{|}}{C}-CH_3$

In accordance with Saytzeff rule

$CH_3CH=\underset{\underset{\displaystyle COOCH_2CH_3}{|}}{C}-CH_3$ will be the major product

7. **Key Idea** The excess of HBr and high temperature in given reaction serves for dual purpose:
(i) Hydrolysis of ether *via* S_N2 mechanism, i.e. Zeisel's method.
(ii) Markownikoff addition at double bond of the branch.

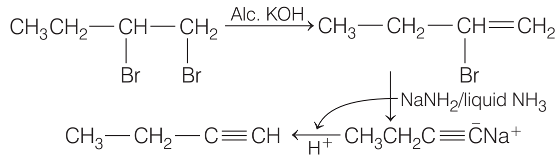
The road map of complete reaction is as follows:



Here, BB = Bond breakage
BF = Bonf formation

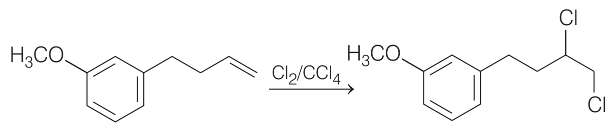
8. **Key Idea** Both alc. KOH and $NaNH_2$ in liquid NH_3 are dehydrohalogenating reagents. On comparative terms $NaNH_2$/liquid NH_3 is stronger in action.

The reaction proceeds as :

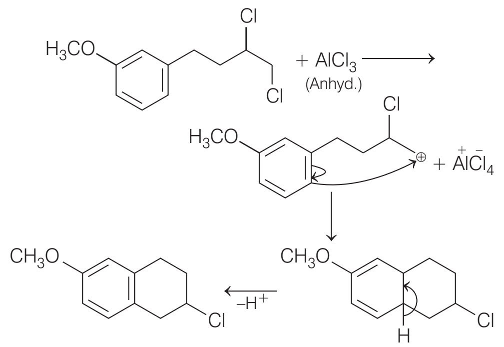


Thus, option (d) is the correct answer.

9. The given reactant in presence of Cl_2/CCl_4, given *vicinal* dihalide. Chlorine adds up to alkene *via* electrophilic addition reaction involving cyclic chlorinium ion formation.



The vicinal dihalide in presence of anhyd. $AlCl_3$ results in the formation of carbocation that rearranges itself to form a cyclic compound.



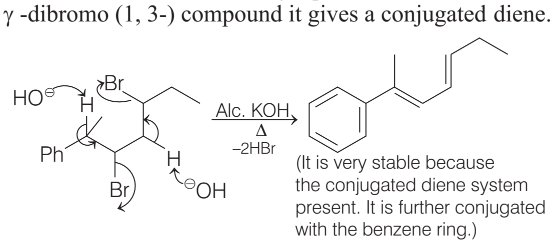
10. The compound (*E*) has two allyl-hydrogen atoms (γ). When *E* reacts with $Br_2/h\nu$, it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene

$$\overset{\delta}{C}H_3-\overset{\gamma}{C}H_2-\overset{\beta}{C}H=\overset{\alpha}{C}H_2 \xrightarrow[-HBr]{Br_2/h\nu}$$
But-1-ene

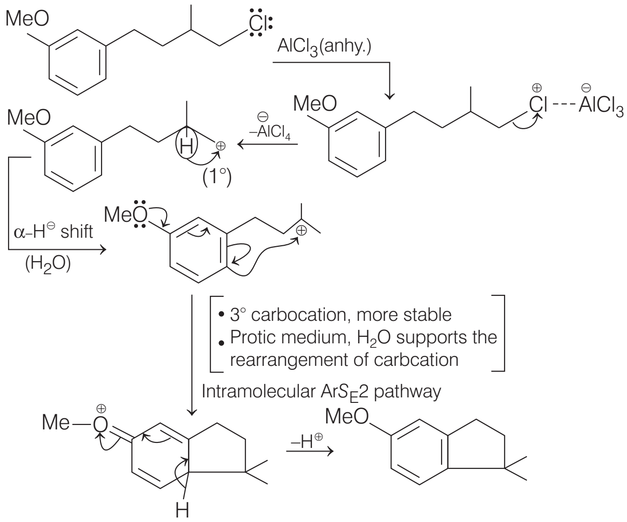
$$\underset{\delta}{C}H_3-\underset{\gamma}{\overset{\overset{\displaystyle Br}{|}}{C}H}-\underset{\beta}{C}H=\underset{\alpha}{C}H_2 \xrightarrow[-HBr]{Br_2/h\nu}$$
3-bromo-but-1-ene

$$\underset{\delta}{C}H_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C_\gamma}}-\underset{\beta}{C}H=\underset{\alpha}{C}H_2$$
3,3- dibromobut-1-ene

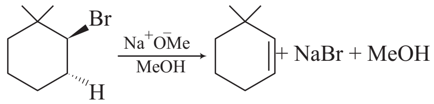
11. The reaction follows α, β-elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a α, γ -dibromo (1, 3-) compound it gives a conjugated diene.



12. In the given reaction, $AlCl_3$ act as Lewis acid and helps in generation of carbocation. The resulting carbocation (1°) rearranges itself to stable carbocation (3°).

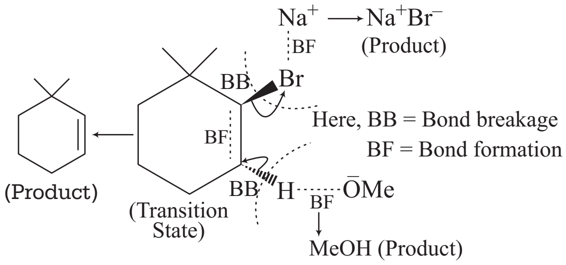


13. Complete reaction can be represented as



Thus, the given reaction is dehydrohalogenation which is a β-elimination proceeding through E_2 mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



14. (i) The rate of S_N1 reaction depends only upon the concentration of the alkyl halide.

(ii) S_N1 reaction proceeds through the formation of carbocation.

The reactivity is decided by ease of dissociation of alkyl halide.

$$R—X \rightleftharpoons R^{\oplus} + X^{\ominus}$$

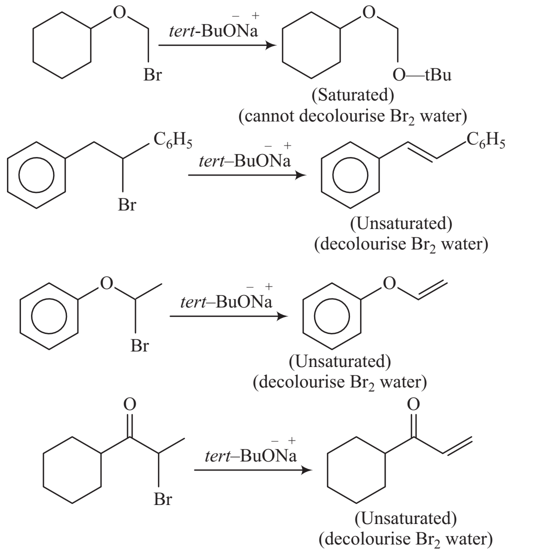
Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N1 reaction.

p-$H_3CO — C_6H_4 — CH_2^{\oplus}$ is the most stable carbocation due to resonance and then $CH_3\overset{\oplus}{C}HCH_2CH_3$ (2° carbocation) while $CH_3CH_2\overset{\oplus}{C}H_2$(1°) is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the S_N1 reaction is

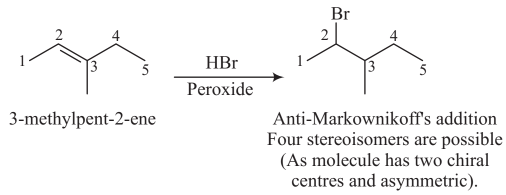
$$\underset{(II)}{CH_3CH_2CH_2Cl} < \underset{(I)}{CH_3\underset{Cl}{\underset{|}{C}}HCH_2CH_3} < \underset{(III)}{p\text{-}H_3COC_6H_4CH_2Cl}$$

15. To show decolourisation, compound must be unsaturated.

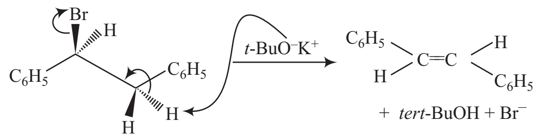


16. The number of stereoisomers in molecules which are not divisible into two equal halves and have n number of asymmetric C-atoms = 2^n.

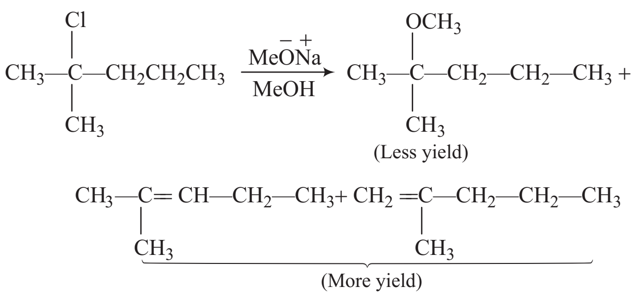
3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible

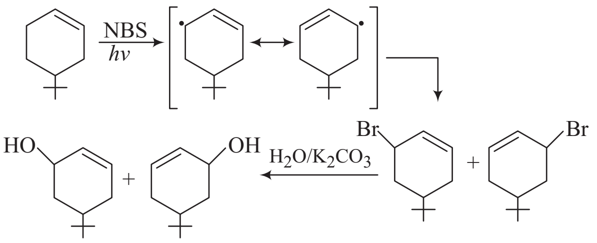


17. An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β-elimination reaction).



18. **Key Idea** Strong nucleophile ($\bar{O}Me$) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



19. 

20. Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow \underset{\text{Methyl fluoride}}{CH_3F} + AgBr$$

But, when aciton of NaI/acetone takes place on alkyl chloride of bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'

$$C_2H_5Cl \xrightarrow[\text{acetone}]{\text{NaI}} C_2H_5I + NaCl$$

Free redical fluorination is highly explosive reaction, so not preferred for the preparation of fluoride.

21. Steric hindrance (crowding) is the basis of S_N2 reaction, by using which we can arrange the reactant in correct order of their reactivity towards S_N2 reaction.

$$\text{Rate of } S_N2 \propto \frac{1}{\text{Steric crowding of 'C'}}$$

$$\underset{\substack{\text{(Less}\\\text{crowded)}}}{CH_3Cl} > \underset{1°}{CH_3CH_2Cl} > \underset{2°}{CH_3-\underset{CH_3}{\underset{|}{CH}}-Cl} > \underset{\text{(More crowded)}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Cl}$$

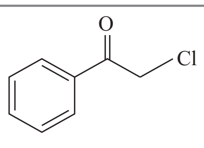
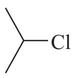
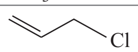
As steric hinderance (crowding) increases, rate of S_N2 reaction decreases.

Note The order of reactivity towards S_N2 reaction for alkyl halides is

$$\underset{(1°)}{\text{Primary halides}} > \underset{(2°)}{\text{Secondary halides}} > \underset{(3°)}{\text{Tertiary halides}}$$

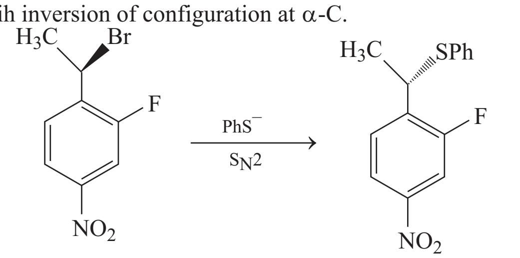
22. PLAN Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus S_N2 reaction is favoured. Also

$$S_N2 \xleftarrow{\quad 1° \quad 2° \quad 3° \quad} \text{Alkyl halides}$$
$$\xrightarrow{\qquad\qquad\qquad} S_N1$$

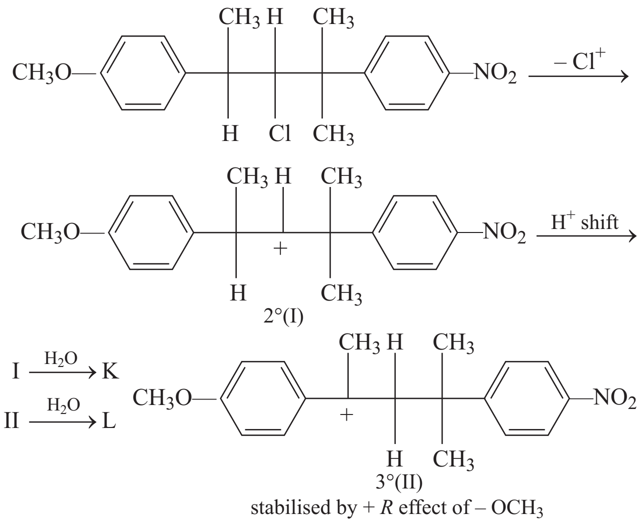
S.		1° alkyl halide but (C—Cl). B.E. is decreased by electron withdrawing [C_6H_5CO] group, (a case of *I*-effect). Thus, maximum rate in S_N2 reaction
Q.		2° alkyl halide, rate is minimum
P.	CH_3-Cl	1° alkyl halide
R.		1° allylic halide but allylic 1° carbocation is resonance stabilised in S_N1 reaction

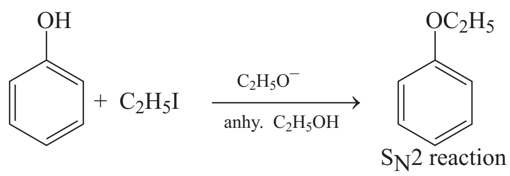
Thus, reactivity order is $S > P > R > Q$

23. Nucleophile PhS^- substitute the Br^- through S_N2 mechanism wih inversion of configuration at α-C.



24. Reaction proceed through carbocation intermediate



25. 

26. $CH_3-CH_2-CH_2Br \xrightarrow[80°C]{\text{Alcoholic NaOH}} CH_3-CH{=}CH_2$

$$\xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$$

27. $H_3C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N^+}}}}-CH_3I^- \longrightarrow CH_3OH + (CH_3)_3N^+I^-$

HO^-

Lack of β-H on quaternary ammonium iodide leads to S_N2 reaction otherwise E2 elimination usually takes place.

28. S_N2 reaction at asymmetric carbon occur with inversion of configuration and a single steroisomer is formed because the reactant and product are not enthtiomer. Therefore the sign of optical rotation may or may not change.

29. If alkyl groups are same, the order of leaving ability of halides in S_N2 reaction is

$$RI > RBr > RCl > RF$$

30. CH_3^-, being the strongest base, has highest nucleophilicity.

31. $$C_6H_5-\underset{H}{\overset{Cl}{C}}-CH_3 + SbCl_5 \rightleftharpoons C_6H_5-\underset{\underset{(I)}{H}}{\overset{+}{C}}-CH_3 + SbCl_6^-T$$

he planar carbocation (I), when return back, forms racemic mixture of the starting compounds.

32. Compound in which metal is directly bonded to carbon, is known are organometallic compound, e.g. CH_3Li.

33. $$CH_3-\underset{CH_3}{\overset{CH_3}{C^-}}MgCl^+ \xrightarrow{D_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-D$$

34. $$CH_3-CH_2-CH_2-CH_2-Cl + KOH \xrightarrow{C_2H_5OH} \underset{\text{1-butene}}{CH_3CH_2-CH=CH_2}$$

35. An alkyl halide containing at least one β-H, on treatment with ethanolic KOH, undergoes dehydrohalogenation, giving alkene.

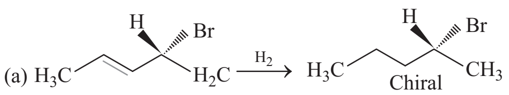
$$CH_3-CH_2-CH_2-Br + KOH \xrightarrow{\text{Ethanol}} CH_3-CH=CH_2$$

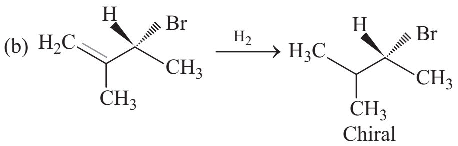
36. During chlorination of alkane, if excess of alkane is treated with $Cl_2(g)$ in presence of light or heat, chance of mono-chlorination predominate.

$$C_2H_6\ (\text{excess}) + Cl_2 \xrightarrow{\text{UV-light}} CH_3CH_2Cl + HCl$$

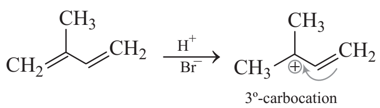
37. (a) Both I and II are 1° halide, undergos S_N2 reaction.
(d) III is a tertiary halide, undergoes S_N2 reaction. I is benzylic bromide, it is very reactive in S_N1 also as if produces stable benzylic carbonation.

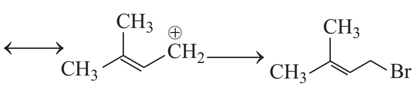
38. In both cases, hydrogenation of olefinic bond will render compound achiral as two identical ethyl group will come at the α-carbon which was earlier chiral carbon. However, in (*a*) and (*c*), chirality will be retained even after hydrogenation.





39. Since, there is no mention of temperature, room temperature will be considered and thermodynamically controlled product would be the major product as:

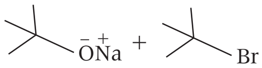




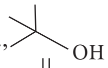
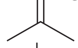
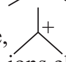
40. Both NH_3 and CF_2Cl_2 are used as refrigerant.

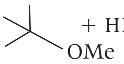
41. Vinyl halide ($CH_2=CH-Cl$) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation ($CH_2=\overset{\oplus}{C}H$). It cannot delocalise its π-electron. In vinyl halide C—Cl bond possess double bond character also.

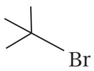
$$CH_2=CH-\ddot{C}l: \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{C}l:$$

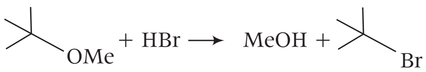
42. **For *P*,** i.e. 

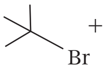
For this reaction 1 and 4 are probable products.

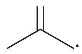
Product 1 i.e.,  is formed due to substitution while product 4 i.e.,  is formed due to elimination. A tertiary carbocation i.e,  formed during the reaction. Remember for 3° carbocation ions elimination product predominates.

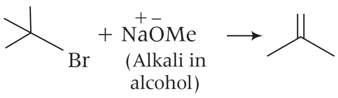
For *Q*, i.e.  + HBr

Correctly matched product for this reaction is 2 i.e., . The reaction proceeds as

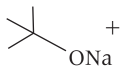


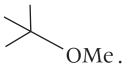
For *R* i.e.,  + NaOMe

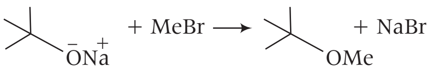
Correctly matched product is 4 i.e., . It is a normal elimination reaction and proceeds as



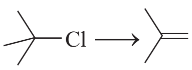
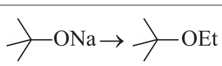
3° alkyl halide preferes elimination.

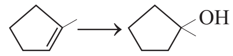
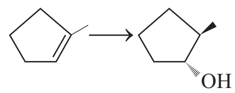
For *S* i.e.,  + MeBr

The correct match is 3 i.e., . The reaction proceeds as



43.

	Column I	Column II	Explanation
P.		NaOEt(2)	$\overline{O}$ Et (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide
Q.		EtBr (3)	3° butoxide undergoes S_N reaction with 1° alkyl halide

R.		(i) $Hg(OAC)_2$ (ii) $NaBH_4$ (1)	Mercuration-demercuration adds H_2O by Markownikoff's rule without rearrangement
S.		(i) BH_3 (ii) H_2O_2/OH^- (4)	Hydroboro-oxidation adds H_2O by anti-Markownikoff's rule

Thus, P — (2), Q — (3), R — (1), S — (4)

44. A. $CH_3—CHBr—CD_3 \xrightarrow[E2]{\text{Alc. KOH}} CH_2=CH—CD_3$

E2 reaction is a single-step reaction in which both deprotonation from β-C and loss of leaving group from α-C occur simultaneously in the rate-determining step.

C-D bond is stronger than C—H bond, C—H is preferably broken in elimination.

B. $Ph—CHBr—CH_3$ reacts faster than $Ph—CHBr—CD_3$ in E2 reaction because in latter case, stronger C—D bond is to be broken in the rate determining step.

C. $Ph—CH_2—CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph—CD=CH_2$

Deuterium incorporation in the product indicates E1CB mechanism

$$Ph—CH_2—CH_2Br \underset{}{\overset{C_2H_5O^-}{\rightleftharpoons}} \underset{\text{carbanion}}{Ph—\bar{C}H—CH_2Br} \overset{C_2H_5OD}{\rightleftharpoons} \underset{\text{I}}{Ph—CHD—CH_2Br}$$

$$\text{I} \xrightarrow{C_2H_5O^-} Ph—\overset{D}{\overset{|}{C}}—CH_2—Br \longrightarrow Ph—\underset{\underset{D}{|}}{C}=CH_2$$

D. Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C—H bond is broken in fast non rate determining step. Also E1 reaction follow first order kinetics.

45. Propene is produced

$(CH_3)_2Cu + CH_2=CHCl \longrightarrow CH_3—CH=CH_2$

46. Vinyl chloride is obtained by the reaction of HCl with ethyne.

47. Chlorine is most reactive.

48. 2-bromo-2-methylpropane is formed as major product.

49. In S_N1 reaction, leaving group is detached in the first step forming carbocation intermediate.

50. True

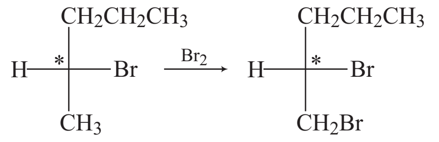
51. Larger the size of donor atom, greater is its polarisability, stronger is the nucleophile.

52. False

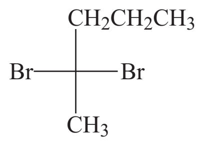
53. CCl_4 is fire retardent, used as fire-extinguisher.

54. Given compound undergoes free-radical bromination under given conditions, replacing H by Br.

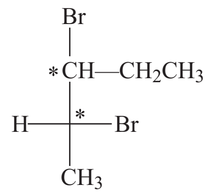
C* is chiral carbon.



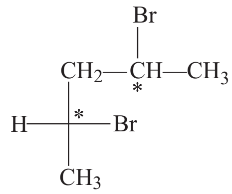
I. Chiral



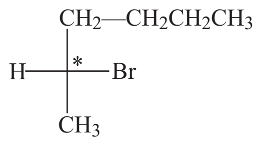
II. Achiral



III. Chiral

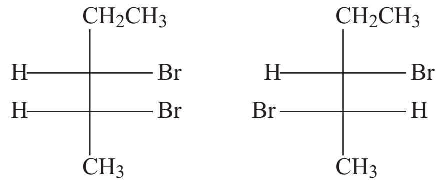


IV. Chiral



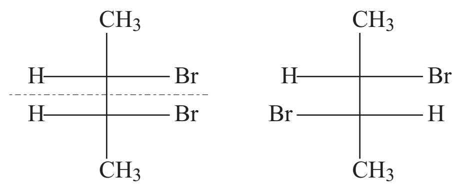
V. Chiral

(III) has two chiral centres and can have two structures.



(III) A (III) B

(IV) has also two chiral centres and can have two structures.

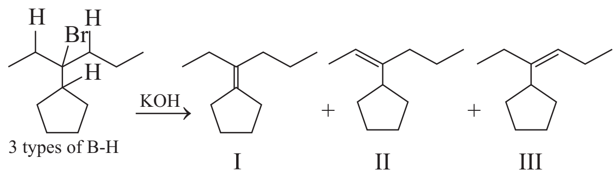


(IV)A (IV)B

It has plane of symmetry thus, achiral.

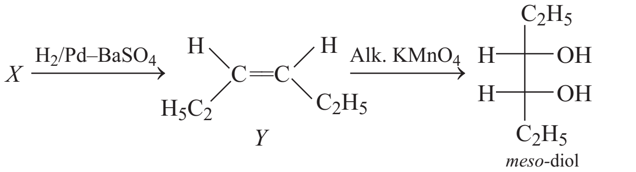
Thus, chiral compounds are five. I, III A, III B, IV B and V.

55. The substrate has three different types of B—H, therefore, first three structural isomers of alkenes are expected as :

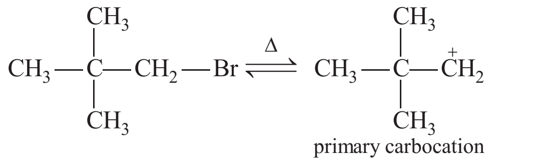


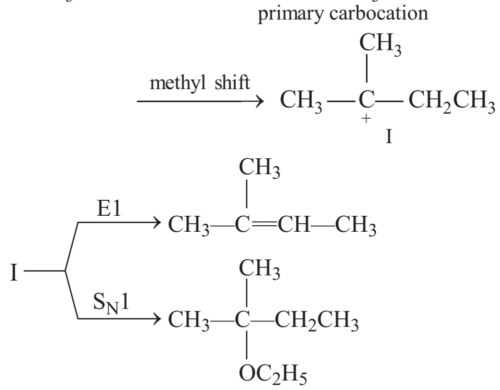
The last two alkenes II and III are also capable of showing geometrical isomerism, hence two geometrical isomers for each of them will be counted giving a total of five isomers.

56. $CH_3CH_2C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} \underset{X}{CH_3CH_2-C{\equiv}C-CH_2CH_3}$

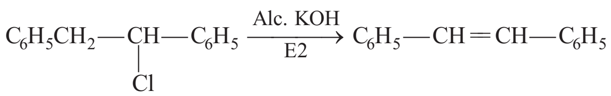


57. Unimolecular reaction occur

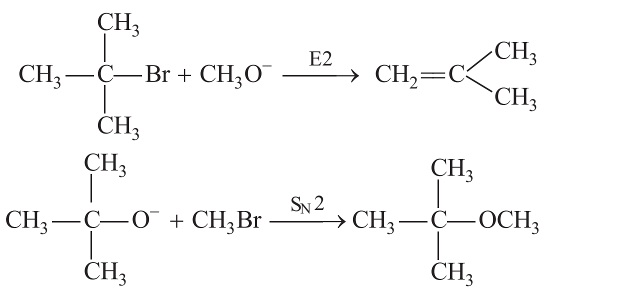




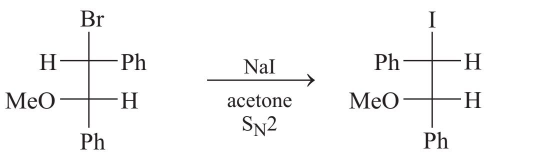
58.



59.

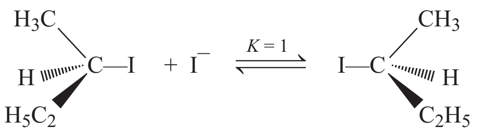


60.



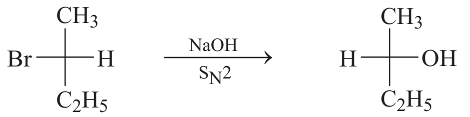
inversion of configuration occur only at α-carbon

61.



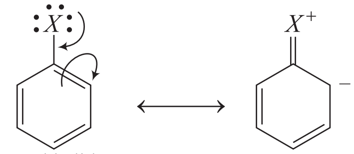
Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

62. S_N2 reactions leads to inversion of configuration at α-C



product with inverted configuration

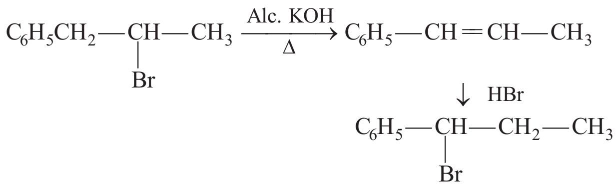
63.



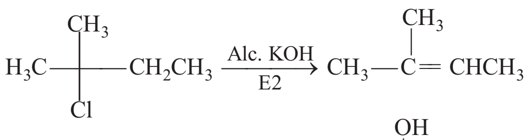
Aryl halide

Due to the above resonance phenomena, C—*X* bond acquire partial double bond character and becomes difficult to break in the rate determining step of S_N2 reaction.

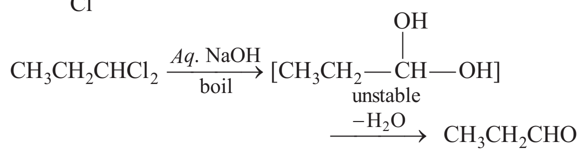
64.



65. (i)



(ii)



66. (i) $H_2O < CH_3OH < HO^- < CH_3O^-$

(ii) $CH_3F < CH_3Cl < CH_3Br < CH_3I$

67. Chloroform in presence of air and sunlight, oxidises slowly to form a highly poisonous compound called phosgene

$$2CHCl_3 + O_2 \xrightarrow{h\nu} \underset{\text{(Phosgene)}}{2COCl_2} + 2HCl$$

To prevent the above oxidation reaction, chloroform is kept in dark bottles.

68. (i)

$$CS_2 + Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

$$CCl_4 + 2\,[H] \xrightarrow{Fe/H_2O} \underset{\text{(Chloroform)}}{CHCl_3} + HCl$$

(ii)

$$CaC_2 + H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

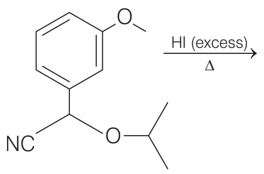
$$C_2H_2 \xrightarrow{H_2/Ni} C_2H_6 \xrightarrow[h\nu]{Cl_2\ \text{(excess)}} \underset{\text{(Hexachloroethane)}}{Cl_3C-CCl_3}$$

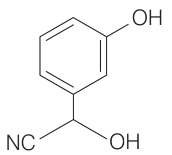
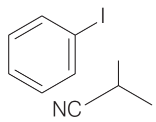
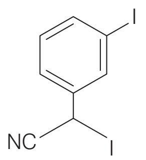
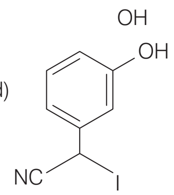
Download Chapter Test
http://tinyurl.com/y54uy6l6 *or*

24
Alcohols and Ethers

Objective Questions I (Only one correct option)

1. The major product of the following reaction is **(2019 Main, 10 April I)**



(a) 
(b) 
(c) 
(d) 

2. The synonym for water gas when used in the production of methanol is **(2019 Main, 10 April I)**

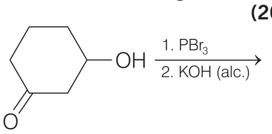
(a) natural gas (b) laughing gas
(c) *syn* gas (d) fuel gas

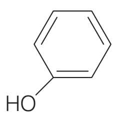
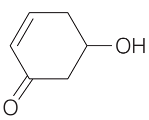
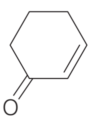
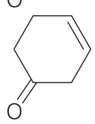
3. The major product of the following reaction is

$CH_3CH = CHCO_2CH_3 \xrightarrow{LiAlH_4}$ **(2019 Main, 9 April I)**

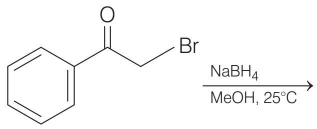
(a) $CH_3CH = CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2CO_2CH_3$ (d) $CH_3CH_2CH_2CHO$

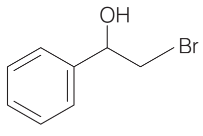
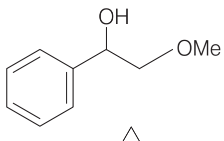
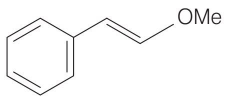
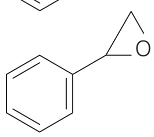
4. The major product of the following reaction is **(2019 Main, 9 April I)**



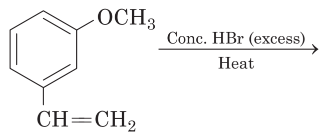
(a) 
(b) 
(c) 
(d) 

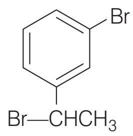
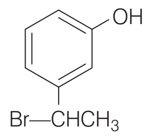
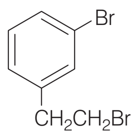
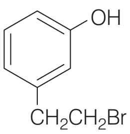
5. The major product of the following reaction is **(2019 Main, 8 April I)**



(a) 
(b) 
(c) 
(d) 

6. The major product of the following reaction is **(2019 Main, 8 April I)**

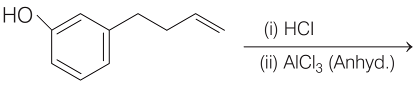


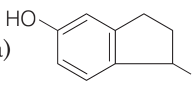
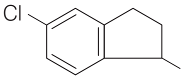
(a) 
(b) 
(c) 
(d) 

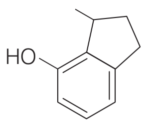
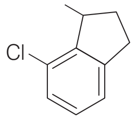
7. $CH_3CH_2 - \underset{\underset{Ph}{|}}{\overset{\overset{OH}{|}}{C}} - CH_3$ cannot be prepared by **(2019 Main, 12 Jan I)**

(a) $CH_3CH_2COCH_3 + PhMgX$
(b) $PhCOCH_3 + CH_3CH_2MgX$
(c) $PhCOCH_2CH_3 + CH_3MgX$
(d) $HCHO + PhCH(CH_3)\,CH_2MgX$

8. The major product of the following reaction is **(2019 Main, 11 Jan II)**



(a)  (b) 

(c)  (d) 

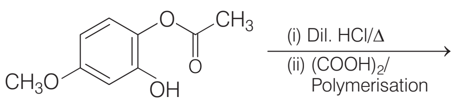
9. Which is the most suitable reagent for the following transformation? **(2019 Main, 10 Jan II)**

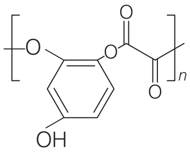
$$CH_3—CH=CH—CH_2—\underset{}{\overset{OH}{\overset{|}{C}}}H—CH_3 \longrightarrow CH_3—CH=CH—CH_2CO_2H$$

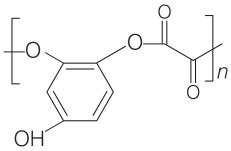
(a) Tollen's reagent (b) $I_2/NaOH$

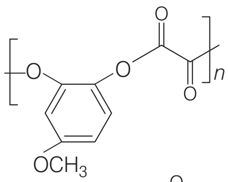
(c) Alkaline $KMnO_4$ (d) CrO_2Cl_2/CS_2

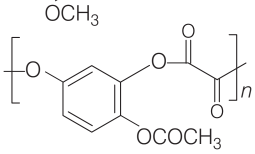
10. The major product of the following reaction is **(2019 Main, 10 Jan II)**



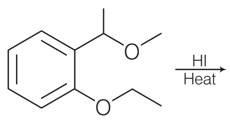
(a) 

(b) 

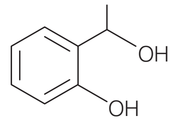
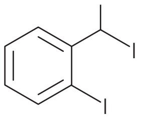
(c) 

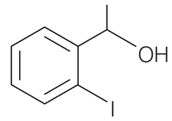
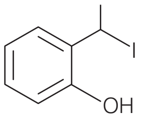
(d) 

11. The major product formed in the following reaction is

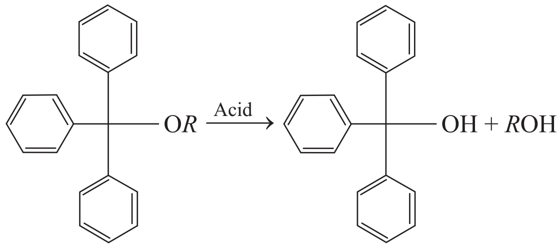


(2018 Main)

(a)  (b) 

(c)  (d) 

12. The acidic hydrolysis of ether (X) shown below is fastest when **(2014 Adv.)**



[X]

(a) one phenyl group is replaced by a methyl group

(b) one phenyl group is replaced by a *para*-methoxyphenyl group

(c) two phenyl groups are replaced by two *para*-methoxyphenyl groups

(d) no structural change is made to X

13. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?

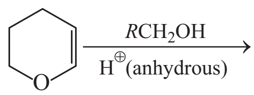
(a) Secondary alcohol by S_N1 **(2013 Main)**

(b) Tertiary alcohol by S_N1

(c) Secondary alcohol by S_N2

(d) Tertiary alcohol by S_N2

14. The major product of the following reaction is



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

15. (I) 1, 2-dihydroxy benzene

(II) 1, 3-dihydroxy benzene

(III) 1, 4-dihydroxy benzene

(IV) Hydroxy benzene

The increasing order of boiling points of above mentioned alcohols is **(2006, 3M)**

(a) I < II < III < IV (b) I < II < IV < III

(c) IV < I < II < III (d) IV < II < I < III

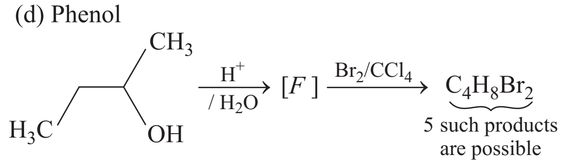
16. The best method to prepare cyclohexene from cyclohexanol is by using **(2005, 1M)**

(a) conc. $HCl + ZnCl_2$ (b) conc. H_3PO_4

(c) HBr (d) conc. HCl

17. When phenyl magnesium bromide reacts with *tert* butanol, which of the following is formed? **(2005, 1M)**

(a) *Tert* butyl methyl ether
(b) Benzene
(c) *Tert* butyl benzene
(d) Phenol

18. 

How many structures of F is possible? **(2003, 1M)**

(a) 2 (b) 5 (c) 6 (d) 3

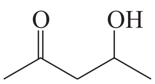
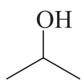
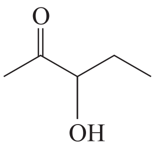
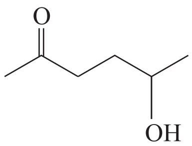
19. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O) 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$ and sodium acetate gives a product 'C'. Identify the structure of 'C'.

(a) $CH_3CH_2CH{=}NNHCONH_2$ **(2002, 3M)**
(b) $H_3C{-}C(CH_3){=}NNHCONH_2$
(c) $H_3C{-}C(CH_3){=}NCONHNH_2$
(d) $CH_3CH_2OH + NCONHNH_2$

20. 1-propanol and 2-propanol can be best distinguished by

(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution **(2001, 1M)**
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

21. Which one of the following will most readily be dehydrated in acidic condition? **(2000, 1M)**

(a) 
(b) 
(c) 
(d) 

22. The products of combustion of an aliphatic thiol (RSH) at 298 K are **(1992)**

(a) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$
(b) $CO_2(g)$, $H_2O(l)$, and $SO_2(g)$
(c) $CO_2(l)$, $H_2O(l)$ and $SO_2(g)$
(d) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$

23. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is **(1988, 1M)**

(a) C—C (b) C—O
(c) C—H (d) O—H

24. Hydrogen bonding is maximum in **(1987, 1M)**

(a) ethanol (b) diethyl ether
(c) ethyl chloride (d) triethyl amine

25. HBr reacts fastest with **(1986, 1M)**

(a) 2-methyl propan-2-ol (b) propan-1-ol
(c) propan-2-ol (d) 2-methyl propan-1-ol

26. An industrial method of preparation of methanol is **(1984, 1M)**

(a) catalytic reduction of carbon monoxide in presence of $ZnO\text{-}Cr_2O_3$
(b) by reacting methane with steam at 900°C with nickel catalyst
(c) by reducing formaldehyde with $LiAlH_4$
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

27. Diethyl ether on heating with conc. HI gives two moles of

(a) ethanol (b) iodoform **(1983, 1M)**
(c) ethyl iodide (d) methyl iodide

28. The compound which reacts fastest with Lucas reagent at room temperature is **(1981 , 1M)**

(a) butan-2-ol (b) butan-1-ol
(c) 2-methyl propan-1-ol (d) 2-methyl propan-2-ol

29. Ethyl alcohol is heated with conc. H_2SO_4. The product formed is

(a) $CH_3COOC_2H_5$ (b) C_2H_2 **(1980 , 1M)**
(c) C_2H_4 (d) C_2H_6

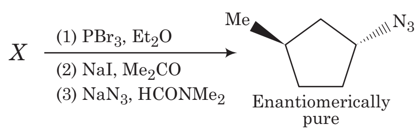
30. Which of the following is soluble in water? **(1980, 1M)**

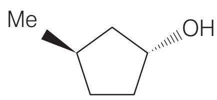
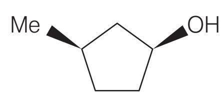
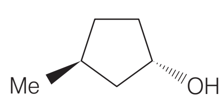
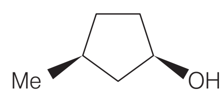
(a) CS_2 (b) C_2H_5OH
(c) CCl_4 (d) $CHCl_3$

Objective Questions II

(One or more than one correct option)

31. In the following reaction sequence, the correct structure (s) of X is (are) **(2018 Adv.)**



(a) 
(b) 
(c) 
(d) 

32. The correct statement(s) about the following reaction sequence is (are)

$$\text{Cumene } (C_9H_{12}) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2} P \xrightarrow{CHCl_3/NaOH}$$

$$Q(\text{major}) + R(\text{minor}),\ Q \xrightarrow[PhCH_2Br]{NaOH} S$$ **(2016 Adv.)**

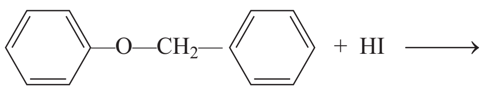
(a) R is steam volatile

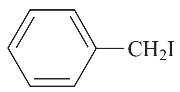
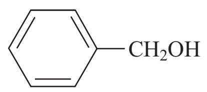
(b) Q gives dark violet colouration with 1% aqueous $FeCl_3$ solution

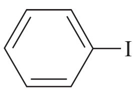
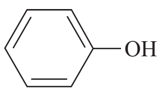
(c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine

(d) S gives dark violet colouration with 1% aqueous $FeCl_3$ solution

33. The following ether, when treated with HI produces **(1999, 3M)**



(a)  (b) 

(c)  (d) 

34. The products of reaction of alcoholic silver nitrate with ethyl bromide are **(1991, 1M)**

(a) ethane (b) ethene

(c) nitroethane (d) ethyl alcohol

(e) ethyl nitrite

Assertion and Reason

Read the following question and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is a correct explanation of Statement I.

(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.

(c) Statement I is correct; Statement II is incorrect.

(d) Statement I is incorrect; Statement II is correct.

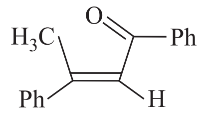
35. **Statement I** Solubility of n-alcohol in water decreases with increase in molecular weight.

Statement II The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water. **(1988 , 2M)**

Passage Based Questions

Passage 1

A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M.

$M =$ 

(2008, 3 × 4M = 12M)

36. The structures of compounds J, K and L respectively, are

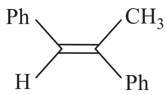
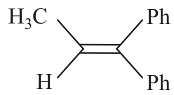
(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

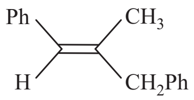
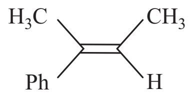
(b) $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$

(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

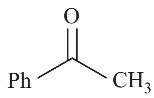
(d) $PhCHO$, $PhCOCH_3$ and $PhCOO^-K^+$

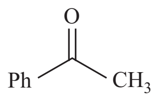
37. The structure of compound I is

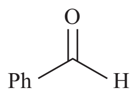
(a)  (b) 

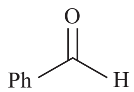
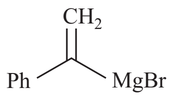
(c)  (d) 

38. Compound H is formed by the reaction of

(a)  ; PhMgBr

(b)  ; $PhCH_2MgBr$

(c)  ; $PhCH_2MgBr$

(d)  ; 

Fill in the Blanks

39. Glycerine contains one ……… hydroxyl group. **(1997, 1M)**

40. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ……… which are formed on prolonged standing in contact with water. **(1992, 1M)**

41. A …… diol has two hydroxyl groups on …… carbon atoms. **(1986, 1M)**

42. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ……… **(1983, 1M)**

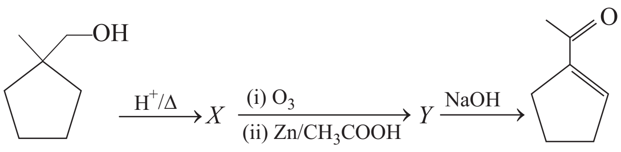
True or False

43. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. **(1985, 1M)**

44. The yield of a ketone when a secondary alcohol is oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. **(1983, 1M)**

Subjective Questions

45.

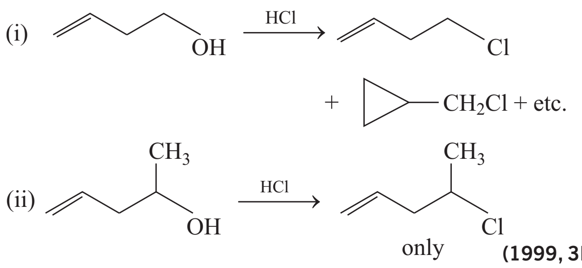


Identify X and Y. **(2005, 2M)**

46. An organic compound P having the molecular formula $C_5H_{10}O$ when treated with dil H_2SO_4 gives two compounds, Q and R both gives positive iodoform test. The reaction of $C_5H_{10}O$ with dil, H_2SO_4 gives reaction 10^{15} times faster than ethylene. Identify organic compound of Q and R. Give the reason for the extra stability of P. **(2004)**

47. Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). **(2001, 5M)**

48. Explain briefly the formation of products giving the structures of the intermediates.



(1999, 3M)

49. Write the structures of the products :

$$(CH_3)_2CH—OCH_3 \xrightarrow[\text{heat}]{\text{HI (excess)}}$$ **(1998, 2M)**

50. Give reasons for the following in one or two sentences. "Acid catalysed dehydration of t-butanol is faster than that of n-butanol. **(1998, 2M)**

51. 2, 2-dimethyloxirane can be cleaved by acid (H^+). Write mechanism. **(1997, 2M)**

52. A compound $D(C_8H_{10}O)$ upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($C_7H_6O_2$). Write the structures of D, E and explain the formation of E. **(1996, 2M)**

53. 3, 3-dimethylbutan-2-ol losses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. **(1996, 2M)**

54. When t-butanol and n-butanol are separately treated with a few drops of dilute $KMnO_4$ in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? **(1994, 2M)**

55. Compound X (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate with excess of MeMgBr, 0.42 g of X gives 224 mL of CH_4 at STP. Treatment of X with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest structure for X and write the equation involved. **(1992, 5M)**

56. Arrange the following in increasing order of boiling point : n-butane, n-butanol, n-butylchloride, *iso*-butane. **(1988, 1M)**

57. How may be the following transformation be carried out (in not more than six steps)?

"Ethyl alcohol to vinyl acetate." **(1986, 3M)**

58. Write down the main product of the following reaction :

$$\text{Ethanol} \xrightarrow{I_2/\text{NaOH}}$$ **(1985, 1M)**

59. Give a chemical test to distinguish between methanol and ethanol. **(1985, 1M)**

60. Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. **(1985, 2M)**

61. An alcohol A, when heated with conc. H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. D can also be obtained either by oxidising A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D. **(1983, 4M)**

62. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

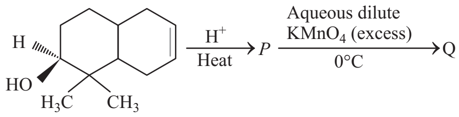
(i) Ethanol from acetylene
(ii) Lead tetraethyl from sodium-lead alloy
(iii) Methyl chloride from aluminium carbide **(1983, 3M)**

63. A compound 'X' containing C, H and O is unreactive towards sodium. It does not add with bromine. It also does not react with Schiff's reagent. On refluxing with an excess of HI, 'X' yields only one organic product 'Y'. 'Y' on hydrolysis yields a new compound 'Z' which can be converted into 'Y' by reaction with red phosphorus and iodine. The compound 'Z' on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of acid is 60. What are the compounds 'X', 'Y' and 'Z'? Write chemical equations leading to the conversion of 'X' to 'Y'. **(1981, 3M)**

64. An organic liquid '*A*' containing C, H and O with boiling point 78°C, possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product '*B*' with the empirical formula, CH_2. '*B*' decolourises bromine water as well as alkaline permanganate solution and takes up one mole of H_2 (per mole of *B*) in presence of finely divided nickel at high temperature. Identify the substances *A* and *B*. **(1979 , 2M)**

Integer Type Question

65. The number of hydroxyl group(s) in Q is **(2015 Adv.)**

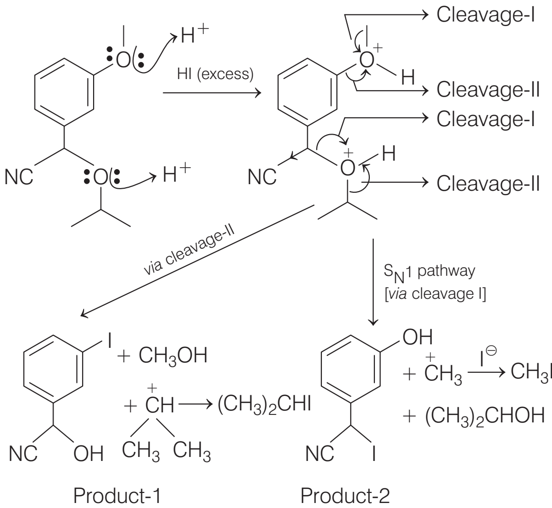


Answers

1. (d)	**2.** (c)	**3.** (a)	**4.** (c)	**25.** (a)	**26.** (a)	**27.** (c)	**28.** (d)
5. (d)	**6.** (b)	**7.** (d)	**8.** (a)	**29.** (c)	**30.** (b)	**31.** (b)	**32.** (b,c)
9. (b)	**10.** (c)	**11.** (d)	**12.** (c)	**33.** (a,d)	**34.** (c,e)	**35.** (c)	**36.** (d)
13. (b)	**14.** (b)	**15.** (c)	**16.** (b)	**37.** (a)	**38.** (b)	**39.** secondary	**40.** Peroxides
17. (b)	**18.** (d)	**19.** (a)	**20.** (c)	**41.** *vicinal*; same	**42.** aldol	**43.** False	**44.** False
21. (a)	**22.** (b)	**23.** (d)	**24.** (a)	**65.** (4)			

Hints & Solutions

1. The given reaction takes place as follows:



Product-2 is formed because

(i) Cleavage-I will give more stable aryl carbocation.

(ii) Cleavage- I will give intermediate which is in conjugation with ring.

2. The production of methanol from water gas is as follows:

$$\underset{\substack{\text{Water gas}\\ \text{or}\\ \textit{syn}\text{ gas}}}{[CO + H_2]} + H_2 \xrightarrow[300\text{ atm, }300^\circ\text{ C}]{ZnO + Cr_2O_3} \underset{\text{Methanol}}{CH_3OH}$$

It is an industrial process used for the production of methanol where volume ratio of the reactant gases is maintained as:

syn gas : $H_2 = 2:1$ and ZnO-Cr_2O_3 act as catalysts

Thus, water gas is also called *syn* gas because it is used for synthesis of methanol.

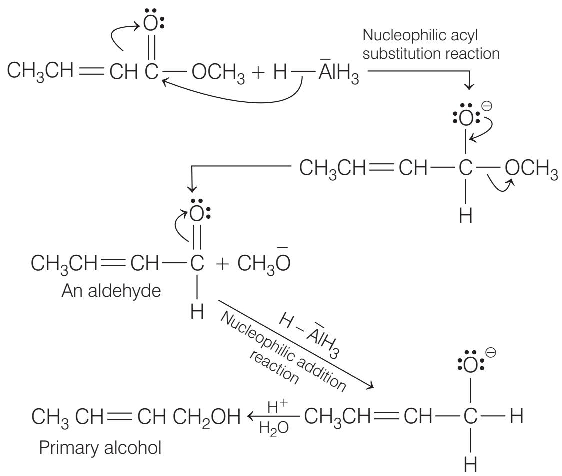
3. **Key Idea** $LiAlH_4$ reagent is used for the reduction of —CHO, $-\overset{O}{\overset{\|}{C}}OCH_3$. It does not reduce double bonds.

The reaction of an ester with $LiAlH_4$ produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.

$$CH_3CH{=}CH\overset{O}{\overset{\|}{C}}{-}OCH_3 \xrightarrow{LiAlH_4} \underset{\text{But-2-en-1-ol}}{CH_3CH{=}CHCH_2OH} + \underset{\text{Methanol}}{CH_3OH}$$

Thus, the major product of the given reactant $CH_3CH{=}CH\overset{O}{\overset{\|}{C}}OCH_3$ in presence of $LiAlH_4$ is $CH_3CH{=}CH\,CH_2OH$ and CH_3OH. The reaction proceeds through following mechanism.

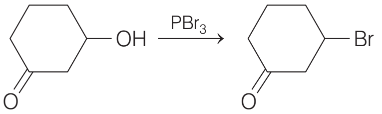
Mechanism



4. **Key Idea** PBr_3 reagent is used for the substitution of —Br group while alc. KOH reagent is used to carry out elimination reaction.

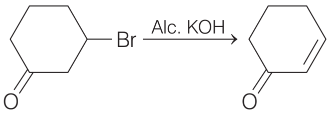
The given reaction proceed in following manner:

Step I In presence of PBr_3, alcohols undergo substitution reactions to give halides. Reagent PBr_3 is usually generated *insitu* by the reaction of red phosphorus with bromine.



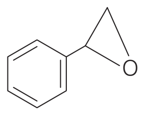
3-bromohexanone

Step II 3-bromohexanone in presence of alc. KOH undergoes elimination reaction and gives cyclohex-2-en-1-one.

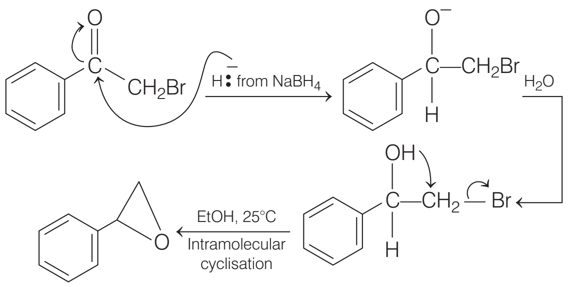


Cyclohex-2-en-1-one

5. Major product obtained in the given reaction is

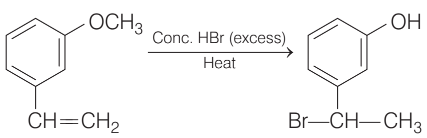


$NaBH_4$ in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in these reductions is hydride ion (H^-). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an H^- followed by an H^+. The mechanism of the given reaction is as follows :



6. **Key Idea** Ethers are least reactive functional groups. The cleavage of C — O bond in ethers take place under drastic conditions with excess of HX.

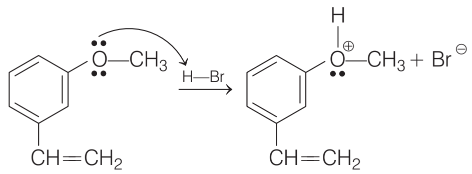
The major product obtained in the reaction is as follows :



As conc. HBr is in excess. So, reaction will take place at both the substituents.

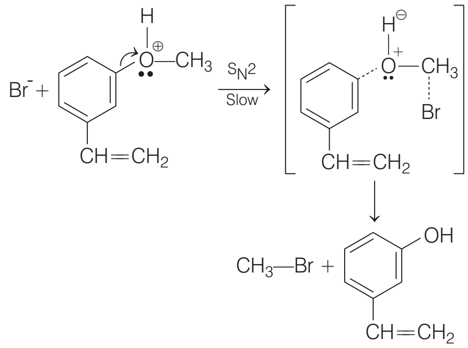
Mechanism

Step 1 Protonation of ether to form oxonium ion.

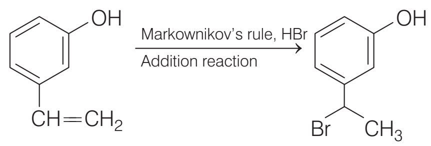


Oxonium ion

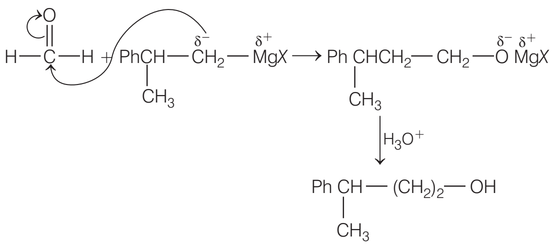
Step 2 Attack of nucleophile at the protonated ether.



Step 3 As HBr is in excess, so, reaction will also take place at alkene.

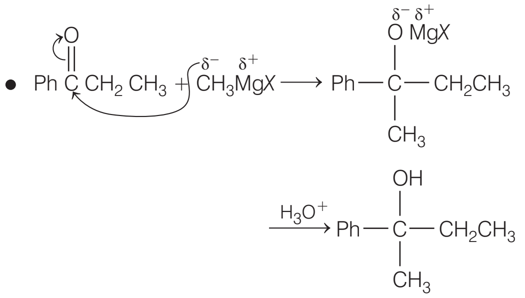


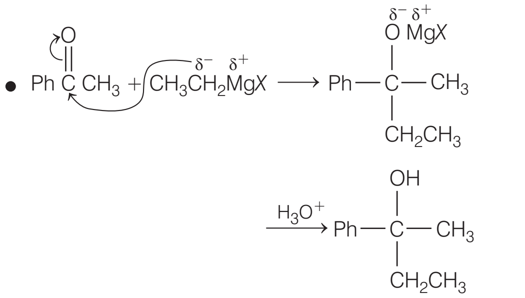
7. $CH_3CH_2—\underset{\displaystyle Ph}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}—CH_3$ cannot be prepared by HCHO and $PhCH(CH_3)CH_2MgX$. This can be easily illustrated by following reaction.

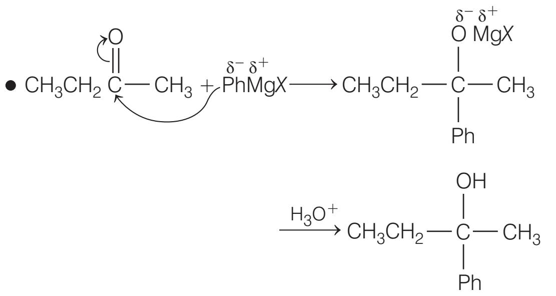


The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

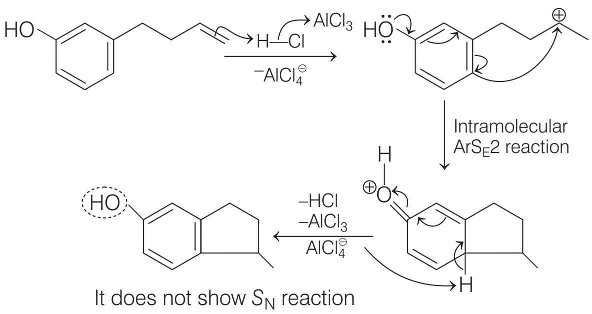
The reactions are as follows :







8. In the given reaction, $AlCl_3$ helps in the generation of electrophile that further undergoes ArS_E2 reaction to give the required product.

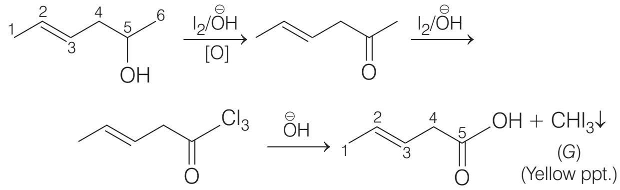


It does not show S_N reaction with HCl because of double bond nature of the O—C bond, (due to $+R$-effect of the —OH group.)

9. The most suitable reagent to carry out given transformation is I_2/NaOH

$$\underset{6}{C}H_3\underset{5}{C}H{=}\underset{4}{C}H{-}\underset{3}{C}H_2{-}\underset{2}{C}H(OH){-}\underset{1}{C}H_3 \xrightarrow[\text{(Oxidative cleavage)}]{\text{Strong oxidation, [O]}} \underset{6}{C}H_3{-}\underset{5}{C}H{=}\underset{4}{C}H{-}\underset{3}{C}H_2{-}\underset{2}{C}(=O){-}OH + CHI_3\downarrow + CO_2\uparrow$$

Here, the haloform reaction will give following reaction:



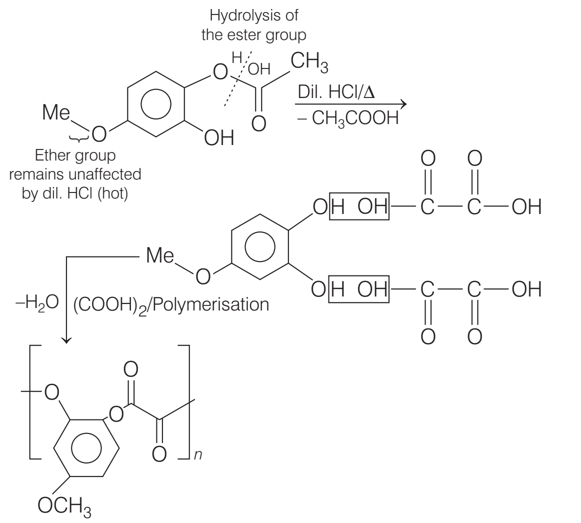
(i) Tollen's reagent ($AgNO_3 + NH_4OH$) is a mild oxidising agent. It does not react with $-CH(OH)-CH_3$ group (2°-alcohol).

(ii) Alkaline $KMnO_4$ cannot perform the oxidative cleavage, rather it will hydroxylate the C=C.

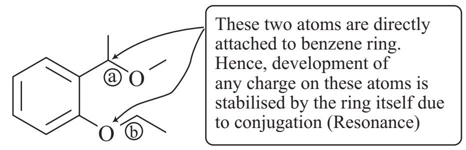
$$\underset{6}{C}H_3{-}\underset{5}{C}H{=}\underset{4}{C}H{-}\underset{3}{C}H_2{-}\underset{2}{C}H(OH){-}\underset{1}{C}H_3 \xrightarrow[OH^-]{KMnO_4} \underset{6}{C}H_3{-}\underset{5}{C}H(OH){-}\underset{4}{C}H(OH){-}\underset{3}{C}H_2{-}\underset{2}{C}H(OH){-}\underset{1}{C}H_3$$

(iv) CrO_2Cl_2/CS_2 will not react here.

10. In the given reaction, ester get cleaved in presence of dil. HCl and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.

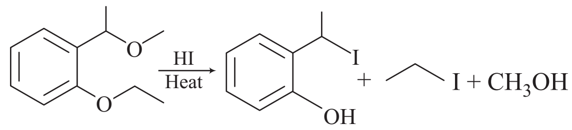


11. **Key idea** The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



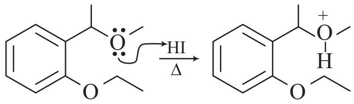
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as



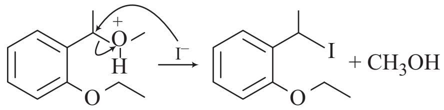
Mechanism

***Step* I** The reaction begins with the attack of H^+ of HI on oxygen to form oxonium ion as

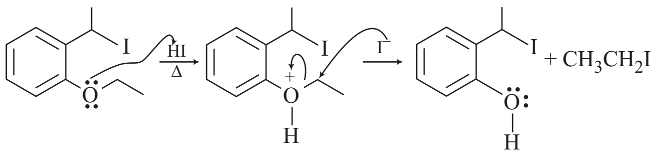


Oxonium ion

***Step* II** This oxonium ion undergoes lysis and addition of I^- to form two products as



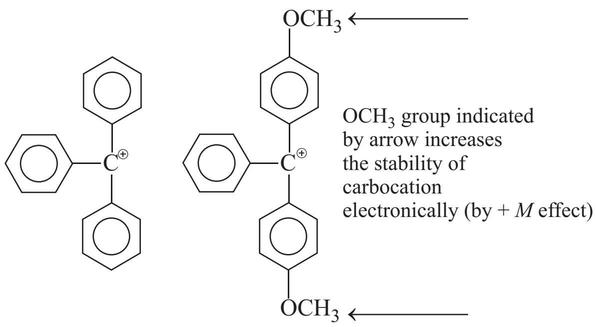
***Step* III** Similar pathway is followed at the other oxygen atom, which can be visualised as



Note Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.

12. **PLAN** This problem can be solved by using the concept of stability of carbocation and S_N1 reaction.

When two phenyl groups are replaced by two *para* methoxy group, carbocation formed will be more stable. As the stability of carbocation formed increases, rate of acidic hydrolysis increases.

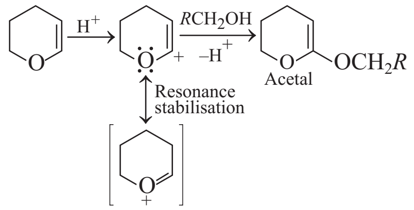


More stable carbocation

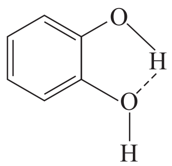
Hence, (c) is the correct choice.

13. The reaction of alcohol with Lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since 3° R—OH forms 3° carbocation (most stable), hence it will react fastest.

14.

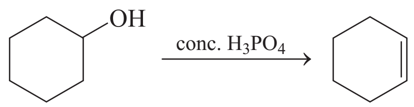


15. All dihydroxy benzene will have higher boiling points than monohydroxy benzene. Also, among dihydroxy benzenes, 1, 2,-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.



(intramolecular H-bonding in 1,2-dihydroxy benzene)

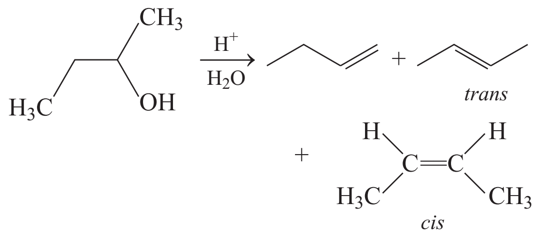
16.



Concentrated H_3PO_4 solution does not involve any substitution product while with others, substitution products are also formed.

17. $C_6H_5MgBr + (CH_3)_3COH \longrightarrow C_6H_6 + Mg[(CH_3)_3CO]Br$

18.



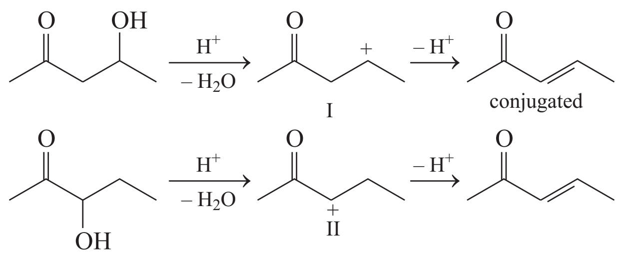
19. *A* is an alcohol and its oxidation product gives Tollen's test, i.e. *B* must be an aldehyde (CH_3CH_2CHO).

$$\underset{}{CH_3CH_2CHO} + \underset{\text{semicarbazide}}{H_2NHN—CO—NH_2} \longrightarrow CH_3CH_2—CH{=}N—NH—CONH_2$$

20. $$\text{1-propanol} \xrightarrow{Cu/\Delta} CH_3—CH_2—CHO \xrightarrow[\text{solution}]{\text{Fehling}} \underset{\text{red}}{Cu_2O\downarrow}$$

$$\text{2-propanol} \xrightarrow{Cu/\Delta} CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3 \xrightarrow[\text{solution}]{\text{Fehling}} \text{No reaction}$$

21.

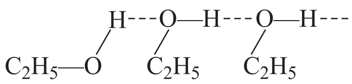


Although both reactions are giving the same product, carbocation I is more stable than II.

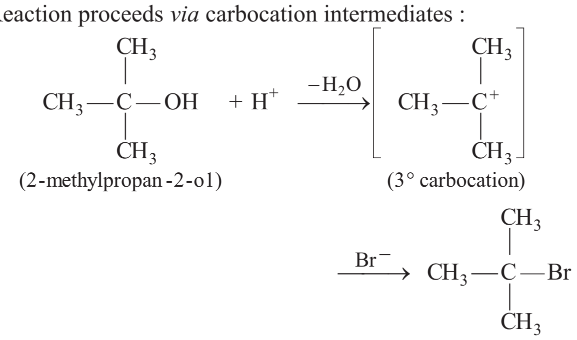
22. Thiol, (RSH), on combustion produces CO_2 (g), SO_2 (g) and $H_2O(l)$. At 298 K, H_2O will be in liquid phase.

23. OH $\longrightarrow$ $O^- + H^+$ (has maximum electronegativity difference)

24. Ethanol is capable in forming intermolecular H-bonds :



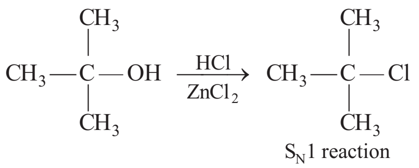
25. Reaction proceeds *via* carbocation intermediates :



26. $CO + H_2 \xrightarrow[\text{heat}]{ZnO\text{-}Cr_2O_3} CH_3OH$

27. $CH_3—CH_2—O—CH_2—CH_3 + HI \longrightarrow 2C_2H_5I$

28. 2-methyl propan-2-ol is a tertiary alcohol, will react fastest with Lucas reagent :



29. On heating with concentrated H_2SO_4, ethanol would undergo dehydration to produce ethene.

30. Ethanol is soluble in water due to its ability to form intermolecular H-bonds with water :

31. **Key idea** All the reactions involved in the problem are Nucleophilic substitution of second order i.e., S_N2 which have the speciality of inversion of configuration at the carbon atom involved.

Of the reactions given

Reaction 1 in its generalised format is seen as

$$R\text{OH} \xrightarrow[\text{In diethyl ether }(Et_2O)]{PBr_3} R\text{Br}$$

Reaction 2 is simple halogen exchange reaction called **Finkelstein reaction**. Its generalised format is

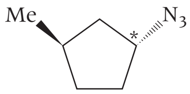
$$RX + \text{NaI} \xrightarrow{\text{In acetone}(Me_2CO)} R\text{I} + \text{Na}X$$

where X =Cl or Br

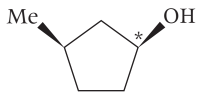
Reaction 3 in its generalised format seen as

$$R\text{I} + NaN_3 \xrightarrow{HCONMe_2} RN_3 + \text{NaI}$$

Now if the given product is

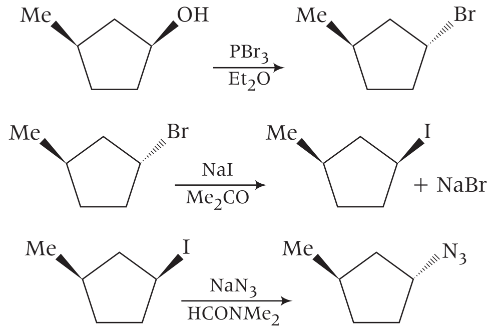


and which is too enantiomerically pure i.e. 100% either dextrorotatory or leavorotatory form, then the 'X' must be

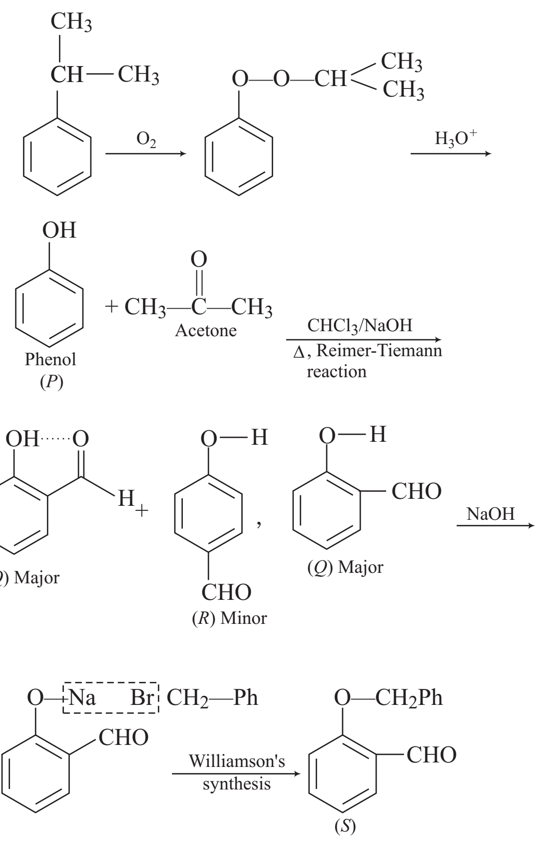


Note The configuration at carbon * atom in 'X' becomes inverted due to S_N2 mechanism which is visible in the product as well.

Thus, the probable reactions will be



32.



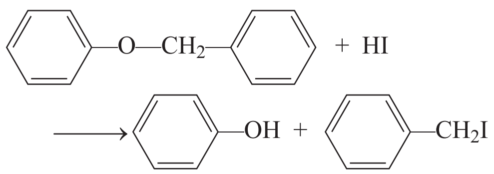
(a) R is not steam volatile, but Q is steam volatile thus, incorrect.

(b) Q has enolic group thus, gives violet colour with 1% aqueous $FeCl_3$ solution thus, correct.

(c) S has carbonyl group hence, gives yellow precipitate with 2, 4-DNP thus, correct.

(d) S does not give colour with $FeCl_3$ thus, incorrect.

33.



Phenol does not react further with HI.

34. $CH_3CH_2Br + \underset{\text{ambident nucleophile}}{O{=}\ddot{N}{-}O^-} \longrightarrow \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{ethyl nitrite}}{CH_3CH_2ONO}$

35. R—OH ← Hydrophilic

Hydrophobic

Increasing molecular weight increases hydrocarbon (R) proportion that lowers the solubility in water.

Passage 1

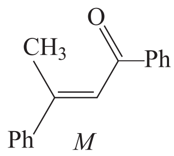
Compound J must be benzaldehyde because it on treatment with KOH undergoing Cannizzaro's reaction producing benzyl alcohol and pot-benzoate (L).

$$\underset{J}{C_6H_5{-}CHO} \xrightarrow{KOH} \underset{\text{benzyl alcohol}}{C_6H_5{-}CH_2OH} + C_6H_5COOK(L)$$

Also M is aldol condensation product formed from acetophenone

$$\underset{\text{acetophenone }(K)}{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \xrightarrow{KOH}$$

$$Ph{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}Ph \xrightarrow{-H_2O}$$



M

$$\Rightarrow I = \begin{matrix} Ph \\ H_3C \end{matrix}\!\!>C{=}CH{-}Ph$$

$$\text{and } H = Ph{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_2{-}Ph$$

3°-alcohol

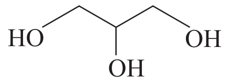
36. $J = C_6H_5CHO$, $K = Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_3$, $L = PhCO\bar{O}K^+$

37. $I = \begin{matrix} Ph \\ H_3C \end{matrix}\!\!>C{=}CH{-}Ph$

38. $Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + Ph{-}CH_2MgBr \xrightarrow{H_2O}$

$$Ph{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_2{-}Ph$$

H

39. Secondary :  C–2(OH) is secondary

40. Peroxides : $H_2O_2 + Fe^{2+} \longrightarrow H_2O + Fe^{3+}$

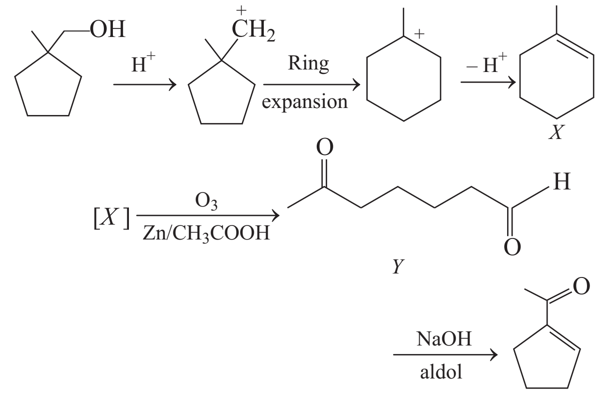
41. *Vicinal*, same

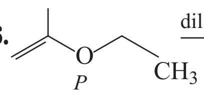
42. $C_2H_5OH \xrightarrow[\Delta]{Cu} CH_3CHO \xrightarrow[H_2O]{NaOH} \underset{\text{aldol}}{CH_3{-}\overset{\overset{OH}{|}}{CH}{-}CH_2{-}CHO}$

43. Ethanol is weaker acid than water, not neutralised with NaOH.

44. 2°-alcohol on oxidation yields ketone while 1°alcohol on oxidation produces aldehyde which can further be oxidised to acid.

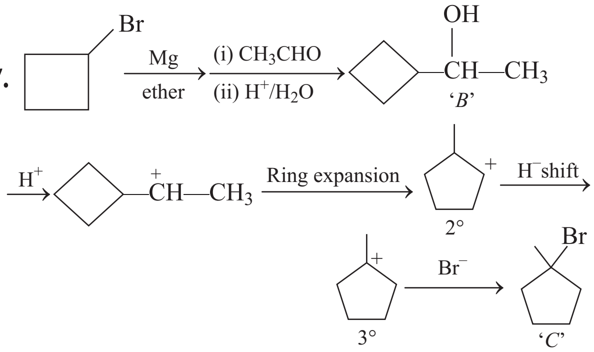
45.

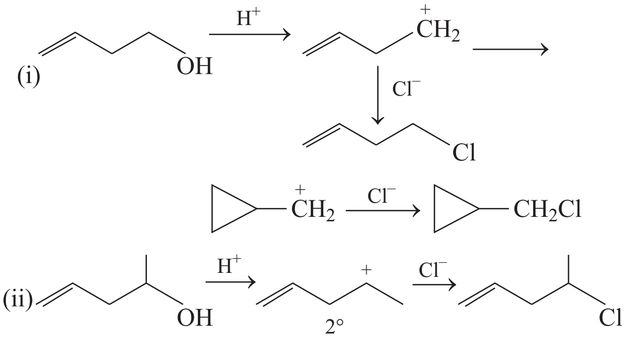


46.  $\xrightarrow{\text{dil. } H_2SO_4/H^+} \underset{Q}{CH_3CH_2OH} + \underset{R}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$

$\xrightarrow{I_2/NaOH}$ Both gives positive iodoform test.

47.



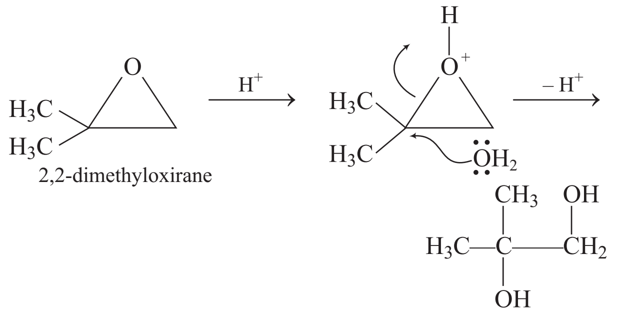
48. 

49. $(CH_3)_2CH-O-CH_3 \xrightarrow{HI} CH_3-\underset{\displaystyle I}{\underset{|}{C}H}-CH_3 + CH_3I$

50. Acid catalysed dehydration proceeds *via* carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :

$$\underset{(t\text{-butanol})}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH} \xrightarrow[-H_2O]{H^+} \underset{(3°\text{ highly stable})}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{+}{C}}}-CH_3}$$

n-butanol forms less stable (1°) carbocation.

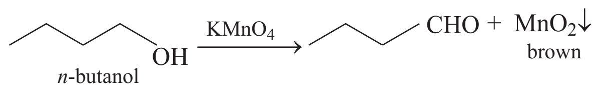
51. 

52. $E = C_6H_5COOH$ (benzoic acid)

$$\Rightarrow D = C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[NaOH]{I_2} C_6H_5-COONa + CHI_3$$

53. $$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3 \xrightarrow{H^+} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\underset{2°}{\overset{+}{C}H}-CH_3$$

$$\xrightarrow[\text{shift}]{\text{Methyl}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{+}{C}}}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3 \xrightarrow{-H^+} (H_3C)_2C=C(CH_3)_2$$

54. 

55. Compound 'X' $\xrightarrow{\text{Lucas reagent}}$ No reaction at room temperature.

$C_5H_8O \xrightarrow[AgNO_3]{\text{Ammoniacal}}$ ppt, $X \xrightarrow[CH_3MgBr]{\text{Excess of}} CH_4$;

$X \xrightarrow[\text{HI excess}]{H_2/Pt}$ n-pentane

Above information suggest that X has a terminal triple bond and it contain primary —OH group.

$$\Rightarrow \underset{X}{H-C\equiv C-CH_2-CH_2-CH_2OH} \xrightarrow{Ag(NH_3)_2^+} Ag-C\equiv C-CH_2CH_2CH_2OH$$

56. Isobutane < n-butane < n-butylchloride < n-butanol

57. $CH_3CH_2OH \xrightarrow[\Delta]{Conc.H_2SO_4} CH_2=CH_2$

$$\xrightarrow{Br_2} \underset{\displaystyle Br}{\underset{|}{C}H_2}-\underset{\displaystyle Br}{\underset{|}{C}H_2} \xrightarrow{NaNH_2} H-C\equiv C-H$$

$$\xrightarrow[CH_3COOH]{Hg(CH_3COO)_2} \underset{\text{vinyl acetate}}{CH_2=CH-OCOCH_3}$$

58. $C_2H_5OH \xrightarrow{I_2/NaOH} \underset{\text{iodoform}}{CHI_3} + HCOONa$

59. $CH_3-CH_2OH + I_2 + NaOH \longrightarrow \underset{\text{yellow}}{CHI_3}\downarrow$ (Iodoform test)

Iodoform test is not given by methanol.

60. Butanol forms intermolecular H-bonds, has higher boiling point than butanal.

61. $(CH_3COO)_2Ca \xrightarrow{\Delta} \underset{D}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} + CaCO_3$

$$\underset{C}{CH_3-C\equiv CH} \xrightarrow[HgSO_4]{H_2SO_4} \underset{D}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}$$

$$CH_3-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3 \xrightarrow[H_2SO_4]{Conc.} \underset{B}{CH_3-CH=CH_2} \xrightarrow[H_2O]{Br_2} \underset{X}{CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-\overset{\displaystyle Br}{\overset{|}{C}H_2}}$$

$$X \xrightarrow[H_2O]{NaNH_2} \underset{C}{CH_3-C\equiv CH}$$

62. (i) $H-C\equiv C-H \xrightarrow[H_2SO_4]{HgSO_4} CH_3-CHO \xrightarrow[H_2]{\text{Catalyst}} CH_3CH_2OH$

(ii) $4\,C_2H_5Br + \underset{\text{sodium-lead alloy}}{4\,(Na/Pb)} \xrightarrow{\text{Heat}} \underset{\text{tetraethyl lead}}{(C_2H_5)_4Pb}$

(iii) $Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + CH_4$

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

63. Compound X must be a symmetrical ether :

$\underset{X}{R-O-R} \xrightarrow{HI} \underset{Y}{2R-I} \xrightarrow{Na}$ No reaction, not an alcohol

$\xrightarrow[\text{reagent}]{\text{Schiffs'}}$ No reaction, not an aldehyde.

$R-I \xrightarrow{H_2O} R-OH(Z) \xrightarrow{[O]} \underset{EW = 60}{\text{Acid}}$

$R-OH(Z) \xrightarrow{I_2/P} R-I$

$\Rightarrow$ Acid is CH_3COOH and $Z = CH_3CH_2OH$

$\Rightarrow$ $X = C_2H_5-O-C_2H_5$, $Y = CH_3-CH_2-I$

$\underset{X}{CH_3CH_2-O-CH_2CH_3} \xrightarrow{HI} \underset{Y}{2CH_3CH_2I}$

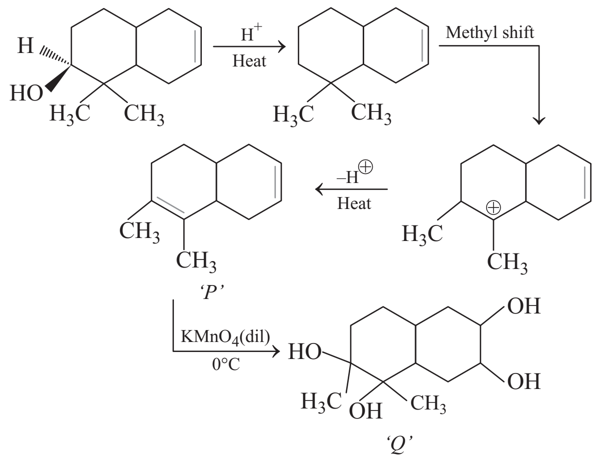
64. A is ethanol because B is an alkene (ethene).

$C_2H_5OH + \text{Conc.}\,H_2SO_4 \longrightarrow CH_2=CH_2 \xrightarrow{H_2/Ni} CH_3-CH_3$

$CH_2=CH_2 + \underset{\text{(brown)}}{Br_2-H_2O} \longrightarrow \underset{\text{colourless}}{\underset{Br\quad\; Br}{CH_2-CH_2}}$

$CH_2=CH_2 + \underset{\text{purple}}{\text{alk. }KMnO_4} \longrightarrow \underset{\text{colourless}}{\underset{OH\quad OH}{CH_2-CH_2}}$

65.



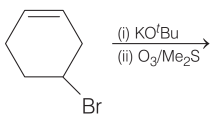
Download Chapter Test
http://tinyurl.com/yy5jdmfu *or*

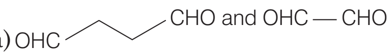
25

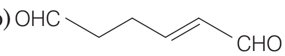
Aldehydes and Ketones

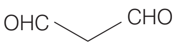
Objective Questions I (Only one correct option)

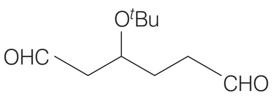
1. The major product(s) obtained in the following reaction is/are **(2019 Main, 12 April I)**



(a) 

(b) 

(c) 

(d) 

2. In the following reaction,

$$\text{Carbonyl compound} + \text{MeOH} \overset{\text{HCl}}{\rightleftharpoons} \text{acetal}$$

Rate of the reaction is the highest for: **(2019 Main, 9 April II)**

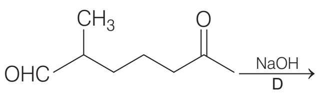
(a) Acetone as substrate and methanol in excess

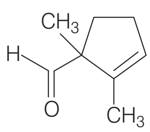
(b) Propanal as substrate and methanol in stoichiometric amount

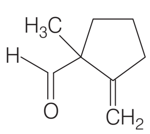
(c) Acetone as substrate and methanol in stoichiometric amount

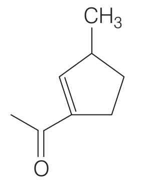
(d) Propanal as substrate and methanol in excess

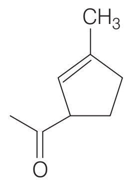
3. The major product obtained in the following reaction is **(2019 Main, 8 April II)**



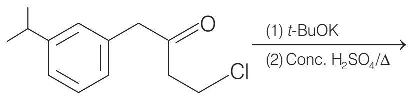
(a) 

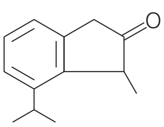
(b) 

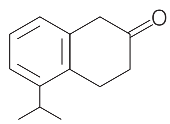
(c) 

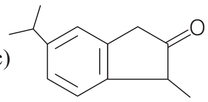
(d) 

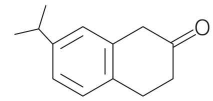
4. The major product of the following reaction is **(2019 Main, 8 April II)**



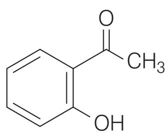
(a) 

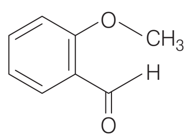
(b) 

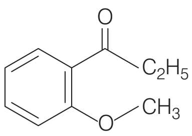
(c) 

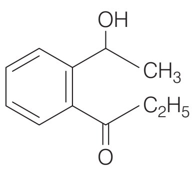
(d) 

5. An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is **(2019 Main, 8 April I)**

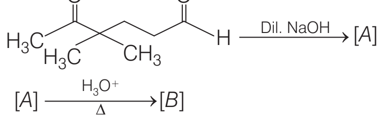
(a) 

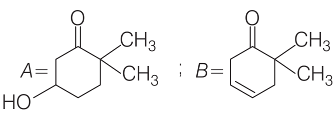
(b) 

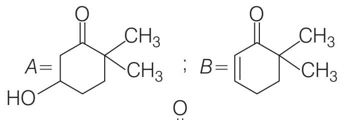
(c) 

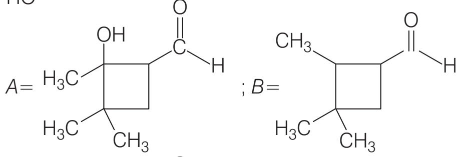
(d) 

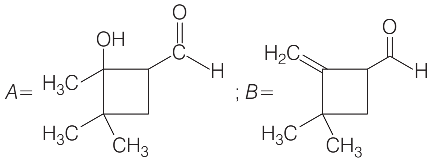
6. In the following reactions, products A and B are **(2019 Main, 12 Jan I)**



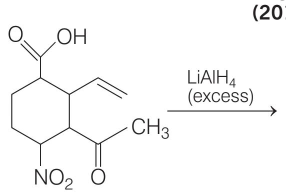
(a) 

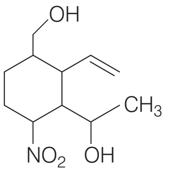
(b) 

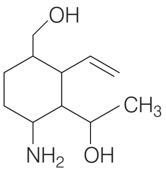
(c) 

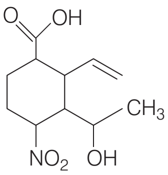
(d) 

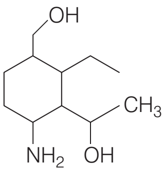
7. The major product obtained in the following reaction is **(2019 Main, 11 Jan II)**



(a) 

(b) 

(c) 

(d) 

8. The correct match between item 'I' and item 'II' is

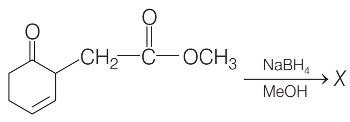
Item 'I' (Compound)		**Item 'II'** (Reagent)	
(A)	Lysine	(P)	1-naphthol
(B)	Furfural	(Q)	Ninhydrin
(C)	Benzyl alcohol	(R)	$KMnO_4$
(D)	Styrene	(S)	Ceric ammonium nitrate

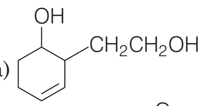
(2019 Main, 10 Jan II)

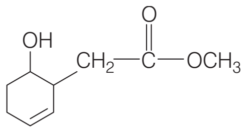
Codes

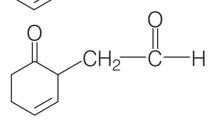
	A	B	C	D
(a)	Q	R	S	P
(b)	R	P	Q	S
(c)	Q	P	S	R
(d)	Q	P	R	S

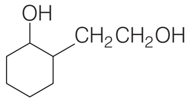
9. The major product 'X' formed in the following reaction is **(2019 Main, 10 Jan I)**



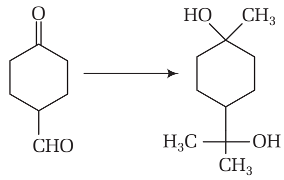
(a) 

(b) 

(c) 

(d) 

10. The correct sequence of reagents for the following conversion will be **(2017 Main)**



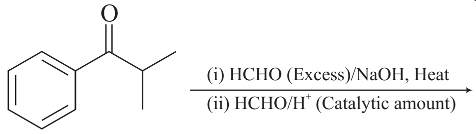
(a) $[Ag(NH_3)_2]^+$ OH^-, H^+ / CH_3OH, CH_3MgBr

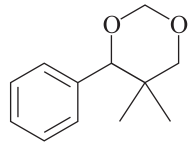
(b) CH_3MgBr, H^+ / CH_3OH, $[Ag(NH_3)_2]^+$ OH^-

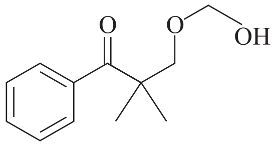
(c) CH_3MgBr, $[Ag(NH_3)_2]^+$ OH^-, H^+ / CH_3OH

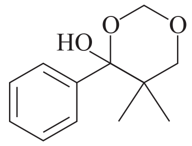
(d) $[Ag(NH_3)_2]^+$ OH^-, CH_3MgBr, H^+ / CH_3OH

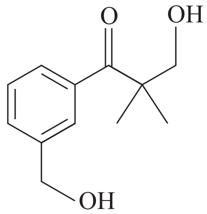
11. The major product of the following reaction sequence is **(2016 Adv.)**



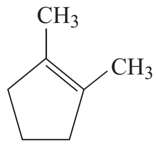
(a) 

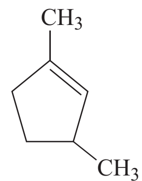
(b) 

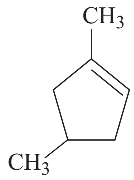
(c) 

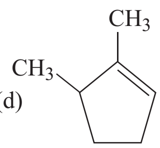
(d) 

12. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **(2015 Main)**

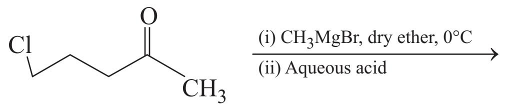
(a) 

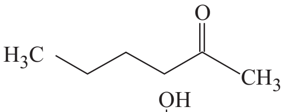
(b) 

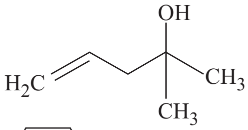
(c) 

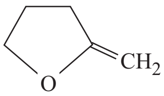
(d) 

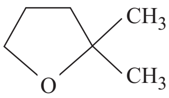
13. The major product in the following reaction is **(2014 Adv.)**



(a) 

(b) 

(c) 

(d) 

14. The most suitable reagent for the conversion of $R—CH_2—OH \rightarrow R—CHO$ is **(2014 Main)**

(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (pyridinium chlorochromate)

15. The major product H in the given reaction sequence is **(2012)**

$$CH_3—CH_2—CO—CH_3 \xrightarrow{CN^{\ominus}} G \xrightarrow{95\%\ H_2SO_4} H$$

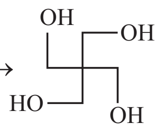
(a) $CH_3—CH{=}C(CH_3)—COOH$

(b) $CH_3—CH{=}C(CH_3)—CN$

(c) $CH_3—CH_2—C(OH)(CH_3)—COOH$

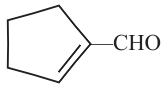
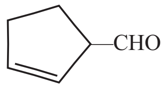
(d) $CH_3—CH{=}C(CH_3)—CO—NH_2$

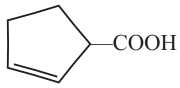
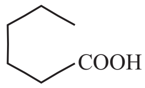
16. The number of aldol reaction(s) that occurs in the given transformation is **(2012)**

$CH_3CHO + 4HCHO \xrightarrow{\text{Conc. } aq. \text{ NaOH}}$ 

(a) 1 (b) 2
(c) 3 (d) 4

17. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is **(2007, 3M)**

(a)  (b) 

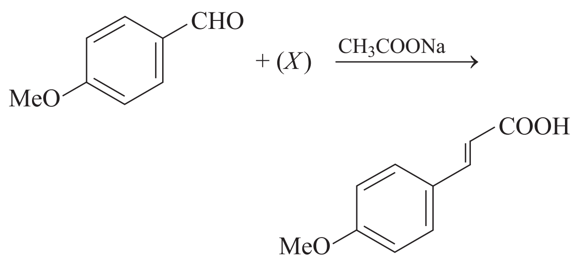
(c)  (d) 

18. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime **(2006)**

(a) two different oximes are formed
(b) three different oximes are formed
(c) two oximes are optically active
(d) all oximes are optically active

19. Butan-2-one can be converted to propanoic acid by which of the following ? **(2006)**

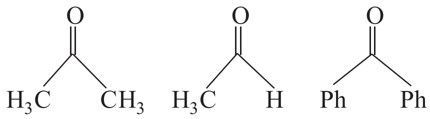
(a) NaOH, NaI/H^+
(b) Fehling's solution
(c) NaOH, I_2/H^+
(d) Tollen's reagent

20. 

What is X?

(a) CH_3COOH (b) $BrCH_2COOH$
(c) $(CH_3CO)_2O$ (d) HOC—COOH

21. The order of reactivity of phenyl magnesium bromide with the following compounds is **(2004, 1M)**



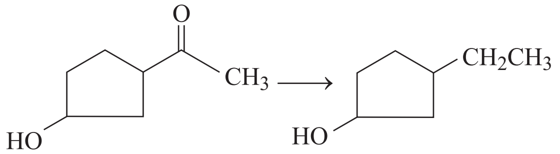
(I) (II) (III)

(a) (II) > (III) > (I)
(b) (I) > (III) > (II)
(c) (II) > (I) > (III)
(d) All of the above

22. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives **(2001, 1M)**

(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol

23. The appropriate reagent for the following transformation:



(a) Zn (Hg), HCl (b) NH_2NH_2, OH^-
(c) H_2/Ni (d) $NaBH_4$

24. Which of the following has the most acidic hydrogen? **(2000, 1M)**
(a) 3-hexanone (b) 2, 4-hexanedione
(c) 2, 5-hexanedione (d) 2, 3-hexanedione

25. The enol form of acetone, after treatment with D_2O, gives **(1999, 2M)**

(a) $H_3C{-}\overset{\displaystyle OD}{\overset{|}{C}}{=}CH_2$ (b) $D_3C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CD_3$

(c) $H_2C{=}\overset{\displaystyle OH}{\overset{|}{C}}{-}CH_2D$ (d) $D_2C{=}\overset{\displaystyle OD}{\overset{|}{C}}{-}CD_3$

26. Which of the following will react with water? **(1998, 2M)**
(a) $CHCl_3$ (b) Cl_3CCHO
(c) CCl_4 (d) $ClCH_2CH_2Cl$

27. Which of the following compounds is oxidised to prepare methyl ethyl ketone? **(1987, 1M)**
(a) 2-propanol (b) 1-butanol
(c) 2-butanol (d) *t*-butyl alcohol

28. The compound that will not give iodoform on treatment with alkali and iodine is **(1985, 1M)**
(a) acetone (b) ethanol
(c) diethyl ketone (d) isopropyl alcohol

29. The Cannizzaro's reaction is not given by **(1983, 1M)**
(a) trimethyl acetaldehyde
(b) acetaldehyde
(c) benzaldehyde
(d) formaldehyde

30. When acetaldehyde is treated with Fehling's solution, it gives a precipitate of **(1983, 1M)**
(a) Cu (b) CuO
(c) Cu_2O (d) Cu + Cu_2O + CuO

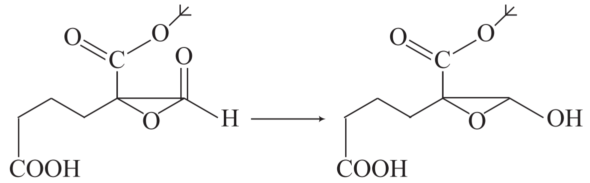
31. A compound that gives a positive iodoform test is **(1982, 1M)**
(a) 1-pentanol (b) 3-pentanone
(c) 2- pentanone (d) pentanal

32. The reagent with which both acetaldehyde and acetone react easily is **(1981, 1M)**
(a) Tollen's reagent (b) Schiff's reagent
(c) Grignard's reagent (d) Fehling's reagent

Objective Questions II

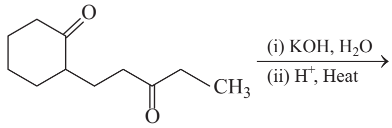
(One or more than one correct option)

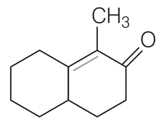
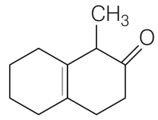
33. Reagent(s) which can be used to bring about the following transformation is (are) **(2016 Adv.)**

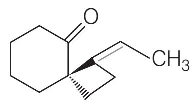
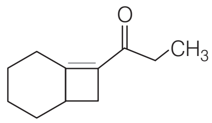


(a) $LiAlH_4$ in $(C_2H_5)_2O$ (b) BH_3 in THF
(c) $NaBH_4$ in C_2H_5OH (d) Raney Ni/H_2 in THF

34. The major product of the following reaction is **(2015 Adv.)**

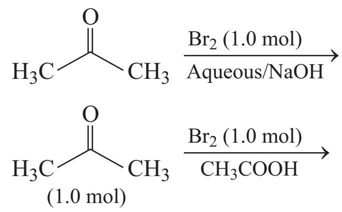


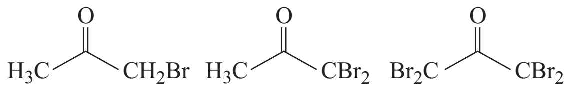
(a)  (b) 

(c)  (d) 

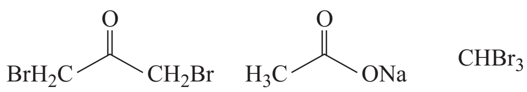
35. After completion of the reactions (I and II), the organic compound (s) in the reaction mixtures is/are **(2013)**

Reaction I
Reaction II





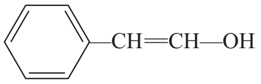
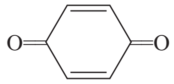
P *Q* *R*

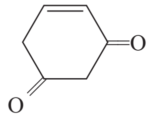
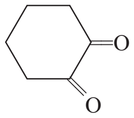


S *T* *U*

(a) reaction I : *P* and reaction II : *P*
(b) reaction I : *U*, acetone and reaction II : *Q*, acetone
(c) reaction I : *T*, *U*, acetone and reaction II : *P*
(d) reaction I : *R*, acetone and reaction II : *S*, acetone

36. Tautomerism is exhibited by **(1998)**

(a)  (b) 

(c)  (d) 

37. A new carbon–carbon bond formation is possible in **(1998, 2M)**

(a) Cannizzaro's reaction
(b) Friedel-Crafts' reaction
(c) Clemmensen's reduction
(d) Reimer-Tiemann reaction

38. Which of the following will undergo aldol condensation? **(1998, 2M)**

(a) Acetaldehyde
(b) Propanaldehyde
(c) Benzaldehyde
(d) Trideutero acetaldehyde

39. Among the following compounds, which will react with acetone to give a product containing $\rangle C{=}N—$?

(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$ **(1998, 2M)**
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$

40. Which of the following is an example of aldol condensation?

(a) $2CH_3CHO \xrightarrow{\text{Dil.NaOH}} CH_3CH(OH)CH_2CHO$ **(1989, 1M)**

(b) $2CH_3COCH_3 \xrightarrow{\text{Dil.NaOH}} H_3C—\overset{OH}{\underset{CH_3}{C}}—CH_2COCH_3$

(c) $2HCHO \xrightarrow{\text{Dil.NaOH}} CH_3OH + HCOONa$

(d) $C_6H_5CHO + HCHO \xrightarrow{\text{Dil.NaOH}} C_6H_5CH_2OH + HCOONa$

41. Which of the following compounds will react with ethanolic KCN? **(1984, 1M)**

(a) Ethyl chloride (b) Acetyl chloride
(c) Chlorobenzene (d) Benzaldehyde

42. Which of the following compounds will give a yellow precipitate with iodine and alkali ? **(1984, 1M)**

(a) 2-hydroxy propane
(b) Acetophenone
(c) Methyl acetate
(d) Acetamide

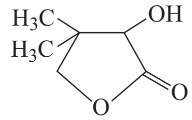
43. Base catalysed aldol condensation occurs with **(1984, 1M)**

(a) propionaldehyde
(b) benzaldehyde
(c) 2-methyl propionaldehyde
(d) 2, 2-dimethyl propionaldehyde

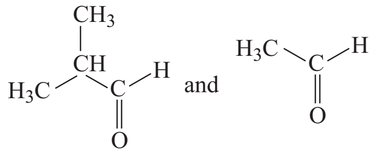
Passage Based Questions

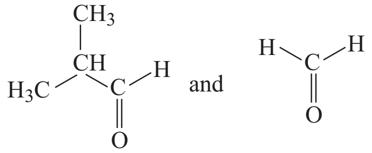
Passage 1

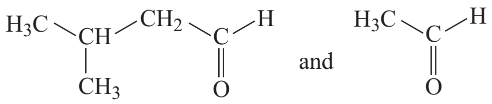
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below : **(2010)**

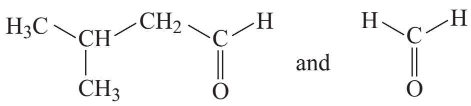


44. The compounds P and Q respectively are

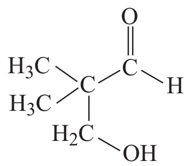
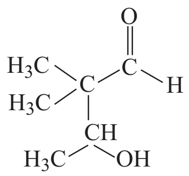
(a) 

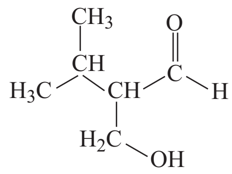
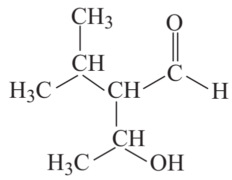
(b) 

(c) 

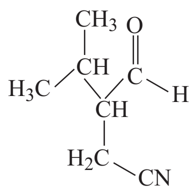
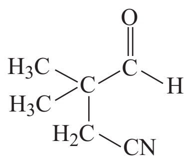
(d) 

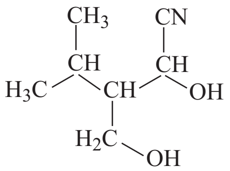
45. The compound R is

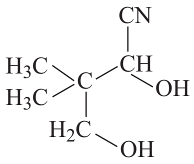
(a)  (b) 

(c)  (d) 

46. The compound S is

(a)  (b) 

(c) 

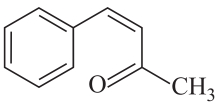
(d) 

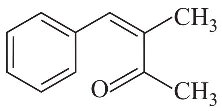
Passage 2

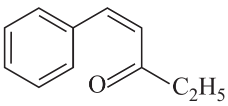
A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*. **(2009)**

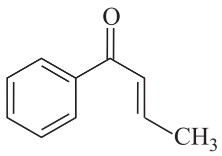
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4\ /\ heat}]{1.\ MeMgBr} Q \xrightarrow{O_3/Zn\text{-}H_2O} R \xrightarrow[heat]{OH^-} S$$

47. The structure of the carbonyl compound *P*, is

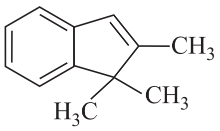
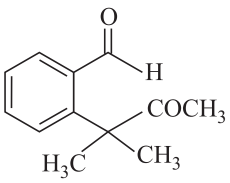
(a) 

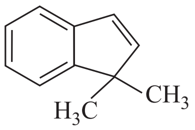
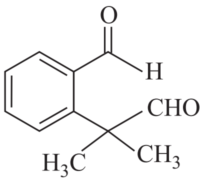
(b) 

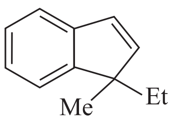
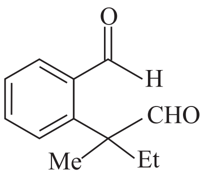
(c) 

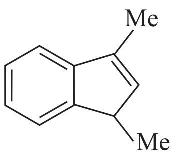
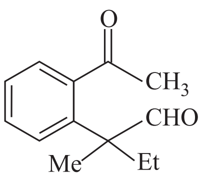
(d) 

48. The structures of the products *Q* and *R*, respectively, are

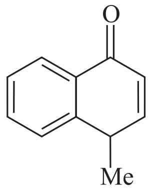
(a)  

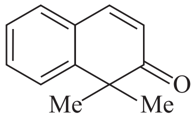
(b)  

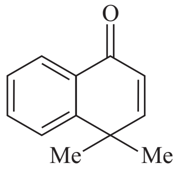
(c)  

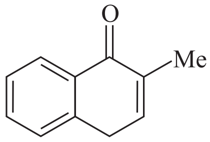
(d)  

49. The structure of the product *S*, is

(a) 

(b) 

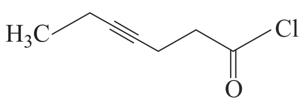
(c) 

(d) 

Passage 3

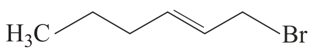
In the following sequence, product *I*, *J* and *L* are formed. *K* represents a reagent.

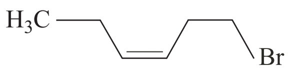
$$\text{Hex-3-ynal} \xrightarrow[\text{(ii) } PBr_3]{\text{(i) } NaBH_4} I \xrightarrow[\text{(iii) } H_3O^+]{\text{(i) Mg/ether, (ii) } CO_2} J \xrightarrow{K}$$

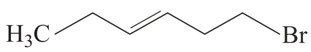
 $\xrightarrow[\text{Pd/BaSO}_4\text{ quinoline}]{H_2} L$

(2008, 3 × 4M = 12M)

50. The structure of the product *I* is

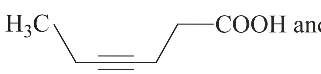
(a) 

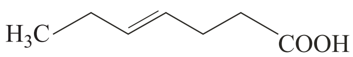
(b) 

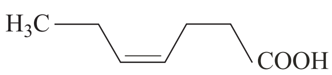
(c) 

(d) 

51. The structures of compounds *J* and *K*, respectively, are

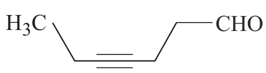
(a)  and $SOCl_2$

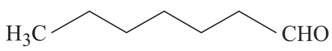
(b)  and SO_2Cl_2

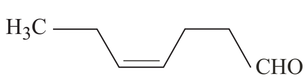
(c)  and $SOCl_2$

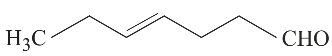
(d)  and CH_3SO_2Cl

52. The structure of product *L* is

(a) 

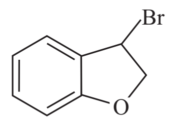
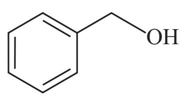
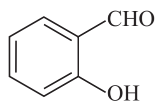
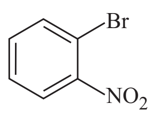
(b) 

(c) 

(d) 

Match the Column

53. Match each of the compounds given in Column I with the reaction(s) that they can undergo, given in Column II.

	Column I		Column II
A.		p.	Nucleophilic substitution
B.		q.	Elimination
C.		r.	Nucleophilic addition
D.		s.	Esterification with acetic anhydride
		t.	Dehydrogenation

54. Match the compounds/ions in Column I with their properties/reactions in Column II. **(2007, 6M)**

	Column I		Column II
A.	C_6H_5CHO	p.	gives precipitate with 2, 4-dinitrophenylhydrazine
B.	$CH_3C{\equiv}CH$	q.	gives precipitate with $AgNO_3$
C.	CN^-	r.	is a nucleophile
D.	I^-	s.	is involved in cyanohydrin formation

Fill in the Blanks

55. Fehling's solution *A* consists of an aqueous solution of copper sulphate, while Fehling's solution *B* consists of an alkaline solution ...... **(1990, 1M)**

True or False

56. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. **(1987, 1M)**

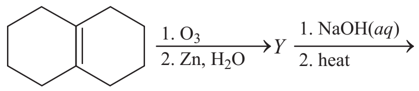
57. Benzaldehyde undergoes aldol condensation in an alkaline medium. **(1982 , 1M)**

Integer Answer Type Questions

58. Consider all possible isomeric ketones including stereoisomers of MW $= 100$. All these isomers are independently reacted with $NaBH_4$. The total number of ketones that gives a racemic product(s) is/are

NOTE (Stereoisomers are also reacted separately). **(2014 Adv.)**

59. In the scheme given below, the total number of intramolecular aldol condensation products formed from *Y* is



(2010)

Subjective Questions

60. $(A),\ C_6H_{12} \xrightarrow{HCl} (B),\ C_6H_{13}Cl + (C),\ C_6H_{13}Cl$

$(B) \xrightarrow{\text{Alcoholic KOH}} (D)$, (an isomer of (A))

$(D) \xrightarrow{\text{Ozonolysis}} (E)$, (positive iodoform and negative Fehling's solution test)

$(A) \xrightarrow{\text{Ozonolysis}} (F) + (G)$, (positive Tollen's test for both)

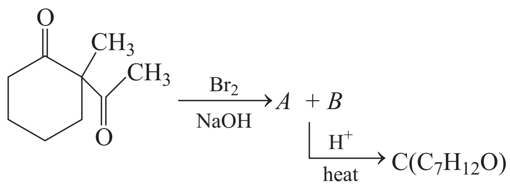
$(F) + (G) \xrightarrow{\text{Conc. NaOH}}$ HCOONa + A primary alcohol

Identify the compounds (*A*) to (*D*). **(2003)**

61. A compound $C_9H_7O_2Cl$ exists predominantly in enol form (*A*) and also in keto form (*B*). On oxidation with $KMnO_4$ it gives *m*-chlorobenzoic acid as one of the products. Identify the compounds (*A*) and (*B*). **(2003)**

62. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with NaOH / I_2 yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2 / Pd – C) gives a racemic mixture. **(2001, 5M)**

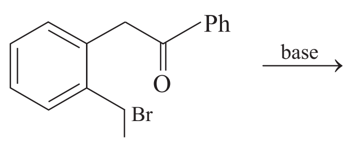
63. Identify *A, B* and *C*, and give their structures.



(2000)

64. An organic compound *A*, $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound *B*. The compound *B* on ozonolysis gives compound *C*, which in presence of a base gives 1-acetyl cyclopentane *D*. The compound *B* on reaction with HBr gives compound *E*. Write the structures of *A*, *B*, *C* and *E*. Show, how *D* is formed from *C*. **(2000, 5M)**

65. What would be the major product in the following reaction ?



(2000, 1M)

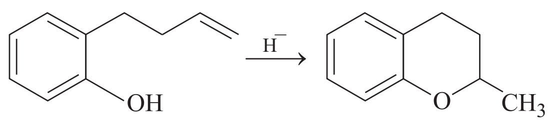
66. (a) Compound *A* (C_8H_8O) on treatment with NH_2OH. HCl given *B* and *C*. *B* and *C* rearrange to give *D* and *E*, respectively, on treatment with acid. *B*, *C*, *D* and *E* are all isomers of molecular formula (C_8H_9NO). When D is boiled with alcoholic KOH, an oil F (C_6H_7N) separates out. F reacts rapidly with CH_3COCl to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G ($C_7H_6O_2$). Identify A-G.

(b) Carry out the following transformation in not more than three steps.

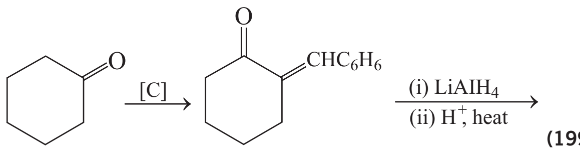
1-butyne $\longrightarrow$ 2-pentanone **(1999, 3M)**

67. Write the intermediate steps for each of the following reactions

(i) $C_6H_5CH(OH)C{\equiv}CH \xrightarrow{H_3O^+} C_6H_5CH{=}CHCHO$

(ii) 

68. Complete the following reactions with appropriate structures of products/reagents.

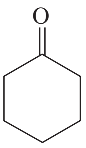


(1998)

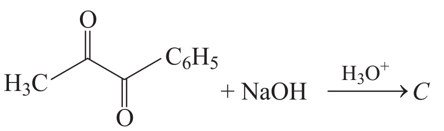
69. An aldehyde A ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B. **(1998, 2M)**

70. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oxime. **(1997, 2M)**

71. Complete the following, giving the structures of the principal organic products,

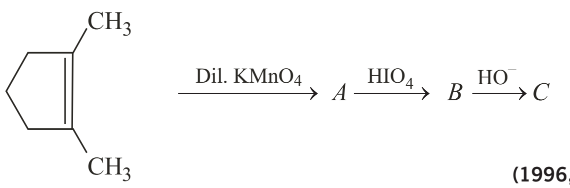
(i)  $+ Ph_3P{=}CH_2 \longrightarrow A$

(ii) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow B$

(iii) 

(1997, 2M)

72. Suggest appropriate structures for the missing compounds. (the number of carbon atoms remains the same throughout the reaction)



(1996, 3M)

73 Complete the following reaction with appropriate structure :

$$\begin{matrix} CH_3CH_2 \\ H \end{matrix}\!\!>C{=}O \xrightarrow[\text{(ii) } LiAlH_4]{\text{(i) } KCN/H_2SO_4}$$

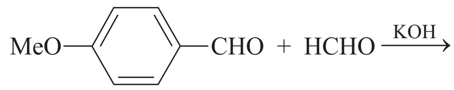
(1996, 1M)

74. Complete the following reaction with appropriate structure.

$$C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH\text{ heat}]{NaOC_2H_5\text{ in absolute}} A$$

(1995, 1M)

75. Write the structure of the major organic product expected from the following reaction. **(1992, 1M)**



76. Arrange the following in the increasing order of expected enol content.

CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$ **(1992, 1M)**

77. Give reason in one or two sentences :

"Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide". **(1991)**

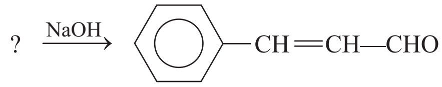
78. A ketone A, which undergoes haloform reaction, gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms mono-ozonide D. D on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. **(1989, 4M)**

79. Answer the followings with suitable equations wherever necessary

(i) suggest a reagent to distinguish acetaldehyde from acetone.

(ii) what happens when excess chlorine is passed through boiling toluene in the presence of sunlight? **(1987, 2M)**

80. Complete the following with appropriate structures



(1986, 1M)

81. How may the following transformation be carried out (in not more than six steps) "benzaldehyde to cyanobenzene"? **(1986, 2M)**

82. Give reason in one or two sentences for the following:

"Hydrazones of aldehydes and ketones are not prepared in highly acidic medium". **(1986, 1M)**

83. Write down product of the following reaction

$$\text{Propanal} \xrightarrow[\text{heat}]{NaOH}$$

(1985, 1M)

84. Arrange the following in order of their increasing reactivity towards HCN :

CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$ **(1985, 1M)**

85. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis:

"Acetoxime from acetaldehyde."

$[K_2Cr_2O_7 / H^+, Ca(OH)_2$ and $NH_2OH, HCl]$ **(1984, 2M)**

86. Show with balanced equation, what happens, when the following are mixed :

"Chloral is heated with aqueous hydroxide" **(1984, 2M)**

87. An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid B. When B is treated with bromine in presence of phosphorus yields a compound C which on hydrolysis gives a hydroxyl acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D. **(1982 , 2M)**

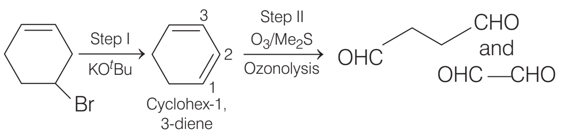
88. Outline the reaction sequence for the conversion of methanal to ethanol (the number of steps should not be more than three). **(1981, 2M)**

89. Write the structural formula of the main organic product formed when methanal reacts with ammonia. **(1981, 1/2M)**

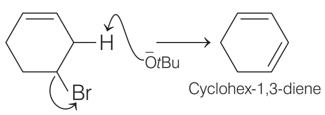
Answers

1. (a)	**2.** (d)	**3.** (c)	**4.** (d)	**37.** (b,d)	**38.** (a,b,d)	**39.** (a,d)	**40.** (a,b)
5. (d)	**6.** (b)	**7.** (b)	**8.** (c)	**41.** (a,b,d)	**42.** (a,b)	**43.** (a,c)	**44.** (b)
9. (b)	**10.** (a)	**11.** (a)	**12.** (b)	**45.** (a)	**46.** (d)	**47.** (b)	**48.** (a)
13. (d)	**14.** (d)	**15.** (a)	**16.** (c)	**49.** (b)	**50.** (d)	**51.** (a)	**52.** (c)
17. (a)	**18.** (b)	**19.** (c)	**20.** (c)	**53.** $A \to p, q, t$	$B \to p, s, t$	$C \to r, s$	$D \to p.$
21. (c)	**22.** (a)	**23.** (b)	**24.** (b)	**54.** $A \to p, q, s$	$B \to q, r$	$C \to q, r, s$	$D \to q, r.$
25. (b)	**26.** (b)	**27.** (c)	**28.** (c)	**55.** Sodium potassium tartarate			
29. (b)	**30.** (c)	**31.** (c)	**32.** (c)	**56.** False	**57.** False		
33. (c)	**34.** (a)	**35.** (c)	**36.** (a,c,d)	**58.** (5)	**59.** (1)		

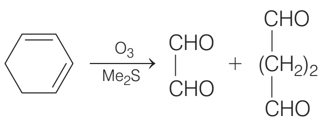
Hints & Solutions

1. 

In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result diene is formed.



Cyclohex -1, 3-diene on ozonolysis gives butane-1, 4- dial and ethane- 1, 2- dial.

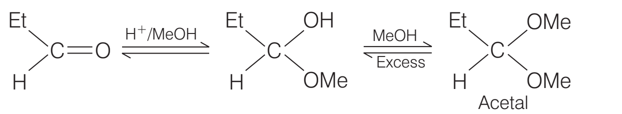


2. **Key Idea** Aldehydes are more reactive than ketones in nucleophilic addition reactions.

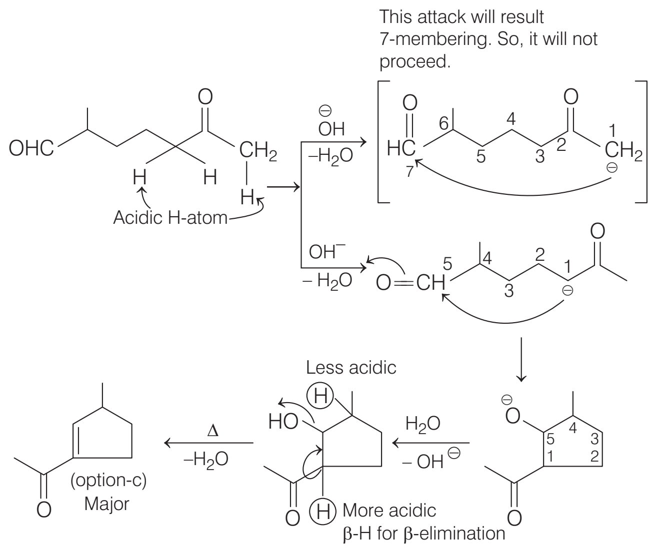
For the reaction,

$$\text{Carbonyl compound} + \text{MeOH} \xrightleftharpoons{\text{HCl}} \text{Acetal}$$

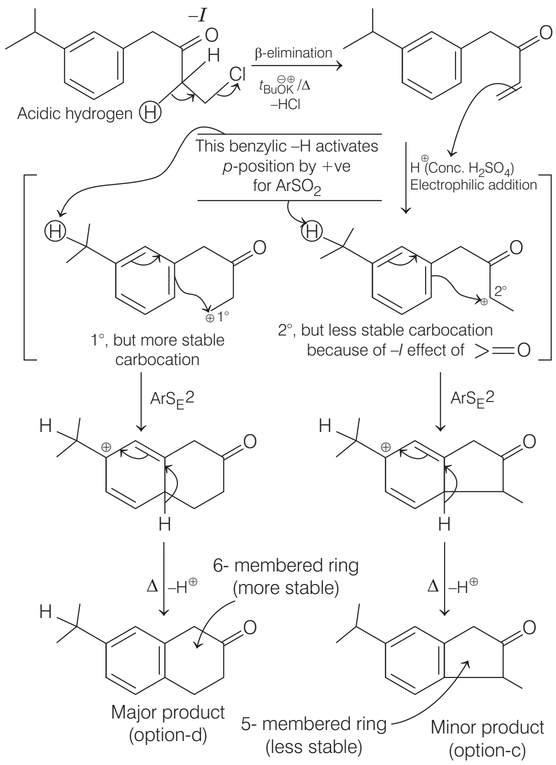
Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :



3. It is an intramolecular aldol condensation reaction.

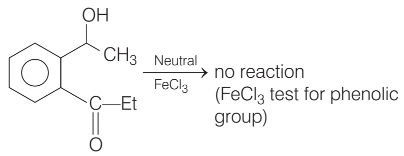


4.

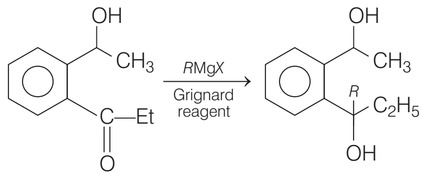


5. According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

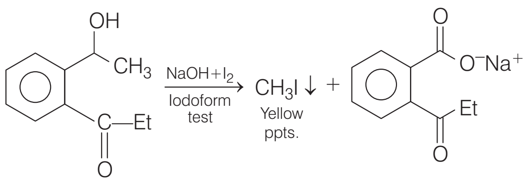
- As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral $FeCl_3$ test.



- Compound gives reaction with RMgX as it contains —C(=O)—Et.

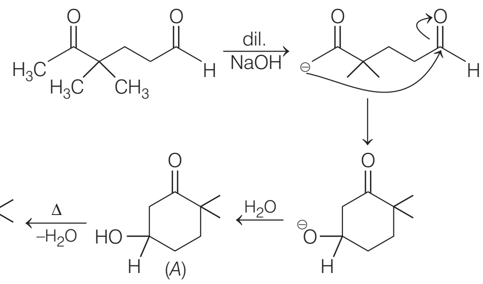


Compound with CH_3CH(OH)— group undergoes iodoform test in presence of NaOH and I_2.

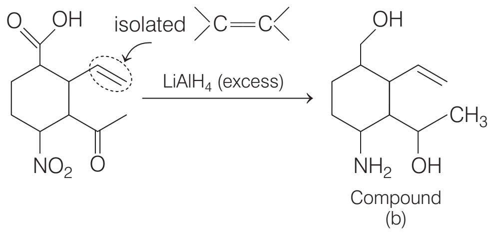


6. The reactant in presence of dil · NaOH undergoes intramolecular aldol condensation reaction.

As a result of this, β-hydroxyketone (A) is obtained which on hydrolysis followed by heating produces α, β-unsaturated ketone (B)

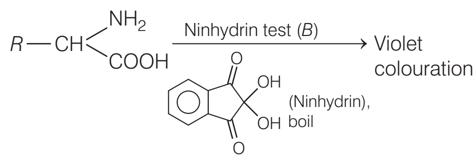


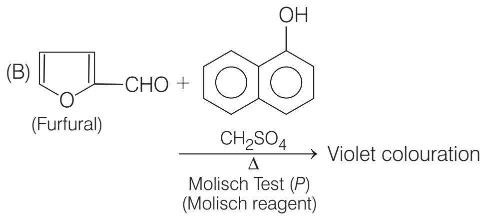
7. $LiAlH_4$ acts as a nucleophilic reducing agent that can reduce —COOH to —CH_2OH, —C(—)=O into —CH(—)—OH and —NO_2 into —NH_2, but it cannot reduce isolated >C=C<

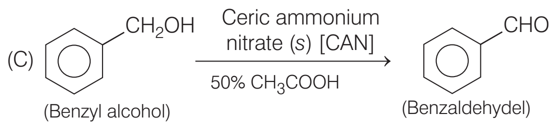


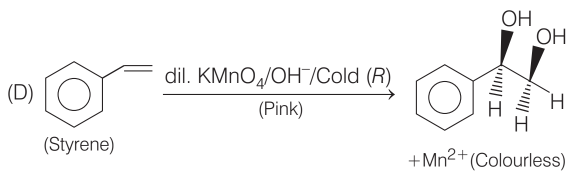
8. (A) → Q; B → (P) ; C → (S), D → (R)

(A) Lysine (R=–$(CH_2)_4$–NH_2)

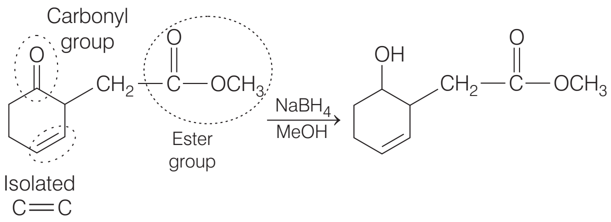




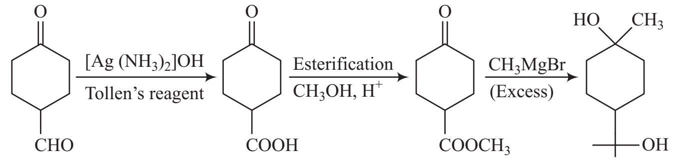




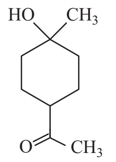
9. $NaBH_4$ is a selective reducing agent. It reduces carbonyl (>C=O) group into an alcohol but cannot reduce an isolated C=C and an ester group too.



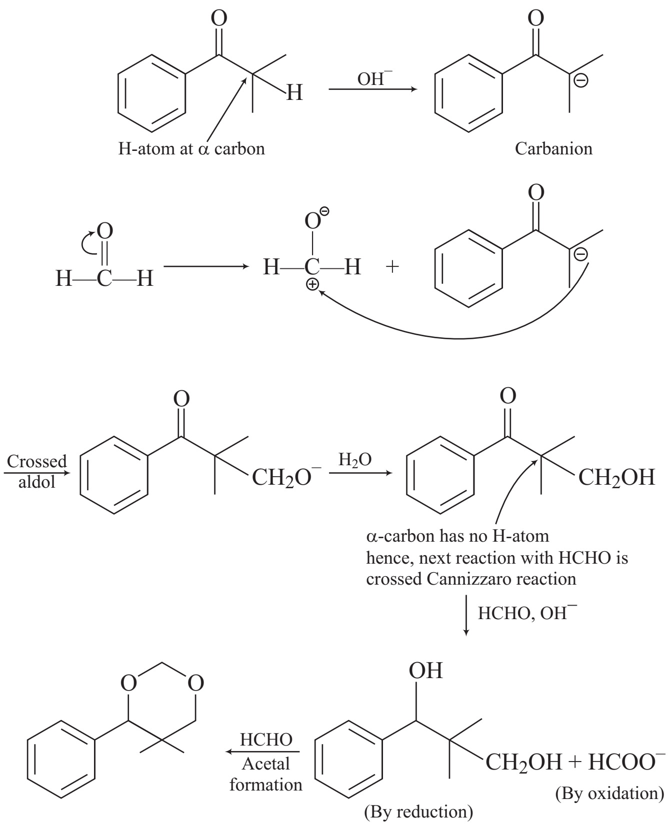
10.



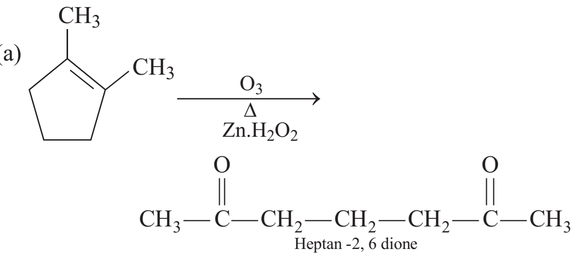
Before final product is formed, intermediate is



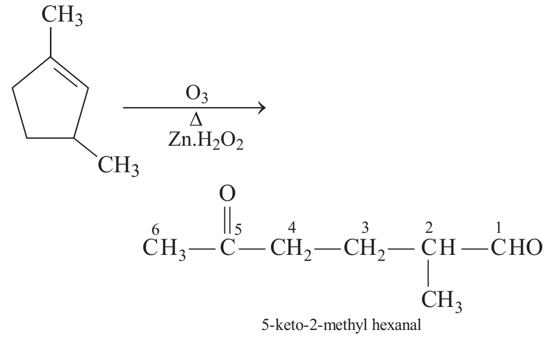
11.



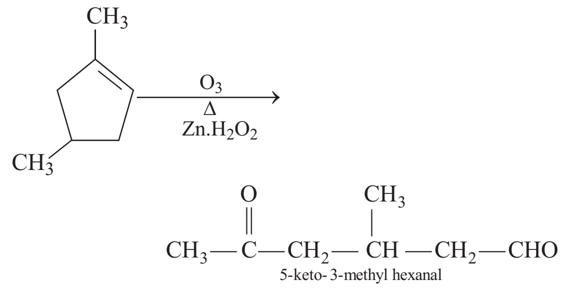
12. (a)



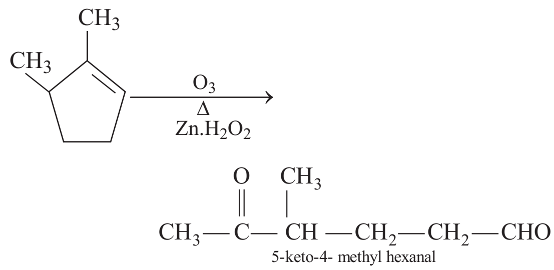
(b)



(c)

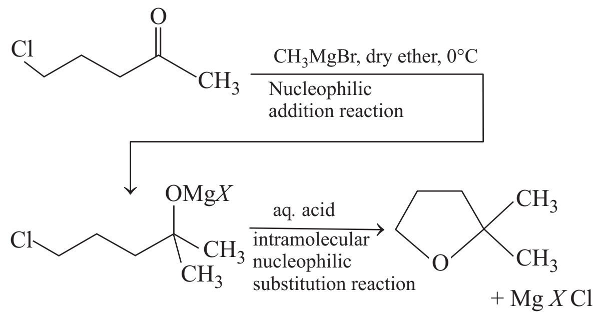


(d)



13. PLAN This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

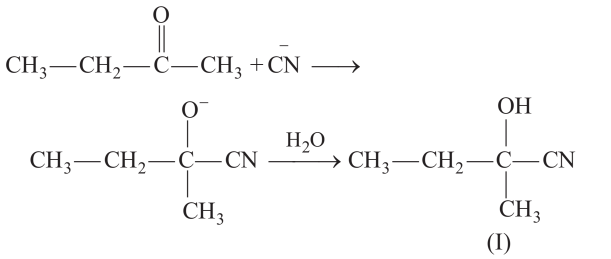
Complete reaction sequence is as shown below:



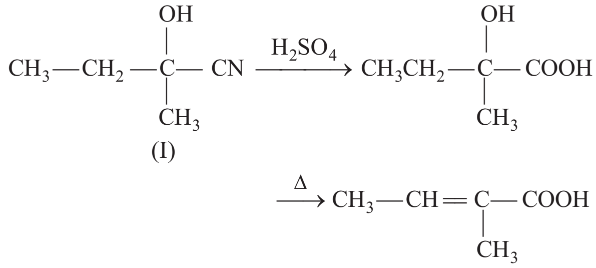
14. $R-CH_2OH \xrightarrow{\text{PCC}} R-CH=O$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

15. The first step is cyanohydrin reaction

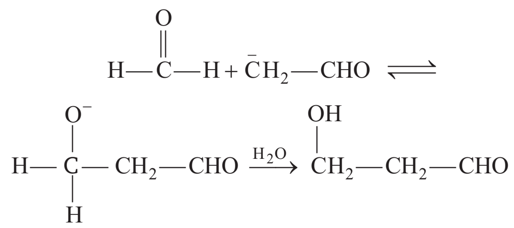


In the second step the — CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc. H_2SO_4.

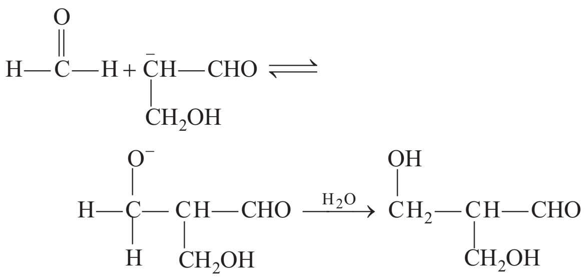


16. The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.

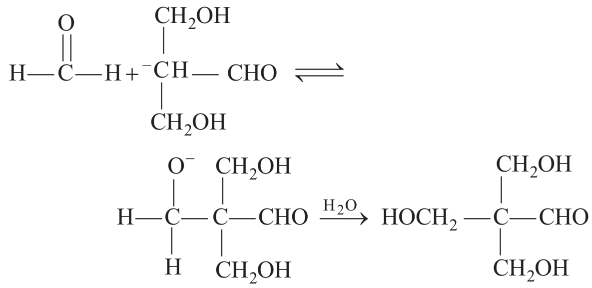
***Step* I** $CH_3CHO + OH^- \longrightarrow \bar{C}H_2-CHO + H_2O$



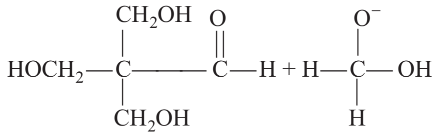
***Step* II** $HOCH_2-CH_2-CHO + HO^- \rightleftharpoons HO-CH_2-\bar{C}H-CHO + H_2O$

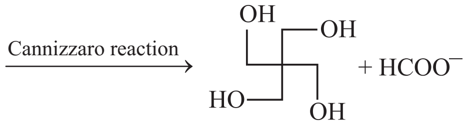


***Step* III** $HOCH_2-CH(CH_2OH)-CHO + HO^- \rightleftharpoons HOCH_2-\bar{C}(CH_2OH)-CHO + H_2O$



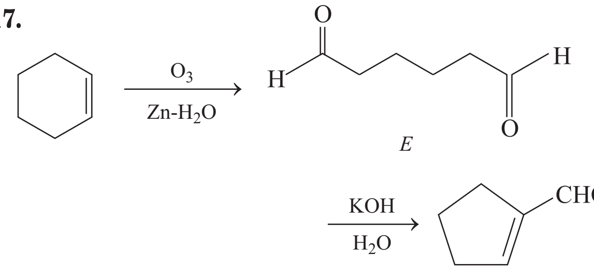
***Step* IV**





In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

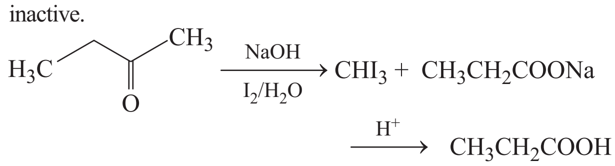
17.



Intramolecular aldol condensation reaction

18. Three different oximes are formed out of which two are optically active i.e.exists as a pair of enantiomers while other is optically inactive.

19.

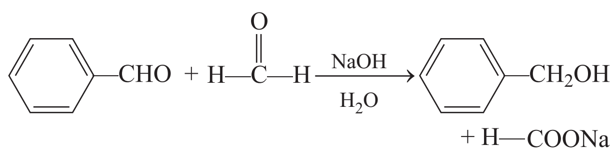


20. X is $(CH_3CO)_2O$ and it is an example of Perkin's reaction.

21. The reactivity of carbonyl compound towards nucleophilic addition of Grignard's reagent depends on extent of steric hindrance at α-carbon. Greater the steric hindrance smaller the reactivity. Hence, reactivity order is

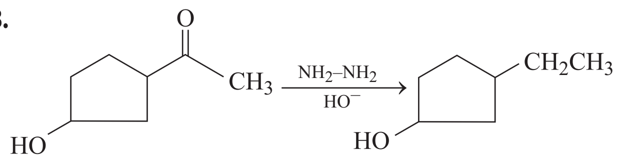
$$\underset{\text{II}}{CH_3CHO} > \underset{\text{I}}{CH_3-CO-CH_3} > \underset{\text{III}}{Ph-CO-Ph}$$

22.



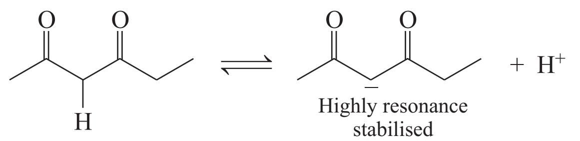
This is an example of cross Cannizzaro reaction in which formaldehyde is always oxidised.

23.



(Wolff-Kishner reduction)

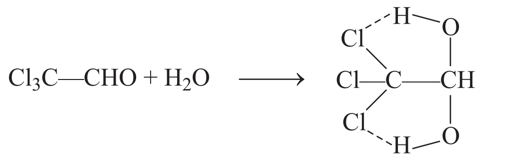
24.



25. $CH_2{=}\overset{OH}{\overset{|}{C}}-CH_3 + D_2O \rightleftharpoons D_3C-\overset{O}{\overset{\|}{C}}-CD_3$

All α-H will be replaced by deuterium.

26.



Highly stable hydrate

27. $\underset{\text{2-butanol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_3} \xrightarrow[\text{catalyst}]{[O]} \underset{\text{Ethyl methyl ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3}$

28. Compounds that contain either CH_3-CO or $CH_3-\underset{OH}{\underset{|}{C}H}-$ group gives iodoform test :

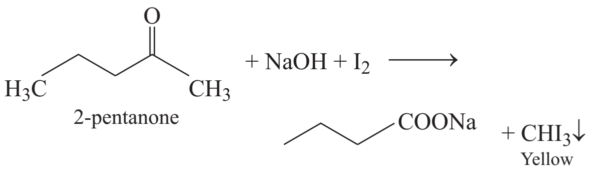
$\underset{\text{Acetone}}{CH_3-\boxed{\overset{O}{\overset{\|}{C}}-CH_3}}$ $\quad$ $\underset{\text{Ethanol}}{\boxed{CH_3-\underset{OH}{\underset{|}{C}H}-}H}$ $\quad$ $\underset{\text{Isopropyl alcohol}}{\boxed{CH_3-\underset{OH}{\underset{|}{C}H}-}CH_3}$

Above three compounds has the desired group for iodoform test. Diethyl ketone does not has the required group for iodoform test.

29. Aldehydes lacking presence of α-H undergo Cannizzaro reaction. When treated with aqueous base CH_3CHO does not undergo Cannizzaro reaction because it has α-H and in the presence of aqueous base it undergoes aldol condensation.

30. $CH_3-CHO + \text{Fehling's solution} \longrightarrow \underset{\text{Red}}{Cu_2O\downarrow}$

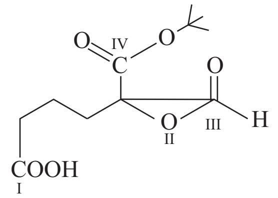
31. For iodoform test, $CH_3-\overset{O}{\overset{\|}{C}}-$ group is required



32. Grignard's reagent reacts with both aldehydes and ketones while other three reagents reacts only with aldehydes, not with ketones.

33. Only — CHO group is to be reduced to $-CH_2OH$.

It can be done using $NaBH_4$ in C_2H_5OH.



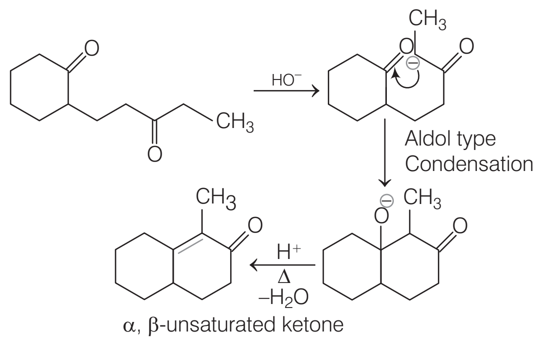
(a) $LiAlH_4 / (C_2H_5)_2O$ reduces I, II and III into $-CH_2OH$, and IV into diol.

(b) BH_3 / THF show same properties as (a).

(c) $NaBH_4 / C_2H_5OH$ reduces III into $-CH_2OH$.

(d) Raney nickel, same as (a) and (b), thus (c) is correct reagent.

34.



35. **Plan** When acetone reacts with Br_2 in basic medium, bromoform is formed.

Reaction I $\underset{\substack{1\text{ mol} \\ \frac{1}{3}\text{mol}}}{CH_3COCH_3} + \underset{\substack{3\text{ mol} \\ 1\text{ mol}}}{3Br_2} + 4NaOH$

$\longrightarrow \underset{(T)}{CH_3COONa} + \underset{(U)}{CHBr_3} + 3NaBr + 3H_2O$

When CH_3COCH_3 and Br_2 are in equimolar quantity, all the Br_2 (limiting reactant) is converted into desired products and 2/3 mole of CH_3COCH_3 remains unreacted, being in excess.

When acetone reacts with Br_2 in acidic medium, there is monobromination of acetone.

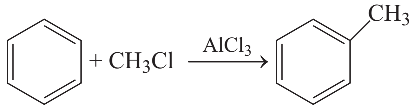
Reactions II

$$\underset{1\text{ mol}}{CH_3COCH_3} + \underset{1\text{ mol}}{Br_2} \xrightarrow{CH_3COOH} \underset{(P)}{CH_3COCH_2Br} + HBr$$

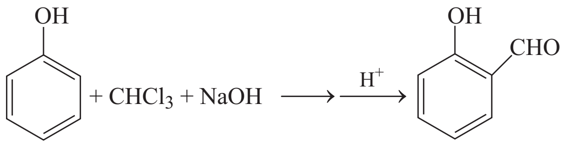
CH_3COCH_3 and Br_2 react in 1 : 1 mole ratio and (*P*) is formed. In reaction I, (*U*) and (*T*) are formed and acetone (reactant) remains unreacted. In reaction II, (*P*) is formed.

36. All those carbonyl compounds containing α-H to sp^2 carbon show keto-enol tautomerism.

37. In both Friedel-Craft's reaction and Reimer-Tiemann reaction new carbon-carbon bond is formed.



Friedel-Crafts' alkylation



Reimer-Tiemann' reaction

38. All carbonyl compounds containing α-H or α-D undergo aldol condensation. In given example, benzaldehyde does not contain α-H to —CHO, hence does not undergo aldol condensation.

39. $$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>C{=}O + C_6H_5NH_2 \longrightarrow \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>C{=}N—C_6H_5$$

$$+ C_6H_5NHNH_2 \longrightarrow \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>C{=}N—NHC_6H_5$$

40. $$2CH_3CHO \xrightarrow{\text{Dil. NaOH}} \underset{\text{Aldol}}{CH_3—\overset{\overset{OH}{|}}{C}H—CH_2CHO}$$

$$2CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{\text{Dil. NaOH}} CH_3—\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$$

Aldol

$$2HCHO \xrightarrow{\text{Dil. NaOH}} \underset{\text{Cannizzaro reaction}}{CH_3OH + HCOONa}$$

$$C_6H_5CHO + HCHO \xrightarrow{\text{Dil. NaOH}} C_6H_5CH_2OH + HCOONa$$

Cannizzaro reaction

41. $$CH_3CH_2Cl + KCN \xrightarrow{S_N2} CH_3CH_2CN + KCl$$

$$CH_3—\overset{\overset{O}{\|}}{C}—Cl + KCN \longrightarrow CH_3—\overset{\overset{O}{\|}}{C}—CN + KCl$$

$$C_6H_5—\overset{\overset{O}{\|}}{C}—H + KCN \longrightarrow C_6H_5—\overset{\overset{O}{\|}}{C}—\underset{\underset{OH}{|}}{C}H—C_6H_5$$

Benzoin

42. Aldehyde, ketones containing $CH_3—\overset{\overset{O}{\|}}{C}—$ group gives iodoform test. Also alcohol containing $CH_3—\underset{\underset{OH}{|}}{C}H—$ group gives iodoform test. $CH_3—\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}—CH_3$ $\;C_6H_5—\overset{\overset{O}{\|}}{C}—CH_3$

Both gives positive iodoform test
Esters and amides do not give iodoform test.

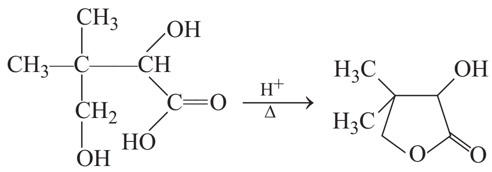
43. For base catalysed aldol condensation, there must be at least one α-H to carbonyl group.

$$\underset{\substack{\text{Propionaldehyde} \\ (2\ \alpha\text{-H})}}{CH_3—CH_2—CHO,}$$

$$\underset{\substack{\text{2-methyl propionaldehyde} \\ (1\ \alpha\text{-H})}}{CH_3—\overset{\overset{CH_3}{|}}{C}H—CHO}\ , \qquad \underset{\substack{\text{2, 2-dimethyl propionaldehyde} \\ (\text{no } \alpha\text{-H})}}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO}$$

Passage 1 (For Q. Nos. 44-46)

The given product is an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin :



Acid above is obtained by acid hydrolysis of cyanohydrin *S* as

$$\underset{S}{H_3C—\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{OH}{|}}{C}H—CN} \xrightarrow[H_2O]{H^+} H_3C—\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{OH}{|}}{C}H—COOH$$

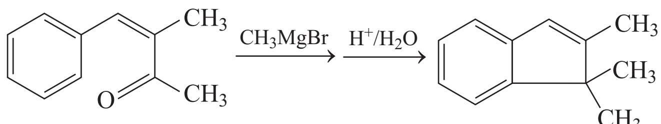
S is obtained by nucleophile addition of HCN on *R*, hence *R* is

$$\underset{R}{H_3C—\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{O}{\|}}{C}—H} + HCN \longrightarrow \underset{S}{H_3C—\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{OH}{|}}{C}H—CN}$$

R is obtained by treatment of *P* and *Q* with aqueous K_2CO_3 through aldol condensation reaction as

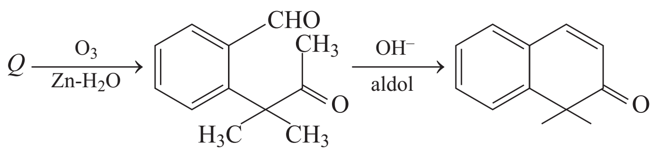
$$\underbrace{CH_3—\overset{\overset{CH_3}{|}}{C}H—CHO + H—\overset{\overset{O}{\|}}{C}—H}_{P\,+\,Q} \xrightarrow{OH^-} \underset{R}{OHC—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2OH}$$

Passage 2 (For Q. Nos. 47-49)



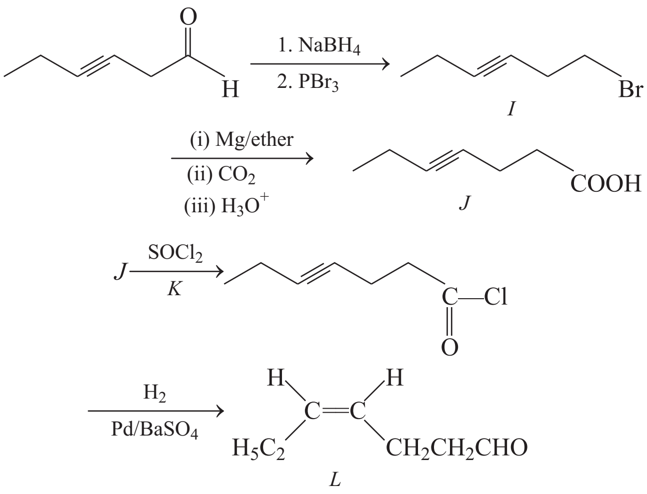
P *Q*

(gives positive iodoform test)

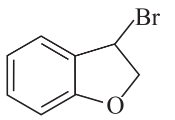
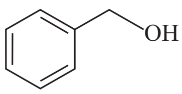
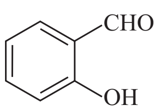
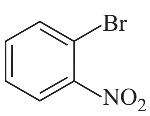


R *S*

Passage 3 (For Q. Nos. 50-52)



53.

	Column I	Column II
A.		Undergo nucleophilic substitution of Br^-. Undergo elimination of HBr. Does not undergo nucleophilic addition. Does not esterify with acetic anhydride, can be dehydrogenated.
B.		Undergo nucleophilic substitution with $SOCl_2$, PCl_5 etc. Does not undergo elimination. Does not undergo nucleophilic addition. Undergo esterification with acetic anhydride. Undergo dehydrogenation to give C_6H_5CHO.
C.		Does not undergo nucleophilic substitution, there is no leaving group. Does not undergo elimination. Undergo nucleophilic addition at carbonyl carbon of —CHO. Undergo esterification with acetic anhydride. Does not undergo dehydrogenation.
D.		Undergo aromatic nucleophilic substitution (S_NAr) Does not undergo elimination, nucleophilic addition, esterification or dehydrogenation.

54.

	Column I	Column II
A.	C_6H_5CHO	Gives phenyl hydrazone with 2, 4-dinitrophenyl hydrazine. Gives precipitate with $AgNO_3$, Tollen's test forms cyanohydrin.
B.	$CH_3—C\equiv CH$	Gives precipitate ($CH_3—C\equiv CAg$) with $AgNO_3$. A nucleophile, undergo electrophilic attack.
C.	CN^-	Forms AgCN with $AgNO_3$. A nucleophile is involved in cyanohydrin formation.
D.	I^-	Gives AgI precipitate with $AgNO_3$ and it is a nucleophile.

55. Sodium potassium tartarate

56. $CH_3MgI + CH_3—\overset{\overset{\large O}{\|}}{C}—CH_3 \xrightarrow{H_2O} CH_3—\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}—OH$

Tertiary alcohol

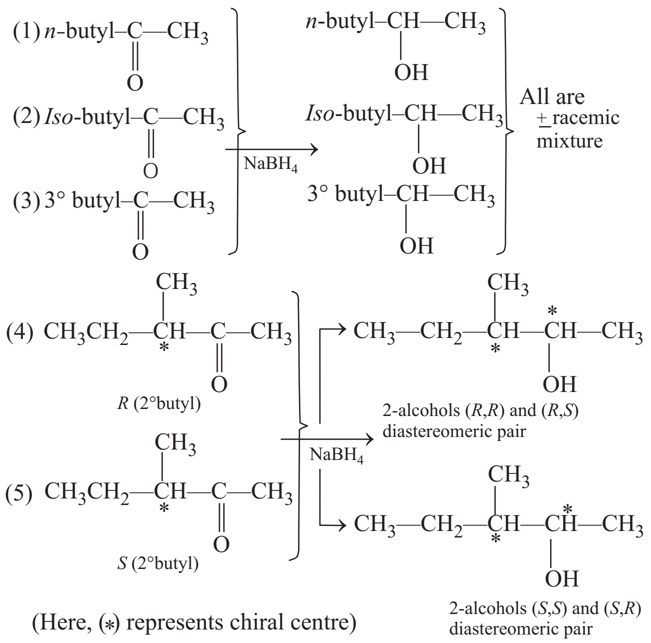
57. Benzaldehyde, lacking α-H does not undergo aldol condensation, rather it undergoes Cannizzaro reaction.

58. Molecular weight of the ketone is 100

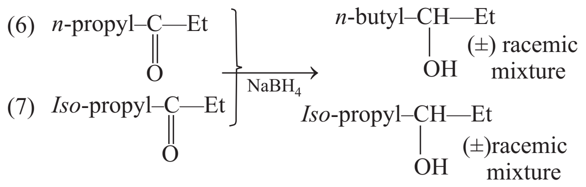
So, molecular formula = $C_6\,H_{12}O$

Degree of unsaturation = $(6 + 1) - \dfrac{12}{2} = 1$

According to question, compound contains ketone group. Since, the compound which contain chiral centre lead to the formation of diastereomer while other produces enantiomers. Various isomers and their possible reduced product are as shown below.

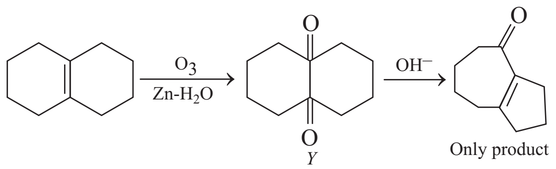


(Here, (*) represents chiral centre)

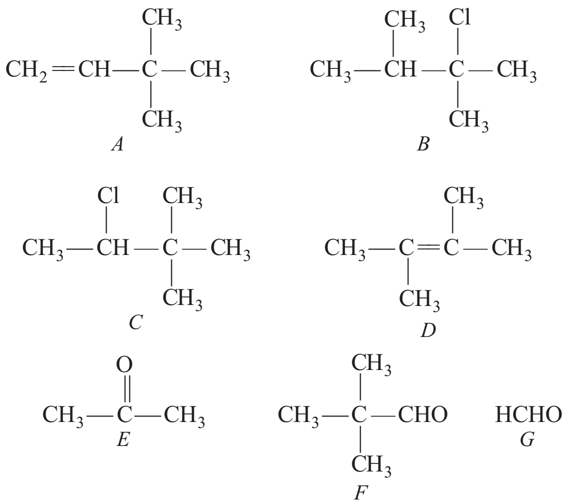


While in case of (4) and (5) they do not produce enantiomer due to the presence of stereogenic centre on ketone.

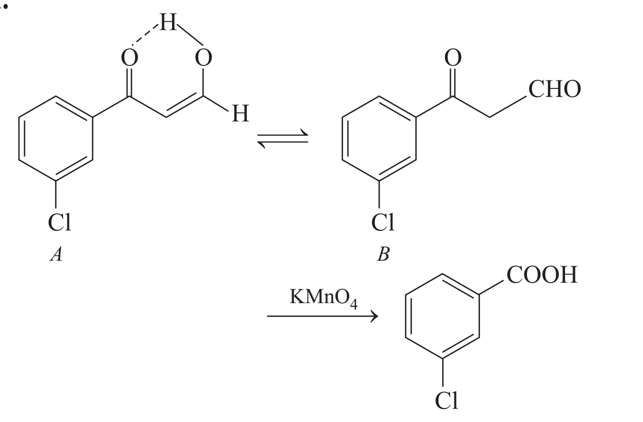
59.



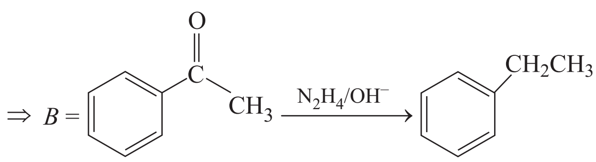
60.

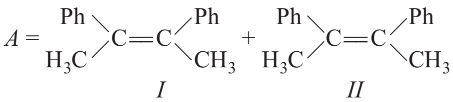


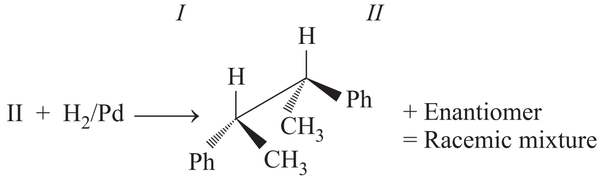
61.



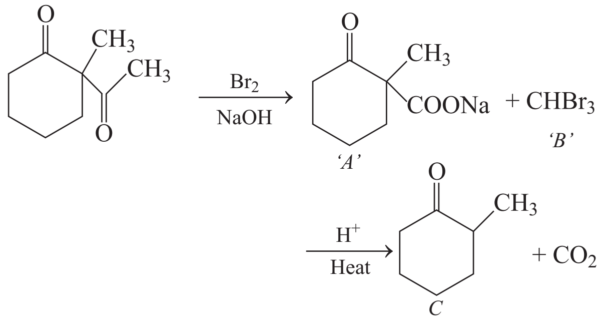
62. $B + NaOH / I_2 \longrightarrow C_6H_5COONa + CHI_3$



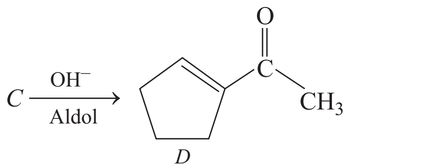


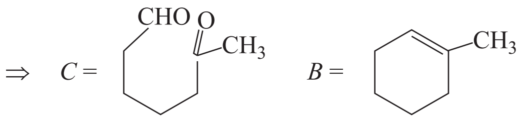


63.

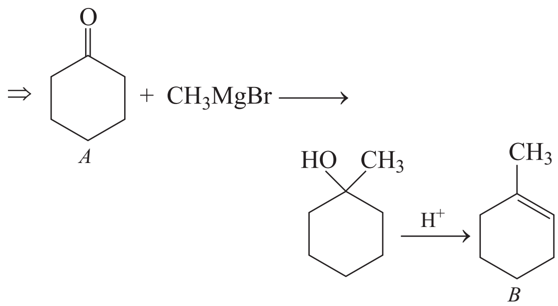


64.

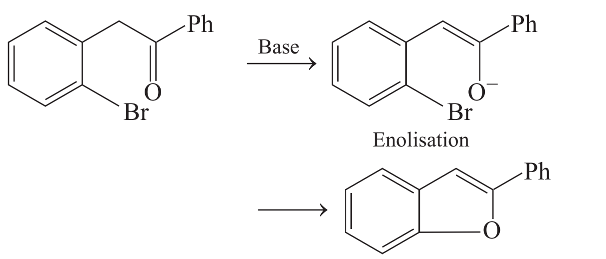




$A\ (C_6H_{10}O) \xrightarrow{MeMgBr} \xrightarrow{H^+} B$

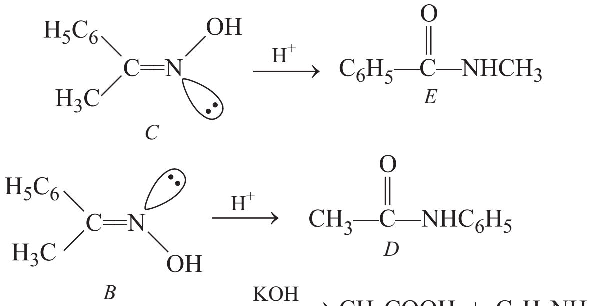


65.



66. (a) G is benzoic acid C_6H_5-COOH, B and C are two stereomeric oximes which undergo Beckmann's rearrangement on treatment with acid to give amides D and E.

$$\underset{E}{C_6H_5-\overset{\overset{O}{\|}}{C}-NHCH_3} \xrightarrow[H_2O]{OH^-} \underset{G}{C_6H_5COOH} + CH_3NH_2$$



$$\xrightarrow[H_2O]{KOH} CH_3COOH + \underset{F}{C_6H_5NH_2}$$

$$F + CH_3COCl \longrightarrow \underset{D}{C_6H_5NHCOCH_3}$$

$$\Rightarrow \quad A = C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$$

(b) $CH_3-CH_2-C\equiv CH$

$$\xrightarrow[H_2O_2/OH^-]{B_2H_6} CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} CH_3CH_2CH_2-\overset{\overset{OH}{|}}{CH}-CH_3$$

$$\xrightarrow{[O]} \underset{\text{2-pentanone.}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

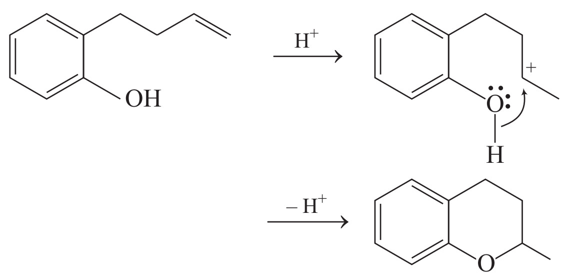
67. (i) $C_6H_5-\underset{\underset{OH}{|}}{CH}-C\equiv C-H$

$$\xrightarrow[-H_2O]{H^+} C_6H_5-\overset{+}{C}H-C\equiv C-H \qquad \ddot{O}H_2$$

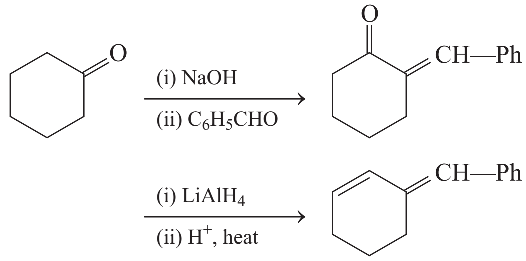
$$\xrightarrow{-H^+} C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-H$$

$$\underset{\text{tautomerisation}}{\rightleftharpoons} C_6H_5-CH=C=\underset{\underset{H}{|}}{C}-OH$$

(ii)



68.



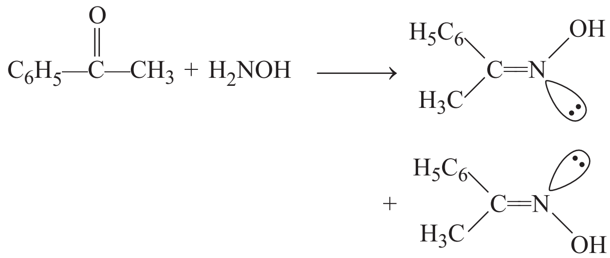
69. Aldehyde A does not has any α-H but undergo ozonolysis to give two moles of compound B and benzaldehyde. Compound B on oxidation gives oxalic acid, so A is

$$\underset{A}{C_6H_5-CH=CH-C\equiv C-CHO} \xrightarrow{O_3}$$

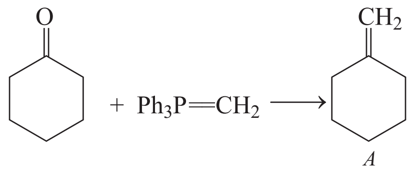
$$C_6H_5-CHO + 2\underset{B}{\begin{matrix}COOH \\ | \\ CHO\end{matrix}}$$

$$B \xrightarrow{Ag^+} \begin{matrix}COOH \\ | \\ COOH\end{matrix}$$

70.

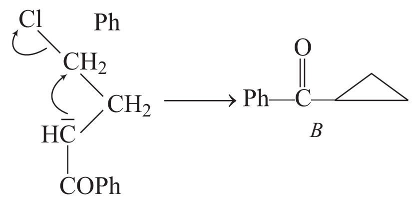


71. (i)

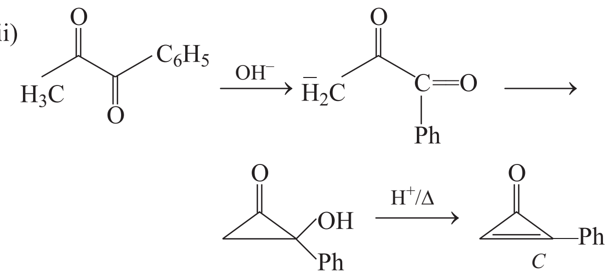


(Wittig reaction)

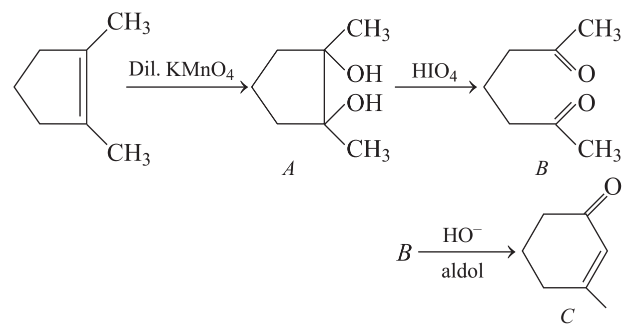
(ii) $Cl-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-Ph \xrightarrow{CH_3O^-}$



(iii)



72.



73. $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$

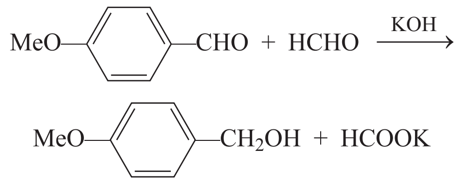
$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \longrightarrow CH_3CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN \quad \text{I}$$

$$\xrightarrow{LiAlH_4} CH_3CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2NH_2 \quad \text{II}$$

I is formed as racemic mixture.

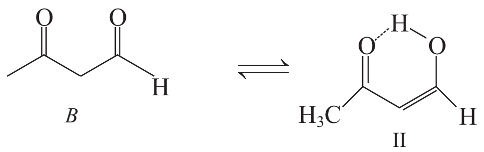
74. $$C_6H_5CHO + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa} C_6H_5-CH=CH-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$$

75.



(Cannizzaro reaction)

In cross-Cannizzaro reaction, methanal is always oxidised.



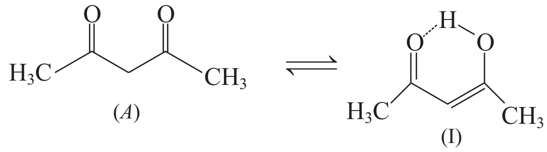
II is less stable than I because II is less substituted enol.
Acetone has greater enol content than ethanal

$$\underset{C}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \rightleftharpoons CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3 \text{ (more substituted)}$$

$$\underset{D}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} \rightleftharpoons CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-H \quad \text{(less substituted)}$$

Therefore, overall enol-content order is $D < C < B < A$

76. $CH_3-CO-CH_2-COCH_3$ has highest enol content due to resonance and formation of six membered ring through intramolecular H-bonding



Also, enol content depends upon the number of substituents on double bond, greater the number of substituents, greater the stability, higher the enol content.

Therefore, CH_3COCH_2CHO forms next most stable enol

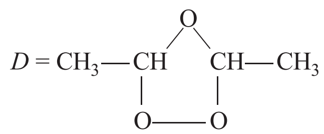
77. Iodoform reaction is an oxidation reaction in which hypoiodite OI^- acts as oxidising agent :

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + OI^- \longrightarrow R-COO^- + CHI_3$$

Iodide (I^-) is a reducing agent, does not give iodoform reaction.

78. $D \xrightarrow{O_3} \xrightarrow[H_2O]{Zn} CH_3CHO$ (only)

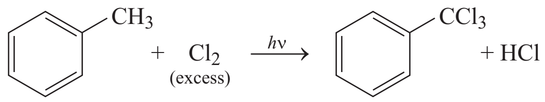
$C = CH_3-CH=CH-CH_3$,



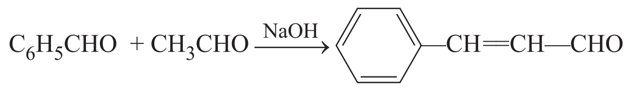
$$B = CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2CH_3 \text{ and } A = CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$$

79. (i) Tollen's reagent gives grey precipitate of Ag, acetone does not.

(ii)

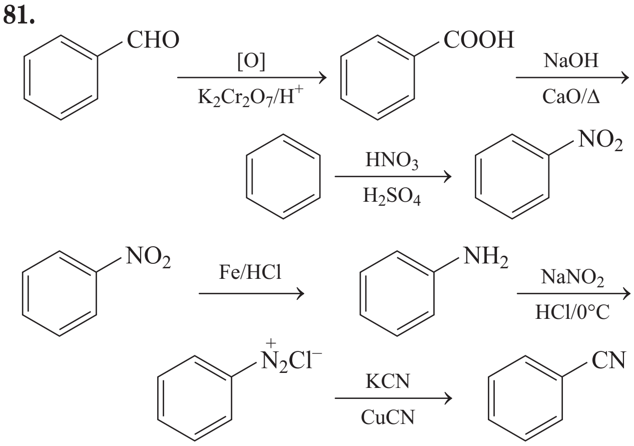


80.



Cross-aldol condensation

81.



82. $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + PhNHNH_2 \longrightarrow \underset{\text{Hydrazone}}{R_2C{=}N{-}NHPh}$

In acidic medium, hydrazine reacts to form salt and hydrazone is hydrolysed back to aldehyde/ketone.

83. $CH_3CH_2CHO \xrightarrow[\text{heat}]{OH^-} CH_3{-}CH_2{-}CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CHO$

Aldol followed by dehydration

84. Steric hindrance at carbonyl carbon determine the reactivity towards nucleophilic addition reaction. Greater the steric hindrance, smaller the reactivity.

$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

85. $CH_3CHO \xrightarrow[K_2Cr_2O_7]{H^+} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$

$(CH_3COO)_2Ca \xrightarrow{\text{heat}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \xrightarrow{H_2NOH} \underset{\text{acetoxime}}{(H_3C)_2C{=}N{-}OH}$

86. $Cl_3C{-}CHO + NaOH(aq) \longrightarrow \underset{\text{Cannizzaro reaction}}{Cl_3C{-}CH_2OH} + Cl_3C{-}COONa$

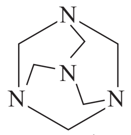
87. $CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \xrightarrow{HCN} CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CN \xrightarrow[H_2O]{H^+} \underset{D}{CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}COOH}$

$\Rightarrow C = CH_3{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}COOH,\ B = CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}COOH$

$\Rightarrow A = CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_3$

88. $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + CH_3MgBr \xrightarrow{\text{Ether}} CH_3CH_2OMgBr \xrightarrow[H_2O]{H^+} CH_3CH_2OH$

89.

$6CH_2O + 4NH_3 \longrightarrow$  "$(CH_2)_6N_4$"

Hexamine

Download Chapter Test
http://tinyurl.com/yx9d32yd *or*

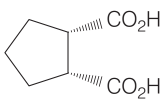
26

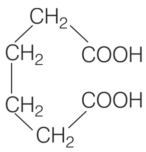
Carboxylic Acids and Their Derivatives

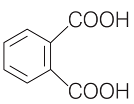
Topic 1 Carboxylic Acids

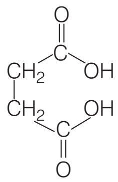
Objective Questions I (Only one correct option)

1 Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride? **(2019 Main, 10 Jan I)**

(a) 

(b) 

(c) 

(d) 

2. In the reaction,

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C$$

The product C is **(2014 Main)**

(a) acetaldehyde (b) acetylene

(c) ethylene (d) acetyl chloride

3. The compound that does not liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is **(2013 Adv.)**

(a) benzoic acid

(b) benzenesulphonic acid

(c) salicylic acid

(d) carbolic acid (Phenol)

4. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is **(2013 Main)**

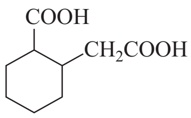
(a) CH_3COOH

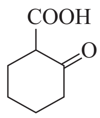
(b) $CH_3CH_2CH_2COOH$

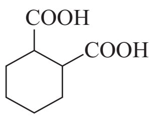
(c) $CH_3—\underset{\underset{CH_3}{|}}{CH}—COOH$

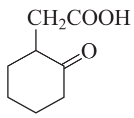
(d) CH_3CH_2COOH

5. The compound that undergoes decarboxylation most readily under mild condition is **(2012)**

(a) 

(b) 

(c) 

(d) 

6. The carboxyl functional group ($—COOH$) is present in

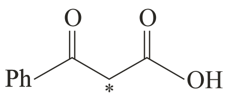
(a) picric acid **(2012)**

(b) barbituric acid

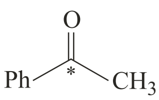
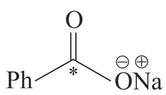
(c) ascorbic acid

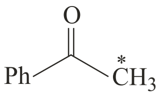
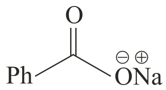
(d) aspirin

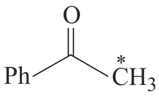
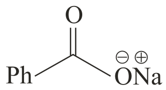
7. In the following reaction sequence, the correct structures of E, F and G are

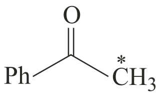
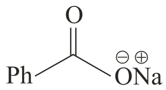
 $\xrightarrow{\text{Heat}} [E] \xrightarrow[\text{NaOH}]{I_2} [F] + [G]$

(* implies ^{13}C labelled carbon) **(2008, 3M)**

(a) $E =$  $F =$  $G = CHI_3$

(b) $E =$  $F =$  $G = CHI_3$

(c) $E =$  $F =$  $G = \overset{*}{C}HI_3$

(d) $E =$  $F =$  $G = \overset{*}{C}H_3I$

8. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively, are **(2006, 3M)**
(a) SO_2, NO_2 (b) SO_2, NO (c) SO_2, CO_2 (d) CO_2, CO_2

9. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be **(2003, S, 1M)**
(a) optically active mixture (b) pure enantiomer
(c) *meso* compound (d) racemic mixture

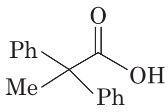
10. Benzoyl chloride is prepared from benzoic acid by **(2000, S, 1M)**
(a) Cl_2, $h\nu$ (b) SO_2Cl_2
(c) $SOCl_2$ (d) Cl_2, H_2O

11. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from **(1999, 2M)**
(a) methyl group
(b) carboxylic acid group
(c) methylene group
(d) bicarbonate group

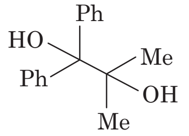
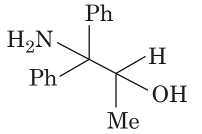
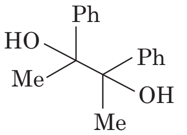
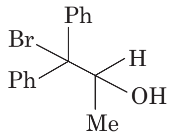
12. Which of the following is basic? **(1980, 1M)**
(a) CH_3CH_2OH (b) H_2O_2
(c) $HOCH_2CH_2OH$ (d) CH_3COOH

Matching Type Questions

13. The desired product *X* can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II.
(given, order of migratory aptitude : aryl > alkyl > hydrogen)



X **(2018 Adv.)**

List–I		List–II
P.	 + H_2SO_4	1. I_2, NaOH
Q.	 + HNO_2	2. $[Ag(NH_3)_2]$ OH
R.	 + H_2SO_4	3. Fehling solution
S.	 + $AgNO_3$	4. HCHO, NaOH
		5. NaOBr

The correct option is
(a) P → 1; Q → 2, 3; R → 1, 4; S → 2,4
(b) P → 1, 5; Q → 3,4; R → 4, 5; S → 3
(c) P → 1, 5; Q → 3,4; R → 5; S → 2,4
(d) P → 1, 5; Q → 2, 3; R → 1,5; S → 2,3

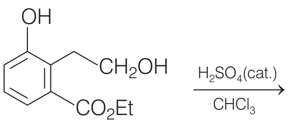
Subjective Questions

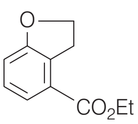
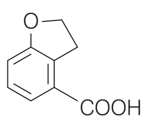
14. How will you bring about the following conversion?
"Ethanal to 2-hydroxy-3-butenoic acid." **(1990, 2M)**

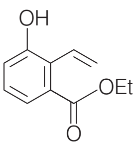
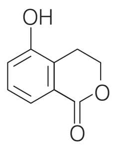
Topic 2 Acid Derivatives

Objective Questions I
(Only one correct option)

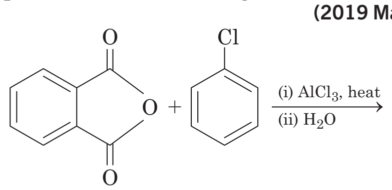
1. The major product of the following reaction is **(2019 Main, 9 April II)**

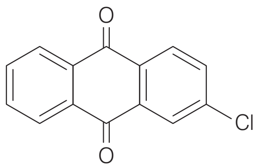
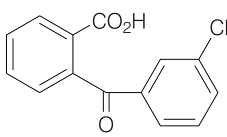


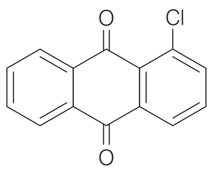
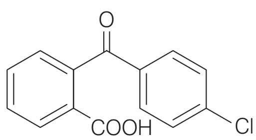
(a)  (b) 

(c)  (d) 

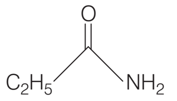
2. The major product of the following reaction is **(2019 Main, 8 April I)**

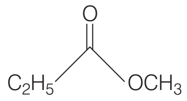


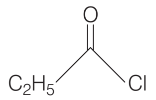
(a)  (b) 

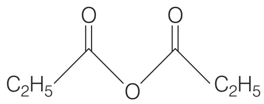
(c)  (d) 

3. The increasing order of the reactivity of the following with $LiAlH_4$ is **(2019 Main, 12 Jan II)**

(*A*) 

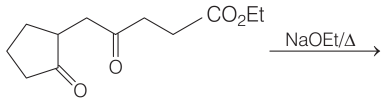
(*B*) 

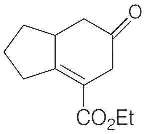
(*C*) 

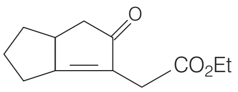
(*D*) 

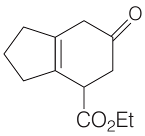
(a) $(A) < (B) < (D) < (C)$
(b) $(A) < (B) < (C) < (D)$
(c) $(B) < (A) < (D) < (C)$
(d) $(B) < (A) < (C) < (D)$

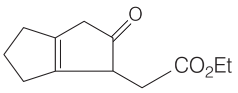
4. The major product obtained in the following reaction is **(2019 Main, 10 Jan II)**



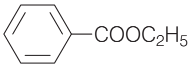
(a) 

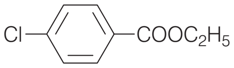
(b) 

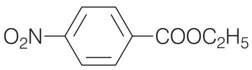
(c) 

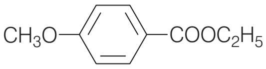
(d) 

5. The decreasing order of ease of alkaline hydrolysis for the following esters is **(2019 Main, 10 Jan I)**


I

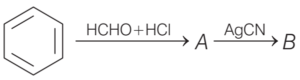

II


III


IV

(a) III > II > IV > I
(b) III > II > I > IV
(c) II > III > I > IV
(d) IV > II > III > I

6. The compounds *A* and *B* in the following reaction are, respectively



(2019 Main, 9 Jan I)

(a) *A* = Benzyl alcohol, *B* = Benzyl isocyanide
(b) *A* = Benzyl alcohol, *B* = Benzyl cyanide
(c) *A* = Benzyl chloride, *B* = Benzyl isocyanide
(d) *A* = Benzyl chloride, *B* = Benzyl cyanide

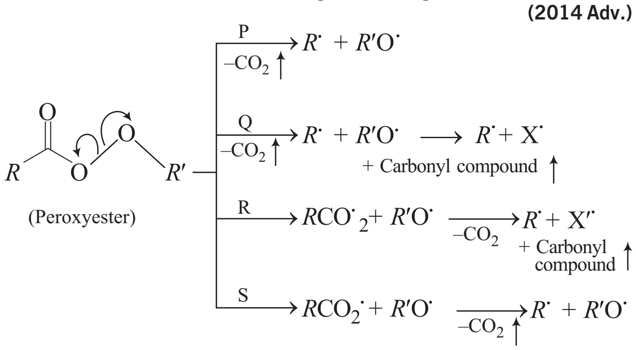
7. The major product of following reaction is

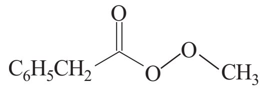
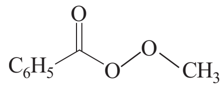
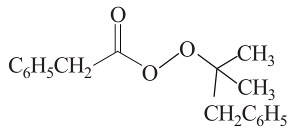
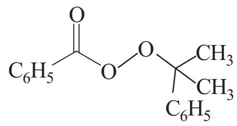
$$R—C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2} ?$$

(2019 Main, 9 Jan I)

(a) *R*CHO
(b) $RCONH_2$
(c) *R*COOH
(d) RCH_2NH_2

8. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column t I with an appropriate structure from Column II and select the correct answer using the code given below the lists. **(2014 Adv.)**



Column I		Column II	
P.	Pathway *P*	1.	
Q.	Pathway *Q*	2.	
R.	Pathway *R*	3.	
S.	Pathway *S*	4.	

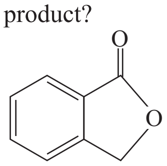
Codes

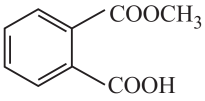
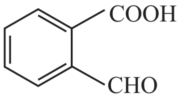
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

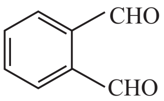
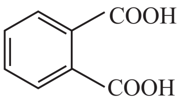
9. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is **(2013 Main)**

(a) 2
(b) 5
(c) 4
(d) 6

10. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? **(2006, 5M)**



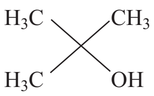
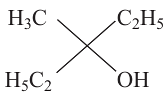
(a)  (b) 

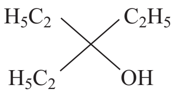
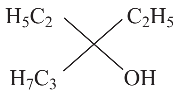
(c)  (d) 

11. Benzamide on treatment with $POCl_3$ gives **(2004, S, 1M)**

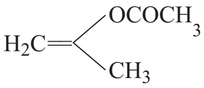
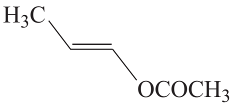
(a) aniline (b) benzonitrile
(c) chlorobenzene (d) benzyl amine

12. Ethyl ester $\xrightarrow[\text{(excess)}]{CH_3MgBr}$ P, the product 'P' will be **(2003, S, 1M)**

(a)  (b) 

(c)  (d) 

13. The product of acid hydrolysis of P and Q can be distinguished by **(2003, S, 1M)**

P :  ; Q : 

(a) Lucas reagent (b) 2, 4-DNP
(c) Fehling's solution (d) $NaHSO_3$

14. Hydrogenation of benzoyl chloride in the presence of Pd on $BaSO_4$ gives **(1992, 1M)**

(a) benzyl alcohol (b) benzaldehyde
(c) benzoic acid (d) phenol

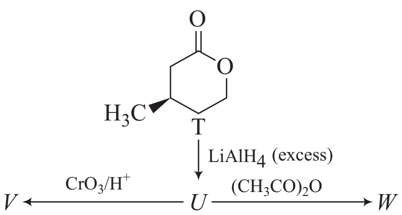
15. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine ? **(1983, 1M)**

(a) PCl_5 (b) $NaOH + Br_2$
(c) Sodalime (d) Hot conc. H_2SO_4

Objective Questions I

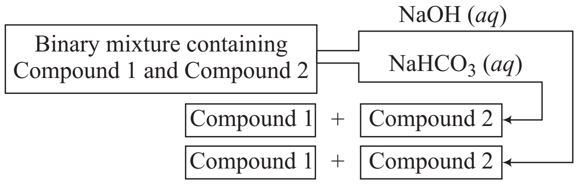
(One or more than one correct options)

16. With reference to the scheme given, which of the given statement(s) about T, U, V and W is/are correct? **(2012)**



(a) T is soluble in hot aqueous NaOH
(b) U is optically active
(c) Molecular formula of W is $C_{10}H_{18}O_4$
(d) V gives effervescence on treatment with aqueous $NaHCO_3$

17. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. **(2012)**



(a) C_6H_5OH and C_6H_5COOH
(b) C_6H_5COOH and $C_6H_5CH_2OH$
(c) $C_6H_5CH_2OH$ and C_6H_5OH
(d) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

18. Reaction of RCONH$_2$ with a mixture of Br_2 and KOH gives R—NH$_2$ as the main product. The intermediates involved in this reaction are **(1992, 1M)**

(a) RCONHBr
(b) RNHBr
(c) R—N=C=O
(d) RCONBr$_2$

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

19. **Statement I** p-hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

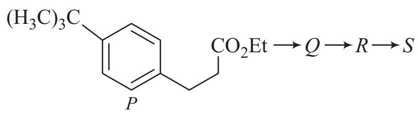
Statement II o-hydroxybenzoic acid has intramolecular hydrogen bonding. **(2007, 3M)**

20. **Statement I** Acetic acid does not undergo haloform reaction.
Statement II Acetic acid has no alpha hydrogen. **(1998, 2M)**

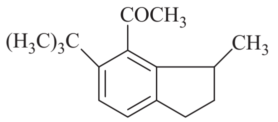
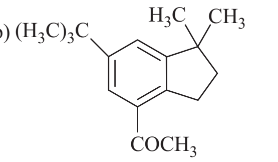
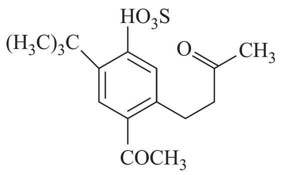
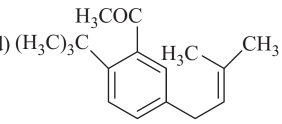
Passage Based Questions

Passage 1

The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives Q. The compound Q on treatment with H_2SO_4 at 0° C gives R. The reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound S. [Et in compound P is ethyl group]



21. The product S is **(2017 Adv.)**

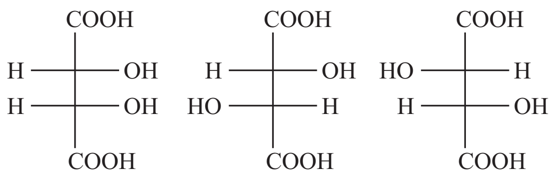
(a) 
(b) 
(c) 
(d) 

22. The reactions, Q to R and R to S, are

(a) Aromatic sulfonation and Friedel-Crafts acylation
(b) Friedel-Crafts alkylation and Friedel-Crafts acylation
(c) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
(d) Dehydration and Friedel-Crafts acylation

Passage 2

P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolourize Br_2/H_2O. On heating, P forms the cyclic anhydride.
Upon treatment with dilute alkaline $KMnO_4$. P as well as Q could produce one or more than one form S, T and U. **(2013 Adv.)**



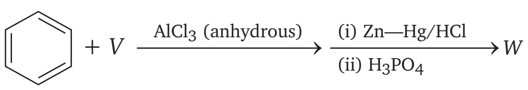
S T U

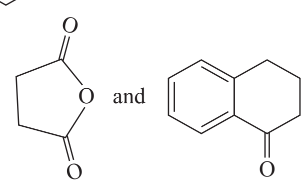
23. Compounds formed from P and Q are, respectively

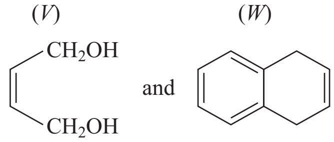
(a) Optically active S and optically active pair (T, U)
(b) Optically inactive S and optically inactive pair (T, U)
(c) Optically active pair (T, U) and optically active S
(d) Optically inactive pair (T, U) and optically inactive S

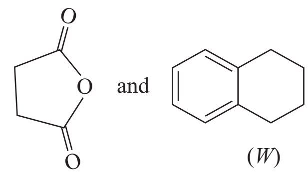
24. In the following reaction sequences V and W are respectively

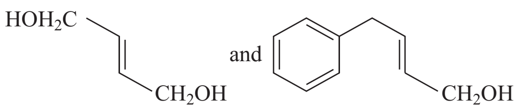
$$Q \xrightarrow[\Delta]{H_2/Ni} V$$



(a) 
(V) (W)

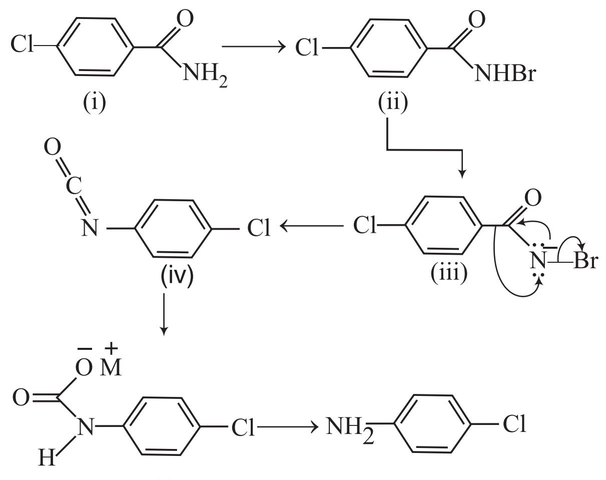
(b) 
(V) (W)

(c) 
(V) (W)

(d) 
(V) (W)

Passage 3

$RCONH_2$ is converted into RNH_2 by means of Hofmann's bromamide degradation.



In this reaction, $RCONHBr$ is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann's degradation reaction is an intramolecular reaction. **(2006, 3 × 4M = 12M)**

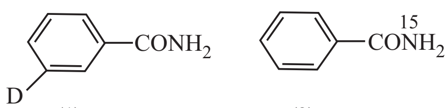
25. How can the conversion of (i) to (ii) be brought about?

(a) KBr
(b) KBr + CH_3ONa
(c) KBr + KOH
(d) Br_2 + KOH

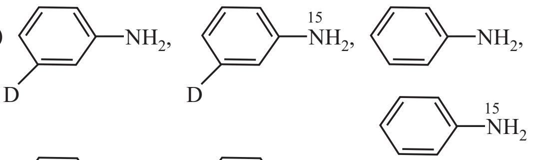
26. Which is the rate determining step in Hofmann's bromamide degradation?

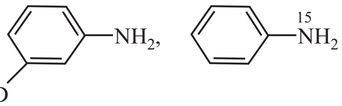
(a) Formation of (i)
(b) Formation of (ii)
(c) Formation of (iii)
(d) Formation of (iv)

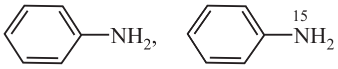
27. What are the constituent amines formed when the mixture of (1) and (2) undergoes Hofmann's bromamide degradation?



(1) (2)

(a) 

(b) 

(c) 

(d) 

Fill in the Blank

28. Formic acid when heated with conc. H_2SO_4 produces ………………… **(1983, 1M)**

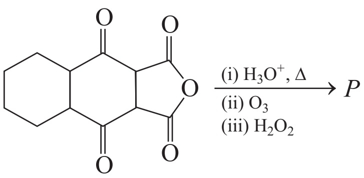
True/False

29. The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. **(1991, 1M)**

30. Hydrolysis of an ester in the presence of a dilute acid is known as saponification. **(1983, 1M)**

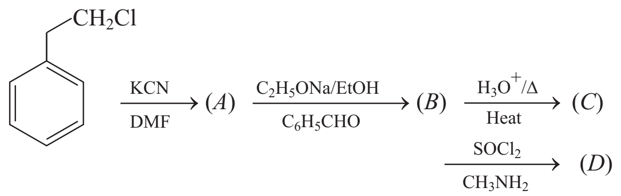
Integer Type Question

31. The total number of carboxylic acid groups in the product *P* is **(2013 Adv.)**



Subjective Questions

32.



Identify *A* to *D*. **(2004, M)**

33. Compound *A* of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form *B*. On oxidation with $KMnO_4$, *A* gives *m*-chlorobenzoic acid. Identify *A* and *B*. **(2003 Main, 2M)**

34. (±) 2-phenylpropanoic acid on treatment with (+) 2-butanol gives (*A*) and (*B*). Deduce their structures and also establish stereochemical relation between them. **(2003)**

35. Identify *X* and *Y* in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde ($H_2\overset{*}{C}O$) as one of the products when compound (*Z*) is treated with HBr and subsequently ozonolysed. Mark the C^* carbon in the entire scheme.

$$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow X \quad (\overset{*}{C} = C^{14} \text{ gas})$$

$$CH_2{=}CH{-}Br \xrightarrow[\text{(ii) } X \text{ (ii) } H_3O^+]{\text{(i) Mg/ether}} Y \xrightarrow{LiAlH_4} Z$$

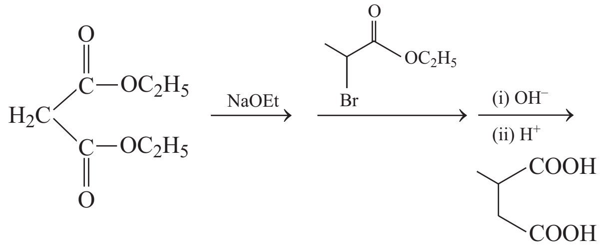
(2001 Main, 5M)

36. Write the structures of the products *A* and *B*.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}C_2H_5 \xrightarrow{H_3O^+} A + B$$

(2000 Main, 3M)

37. Explain briefly the formation of the products giving the structures of the intermediates



(1999, 5M)

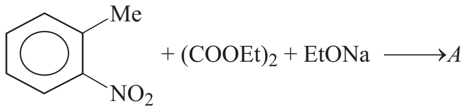
38. Write the structures of the products :

$$CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ heat}$$

(1998)

39. An ester *A* ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved. **(1998)**

40. Complete the following, giving the structures of the principal organic products

(i) 

(ii) $(COOH)_2 + (CH_2OH)_2 \xrightarrow{conc.\ H_2SO_4} B$

(iii) $H_3CCOCOC_6H_5 + NaOH \xrightarrow{H_3O^+} C$ **(1997, 2M)**

41. A hydrocarbon *A* of the formula C_8H_{10}, on ozonolysis gives compound *B* ($C_4H_6O_2$) only. The compound *B* can also be obtained from the alkyl bromide *C* (C_3H_5Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify *A*, *B* and *C* and also give equations for the reactions. **(1996, 3M)**

42. Complete the following sequence of reactions with appropriate structures

$$CH_3-CH_2-COOH \xrightarrow[Br_2]{Red\text{-}P} A$$

$$A \xrightarrow[\text{(ii) } H^+]{\text{(i) Alc. KOH (excess)}} B$$

(1995, 2M)

43. Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly.

(i) $C_6H_5COCH_2COOH$
(ii) $C_6H_5COCOOH$
(iii) $C_6H_5CH(OH)COOH$
(iv) $C_6H_5CH(NH_2)$ COOH **(1995, 2M)**

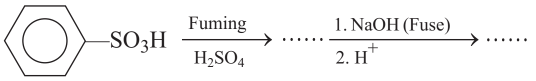
44. Predict the major product in the following reaction :

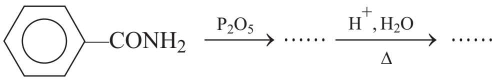
$$C_6H_5—CH_2COCH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr \text{ (excess)}}$$ **(1994, 1M)**

45. In the following reactions, identify the compounds A, B, C and D.

(i) $PCl_5 + SO_2 \longrightarrow A + B$
(ii) $A + CH_3COOH \longrightarrow C + SO_2 + HCl$
(iii) $2C + (CH_3)_2 Cd \longrightarrow 2D + CdCl_2$ **(1994, 1M × 4 = 4M)**

46. Complete the following sequence of the reactions with appropriate structures

(i) 

(ii) 

(1992, 1M)

47. In the following identify the compounds/reaction conditions represented by the alphabets A, B, and C :

$$C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{NH_3}$$
$$B \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} C$$ **(1991, 2M)**

48. Arrange the following as stated:
"Increasing order of acidic strength."

$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH **(1991, 1M)**

49. How will you bring about the following conversion?
"Ethanoic acid to a mixture of methanoic acid and diphenyl ketone." **(1990, 2M)**

50. Give reasons for :
"Carbon-oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both the carbon-oxygen bonds in sodium formate have the same value, i.e. 1.27Å." **(1988, 2M)**

51. Write balanced equations for the following reaction :
"Acetamide is reacted with bromine in the presence of potassium hydroxide." **(1987, 1M)**

52. A liquid X, having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid Y and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z ? **(1986, 3M)**

53. An ester A ($C_4H_8O_2$) on treatment with excess of methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce structures of A and B. Show the reactions involved. **(1998)**

54. Complete the following with appropriate structures :

$$(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$$ **(1986, 1M)**

55. Arrange the following in order of their increasing ease of hydrolysis : **(1986, 1M)**

$CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$, CH_3CONH_2

56. Give reasons in one or two sentences for the following :
"Formic acid is a stronger acid than acetic acid." **(1985, 1M)**

57. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis.
"Propionic anhydride from propionaldehyde"
$[AgNO_3, NH_4OH, P_2O_5]$ **(1984, 2M)**

58. Give reasons for the following in one or two sentences.
''Acetic acid can be halogenated in the presence of P and Cl_2, but formic acid cannot be halogenated in the same way.'' Why? **(1983, 1M)**

59. State with balanced equation, what happens when, "Acetic anhydride reacts with phenol in presence of a base." **(1982, 1M)**

60. Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. **(1981, 1/2 M)**

61. Write the chemical equation to show what happens when, "Ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified". **(1981, 2 M)**

Answers

Topic 1

1. (b)	**2.** (c)	**3.** (d)	**4.** (d)
5. (b)	**6.** (d)	**7.** (c)	**8.** (d)
9. (d)	**10.** (c)	**11.** (d)	**12.** (a)
13. (d)			

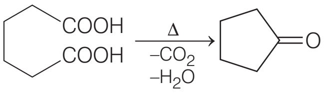
Topic 2

1. (d)	**2.** (d)	**3.** (a)	**4.** (b)
5. (b)	**6.** (c)	**7.** (a)	**8.** (a)
9. (b)	**10.** (c)	**11.** (b)	**12.** (a)
13. (c)	**14.** (b)	**15.** (b)	**16.** (a,c,d)
17. (b,d)	**18.** (a,c)	**19.** (d)	**20.** (c)
21. (a)	**22.** (c)	**23.** (b)	**24.** (a)
25. (d)	**26.** (d)	**27.** (b)	
28. H_2O and CO gas		**29.** False	**30.** False
31. (2)			

Hints & Solutions

Topic 1 Carboxylic Acids

1. Heating of $(CH_2)_4{<}^{COOH}_{COOH}$ (adipic acid) with a dehydrating agent, decarboxylates ($—CO_2$) to give a ketone (cyclopentanone), not an anhydride.



Codes

$P \to 1, \quad Q \to 3, \quad R \to 4, \quad S \to 2$

Thus, (a) is the correct choice.

2. This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.

(i) $LiAlH_4$ causes reduction
(ii) PCl_5 causes chlorination
(iii) Alc. KOH causes elimination reaction

$$\underset{}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH}$$

$$\xrightarrow{PCl_5} \underset{(B)}{CH_3CH_2Cl} \xrightarrow[-HCl]{Alc.KOH} \underset{\substack{(C)\\ \text{Ethylene}}}{CH_2 = CH_2}$$

3. **PLAN** $NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$

HCO_3^- is decomposed by acid releasing CO_2

$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

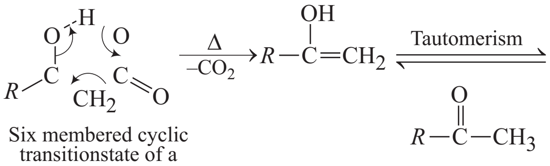
If acid is stronger than HCO_3^- then CO_2 is released. Phenol is less acidic and thus does not liberate CO_2 with $NaHCO_3$.

4. $\underset{(A)}{CH_3CH_2—\overset{\overset{O}{\|}}{C}—OH} \xrightarrow{NH_3}$

$$\underset{(B)}{CH_3CH_2COONH_4} \xrightarrow{\Delta} \underset{(C)}{CH_3—CH_2—\overset{\overset{O}{\|}}{C}—NH_2}$$

$$\xrightarrow[\text{Hoffmann's bromamide reaction}]{Br_2,\,KOH} CH_3—CH_2—NH_2$$

5. It is a β-keto acid which undergo decarboxylation in very mild condtion, i.e. on simple heating. This occur through a six member cyclic transition state as

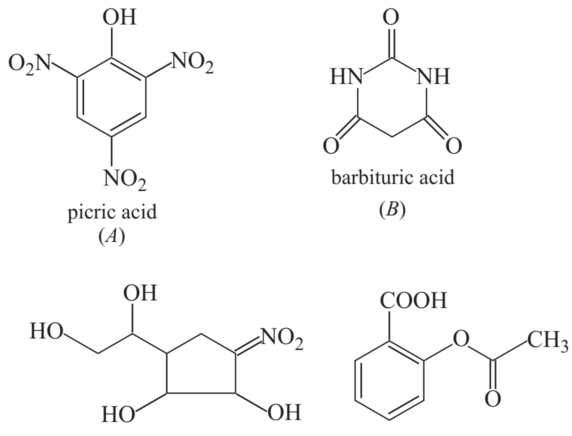


Six membered cyclic transitionstate of a β-keto acid

NOTE

- Ordinary carboxylic acid require soda-lime catalyst for decarboxylation.
- Final step of decarboxylation in the above shown mechanism involve tautomerism, therefore, for decarboxylation of β-keto acid by above mechanism, the acid must contain an α-H].

6. Structures of the various compounds are



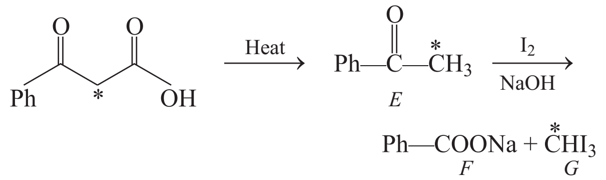
picric acid (*A*)

barbituric acid (*B*)

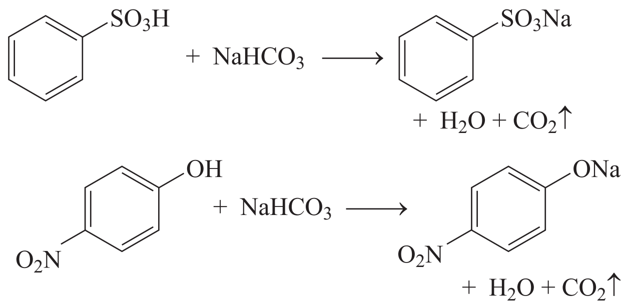
ascorbic acid (*C*)

aspirin (*D*)

7.



8.



9. $R—\overset{\overset{O}{\|}}{C}—OH + H\diagdown\ddot{O}R' \xrightarrow{-H^+} R—\underset{\underset{OR'}{|}}{\overset{\overset{O^-}{|}}{C}}—OH$

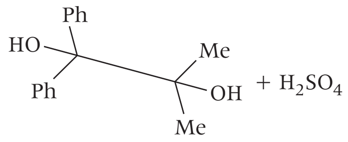
Reaction occur at planar sp^2 carbon giving racemic mixture of product.

10. $C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5—COCl$

11. $CH_3—CH_2—COOH + NaH\overset{*}{C}O_3 \longrightarrow CH_3CH_2COONa + H_2O + \overset{*}{C}O_2$

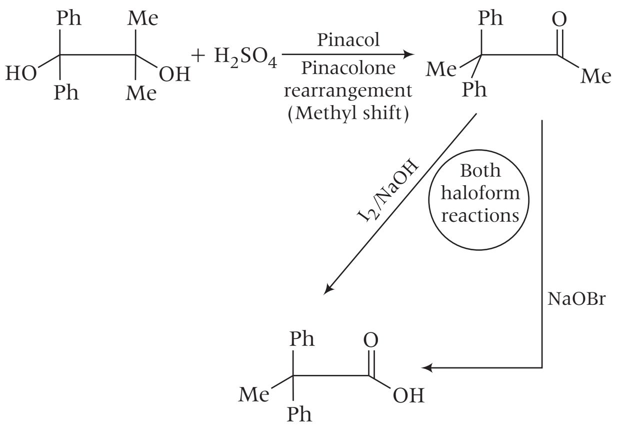
12. Ethanol is the weakest acid among these, hence it is most basic.

13. (d)

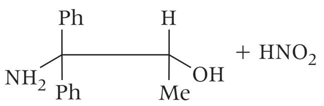
For *P*, i.e. 

The correct match is 1 i.e., I_2, NaOH and 5 i.e., NaOBr

The reactions proceed as

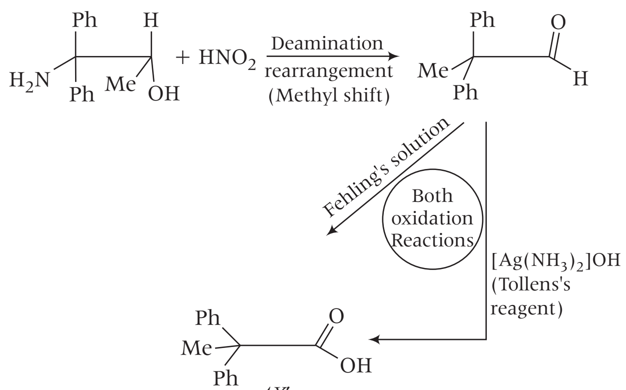


'X'

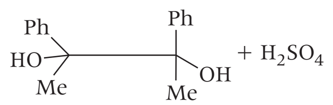
For *Q*, i.e. 

The correct match is 2 i.e. $[Ag(NH_3)_2]OH$ and 3 i.e., Fehling's solution.

The reactions proceed as

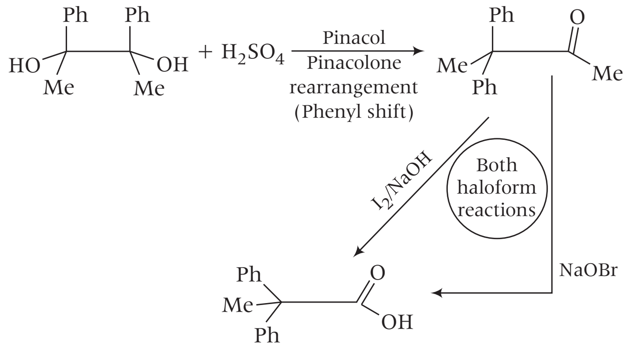


'X'

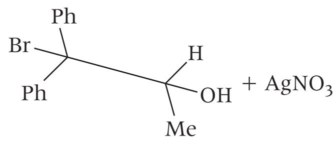
For *R*, i.e. 

The correct match is 1, 5 again.

The reaction proceed as

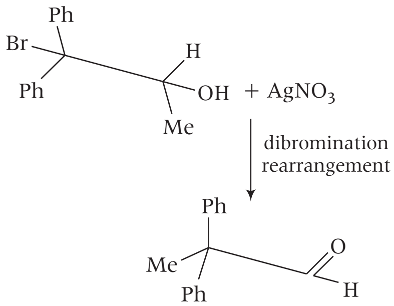


X

For *S*, i.e. 

The correct match is 2, 3.

The reaction proceed as



Rest procedure is same as seen for *Q* above i.e., via oxidation.

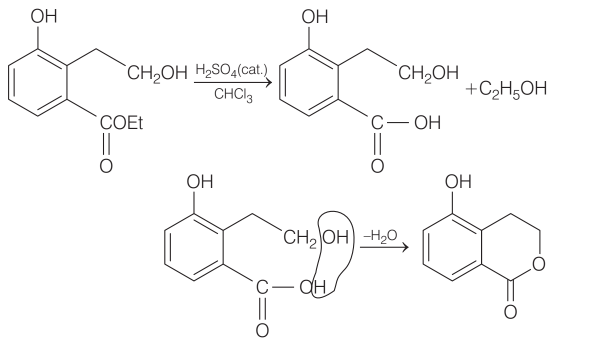
14. $CH_3CHO + HCHO \xrightarrow{NaOH} \underset{\text{Aldol}}{H-\overset{OH}{\underset{H}{C}}-CH_2-CHO} \xrightarrow{\Delta}$

$CH_2{=}CH-CHO \xrightarrow{HCN} \underset{\text{Cyanohydrin}}{CH_2{=}CH-\overset{OH}{CH}-CN}$

$CH_2{=}CH-\overset{OH}{CH}-CN \xrightarrow[H_2O]{H^+} CH_2{=}CH-\overset{OH}{CH}-COOH$

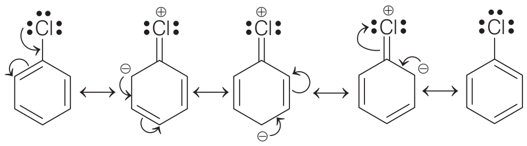
Topic 2 Acid Derivatives

1. Given reaction involves acidic hydrolysis of esters followed by the intramolecular cyclisation. The chemical equation is as follows:

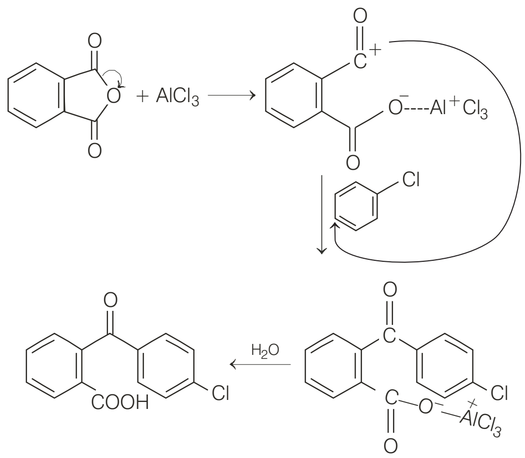


2. The major product of the given reaction is (d).

This reaction proceed *via* Friedel-Craft acylation. Here, — Cl group present on chlorobenzene is *ortho* and *para*-directing. It can be easily understood by resonating structures of chlorobenzene.



The given reaction proceed as follows :



3. All the given compounds are acid derivatives, thus contain carbonyl group in them. $LiAlH_4$ reduces these compounds through nucleophilic substitution *via* addition elimination ($S_{N_A}E$) reaction. The rate of reaction depends upon the following factors :

(i) Size of alkyl group.

(ii) Steric hinderance around the $>C=O$ group.

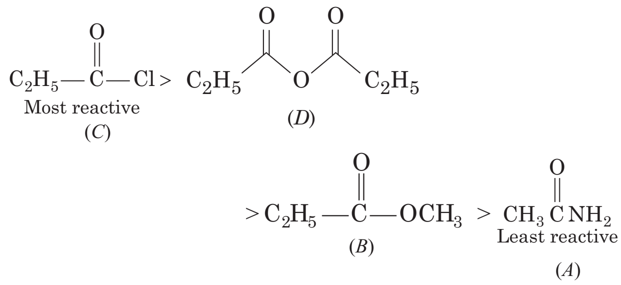
(iii) (+) ve charge on the C-atom of $>C=O$ group.

The alkyl groups are more or less same in the given compounds. Thus, the reactivity order of given compounds depends upon 2nd and 3rd factor written above. The cumulative effect of these two factors results to leaving group ability (LGA) of the substituents in the following order :

$$\underset{\text{Good leaving group}}{Cl^-} > O^- —\overset{\overset{\large O}{\|}}{C}—CH_3 > \bar{O}—CH_3 > \underset{\text{Poor leaving group}}{NH_2}$$

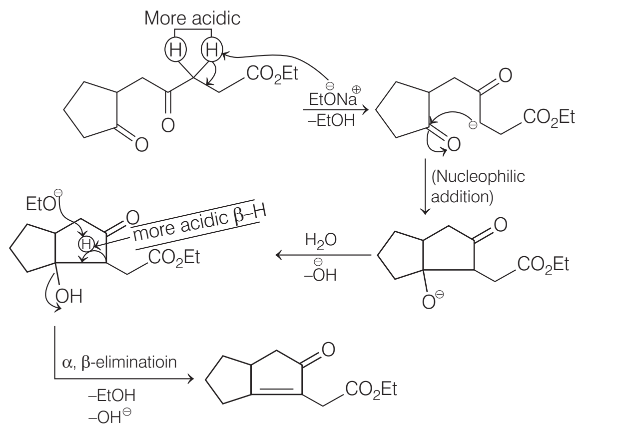
This leaving group ability (weak conjugate base) corresponds directly to the reactivity order.

Hence, the correct reactivity order is:

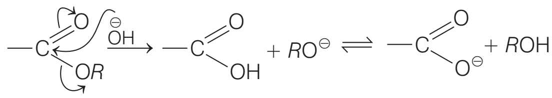


Note The $-I$ effect of — Cl and + m effects of $—\ddot{N}H_2$— $O—\overset{\overset{O}{\|}}{C}—C_2H_5$ and — OCH_3 groups while attached to $—\underset{\underset{O}{\|}}{C}—$ group to be reduced. Also add to the group leaving ability.

4. In presence of strong base, acidic H can easily be removed that result in formation of anion. The resulting anion undergoes intramolecular nucleophilic addition which on hydrolysis followed by heating gives the required product.



5. Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl S_N2 mechanism.



Rate of S_N2 mechanism depends on the polarity of $>C=O$ group of —COOR group. Electron withdrawing group ($-R > -I$) increases the rate of S_N2 reaction whereas electron donating group ($+R > +I$) decreases the rate of S_N2 reaction.

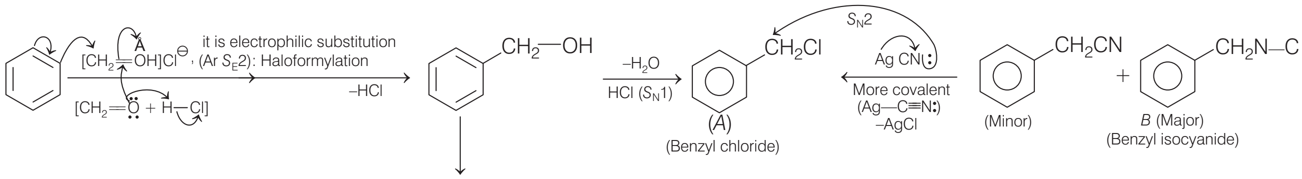
Here, the nature of functional groups attached *para* to the benzene ring are:

$$\underset{(-R)}{—NO_2} > \underset{(-I)}{—Cl} > \underset{(+R)}{—OCH_3}$$

So, the order of hydrolysis will be,

$$\underset{(-R)}{III} > \underset{(-I)}{II} > I > \underset{(+R)}{IV}$$

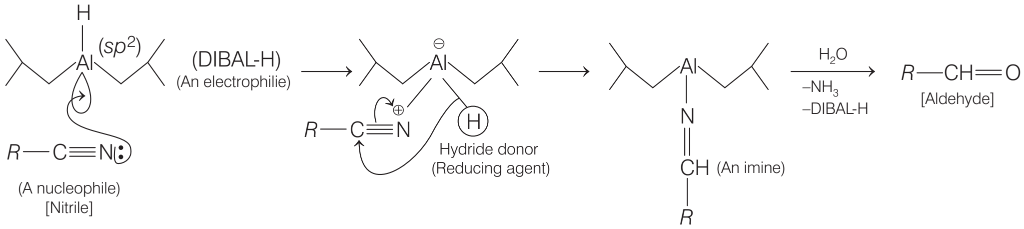
6. The mechanism of the given reaction is as follows:



Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

7. **Key Idea** DIBAL-H is diisobutyl aluminium hydride, $[(CH_3)_2CHCH_2]_2AlH$. It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

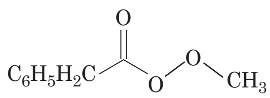
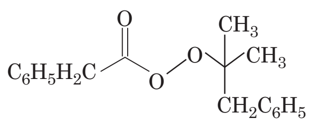
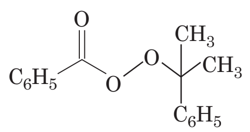
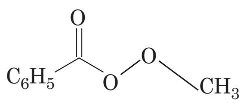
The mechanism of the reaction is as follows:



So, $R-\underset{\underset{O}{\|}}{C}H$ is the correct answer.

8. **PLAN** his problem can be solved by usin the stability of radical obtained after fra mentation of peroxyester.

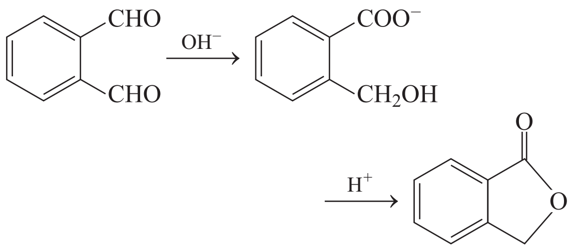
Allylic radical are more stable than alkyl radical, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical. i.e. fragmentation produces stable radical.
On the basis of stability of radical, fragmentation can be done as

Column I	Column II		Explanation
P.	1.		$C_6H_5-\dot{C}H_2 + CO_2 + CH_3O^{\bullet}$
Q.	3.		$C_6H_5-\dot{C}H_2 + CO_2 + Ph-CH_2-\underset{CH_3}{\overset{O^{\bullet}}{C}}-CH_3 \longrightarrow Ph-\dot{C}H_2 + CH_3-CO-CH_3$
R.	4.		$C_6H_5-\dot{C}O_2 + CH_3-\underset{C_6H_5}{\overset{O^{\bullet}}{C}}-CH_3 \xrightarrow{-CO_2} \dot{Ph} + CH_3-CO-Ph + \dot{C}H_3 + CO_2$
S.	2.		$C_6H_5-\dot{C}O_2 + \dot{C}H_3O$ $\longrightarrow C_6\dot{H}_5 + CO_2$

9. $R\text{—}NH_2 + CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Cl \xrightarrow[(-HCl)]{} R\text{—}NH\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$

Since, each —$COCH_3$ group displace one H atom in the reaction of one mole of $CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Cl$ with one —NH_2 group, the molecular mass increases with 42 unit.

Since the mass increases by $(390 - 180) = 210$, hence the number of —NH_2 group is $\dfrac{210}{42} = 5$.

10. 

11. $C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 \xrightarrow{POCl_3} C_6H_5\text{—}CN$

12. $CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OC_2H_5 \xrightarrow[\text{excess}]{CH_3MgBr} CH_3\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}\text{—}CH_3$

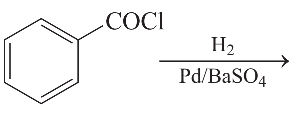
$\xrightarrow{H_2O} CH_3\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{—}OH$

13. $P \xrightarrow[H_2O]{H^+} CH_3\text{—}\overset{\overset{\displaystyle OH}{|}}{C}{=}CH_2 \rightleftharpoons CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$

$\xrightarrow[I_2]{NaOH} \underset{\text{Yellow}}{CHI_3\downarrow}$

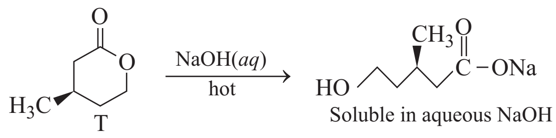
$Q \xrightarrow[H_2O]{H^+} CH_3\text{—}CH{=}CH\text{—}OH \rightleftharpoons CH_3CH_2OH$

$\xrightarrow{\text{Fehling solution}} \underset{\text{Red}}{Cu_2O\downarrow}$

14.  "Rosenmund reduction"

15. $CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 + Br_2 + NaOH \longrightarrow CH_3NH_2$ "Hofmann's bromamide reaction".

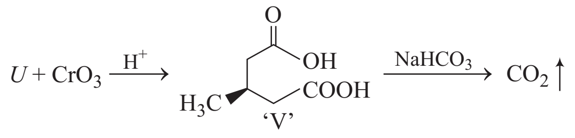
16. (a) T undergoes an ester hydrolysis in hot aqueous alkali as



(b) $LiAlH_4$ reduces ester to alcohol as
"U" No chiral carbon optically inactive.

(c) U on treatment with excess of acetic anhydride forms a diester as

(d) U on treatment with $CrO_3|H^+$ undergo oxidation to diacid which gives effervescence with $NaHCO_3$.



17. For separation by differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

(a) Both phenol and benzoic acid forms salt with NaOH, hence this mixture can't be separated.

(b) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also benzoic acid forms salt with $NaHCO_3$ but benzyl alcohol does not, hence $NaHCO_3$ can be used for separation.

(c) Neither benzyl alcohol nor phenol forms salt with $NaHCO_3$, mixture cannot be separated using $NaHCO_3$.

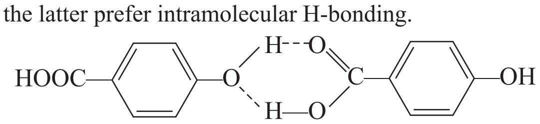
(d) $C_6H_5CH_2COOH$ forms salt with NaOH, $C_6H_5CH_2OH$ does not, hence mixture can be separated using NaOH. $C_6H_5CH_2COOH$ forms salt with $NaHCO_3$. $C_6H_5CH_2OH$ does not, hence mixture can be separated using $NaHCO_3$.

18. $R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 + OH^- + Br_2 \longrightarrow \underset{(A)}{R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NHBr}$

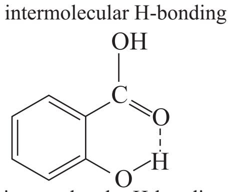
$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NHBr + OH^- \longrightarrow \underset{(B)}{R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{-}{N}\text{—}Br}$

$\longrightarrow \underset{(C)}{R\text{—}N{=}C{=}O} + Br^-$

19. p-hydroxy benzoic acid has higher boiling point than o-hydroxy benzoic acid because former prefers intermolecular H-bonding while the latter prefer intramolecular H-bonding.



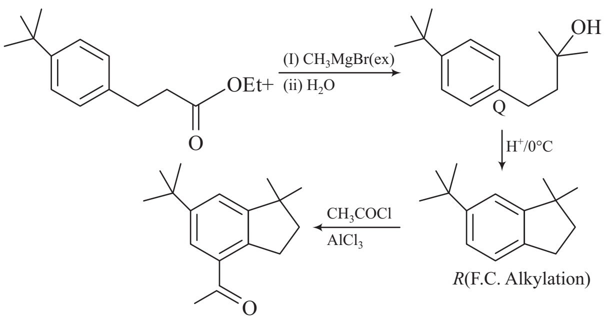
intermolecular H-bonding



intramolecular H-bonding

20. Compounds with $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—$ or $CH_3—CH(OH)$–group gives haloform reaction but this reaction is given only by aldehydes, ketones and alcohols, so acetic acid does not give haloform reaction. However acetic acid has three α-H, therefore, statement I is true but statement II is false.

Passage-1



S(F.C. Acylation)

22. (a)

22. (c)

23. **PLAN** lkenes decolourise Br_2 water

-isomer $\xrightarrow{\text{dil·KMnO}_4}$ isomers by addition

-isomer $\xrightarrow{\text{dil·KMnO}_4} d(+)$ and $l(-)$ isomers by

Formation of anhydride from dicarboxylic acid indicates -isomer.

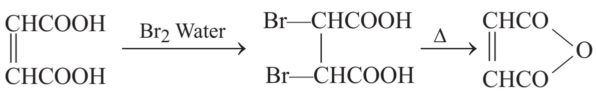
P and Q are isomers of dicarboxylic acids.

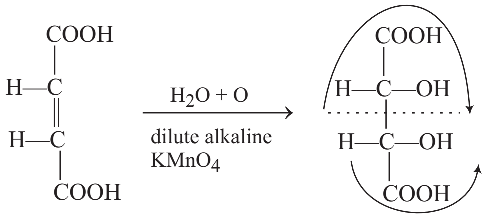
$$P, Q \xrightarrow{Br_2 \text{ water}} \text{decolourised}$$

P and Q have (C═C) bond

$$P \xrightarrow{\Delta} \text{anhydride}$$

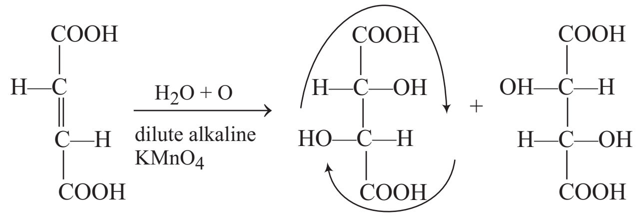
Thus, P is *cis*-isomer.





(P) (maleic acid)

(S) Optically inactive due to internal compensation of rotation (*meso*-isomer)

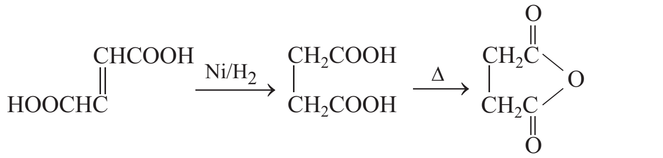


(fumaric acid) (T) d(+) (U) l(–)

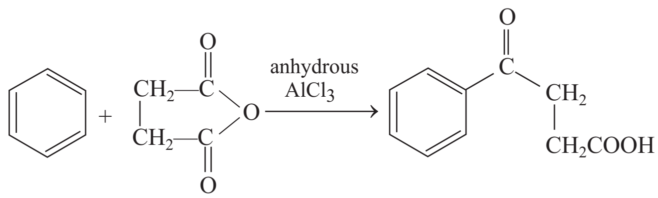
T and U (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation.

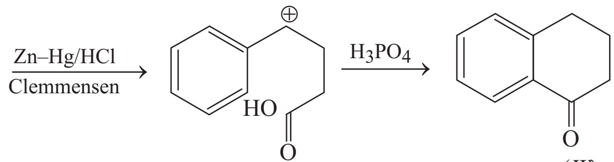
24. **PLAN** Ni / H_2 reduces (C═C) bond.

Benzene undergoes Friedel-Crafts reaction Zn-Hg/HCl reduces carbonyl group (Clemmensen reduction)

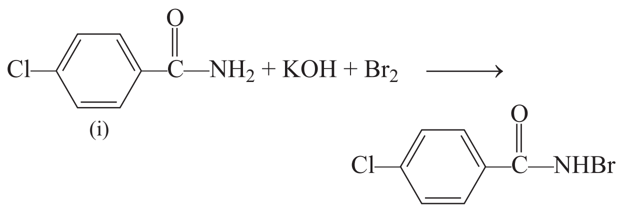


succinic anhydride (V)



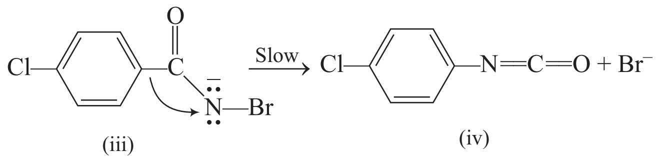


(W)

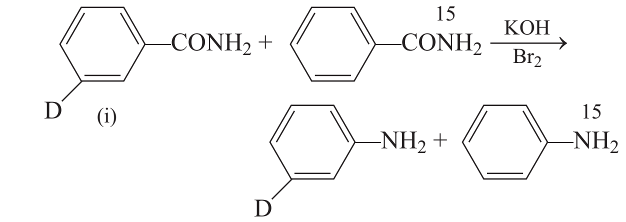
25. 

an intermediate (ii)

26. Rearrangement of (iii) to (iv) is the rate determining step :



27. The rate determining step of Hofmann's bromamide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.



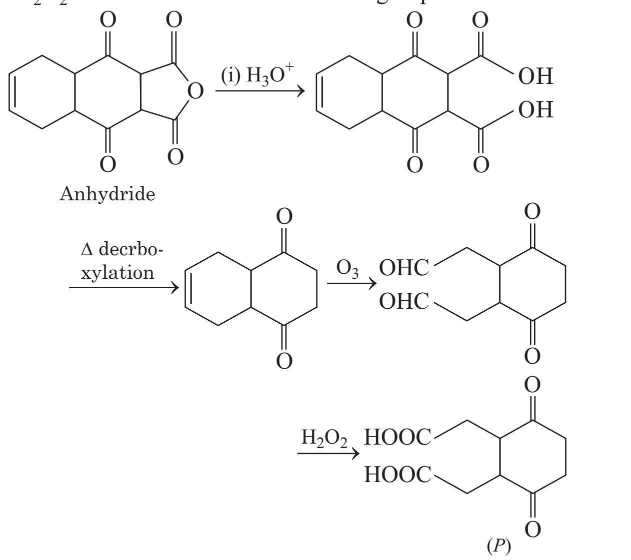
28. $HCOOH + \underset{\text{conc.}}{H_2SO_4} \xrightarrow{\Delta} H_2O + CO\uparrow$

29. Propanoic acid has higher boiling point than *n*-butanol because of more exhaustive H-bonding in former case.

30. Saponification is hydrolysis of ester in presence of dilute base rather in presence of dilute acid.

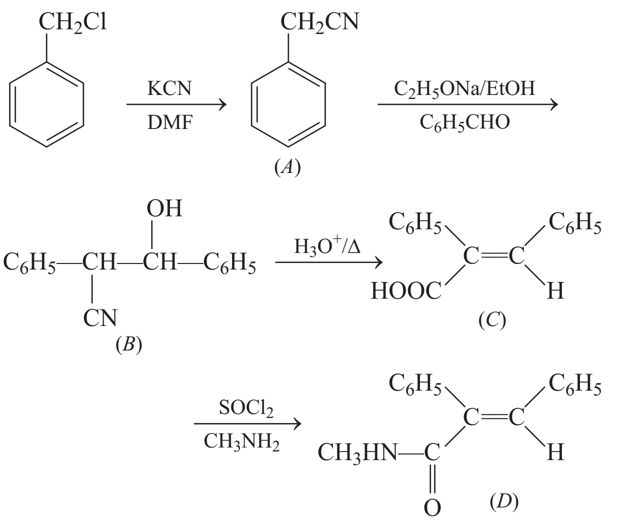
31. **PLAN** eactant is cyclic anhydride and chan es to dicarboxylic acid on hydrolysis.

Also there is decarboxylation on heating if there is keto group *w.r.t* —COOH group. Ozonolysis cleaves (C=C) bond and H_2O_2 oxidises —CHO to —COOH group.

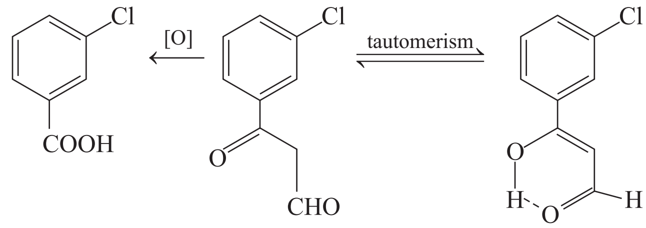


Thus, number of —COOH groups in *P* = 2.

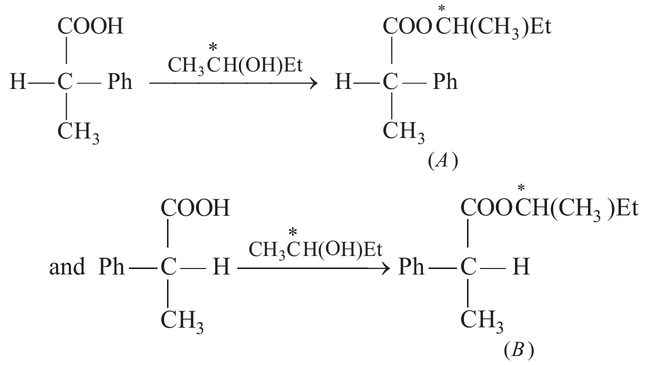
32.



33. Compound *A* of molecular formula $C_9H_7O_2Cl$ exist in keto and predominantly in enolic form *B*. Hence, *A* must be a carbonyl compound which contain α-H. Enolic forms of *B* predominates because of presence of intramolecular H-bonding.



34. The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :

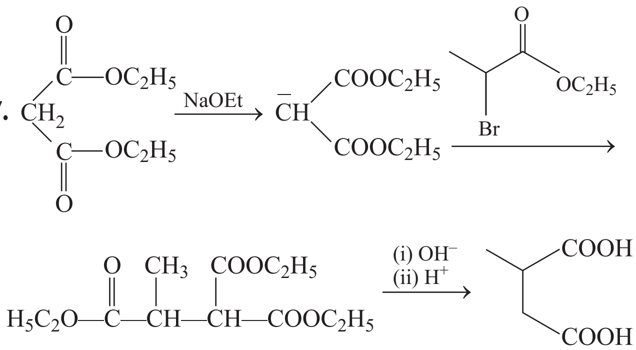


Here *A* and *B* are diastereomers.

35. $H_2C{=}CH{-}Br \xrightarrow[\text{(ii) } X \text{ (iii) } H_3O^+]{\text{(i) Mg/ether}} \underset{Y}{H_2C{=}CH{-}\overset{*}{C}({=}O){-}OH} \xrightarrow{LiAlH_4} \underset{Z}{H_2C{=}CH{-}\overset{*}{C}H_2OH}$

36. $CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{18}{O}C_2H_5 \xrightarrow{H_3O^+} \underset{(A)}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{(B)}{C_2H_5{-}\overset{18}{O}H}$

37.

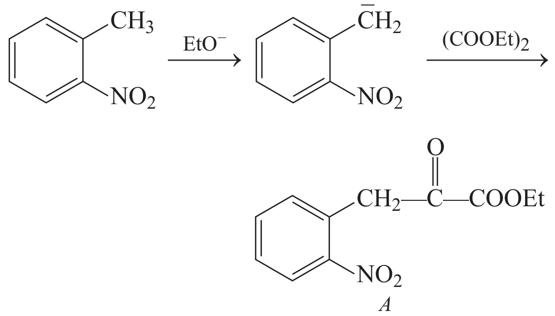


38. $CH_3CH_2NH_2 \xrightarrow[\text{Heat}]{(CH_3CO)_2O} CH_3CH_2NH{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

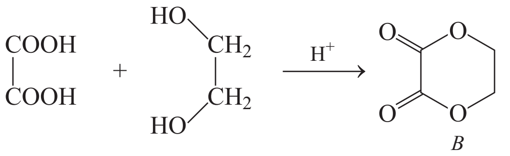
39. $$\mathrm{H-\overset{\overset{O}{\|}}{C}-O-\underset{A}{\overset{\overset{CH_3}{|}}{C}H}-CH_3 \xrightarrow[\text{excess}]{MeMgBr/H_2O} \underset{B}{CH_3-\underset{\underset{CH_3}{|}}{C}H-OH}}$$

$$\xrightarrow{\mathrm{NaOCl}} \mathrm{CH_3COOH + CHCl_3}$$

40. (i)



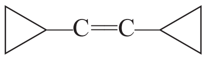
(ii)

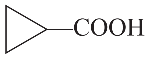


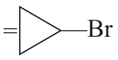
(iii) $$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow[H_2O]{NaOH} \underset{C}{C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH}}$$

41. B is C_3H_5COOH and A is $C_3H_5-C\equiv C-C_3H_5$

Also A on ozonolysis gives B indicates that there is no olefinic bond in C_3H_5-unit of A and it is cyclopropyl group.

$\Rightarrow$ $A =$ 

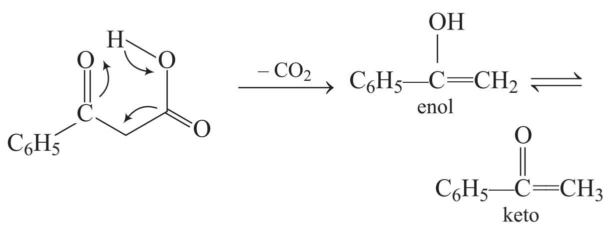
$B =$ 

and $C =$ 

42. $$\mathrm{CH_3CH_2COOH \xrightarrow[Br_2]{red\text{-}P} \underset{A}{CH_3-\underset{\underset{Br}{|}}{C}H-COOH}}$$ (HVZ reaction)

$$\xrightarrow[\text{(ii) } H^+]{\text{(i) alc.KOH}} \underset{B}{\mathrm{CH_2=CH-COOH}}$$

43. A β-keto acid undergo very fast decarboxylation



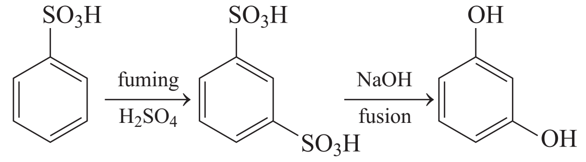
44. $$\mathrm{C_6H_5CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} C_6H_5-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

45. (i) $\mathrm{PCl_5 + SO_2 \longrightarrow \underset{B}{POCl_3} + \underset{A}{SOCl_2}}$

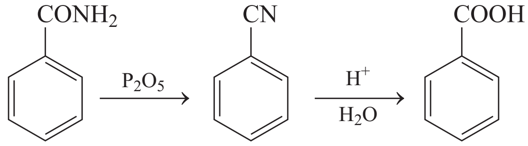
(ii) $\mathrm{SOCl_2 + CH_3COOH \longrightarrow \underset{(A)}{CH_3COCl} + SO_2 + HCl}$

(iii) $\mathrm{2CH_3COCl + Cd(CH_3)_2 \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CdCl_2}$

46. (i)



(ii)



47. $$\mathrm{C_6H_5COOH \xrightarrow{PCl_5} \underset{A}{C_6H_5COCl} \xrightarrow{NH_3} \underset{B}{C_6H_5-\overset{\overset{O}{\|}}{C}-NH_2}}$$

$$\mathrm{\xrightarrow{P_2O_5} C_6H_5-CN \xrightarrow{H_2/Ni} \underset{C}{C_6H_5CH_2NH_2}}$$

48. Electron withdrawing inductive effect increases acid strength while electron donating inductive effect decreases acid strength.

+*I*-effect

$$\mathrm{H_3C-\underset{\underset{CH_3}{|}}{C}H-COOH < CH_3CH_2COOH < CH_3COOH}$$

+*I*-effect   +*I*-effect   +*I*-effect

$$\mathrm{< \underset{\underset{Cl}{|}}{C}H_2-CH_2COOH < \underset{\underset{Cl}{|}}{C}H_2-COOH}$$

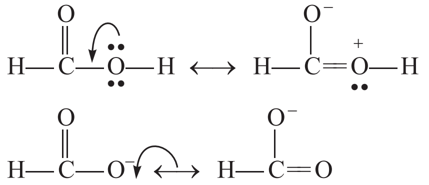
−*I*-effect (greater distance)   −*I*-effect

49. $$\mathrm{CH_3-COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow[AlCl_3]{C_6H_6} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3}$$

$$\mathrm{\xrightarrow[H_2O]{C_6H_5MgBr} C_6H_5-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[\Delta]{H^+} C_6H_5-\overset{\overset{C_6H_5}{|}}{C}=CH_2}$$

$$\mathrm{\xrightarrow{O_3/H_2O_2} C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 + H-COOH}$$

50. Both formic acid and sodium formate exhibit the phenomenon of resonance as :



In formic acid, the extent of delocalisation is less compared to sodium formate because of charge separation in the former case. Due to this reason, the bond length between carbon and sp^3 oxygen in formic acid is slightly greater than the same between carbon and sp^2 oxygen. In formate ion, there is no separation of charge and both the resonance structures are equivalent giving equal bond length of both carbon oxygen bonds.

51. $CH_3CONH_2 + Br_2 \xrightarrow{NaOH} \underset{\text{Hoffman bromamide reaction}}{CH_3NH_2 + Na_2CO_3}$

52. X is an ester and both its acid and alcohol fragments have same number of carbons. Hence, X is :

$$\underset{X}{CH_3CH_2COOCH_2CH_2CH_3} \xrightarrow[H_2O]{H^+} \underset{Y}{CH_3CH_2COOH} + \underset{Z}{CH_3CH_2CH_2OH}$$

$$Z \xrightarrow{[O]} \underset{Y}{CH_3CH_2COOH}$$

53. $$\underset{A}{H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{|}}{CH}-CH_3} \xrightarrow[\text{excess}]{MeMgCl} \xrightarrow{H^+/H_2O} \underset{B}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_3}$$

$$B + NaOCl \longrightarrow CHCl_3 + CH_3COOH$$

54. $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$

55. Among acid derivatives, the reactivity towards nucleophilic acyl substitution is in the order of :

Amide < Ester < Anhydride < Acid chloride

Hydrolysis is an example of nucleophilic acyl substitution, hence the reactivity towards hydrolysis is :

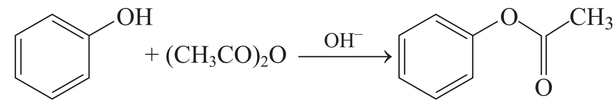
$CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

56. $$\underset{\substack{+I\text{-effect} \\ \text{decreases acid-strength}}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} < \underset{\text{does not affect acidity.}}{H-\overset{\overset{O}{\|}}{C}-OH}$$

57. $CH_3CH_2CHO + AgNO_3 \xrightarrow{NH_4OH} CH_3CH_2COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CH_2CO)_2O$

58. $CH_3-COOH + Cl_2 \xrightarrow{\text{Red-P}} \underset{\underset{Cl}{|}}{CH_2}-COOH$ (HVZ reaction)

For this reaction to occur, presence of a α-H is essential requirement. Formic acid does not has any α-H, fails in HVZ reaction.

59. 

60. $$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + 2CH_3MgBr \longrightarrow CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

61. $$CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-} \bar{C}H_2COOC_2H_5 \xrightarrow{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_2} \underset{\text{Claisen condensation}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COO_2H_5}$$

$$\xrightarrow[H_2O]{H^+} C_2H_5OH + CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOH$$

27

Aliphatic Compounds Containing Nitrogen

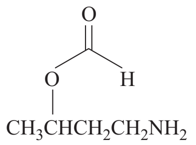
Objective Questions I (Only one correct option)

1. The major product of the following reaction is

$$CH_3\underset{\displaystyle |}{\overset{\displaystyle OH}{C}}HCH_2CH_2NH_2 \xrightarrow[\text{Triethylamine}]{\text{Ethyl formate (1 equiv.)}}$$

(2019 Main, 10 April I)

(a) $CH_3\overset{OH}{\underset{|}{C}}HCH_2CH_2NHCHO$ (b) $CH_3CH{=}CH{-}CH_2NH_2$

(c) $CH_3{-}\overset{OH}{\underset{|}{C}}H{-}CH{=}CH_2$ (d) 

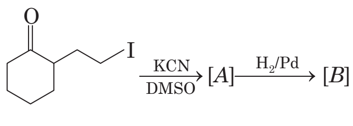
2. Ethylamine ($C_2H_5NH_2$) can be obtained from *N*-ethylphthalimide on treatment with **(2019 Main, 10 April I)**

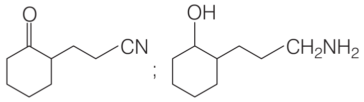
(a) $NaBH_4$ (b) NH_2NH_2 (c) H_2O (d) CaH_2

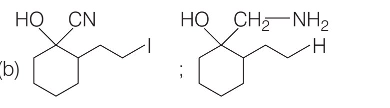
3. Hinsberg's reagent is **(2019 Main, 9 April II)**

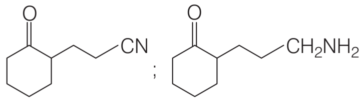
(a) $SOCl_2$ (b) C_6H_5COCl (c) $C_6H_5SO_2Cl$ (d) $(COCl)_2$

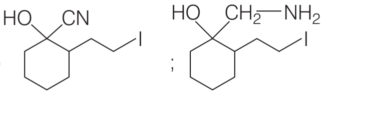
4. The major products *A* and *B* for the following reactions are, respectively **(2019 Main, 9 April II)**



(a) 

(b) 

(c) 

(d) 

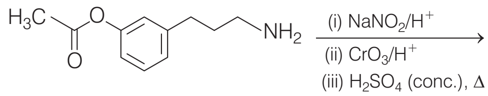
5. Which of the following amines can be prepared by Gabriel phthalimide reaction? **(2019 Main, 8 April I)**

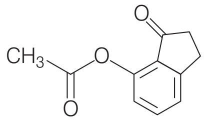
(a) *n* - butylamine
(b) triethylamine
(c) *t*-butylamine
(d) *neo* -pentylamine

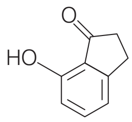
6. In the following compounds, the decreasing order of basic strength will be **(2019 Main, 8 April I)**

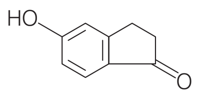
(a) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$
(b) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(d) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

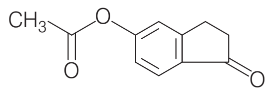
7. The major product of the following reaction is **(2019 Main, 12 Jan II)**



(a) 

(b) 

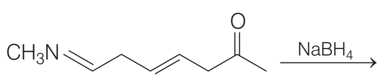
(c) 

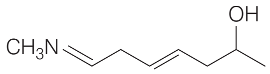
(d) 

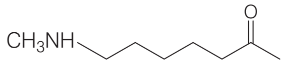
8. A compound '*X*' on treatment with Br_2 / NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound '*X*' is **(2019 Main, 11 Jan II)**

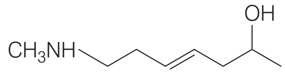
(a) $CH_3COCH_2NHCH_3$
(b) $CH_3CH_2CH_2CONH_2$
(c) $CH_3CON(CH_3)_2$
(d) $CH_3CH_2COCH_2NH_2$

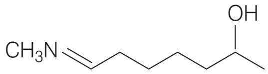
9. The major product of the following reaction is **(2019 Main, 10 Jan II)**



(a) 

(b) 

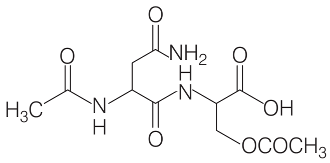
(c) 

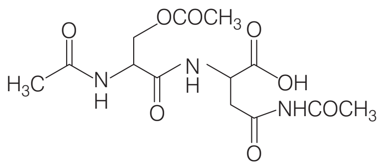
(d) 

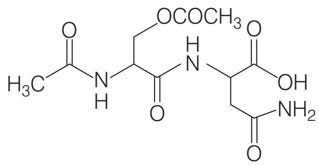
10. The correct structure of product 'P' in the following reaction is

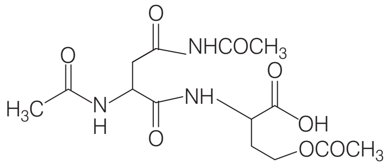
$$\text{Asn} - \text{Ser} + \underset{\text{(Excess)}}{(\text{CH}_3\text{CO})_2\text{O}} \xrightarrow{\text{NEt}_3} P$$

(2019 Main, 10 Jan I)

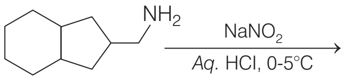
(a) 

(b) 

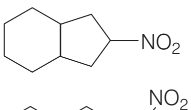
(c) 

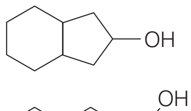
(d) 

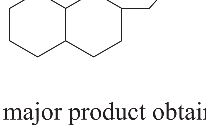
11. The major product formed in the reaction given below will be

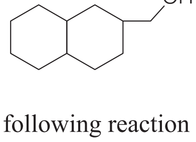


(2019 Main, 10 Jan I)

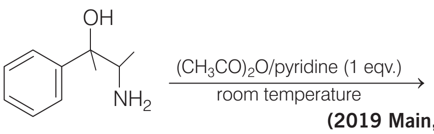
(a) 

(b) 

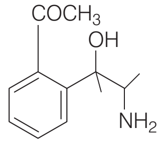
(c) 

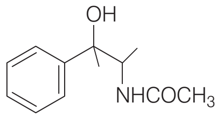
(d) 

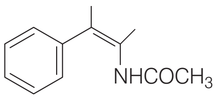
12. The major product obtained in the following reaction is

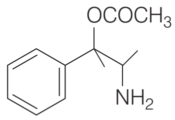


(2019 Main, 9 Jan II)

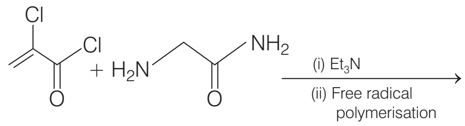
(a) 

(b) 

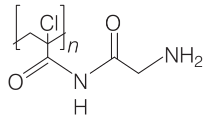
(c) 

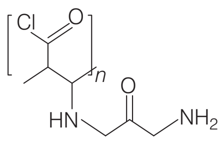
(d) 

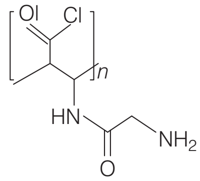
13. Major product of the following reaction is

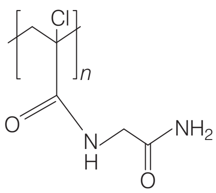


(2019 Main, 9 Jan I)

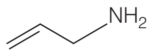
(a) 

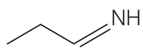
(b) 

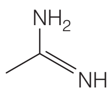
(c) 

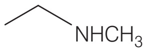
(d) 

14. The increasing order of basicity of the following compounds is

I. 

II. 

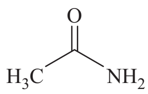
III. 

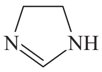
IV. 

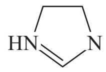
(2018 Main)

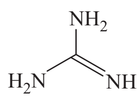
(a) (I) < (II) < (III) < (IV)
(b) (II) < (I) < (III) < (IV)
(c) (II) < (I) < (IV) < (III)
(d) (IV) < (II) < (I) < (III)

15. The order of basicity among the following compounds is **(2017 Adv.)**


(I)


(II)


(III)


(IV)

(a) II > I > IV > III
(b) I > IV > III > I
(c) IV > I > II > I
(d) IV > I > II > III

16. In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are **(2016 Main)**

(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and one mole of Br_2

17. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **(2014 Main)**

(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

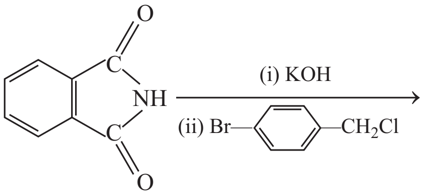
18. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is **(2014 Main)**

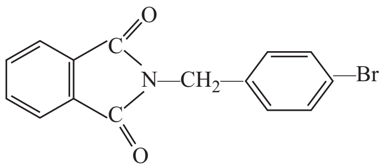
(a) an alkanol (b) an alkanediol
(c) an alkyl cyanide (d) an alkyl isocyanide

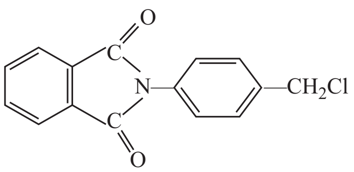
19. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was **(2013 Main)**

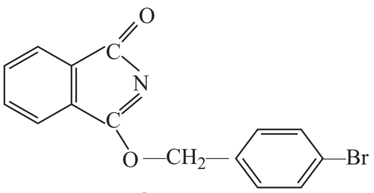
(a) methyl isocyanate
(b) methylamine
(c) ammonia
(d) phosgene

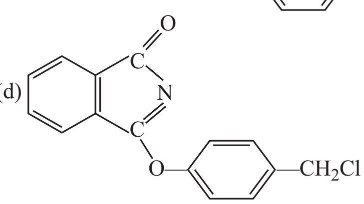
20. The major product of the following reaction is **(2011)**



(a)


(b)


(c)


(d)


21. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + $KCl + H_2O$. Nitrogen containing compound is **(2006)**

(a) CH_3CN (b) CH_3NHCH_3
(c) $CH_3—\overset{-}{N}\equiv\overset{+}{C}$ (d) $CH_3—\overset{+}{N}\equiv\overset{-}{C}$

22. Benzamide on treatment with $POCl_3$ gives **(2004)**

(a) aniline (b) benzonitrile
(c) chlorobenzene (d) benzyl amine

23. The correct order of basicities of the following compounds is

$$\underset{1}{H_3C—C\overset{\nearrow NH}{\underset{\searrow NH_2}{}}}, \quad \underset{2}{CH_3—CH_2—NH_2}, \quad \underset{3}{(CH_3)_2NH}, \quad \underset{4}{H_3C—\overset{\overset{O}{\|}}{C}—NH_2}$$

(2001, 1M)

(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4 (c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

24. A positive carbylamine test is given by **(1999, 2M)**

(a) N, N-dimethylaniline (b) 2, 4-dimethylaniline
(c) N-methyl-*o*-methylaniline (d) *p*-methylbenzylamine

25. *p*-chloroaniline and anilinium hydrochloride can be distinguished by **(1998, 2M)**

(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

26. Carbylamine test is performed in alc. KOH by heating a mixture of **(1984, 1M)**

(a) chloroform and silver powder
(b) trihalogenated methane and a primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

27. Acetamide is treated separately with the following reagents. Which of these would give methylamine? **(1983, 1M)**

(a) PCl_5 (b) Sodalime
(c) $NaOH + Br_2$ (d) Hot, conc. H_2SO_4

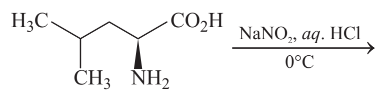
28. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine, is **(1981, 1M)**

(a) methylamine (b) ethylamine
(c) diethylamine (d) triethylamine

Objective Question II

(Only one more than one correct option)

29. The major product of the reaction is **(2015, Adv.)**



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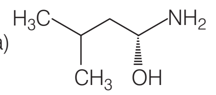

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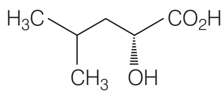

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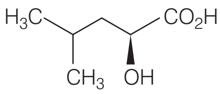

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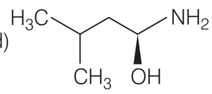


30. A positive carbylamine test is given by **(1999, 2M)**

(a) N, N-dimethyl aniline (b) 2, 4-dimethyl aniline
(c) N-methyl-*o*-methyl aniline (d) *p*-methyl benzyl amine

Fill in the Blanks

31. $(CH_3OH_2^+)$ is …… acidic than $(CH_3NH_3^+)$. **(1997 C, 1M)**

Match the Columns

32. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. **(2016, Adv.)**

Column I		Column II
(A) $CH_3CH_2CH_2CN$	(p)	Reduction with Pd - C/H_2
(B) $CH_3CH_2OCOCH_3$	(q)	Reduction with $SnCl_2/HCl$
(C) $CH_3CH{=}CHCH_2OH$	(r)	Development of foul smell on treatment with chloroform and alcoholic KOH.
(D) $CH_3CH_2CH_2CH_2NH_2$	(s)	Reduction with diisobutylaluminium hydride (DIBAL-H)
	(t)	Alkaline hydrolysis

Subjective Questions

33. $\underset{\substack{\text{optically active}\\ X}}{C_5H_{13}N} \xrightarrow[-N_2]{NaNO_2,\ HCl} Y$(tertiary alcohol + other products)

Find X and Y. Is Y optically active ? Write the intermediate steps **(2005, 4M)**

34. Give reasons for the following in one or two sentences. Dimethylamine is a stronger base than trimethylamine. **(1998, 2M)**

35. Following reaction gives two products. Write the structures of the products.

$$CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ heat}$$ **(1998, 2M)**

36. Give the structure of A. 'A (C_3H_9N) reacts with benzenesulphonyl chloride to give a solid, insoluble in alkali'. **(1993, 1M)**

37. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic KOH. A 0.295 g sample of the substance dissolved in *aq*. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless, odourless gas whose volume corresponds to 112 mL at STP.

After evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance assuming that it contains one N-atom per molecule. **(1993, 4M)**

38. Arrange the following in increasing order of basic strength: methylamine, dimethylamine, aniline, N-methylaniline. **(1988, 1M)**

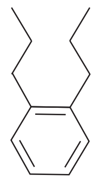
39. Give a chemical test and the reagent used to distinguish between the following : "Ethylamine and diethylamine". **(1988, 1M)**

40. For nitromethane molecule, write structures
(i) showing significant resonance stabilisation
(ii) indicating tautomerism **(1986, 1M + 1M = 2M)**

41. State the equation for the preparation of following compounds : *n*-propyl amine from ethyl chloride. **(1982, 2 × 1M = 2M)**

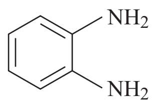
Passage Based Questions

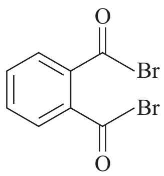
Treatment of compound O with $KMnO_4/H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with $Br_2/NaOH$ produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.4 **(2016 Adv.)**

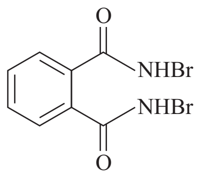


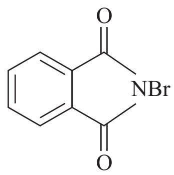
(O)

42. The compound R is

(a) 

(b) 

(c) 

(d) 

43. The compound T is
(a) glycine (b) alanine
(c) valine (d) serine

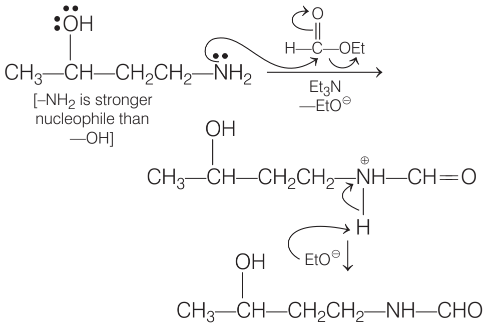
Answers

1. (a)	**2.** (b)	**3.** (c)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (c)	**8.** (b)
9. (c)	**10.** (a)	**11.** (*)	**12.** (b)	**13.** (d)	**14.** (c)	**15.** (d)	**16.** (c)
17. (a)	**18.** (d)	**19.** (a)	**20.** (a)	**21.** (d)	**22.** (b)	**23.** (b)	**24.** (d)
25. (c)	**26.** (b)	**27.** (c)	**28.** (c)	**29.** (c)	**30.** (b,d)	**31.** (more)	

32. A → p, q, s, t; B → p, s, t; C → p; D → r **42.** (a) **43.** (b)

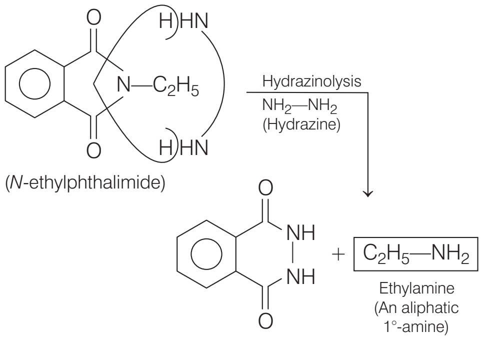
Hints & Solutions

1. The mechanism of the given reaction is as follows:



The basic mechanism of the reaction is acyl S_N2 because the nucleophile, $CH_3(OH)CH_2CH_2\ NH_2$ attacks the sp^2 carbon of the ester $(H-CO_2Et)$ and gets substituted.

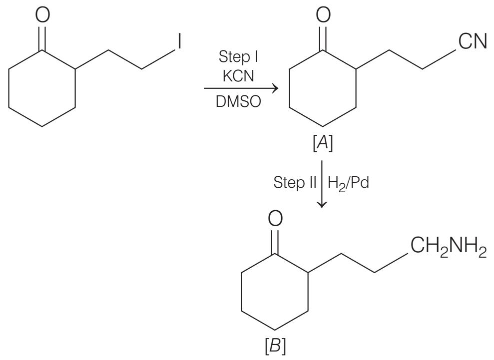
2. The reaction for the production of ethylamine from N-ethylphthalimide can be takes place as follows:



This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step concentrated alkali can also be used in place of hydrazine.

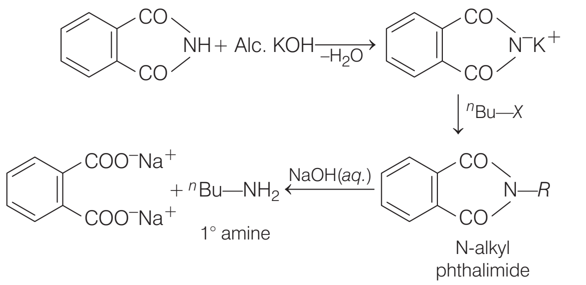
3. Hinsberg's reagent is $C_6H_5SO_2Cl$ (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.

4.



Step I involves the nucleophilic substitution reaction in which I (Iodine) is substituted by
— CN group. **In step II**, H_2/Pd reagent is used for reduction process. Here, — CN group reduces itself to $—CH_2NH_2$.

5. n-butylamine $(CH_3CH_2CH_2CH_2NH_2)$ can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines. In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



Triethylamine, t-butylamine and neo-pentylamine cannot be prepared by Gabriel phthalimide reaction.

6. Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.

$$R-\ddot{N}H_2 + H^+ \rightleftharpoons R-NH_3^+$$

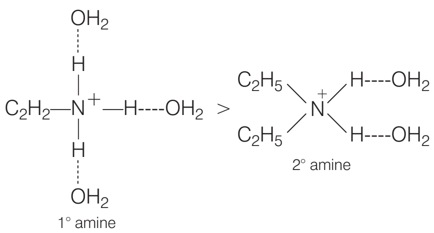
$$H-\ddot{N}H_2 + H^+ \rightleftharpoons H-NH_3^+$$

Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

(a) + I effect (b) Steric effect

(c) Solvation effect

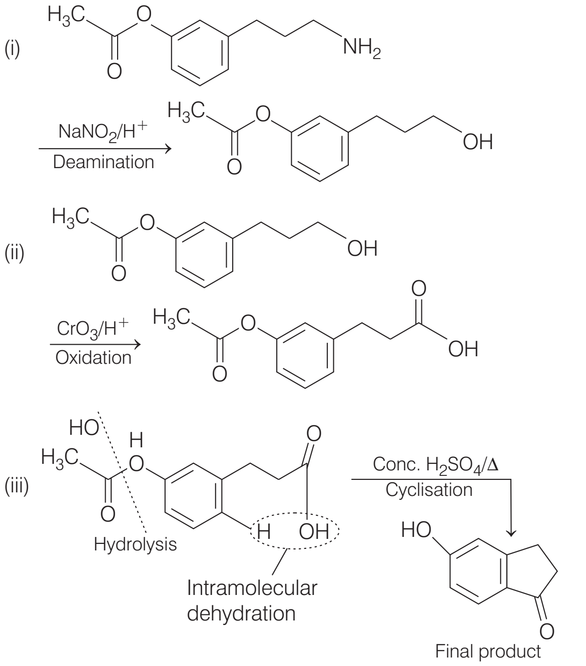
In first case, on increasing the size of alkyl group + I effect increases and the positive charge of ammonium cation gets dispersed more easily, Therefore, order of basicity is 2º amine > 1º amine > ammonia. In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.



Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium cation. But in case of $-C_2H_5$ group, $+I$ effect predominates over H-bonding. Therefore, order is 2° amine > 1° amine > ammonia i.e. $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

7. **Key Idea** The reaction involves:
A. Deamination in step (i)
B. Oxidation in step (ii)
C. Hydroysis in step (iii)

The complete pathway of reactions is as follows:



Thus, option (c) is the correct answer.

8. The molecular formula, C_3H_9N refers to four structural isomers of amines

(a) $CH_3CH_2CH_2NH_2$ (b) $CH_3-CH(NH_2)-CH_3$ — Primary amine

(c) $CH_3-NH-CH_2CH_3$ — Secondary amine (d) $CH_3-N(CH_3)-CH_3$ — Tertiary amine

Here, only *a* and *b* (primary amines) can be prepared from their respective amides by Hoffmann bromamide (Br_2/NaOH) method and can give positive carbylamine test.

$$\Rightarrow CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[NaOH,\ -Na_2CO_3]{Br_2} CH_3CH_2CH_2-NH_2$$

$$\Rightarrow CH_3-\underset{}{\overset{H_2N-C=O}{\overset{|}{CH}}}-CH_3 \xrightarrow[-Na_2CO_3]{Br_2/NaOH} CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3$$

So, '*X*' can be $CH_3CH_2CH_2-CONH_2$ (a) or $CH_3CH(CONH_2)CH_3$ (b).

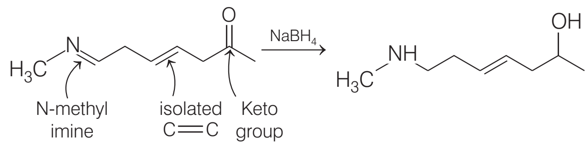
Carbylamine test given by (a) and (b)

$$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3(CH_2)_2NC + 3KCl + 3H_2$$

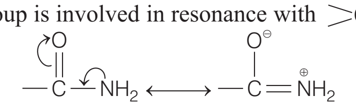
$$CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-\overset{NC}{\overset{|}{CH}}-CH_3 + 3KCl + 3H_2$$

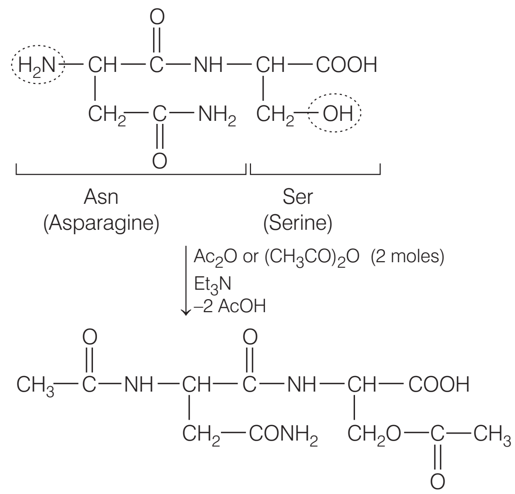
As (b) is not among the given options So, it is ruled out and compound (X) is $CH_3CH_2CH_2CONH_2$.

9. $NaBH_4$ is a selective reducing agent. It can reduce $>C=O$ group into alcohol, N-methyl imine group, $Me-N=CH-$ into 2°-amine but cannot reduce an isolated $C=C$.



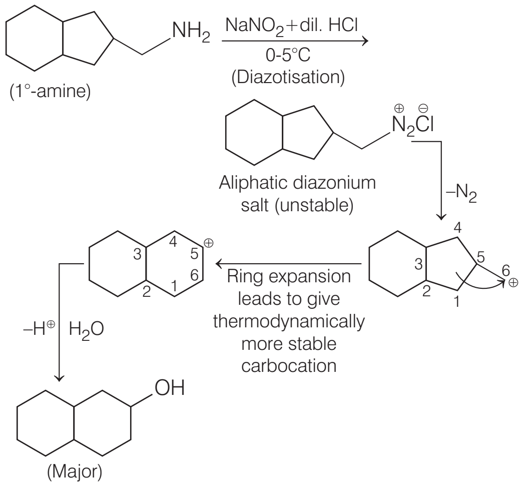
10 Acetylation by Ac_2O/Et_3N is possible with $-NH_2$ (1°-amine) and $-OH$ (alcohol) groups only, but not with '$-NH_2$' part of $-\overset{O}{\overset{\|}{C}}-NH_2$ (amide) groups, because the *lp* of nitrogen in amide group is involved in resonance with $>C=O$ part.



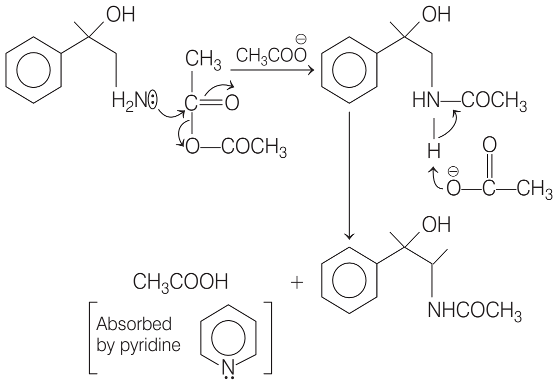


11. No option is the correct answer.

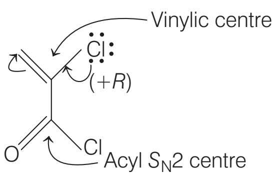
Amines in presence of $NaNO_2$ + dil. HCl undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

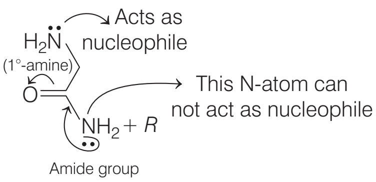


12. Rate of acetylation : $—NH_2 > —OH$ because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom. So, N-atom of the $—\ddot{N}H_2$ group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the $—\ddot{O}H$ group.

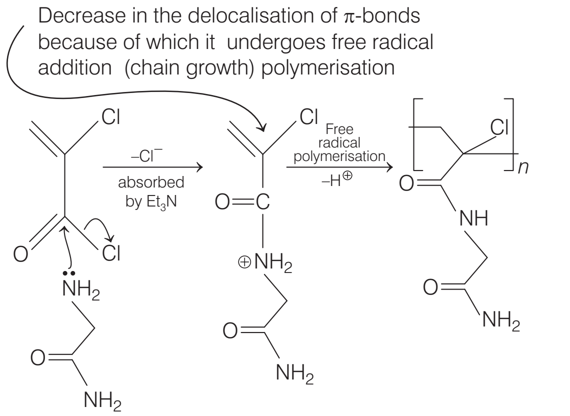


13. The analysis of both the substrates :

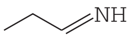


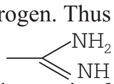


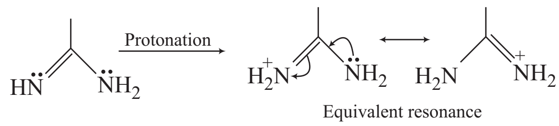
So, the reaction can take place as follows:

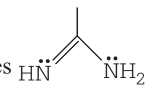


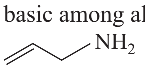
14. **Key Idea** Among the given compounds the basic nature depends upon their tendency to donate electron pair.

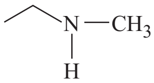
Among the given compounds in , Nitrogen is sp^2-hybridised. This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen. Thus making compound least basic.

Among the rest  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π bond i.e. As a result of this conjugation the cation formed after protonation becomes resonance stabilised



This equivalent resonance in cation makes  most basic among all.

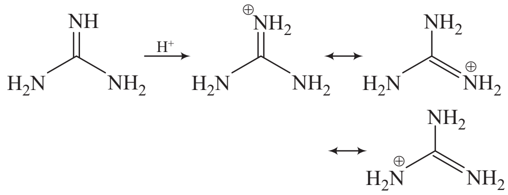
 Categorisation is very simple between rest two as

 (primary amine) is less basic than (secondary amine)

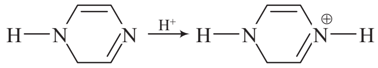
Hence, the correct order is

(II) < (I) < (IV) < (III) i.e. option (c) is correct.

15. IV is most basic as conjugate acid is stabilised by resonance of two — NH_2.



III is least basic as



Destablised by $-I$-effect of sp^2-carbons.

16. Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow \underset{(1^\circ \text{amine})}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Hence, four moles of NaOH and one mole of Br_2 are used.

17. This problem can be solved by using the concept of effect of steric hindrance, hydration and H-bonding in basic strength of amines. Order of basic strength of aliphatic amine in aqueous solution is as follows (order of K_b)

$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

As we know, $pK_b = -\log K_b$

So, $(CH_3)_2\ddot{N}H$ will have smallest pK_b value. In case of phenyl amine, N is attached to sp^2-hybridised carbon, hence it has highest pK_b and least basic strength.

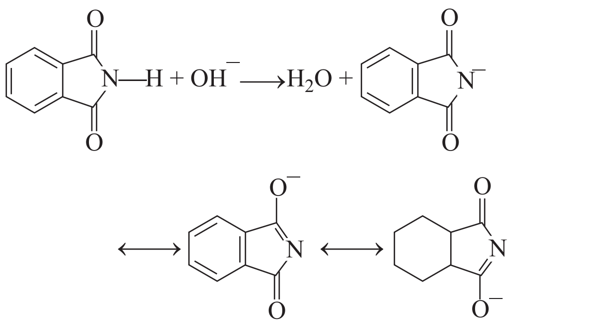
18. This reaction is an example of carbylamine test which includes conversion of amine to isocyanide.

$$\underset{1^\circ \text{ amine}}{R-\ddot{N}H_2} + CHCl_3 \xrightarrow[KOH]{C_2H_5OH} \underset{\text{Alkyl isocyanide}}{R-\overset{+}{N}\equiv\overset{-}{C}:}$$

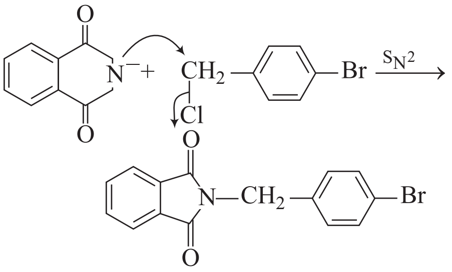
NOTE The mechanism of this reaction included rearrangement of nitrene in which migration of alkyl group from carbon to nitrogen takes place.

19. Methyl isocyanate $CH_3-N=C=O$ (MIC) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

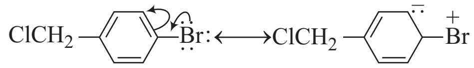
20. It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two α-carbonyls.



The conjugate base formed above act as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exist in three resonating form, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen act as donor as it is better donor than oxygen.



Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



21. $CH_3NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{isocyanide}}{CH_3-\overset{+}{N}\equiv\overset{-}{C}} + KCl + H_2O$

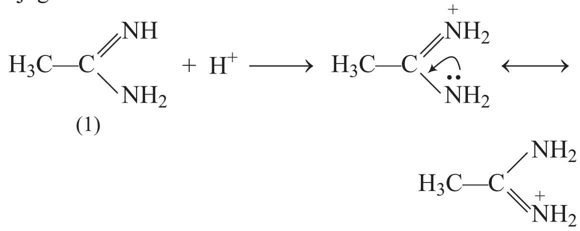
22. $C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{POCl_3} C_6H_5-C\equiv N + H_2O$

$POCl_3$ brings about dehydration of primary amide.

23. 4, (acetamide) is least basic because lone pair of nitrogen is involved in delocalisation.

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H_2$$

'1' is most basic due to formation of resonance stabilised conjugate acid.

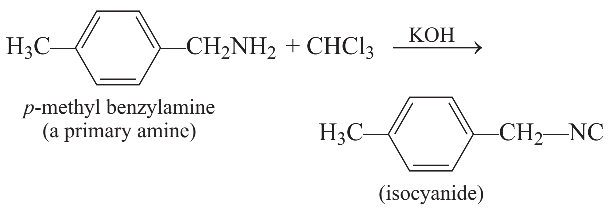


3 (secondary amine) is stronger base than 2 (primary amine).

Hence, overall order of basic strength is :

$$1 > 3 > 2 > 4$$

24.



Carbylamine test is not given by secondary or tertiary amine.

25. $\underset{\substack{\text{anilinium}\\ \text{hydrochloride}}}{C_6H_5\overset{+}{N}H_3Cl^-} + AgNO_3 \longrightarrow C_6H_5\overset{+}{N}H_3NO_3^- + AgCl(s)\downarrow$

No such precipitate of AgCl(s) would be formed with p-chloroaniline.

26. $R-NH_2 + CHCl_3 \xrightarrow{KOH} \underset{\substack{\text{isocyanide}\\ \text{(foul smell)}}}{R-NC}$ 'Carbylamine test'

The above test is characteristic of primary amine and used to distinguish primary amine from other amines.

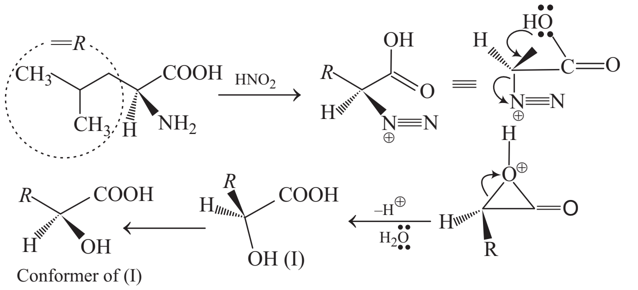
27. $\underset{\text{acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + Br_2 \xrightarrow{NaOH} \underset{\text{methylamine}}{CH_3NH_2}$

(Hofmann's bromamide reaction)

28. A secondary amine, on treatment with aqueous nitrous acid at low temperature produces oily nitrosamine.

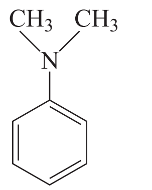
$$(C_2H_5)_2NH + HNO_2 \longrightarrow \underset{\text{nitrosamine}}{(C_2H_5)_2N{-}NO} + H_2O$$

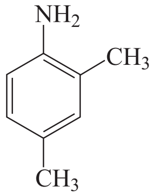
29. Reaction proceeds *via* diazonium salt with neighbouring group participation.

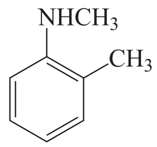


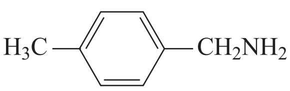
Conformer of (I)

30. Carbylamine test is given by primary amines only.


N,N-dimethylaniline (3°-amine)


2,4-dimethylaniline (1°-amine)


N-methyl-*o*-methylaniline (2°-amine)


p-methyl benzylamine (1°-amine)

31. More : CH_3NH_2 is stronger base than CH_3OH.

32.

	Column I	Column II
(A)	$CH_3CH_2CH_2CN$:	Gives amine with Pd-C/H_2 Gives aldehyde with $SnCl_2$/HCl Gives amide with diisobutyl- aluminium hydride. Gives carboxylic acid on alkaline hydrolysis.
(B)	$CH_3CH_2OCOCH_3$: ester	Reduced to alcohol with Pd - C/H_2 Reduced with diisobutylaluminium hydride into aldehyde. Undergo alkaline hydrolysis.
(C)	$CH_3CH{=}CHCH_2OH$:	Reduced to butanol when treated with Pd-C/H_2.
(D)	$CH_3CH_2CH_2CH_2NH_2$	A primary amine, gives carbylamine test.

33. $CH_3{-}\overset{*}{C}H(NH_2){-}CH(CH_3){-}CH_3$ (X) or $CH_3{-}\overset{*}{C}H(C_2H_5){-}CH_2NH_2$

$$CH_3{-}\overset{*}{C}H(NH_2){-}CH(CH_3){-}CH_3 \xrightarrow[HCl]{NaNO_2} CH_3{-}CH_2{-}C(CH_3)(OH){-}CH_3$$

Y-optically inactive

Above reaction proceeds *via* carbocation intermediate, hence rearrangement takes place.

34. Conjugate acid of dimethylamine is more stable than conjugate base of triethyl amine due to exhaustive H-bonding with water.

35. $$CH_3CH_2NH_2 \xrightarrow[\text{Heat}]{(CH_3CO)_2O} CH_3CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CH_3COOH$$

36. A must be a secondary amine :

$CH_3CH_2NHCH_3$ + benzene sulphonylchloride $\longrightarrow$

$$CH_3CH_2{-}N(CH_3){-}SO_2{-}C_6H_5 \xrightarrow{NaOH} \text{Insoluble}$$

37. Starting compound is a primary amine.

$$R{-}NH_2 + CHCl_3 + KCl \longrightarrow \underset{\text{foul smell}}{R{-}NC}$$

Also, $R{-}NH_2 + HNO_2 \longrightarrow R{-}OH + N_2$

$$\text{Moles of } N_2 = \frac{112}{22500} = 5 \times 10^{-3}$$

$\because$ One mole of N_2 is obtained from 1.0 mole of $R{-}NH_2$, mole of $R{-}NH_2 = 5 \times 10^{-3}$

$\Rightarrow$ 5×10^{-3} mol $R{-}NH_2$ weigh = 0.295 g

$$1 \text{ mole of } R{-}NH_2 \text{ will weigh} = \frac{0.295}{5 \times 10^{-3}} = 59 \text{ g}$$

In $R{-}NH_2$, $-NH_2$ has molar mass = 16

$\Rightarrow$ $R-$ has molar mass = 43

Also, the alcohol $R{-}OH$ gives iodoform test; it must has the following skeleton :

$$R'{-}CH(OH){-}CH_3$$

$\Rightarrow$ $R'-$ has molar mass = 15 (CH_3)

$\Rightarrow$ Original compound is $CH_3{-}CH(CH_3){-}NH_2$

38. Aniline > N-methylaniline < methylamine < dimethylamine.

39. Carbylamine test given only by primary amine.

$$\underset{\text{primary amine}}{CH_3CH_2—NH_2} + CHCl_3 \xrightarrow{KOH} \underset{\text{foul smell}}{CH_3—CH_2—NC}$$

Nitrosamine test is given only by secondary amine.

$$(CH_3CH_2)_2NH + HNO_2 \longrightarrow \underset{\text{oily nitrosamine}}{(CH_3CH_2)_2N—NO}$$

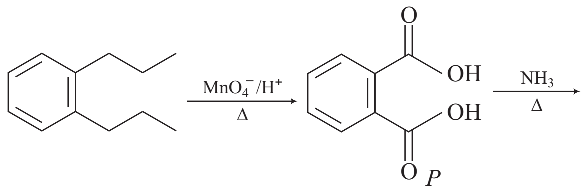
40. (i) $CH_3—\overset{+}{N}(=O)—O^- \longleftrightarrow CH_3—\overset{+}{N}(—O^-)=O \equiv CH_3—\overset{+}{N}(\dot{=}O)_2^{\,-}$

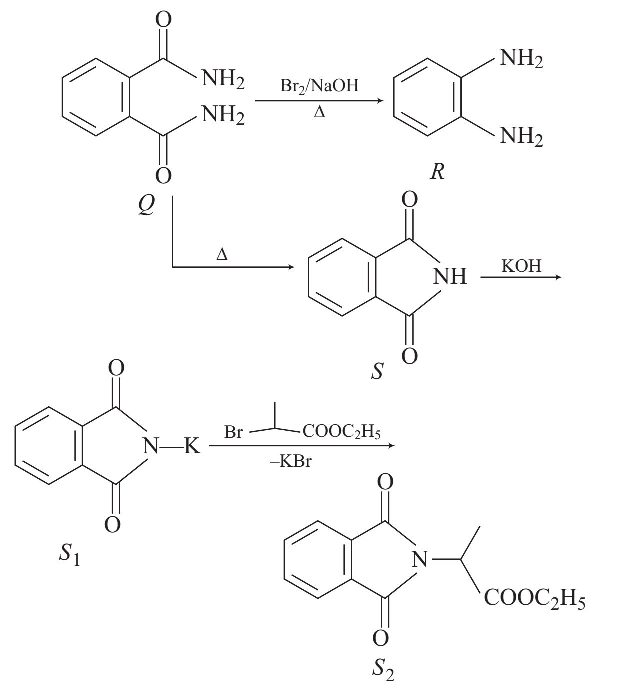
(ii) $CH_3—\overset{+}{N}(=O)—O^- \rightleftharpoons CH_2=\overset{+}{N}(—OH)—O^-$: Tautomerism

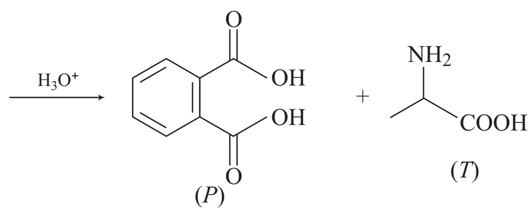
41. $CH_3CH_2Cl \xrightarrow[S_N2]{NaCN} CH_3CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$

42. (a)

43. Explanation







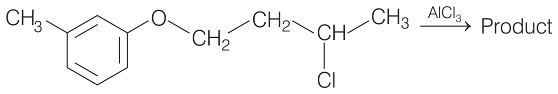
Download Chapter Test
http://tinyurl.com/y6nlww9e *or*

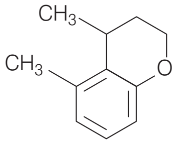
28

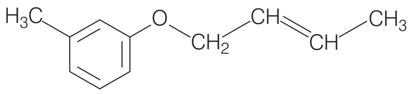
Benzene and Alkyl Benzene

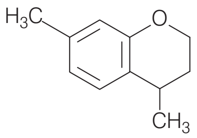
Objective Questions I (Only one correct option)

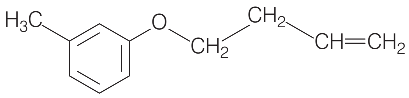
1. The major product obtained in the given reaction is **(2019 Main, 10 April II)**



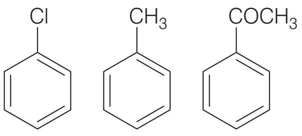
(a) 

(b) 

(c) 

(d) 

2. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is **(2019 Main, 10 April I)**

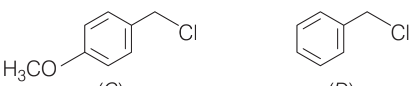


(I) (II) (III)

(a) III < I < II (b) II < I < III
(c) III < II < I (d) I < III < II

3. Increasing order of reactivity of the following compounds for S_N1 substitution is **(2019 Main, 9 April II)**

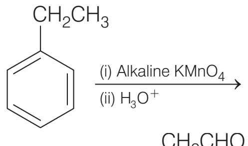
(*A*) (*B*)

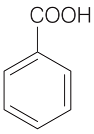
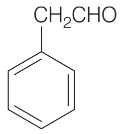


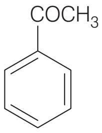
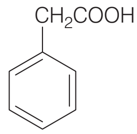
(*C*) (*D*)

(a) (*A*) < (*B*) < (*D*) < (*C*)
(b) (*B*) < (*C*) < (*D*) < (*A*)
(c) (*B*) < (*A*) < (*D*) < (*C*)
(d) (*B*) < (*C*) < (*A*) < (*D*)

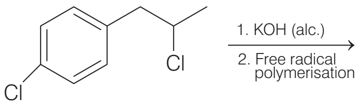
4. The major product of the following reaction is **(2019 Main, 9 April I)**

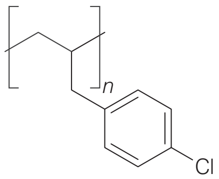
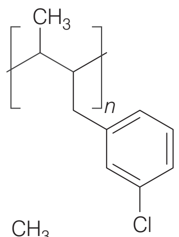


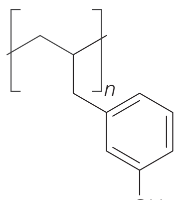
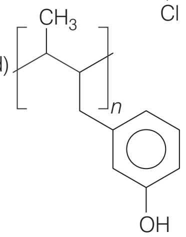
(a)  (b) 

(c)  (d) 

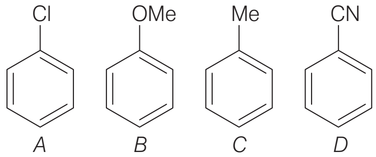
5. The major product of the following reaction is **(2019 Main, 9 April I)**



(a)  (b) 

(c)  (d) 

6. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is **(2019 Main, 9 April I)**

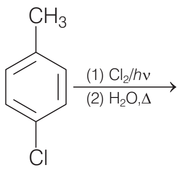


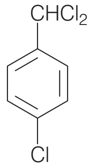
A *B* *C* *D*

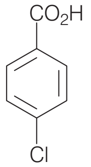
(a) $A < B < C < D$ (b) $B < C < A < D$
(c) $D < A < C < B$ (d) $D < B < A < C$

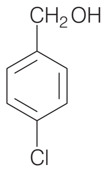
7. Polysubstitutiion is a major drawback in **(2019 Main, 8 April II)**
(a) Friedel-Craft's alkylation
(b) Reimer-Tiemann reaction
(c) Friedel-Craft's acylation
(d) Acetylation of aniline

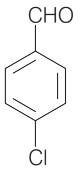
8. The major product of the following reaction is **(2019 Main, 8 April II)**



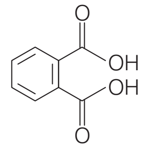
(a) 

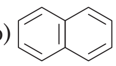
(b) 

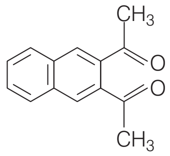
(c) 

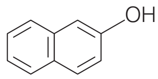
(d) 

9. Among the following four aromatic compounds, which one will have the lowest melting point? **(2019 Main, 12 Jan I)**

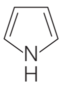
(a) 

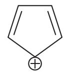
(b) 

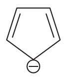
(c) 

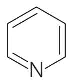
(d) 

10. Which of the following compounds is not aromatic? **(2019 Main, 9 Jan II)**

(a) 

(b) 

(c) 

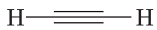
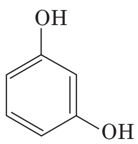
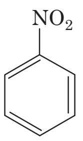
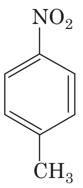
(d) 

11. In the following sequence of reactions **(2015 Main)**

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C\text{, the product C is}$$

(a) C_6H_5COOH (b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

12. Match the four starting materials given in Column I with the corresponding reaction schemes provided in Column II and select the correct answer using the code given below the lists.

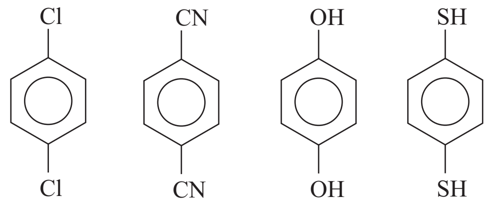
	Column I		Column II
A.		p.	**Scheme I** $? \xrightarrow[\text{(iii) } SOCl_2 \text{ (iv) } NH_3]{\text{(i) } KMnO_4,\, HO^-,\text{ heat (ii) } H^+,\, H_2O} C_7H_6N_2O_3$
B.		q.	**Scheme II** $? \xrightarrow[\text{(iv) } HNO_3 \text{ (v) Dil. } H_2SO_4,\text{ heat (vi) } HO^-]{\text{(i) Sn/HCl (ii) } CH_3COCl \text{ (iii) Conc. } H_2SO_4} C_6H_6N_2O_2$
C.		r.	**Scheme III** $? \xrightarrow[\text{(iii) } H_2S\,.\,NH_3 \text{ (iv) } NaNO_2,\, H_2SO_4 \text{ (v) hydrolysis}]{\text{(i) Red hot iron, 873 K (ii) fuming } HNO_3,\, H_2SO_4,\text{ heat}} C_6H_5NO_3$
D.		s.	**Scheme IV** $? \xrightarrow[\text{(ii) Conc. } HNO_3,\text{ conc. } H_2SO_4 \text{ (iii) Dil. } H_2SO_4,\text{ heat}]{\text{(i) Conc. } H_2SO_4, 60°C} C_6H_5NO_4$

Codes

	A	B	C	D
(a)	p	s	q	r
(b)	r	p	s	q
(c)	r	s	q	p
(d)	s	p	r	q

(2014 Adv.)

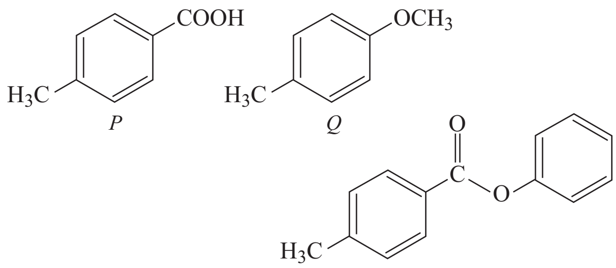
13. For which of the following molecule significant $\mu \neq 0$?



I II III IV

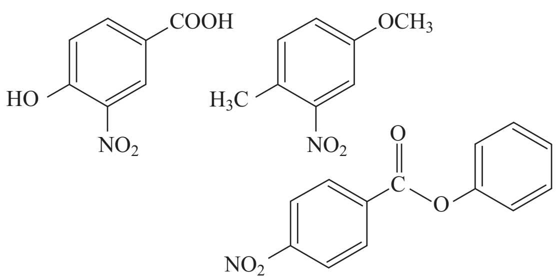
(a) Only I (b) I and II **(2014 Main)**
(c) Only III (d) III and IV

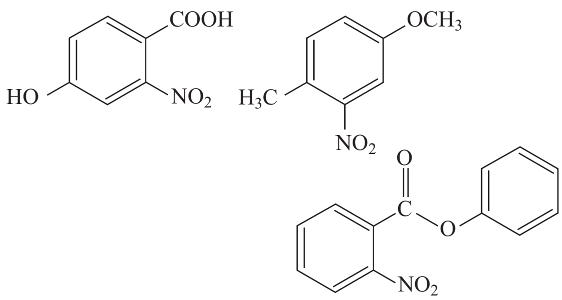
14. The compounds *P*, *Q* and *S*

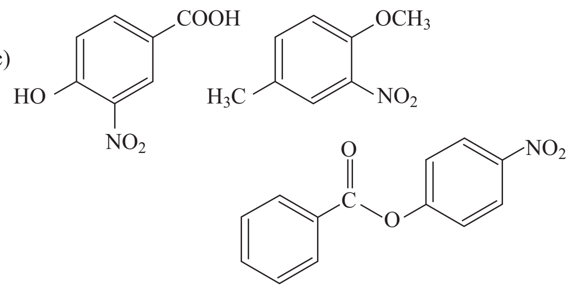


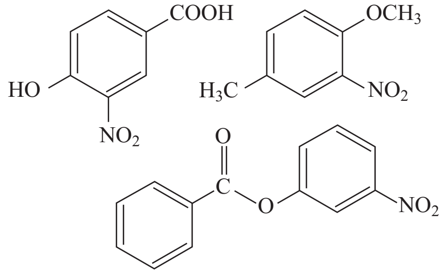
P *Q* *S*

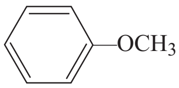
were separately subjected to nitration using HNO_3 / H_2SO_4 mixture. The major product formed in each case respectively, is **(2010)**

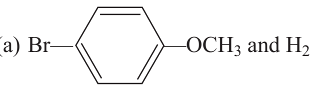
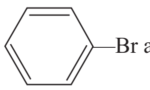
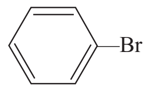
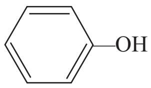
(a) 

(b) 

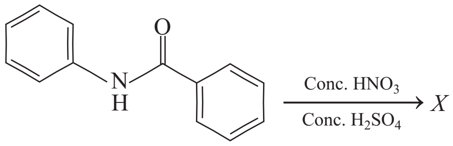
(c) 

(d) 

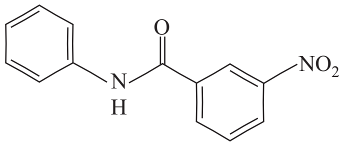
15. In the reaction,  $\xrightarrow{HBr}$ the products are, **(2010)**

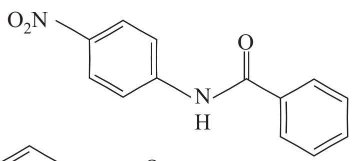
(a)  and H_2
(b)  and CH_3Br
(c)  and CH_3OH
(d)  and CH_3Br

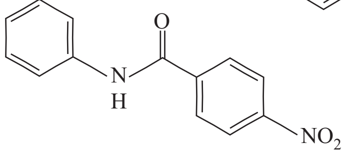
16. In the following reaction,

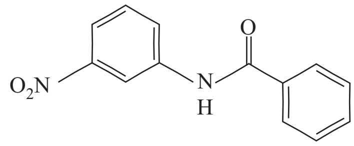


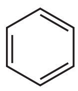
The product *X* is **(2007, 3M)**

(a) 

(b) 

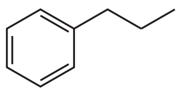
(c) 

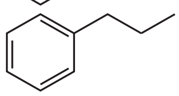
(d) 

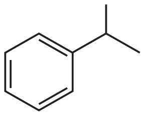
17.  $+ Cl-CH_2CH_2-CH_3 \xrightarrow{AlCl_3}$

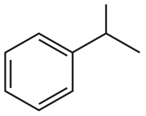
$P \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2/\Delta} Q +$ Phenol

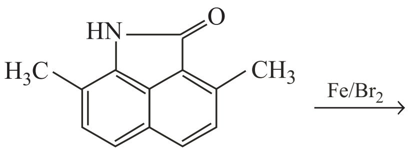
P and *Q* are respectively **(2006, 5M)**

(a)  + CH_3CH_2CHO

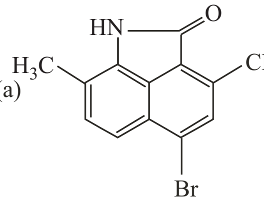
(b)  + CH_3COCH_3

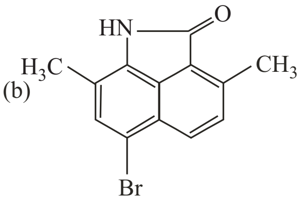
(c)  $+ \ CH_3COCH_3$

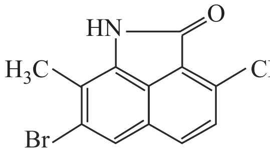
(d)  $+ \ CH_3CH_2CHO$

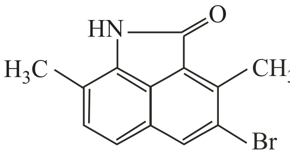
18. 

product on monobromination of this compound is **(2004, 1M)**

(a) 

(b) 

(c) 

(d) 

19. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds Benzene (1), Toluene (2), Chlorobenzene (3) and Nitrobenzene (4) **(2002)**

(a) $1 > 2 > 3 > 4$ (b) $4 > 3 > 2 > 1$
(c) $2 > 1 > 3 > 4$ (d) $2 > 3 > 1 > 4$

20. A solution of (+) -2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of **(1999, 2M)**

(a) carbanion (b) carbene
(c) free-radical (d) carbocation

21. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with **(1998, 2M)**

(a) SO_2Cl_2 (b) $SOCl_2$ (c) Cl_2 (d) NaOCl

22. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives **(1990, 1M)**

(a) *o*-cresol (b) *p*-cresol
(c) 2, 4-dihydroxy toluene (d) benzoic acid

23. The reaction of toluene with chlorine in the presence of ferric chloride ($FeCl_3$) gives predominantly **(1986, 1M)**

(a) benzoyl chloride (b) *m*-chlorotoluene
(c) benzyl chloride (d) *o*- and *p*-chlorotoluene

24. The compound that is most reactive towards electrophilic substitution is **(1985, 1M)**

(a) toluene (b) benzene
(c) benzoic acid (d) nitrobenzene

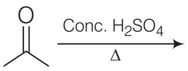
25. Among the following, the compound that can be most readily sulphonated is **(1982)**

(a) benzene (b) nitrobenzene
(c) toluene (d) chlorobenzene

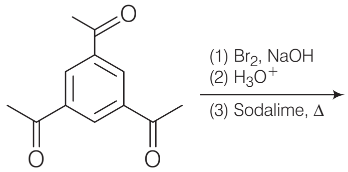
Objective Questions II

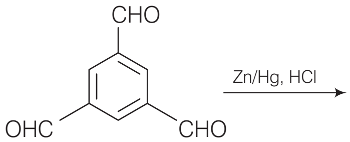
(One or more than one correct option)

26. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) **(2018 Adv.)**

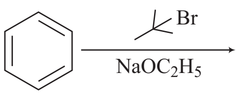
(a) 

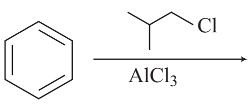
(b) 

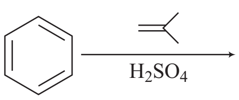
(c) 

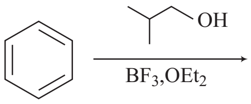
(d) 

27. Among the following reactions(s), which gives(give) *tert*-butyl benzene as the major product? **(2016 Adv.)**

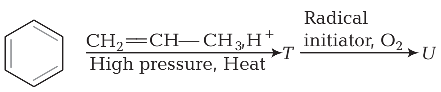
(a) 

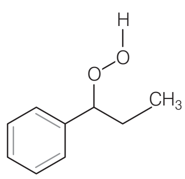
(b) 

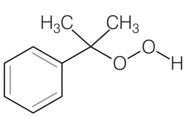
(c) 

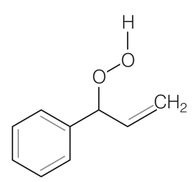
(d) 

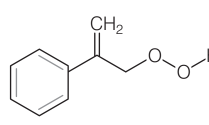
28. The major product *U* in the following reaction is **(2015 Adv.)**



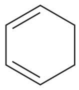
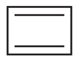
(a) 

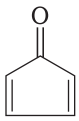
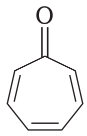
(b) 

(c) 

(d) 

29. Which of the following molecules, in pure form, is/are unstable at room temperature? **(2012)**

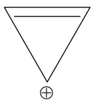
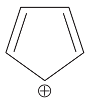
(a)  (b) 

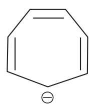
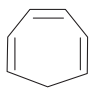
(c)  (d) 

30. An aromatic molecule will **(1999, 3M)**

(a) have $4n\,\pi$-electrons
(b) have $(4n+2)\pi$-electrons
(c) be planar
(d) be cyclic

31. Which compound(s) out of the following is/are not aromatic? **(2019 Main, 11 Jan I)**

(a)  (b) 

(c)  (d) 

32. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the CH_3 group **(1999, 3M)**

(a) is *para*-directing
(b) is *meta*-directing
(c) activates the ring by hyperconjugation
(d) deactivates the ring

33. A new carbon–carbon bond formation is possible in **(1998)**

(a) Cannizzaro's reaction (b) Friedel-Craft's alkylation
(c) Clemmensen reduction (d) Reimer-Tiemann reaction

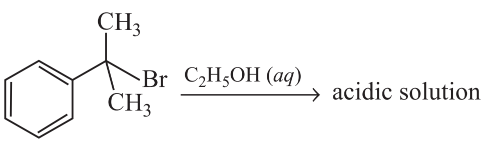
True or False

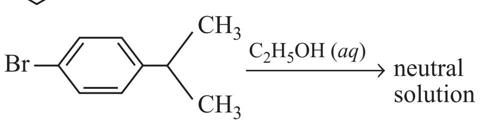
34. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta*-position. **(1987, 1M)**

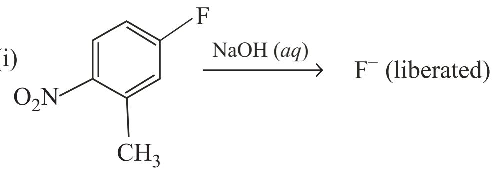
35. In benzene, carbon uses all the three *p*-orbitals for hybridisation. **(1987, 1M)**

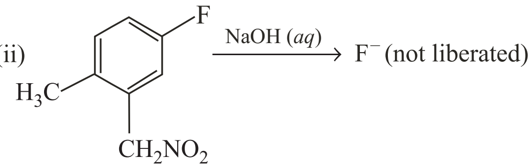
Subjective Questions

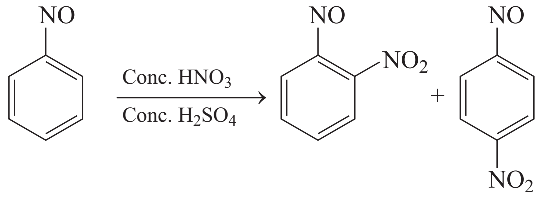
36. Explain the followings :

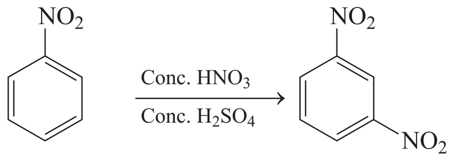
(a) (i) 

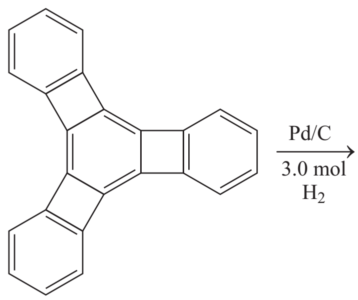
(ii) 

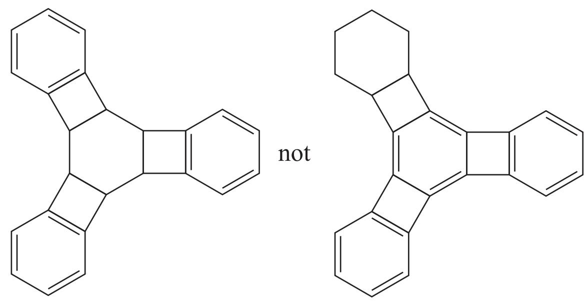
(b) (i) 

(ii) 

(c) (i) 

(ii) 

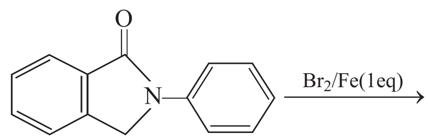
(d) 



(2005)

37. 7-bromo-1, 3, 5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1,3-cyclopentadiene doesn't ionise even in presence of $Ag^+(aq)$. Explain. **(2004)**

38. What would be the major product in the following reaction? **(2000, Main, 1M)**



39. Give reasons for the following :

(i) *tert*-butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$.

(ii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond. **(2000)**

40. Show the steps to carry out the following transformations.

(i) Ethylbenzene $\rightarrow$ benzene

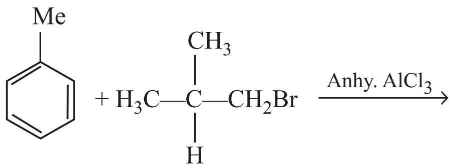
(ii) Ethylbenzene $\rightarrow$ 2-phenylpropionic acid

41. Write the structures of the products.

$$CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$$ **(1998, 2M)**

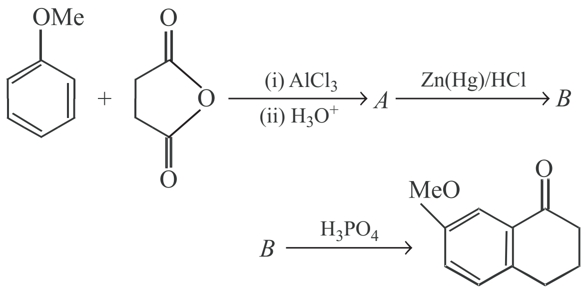
42. Give reasons for the following in one or two sentences "Nitrobenzene does not undergo Friedel-Craft's alkylation." **(1998, 2M)**

43. Complete the following, giving the structures of the principal organic products. **(1997)**

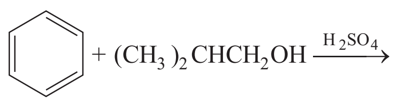


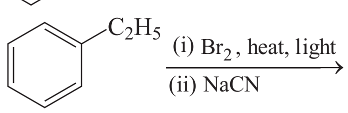
44. Toluene reacts with bromine in the presence of the light to give benzyl bromide, while in presence of $FeBr_3$ it gives *p*-bromotoluene. Give explanation for the above observation. **(1996)**

45. Predict the structures of the intermediates/products in the following reaction sequences **(1996)**



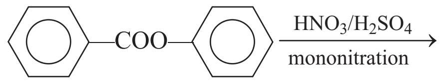
46. Predict the major product in the following reactions **(1994)**

(i) 

(ii) 

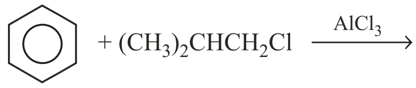
47. Give reason for the following 'In acylium ion the structure $R—C\equiv O^+$ is more stable than $R—C^+=O$' **(1994, 1M)**

48. Identify the major product in the following reactions :

(i) 

(ii) $C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$ **(1993, 2M)**

49. Write the structure of the major organic product expected from the following reaction



(1992, 1M)

50. Give reasons in two or three sentences only for the following:

Phenyl group is known to exert negative inductive effect, but each phenyl ring in biphenyl ($C_6H_5—C_6H_5$) is more reactive than benzene towards electrophilic substitution. **(1992, 1M)**

51. Arrange the following in increasing order of reactivity towards sulphonation with fuming sulphuric acid.

Benzene, toluene, methoxy benzene, chlorobenzene. **(1988, 1M)**

52. Answer the following with suitable equation wherever necessary

(i) How can you prepare benzene from lime ?

(ii) How will you convert toluene to *m*-nitrobenzoic acid ? **(1987, 2M)**

53. Write down the main product of the following reaction

$$\text{Benzene} \xrightarrow{CH_3CH_2COCl/AlCl_3}$$ **(1985, 1M)**

54. How many sigma and pi-bonds are present in a benzene molecule ? **(1985, 1M)**

55. Write down the reaction involved in the preparation of following using the reagents indicated against in parenthesis.

"Ethyl benzene from benzene."

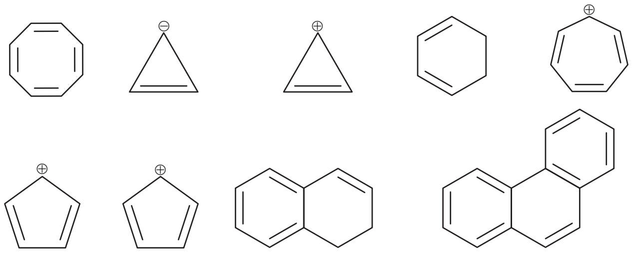
$[C_2H_5OH, PCl_5, \text{anhyd. } AlCl_3]$ **(1984, 2M)**

56. Show with balanced equation what happens when the '*p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH'. **(1984, 1M)**

57. Give reasons for the following in one or two sentences : 'Although benzene is highly unsaturated, normally it does not undergo addition reaction.' **(1983, 1M)**

Integer Type Questions

58. Among the following, the number of aromatic compound(s) is

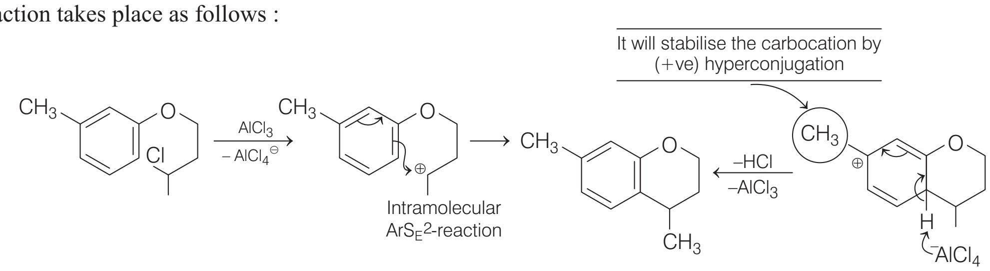


Answers

1. (c)	**2.** (a)	**3.** (c)	**4.** (a)	**21.** (a)	**22.** (d)	**23.** (d)	**24.** (a)
5. (a)	**6.** (c)	**7.** (a)	**8.** (d)	**25.** (c)	**26.** (a,b,d)	**27.** (b,c,d)	**28.** (b)
9. (b)	**10.** (b)	**11.** (d)	**12.** (c)	**29.** (b,c)	**30.** (b,c,d)	**31.** (b,c,d)	**32.** (a,c)
13. (d)	**14.** (c)	**15.** (d)	**16.** (b)	**33.** (b,d)	**34.** False	**35.** False	**54.** (12σ, 3π)
17. (c)	**18.** (b)	**19.** (c)	**20.** (d)	**58.** (5)			

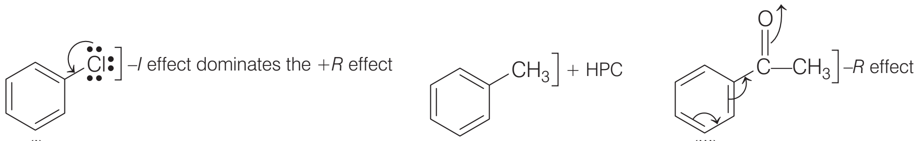
Hints & Solutions

1. The given reaction takes place as follows :



2. **Key Idea** In electrophilic aromatic substitution (Ar S_E 2) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction. Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their $+R/+M$ and hyperconjugative (HPC) effects. Now, let us consider the given substrate.

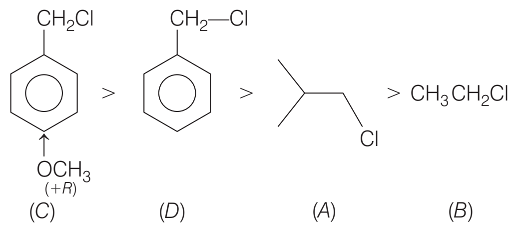


(I) (II) (III)

As $-R$ effect is more powerful than $-I$ effect, the order of their reactivity, towards an electrophile will be

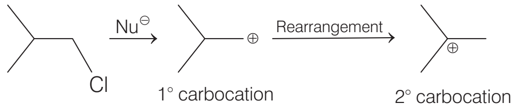
$$\underset{(-R)}{\text{III}} < \underset{(-I>+R)}{\text{I}} < \underset{(+\text{ HPC})}{\text{II}}$$

3. Reactivity of substitution nucleophilic unimolecular (S_N1) reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide and faster will be the rate of reaction. So, the correct order of (S_N1) reactivity is



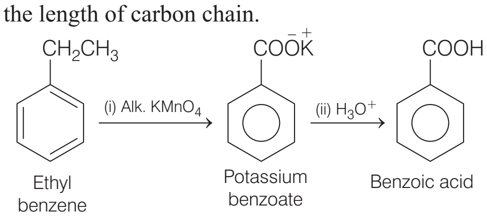
(C) (D) (A) (B)

In compound C, the carbocation formed is stabilised by activating group ($—OCH_3$). Compound D forms benzyl carbocation ($C_6H_5—\overset{+}{C}H_2$) that is stabilised by resonance. Compound A produces a primary carbocation that further rearranges itself to secondary carbocation.

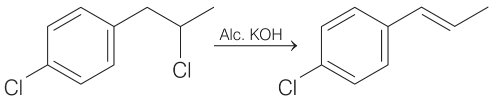


Compound B produces primary carbocation which is least stable among all the given options.

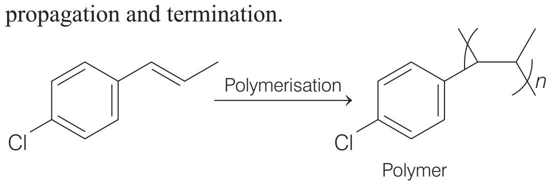
4. The major product of the given reaction is benzoic acid (C_6H_5COOH). On vigorous oxidation of alkyl benzene with acidic or alkaline $KMnO_4$, aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.



5. In presence of alc. KOH, the given halide undergoes elimination reaction



The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.

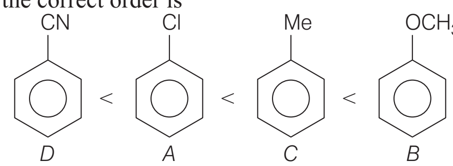


6. Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong –*I* effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene due to resonance. Therefore, activates the benzene ring for the attack by an electrophile. Hence, called as activating groups.

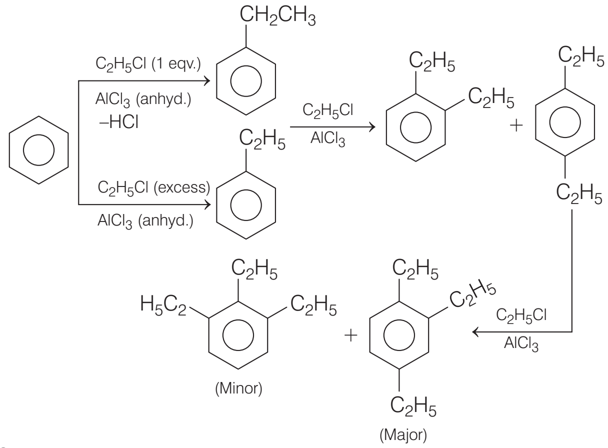
In given options, Activating groups are $\underset{(+I,+R)}{—CH_3} < \underset{\text{Strong }+R\text{ effect}}{—\ddot{O}CH_3}$

Deactivating groups are $\underset{\text{Strong }-I\text{ effect}}{—CN} > \underset{(-I>-R)}{—Cl}$

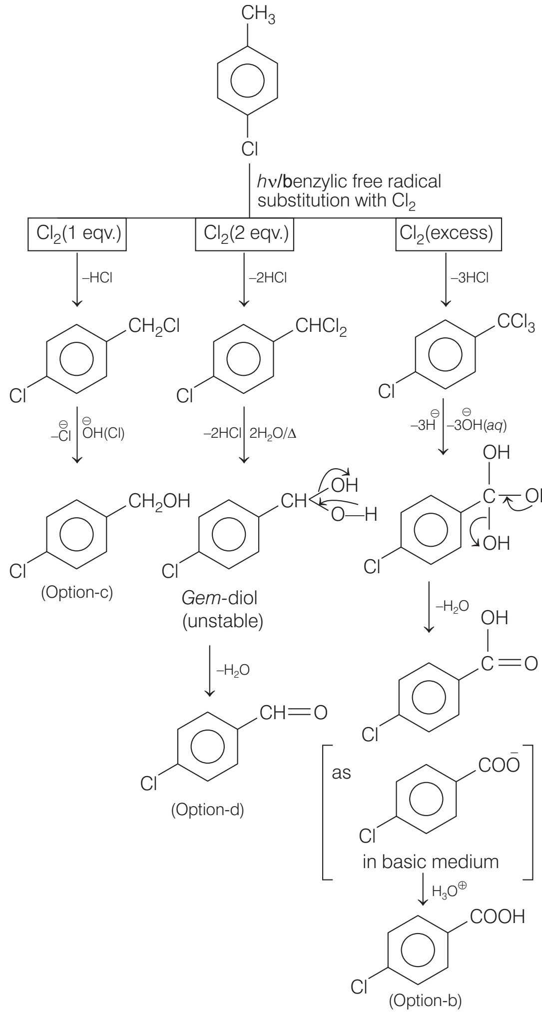
So, the correct order is



7. Through aromatic electrophilic substitution mechanism (ArS_E2) when mono-alkylation (Friedel-Craft's reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards ArS_E2) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



8.



So, considering the second reaction condition, Cl^-, H_2O, Δ in the statement of the question, the correct answer is option (d).

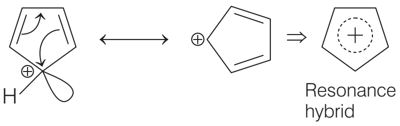
9. Melting point of a compound depends on size and force of attraction between the molecules. Compound (c) has largest size and also possess weak intermolecular association due to dipole - dipole interactions.

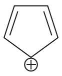
Compound (a) is a dicarboxylic acid and possess high melting point due to intermolecular hydrogen bonding.

As a result, it exist as associated molecule. Compound (d) is an alcohol and possess intermolecular H-bonding. No interactions are present in hydrocarbon (naphthalene) compound (b).

Hence, melting point is lowest for naphthalene ($\simeq 80°C$), i.e. compound (b).

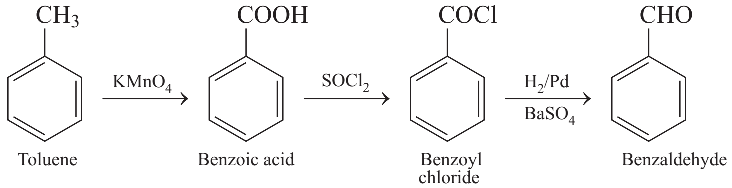
10. Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:



Hence,  is anti-aromatic does not follow

Huckel's rule as it has conjugated 4π-electron ($4n\pi$, $n = 1$) system. Rest of the species are aromatic as each of them belongs to 6π-electron $[(4n+2)\pi,\ n = 1]$ system.

11.



12. **PLAN** This problem can be solved by using the various concepts synthesis of benzene, electrophilic substitution reaction and directive influence of various substituents, including oxidation and reduction.

$\Rightarrow$ —OH and —NH_2 are *o/p*-directing groups.

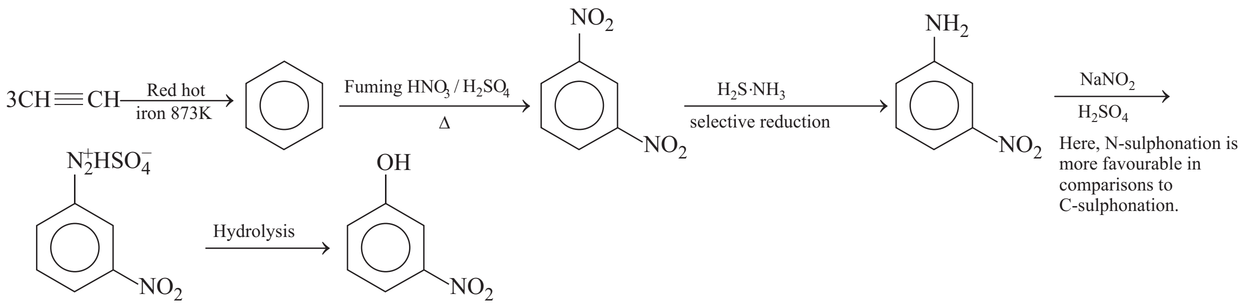
$\Rightarrow$ N-acetylation is more favourable than C-acylation.

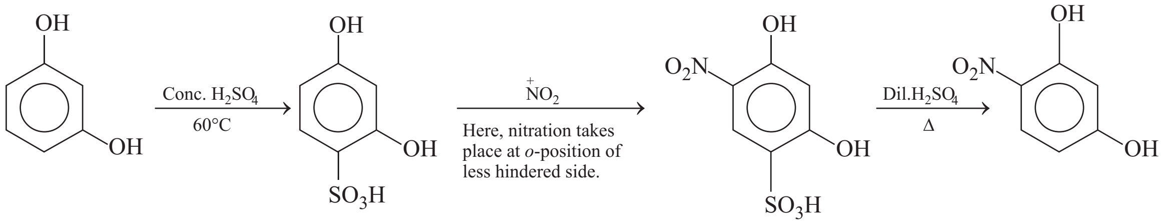
$\Rightarrow$ N-sulphonation is more favourable than C-sulphonation.

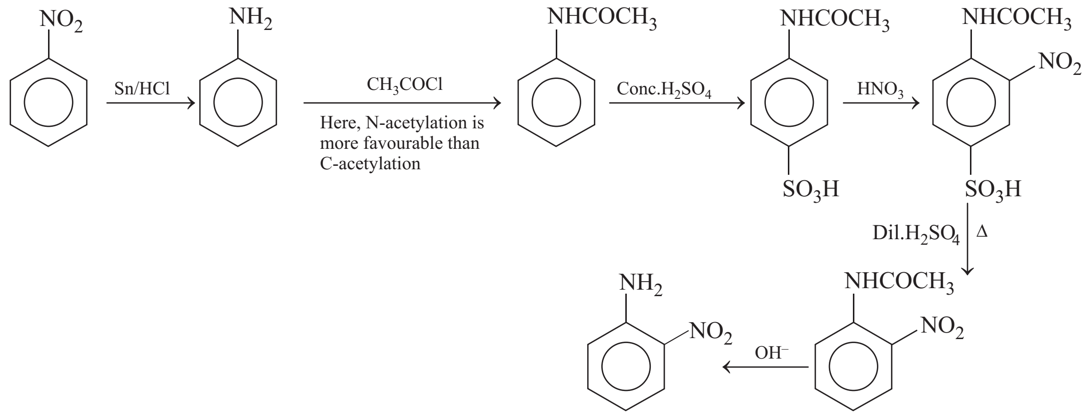
$\Rightarrow$ NO_2 is a meta-directing group.

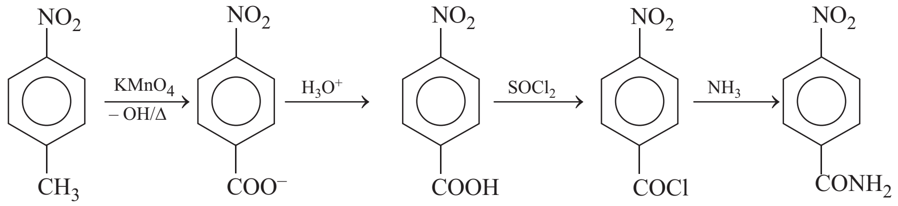
$\Rightarrow$ $H_2S\cdot NH_3$ reduces only one NO_2 group selectively in the presence of two NO_2 groups.

Using above concepts the correct sequence of reaction can be written as

A. 

B. 

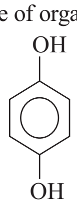
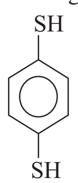
C. 

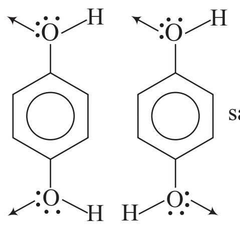
D. 

Above reaction proceeds through oxidation, chlorination and amide formation sequentially.

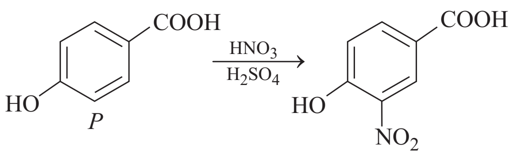
$\therefore$ A $\rightarrow$ r, B $\rightarrow$ s, C $\rightarrow$ q, D $\rightarrow$ p Hence, the correct choice is (c).

13. Draw the structure of organic compounds indicating net dipole moment which includes lone pair and bond angle also.

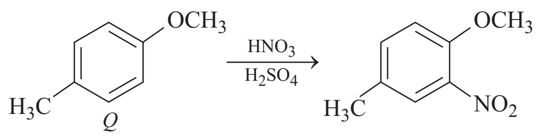
In the quinol  and thioquinol 

 same as in thioquinol.

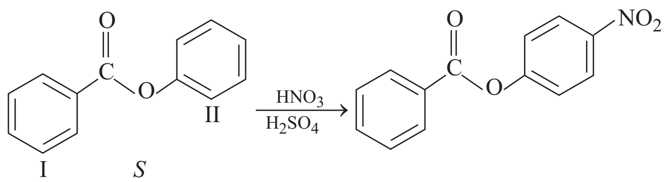
— OH groups and —SH groups do not cancel their dipole moment as they exist in different confirmation.

14. 

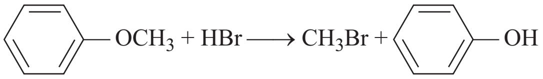
— OH is activating while — COOH is deactivating group in S_EAr reaction. Therefore, electrophile attack to *ortho* of the activating — OH group.



Both — OCH_3 and — CH_3 are activating *ortho/para* directing groups but — OCH_3 is stronger activator, electrophile attack to *ortho* of — OCH_3.

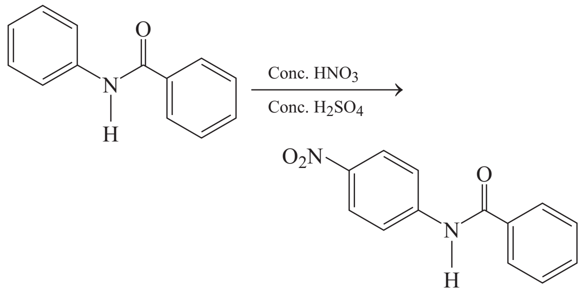


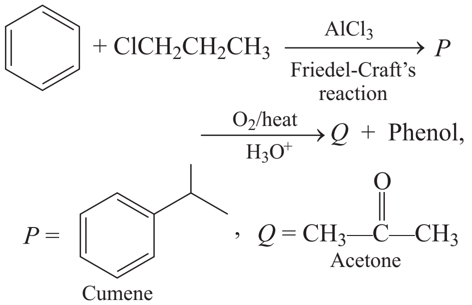
Ring II is activated while ring I is deactivated in S_EAr reaction. Therefore, electrophile attack at *para* to ring-II, the less hindered position.

15. 

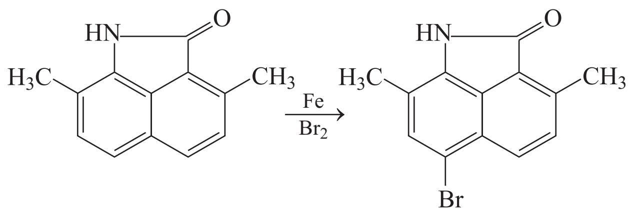
—OH of phenol is not further substituted by bromide due to resonance with the ring.

16. Ring attached to nitrogen is activated while ring attached to C=O is deactivated. Also, electrophilic substitution occur predominantly at *para* position of the activated ring due to immense steric hindrance at *ortho* position.



17. 

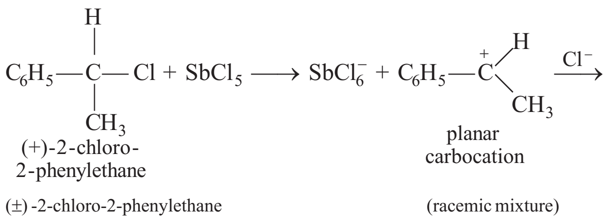
18. Ring attached to nitrogen is activated by electron donating resonance effect while ring attached to carbonyl group is deactivated by electron withdrawing resonance effect :



19. Both chloro and nitro groups are deactivating in electrophilic aromatic substitution reaction. Also nitro group is stronger deactivating group. Methyl group is activator in electrophilic aromatic substitution.

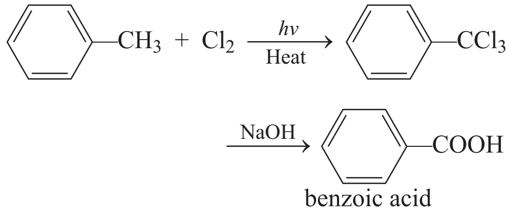
Hence, overall order of reactivity is :

nitrobenzene < chlorobenzene < benzene < toluene

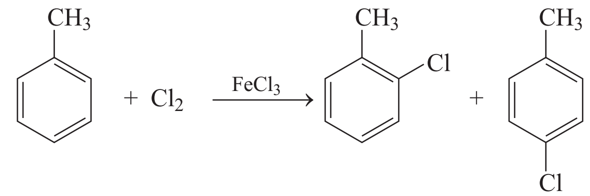
20. 

21. SO_2Cl_2 brings about free-radical chlorination at —CH_3 group.

22. Free radical chlorination occur at —CH_3.



23. The methyl group in toluene is *ortho/para* directing activating group :

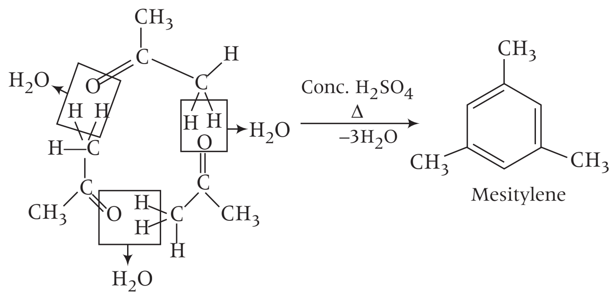


24. Toluene is most reactive among these. Nitro and carboxylic groups are deactivating in aromatic electrophilic substitution reaction.

25. Toluene is most readily sulphonated among these because methyl group is electron donating (+ *I* effect), activate benzene ring for electrophilic aromatic substitution.

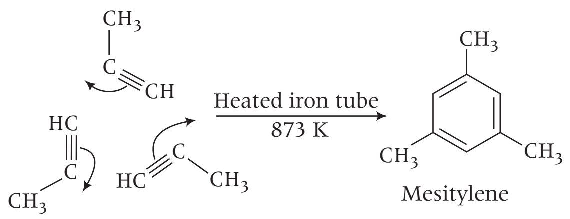
26. Reaction shown in option (a) is aldol condensation in the presence of conc. H_2SO_4 at high temperature.

In summerised way the formation of mesitylene through this can be visualised as



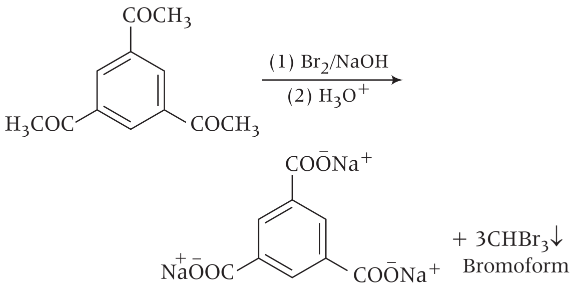
Reaction given in option (b) is simple polymerisation (trimerisation) reaction of alkyne i.e.,

Me—≡—H or $CH_3—C≡CH$ when passed through heated iron tube at 873K then mesitylene is formed as

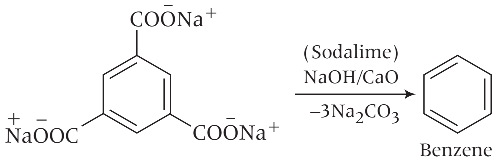


This reaction is also called aromatisation.

(1) and (2) reactions of option (c) combined to give haloform reaction while (3) reaction given in this option is decarboxylation reaction i.e.,



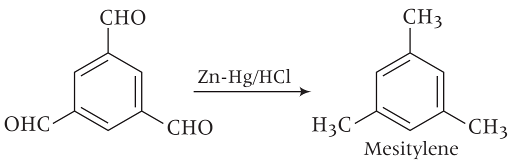
The above product of haloform reaction on decarboxylation gives benzene as



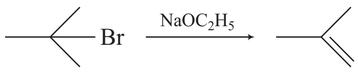
The reaction given in option (d) is Clemmensen reduction i.e.,

$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

Hence, the final product of this reaction is also mesitylene which can be seen as

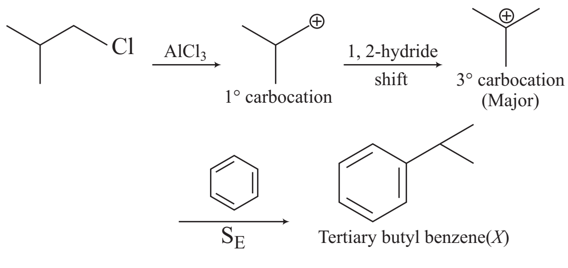


27. (a)

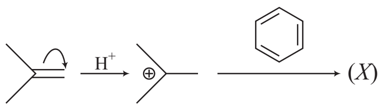


$C_2H_5O^-$ (a strong nucleophile) causes E1 reaction to form isobutene as the major product.

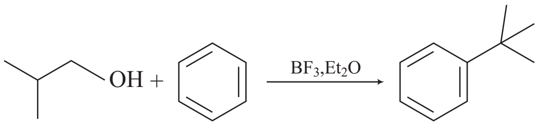
(b)



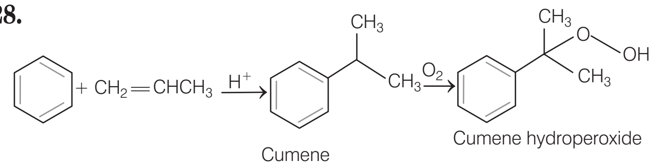
(c)



(d)

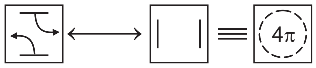


28.

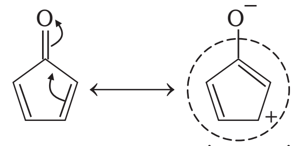


Cumene hydroperoxide formed above is an intermediate in the synthesis of phenol.

29. According to Huckel rule, the compounds which have $4n$ ($n = 0, 1, 2, 3…$) delocalised π-electrons in a close-loop are anti-aromatic and characteristically unstable. Compound *B* satisfy the criteria of anti-aromaticity as :



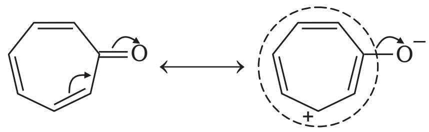
Compound *C* is anti-aromatic in its resonance form :



anti-aromatic

Compound *A* has 4π-electrons which are also delocalised but do not constitute close loop, hence non-aromatic.

Compound *D* is aromatic, characteristically stable.



Tropyllium ion, aromatic

Order of stability Aromatic > Non-aromatic > Anti-aromatic

30. Aromatic molecule must.

(b) have $(4n + 2)\pi$ electrons. (c) be planar.

(d) be cyclic.

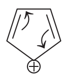
31. A compound is considered to be aromatic, if it follows three rules:

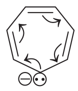
(a) Must be cyclic and planar.

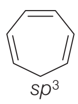
(b) Must have conjugated system in it.

(c) It must follow Huckel rule which states that number of π-electrons = $(4n + 2)$

(A)  $\Rightarrow$ 2π-e^- system $[(4n + 2)\pi, n = 0] \Rightarrow$ Aromatic

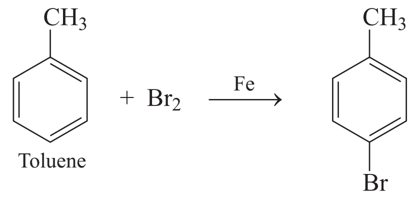
(B)  $\Rightarrow$ 4π-e^- system $[4n\pi, n = 1] \Rightarrow$ Anti-aromatic

(C)  $\Rightarrow$ 8π-e^- system $[4n\pi, n = 2] \Rightarrow$ Anti-aromatic

(D)  $\Rightarrow$ The sp^3-carbon does not support conjugation and also devoids planarity.

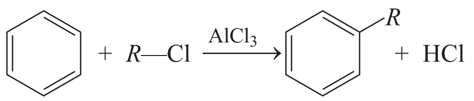
$\Rightarrow$ Non-aromatic

32.

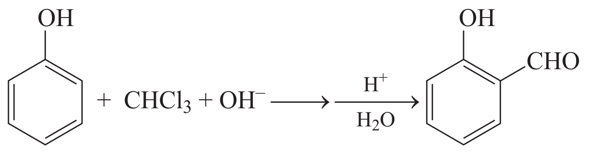


— CH_3 in toluene is *para* directing group.It activates the ring by both inductive and hyperconjugation effect.

33. In both Friedel-Craft's reaction and Reimer-Tiemann reaction, new carbon-carbon bond is formed :



Friedel-Craft's reaction

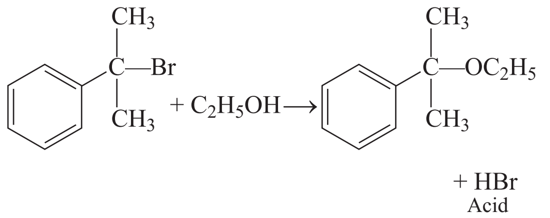


Reimer-Tiemann reaction

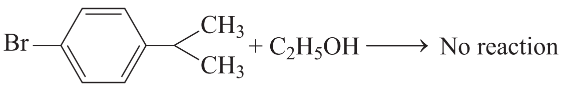
34. An electron donating substituent in benzene orient *ortho/para* substitution.

35. In benzene, carbons are sp^2-hybridised only, hence only two *p*-orbitals are involved in hybridisation.

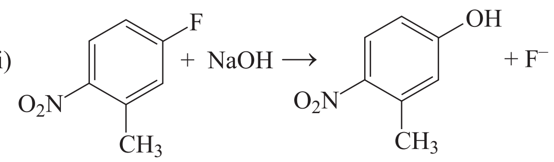
36. (a) (i)



(ii)

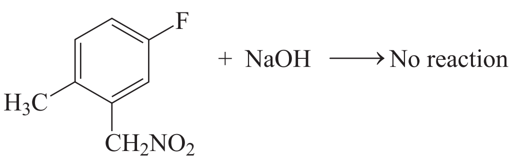


(b) (i)



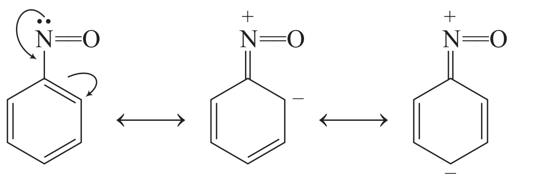
Nitro group from *para* position activate aromatic nucleophilic substitution.

(ii)



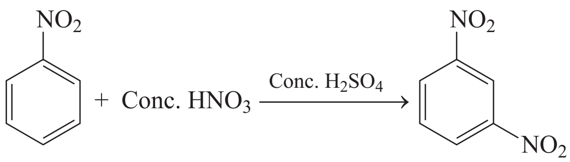
—NO_2 is not in resonance with benzene ring, does not activate the aromatic nucleophilic substitution reaction, hence fluoride is not formed.

(c) (i)



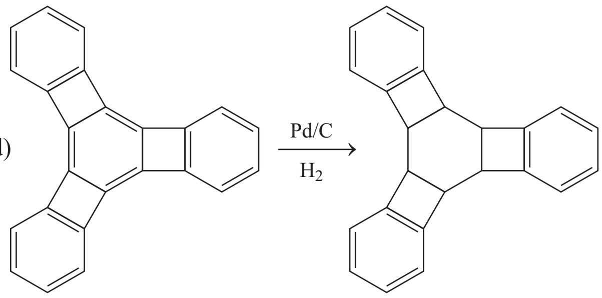
Hence, —NO is *ortho/para* directing although deactivating group. Therefore, *ortho/para* nitro derivatives are formed on treatment with mixed acid.

(ii)



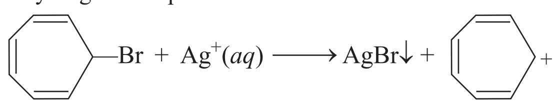
Nitro group is *meta* directing as well as strongly deactivating.

(d)



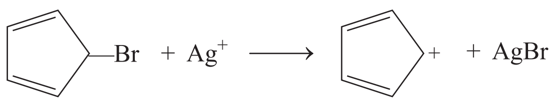
In the above hydrogenation reaction, the anti-aromatic character of three cyclobutadiene rings are relieved that provide stability to the hydrogenation product.

37.



7-bromo-1,3,5-cycloheptatriene

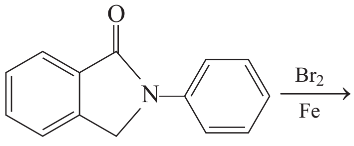
Tropylium ion (aromatic, stable)



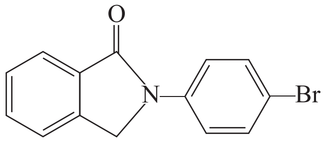
5-bromo-1,3-cyclopentadiene

anti-aromatic (unstable)

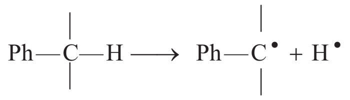
38.



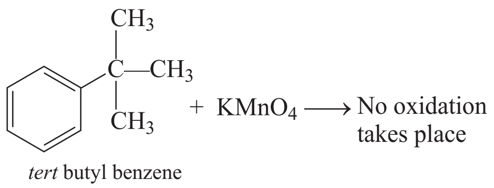
deactivated activated



39. (i) Oxidation of side-chain alkyl group of benzene occur through free radical mechanism and it initiates at $\alpha-$C as.

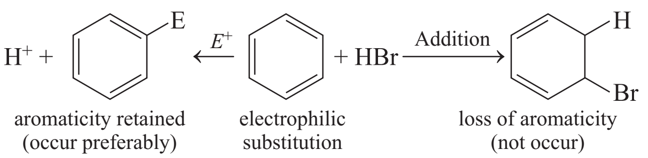


In tertiary butyl benzene, there is no $\alpha-$H, required to initiate free radical oxidation reaction, hence not oxidised with $KMnO_4$.

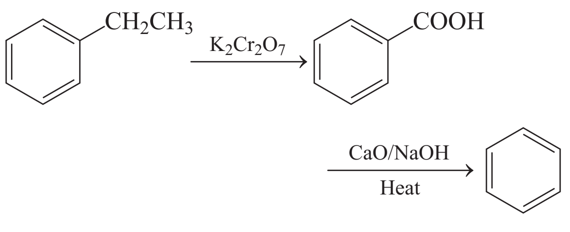


tert butyl benzene
(no α-H)

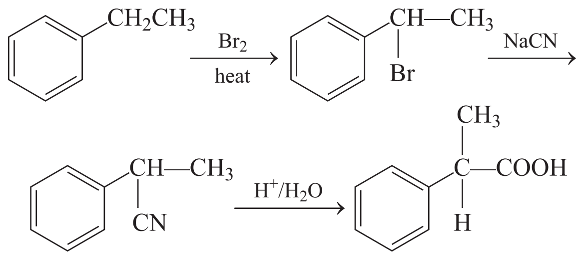
(ii) Pi-electrons of double bonds are involved in aromatic delocalisation (aromaticity), hence electrophilic addition do not occur as it would destroy aromatic stability. However, electrophilic substitution do not destroy aromaticity.



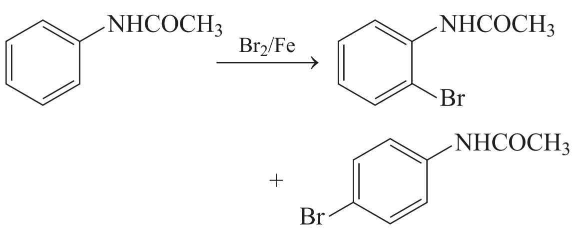
40. (i)



(ii)



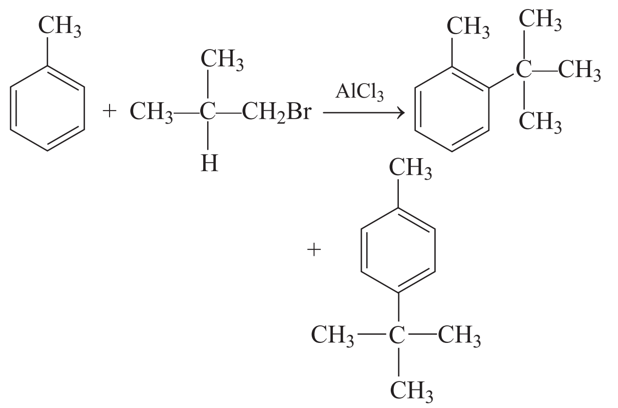
41.



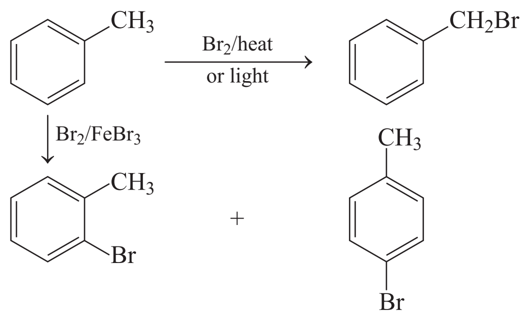
$NHCOCH_3$ is *ortho/para* directing although deactivating group. Therefore, *Ortho/pare* bromoderivatives are fomed or treatment.

42. Nitro group is a very strong deactivating group, the very slow Friedel-Craft's reaction does not takes place in presence of nitro group.

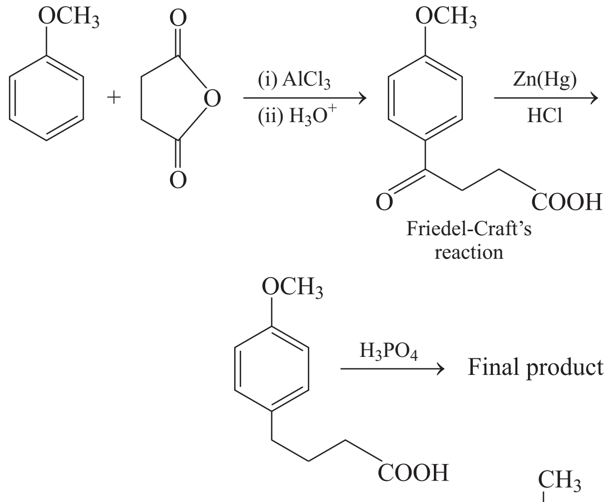
43.



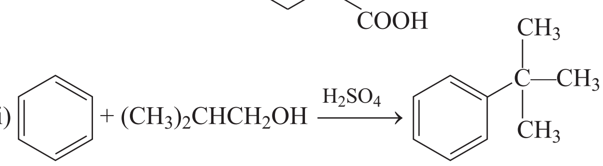
44. In presence of light, free radical reaction takes place at —CH_3 group while in presence of $FeBr_3$, electrophilic substitution occur in the ring.



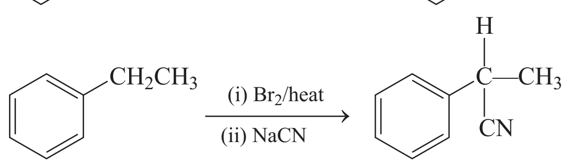
45.



46. (i)



(ii)

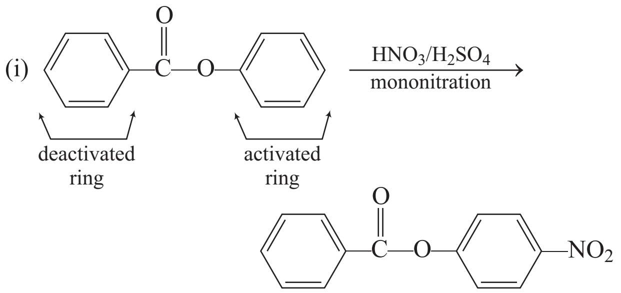


47. $R—C\equiv\overset{+}{O} \longleftrightarrow R—\overset{+}{C}=O$
I II

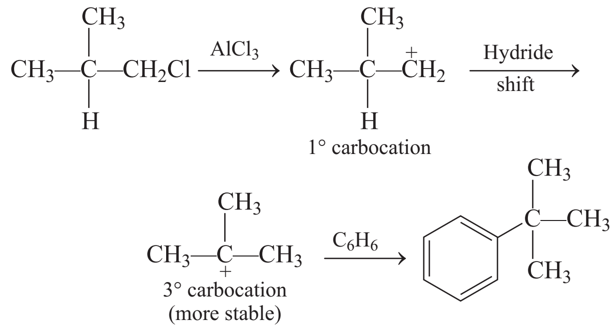
I is more stable resonance structure of acylium ion than II on the following grounds.

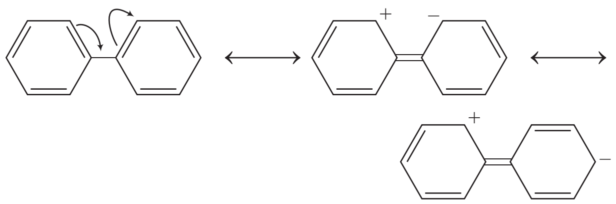
It has more covalent bonds.

It has complete octet of both carbon and oxygen.

48. (i) 

(ii) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + Mg(OOCC_6H_5)I$

49. 

50. 

The above resonance activate an aromatic ring for electrophilic substitution reaction.

51. Both $—CH_3$ and $—OCH_3$ are activating groups but chloro is deactivating group in electrophilic aromatic substitution reaction.

Also $—OCH_3$ activate more than $—CH_3$ due to resonance effect by the former group. Therefore, the overall order of reactivity is:

Chlorobenzene < benzene < toluene < methoxy benzene

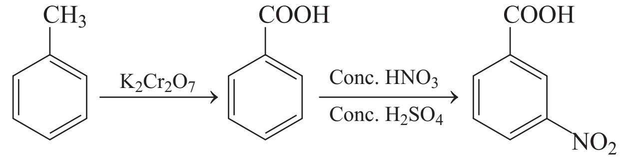
52. (i) Lime is heated with coke at high temperature and then, hydrolysed to form acetylene. This acetylene on passing red hot tube polymerises to form benzene :

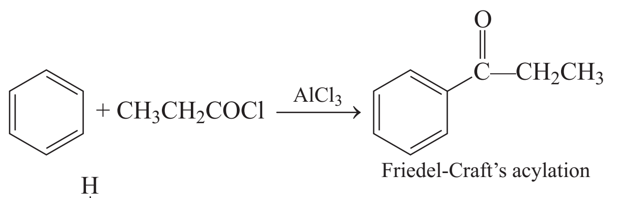
$$\underset{\text{Lime}}{CaO} + \underset{\text{Coke}}{3C} \xrightarrow{2000°C} CaC_2 + CO\uparrow$$

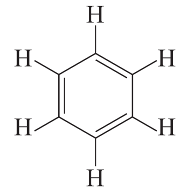
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

$$3C_2H_2 \xrightarrow[\Delta]{Cu} \underset{\text{Benzene}}{C_6H_6}$$

(ii) $—CH_3$ in toluene is *ortho/para* directing group, first oxidised to $—COOH$ in order to make it *meta* directing and then nitrated.



53. 

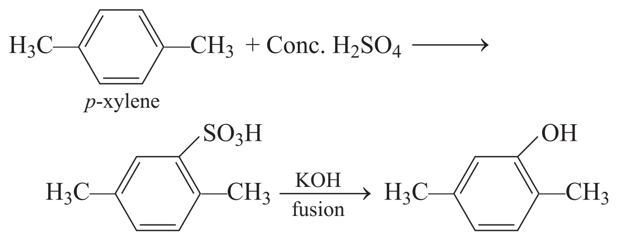
54. 

It has 12 sigma and 3 pi-bonds.

55. $CH_3CH_2OH + PCl_5 \longrightarrow POCl_3 + HCl + CH_3CH_2Cl$

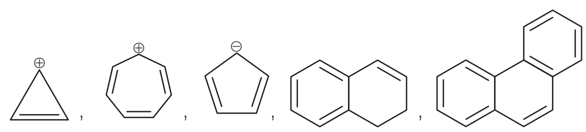
$$C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5—CH_2CH_3$$

Friedel-Craft's reaction

56. 

57. Pi-bonds of benzene are involved in aromaticity, not open for electrophilic addition reaction. Rather, it undergo electrophilic substitution reaction.

58. The aromatic systems are

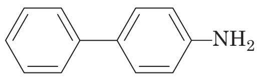


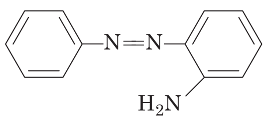
29

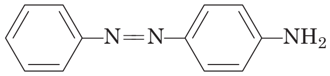
Aromatic Compounds Containing Nitrogen

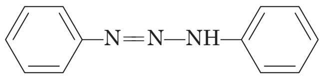
Objective Questions I (Only one correct option)

1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives **(2019 Main, 12 April II)**

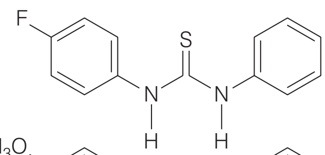
(a) 

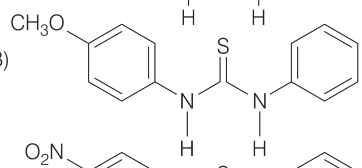
(b) 

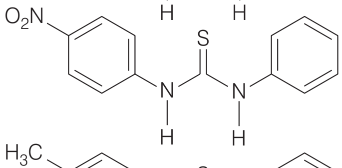
(c) 

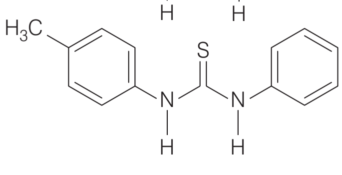
(d) 

2. The increasing order of the pK_b of the following compound is

(A) 

(B) 

(C) 

(D) 

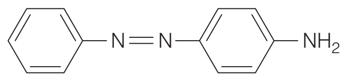
(2019 Main, 12 April I)

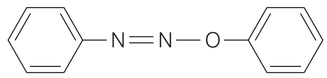
(a) (A) < (C) < (D) < (B)
(b) (C) < (A) < (D) < (B)
(c) (B) < (D) < (A) < (C)
(d) (B) < (D) < (C) < (A)

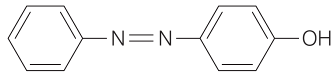
3. Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene?

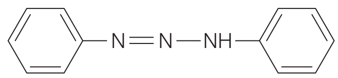
(a) H_2 / Ni **(2019 Main, 10 April II)**
(b) (i) HCl/H_2O (ii) $NaBH_4$
(c) (i) $LiAlH_4$ (ii) H_3O^+
(d) (i) $SnCl_2 + HCl$(gas) (ii) $NaBH_4$

4. Aniline dissolved in dil. HCl is reacted with sodium nitrite at 0°C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil.HCl. The structure of the major product is **(2019 Main, 9 April I)**

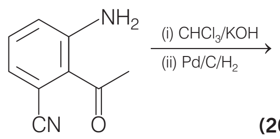
(a) 

(b) 

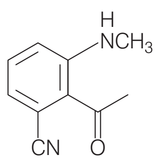
(c) 

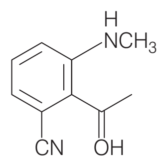
(d) 

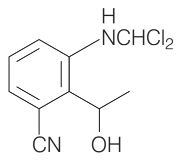
5. The major product obtained in the following reaction is

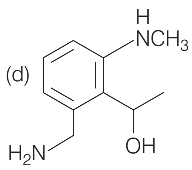


(2019 Main, 8 April II)

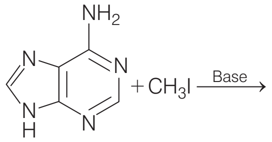
(a) 

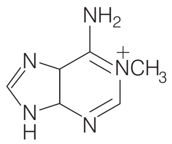
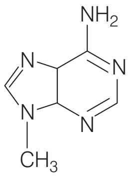
(b) 

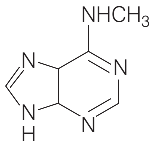
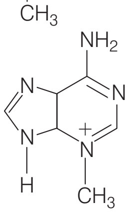
(c) 

(d) 

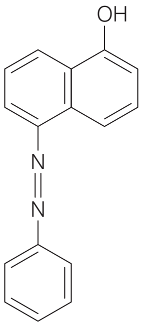
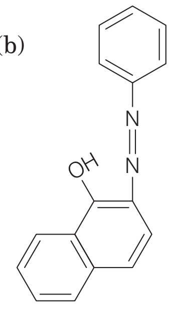
6. The major product in the following reaction is **(2019 Main, 8 April II)**

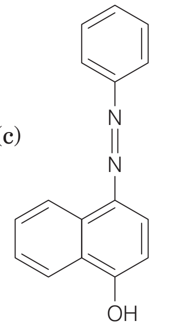
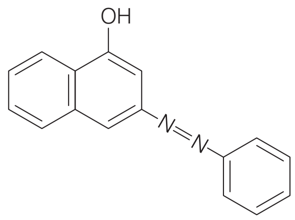


(a)  (b) 

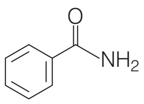
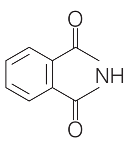
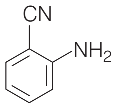
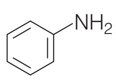
(c)  (d) 

7. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give **(2019 Main, 8 April I)**

(a)  (b) 

(c)  (d) 

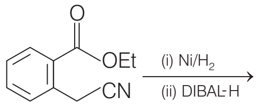
8. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is **(2019 Main, 12 Jan I)**

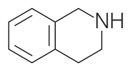
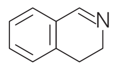
   

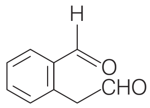
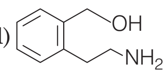
(*A*) (*B*) (*C*) (*D*)

(a) $(A) < (C) < (D) < (B)$
(b) $(B) < (A) < (C) < (D)$
(c) $(B) < (A) < (D) < (C)$
(d) $(A) < (B) < (C) < (D)$

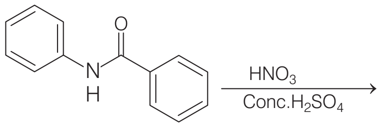
9. The major product of the following reaction is **(2019 Main, 11 Jan I)**

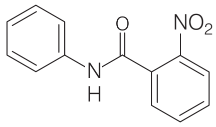
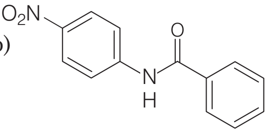


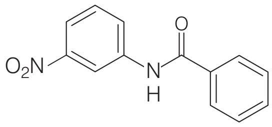
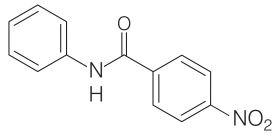
(a)  (b) 

(c)  (d) 

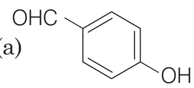
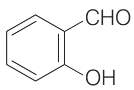
10. What will be the major product in the following mononitration reaction ? **(2019 Main, 10 Jan II)**

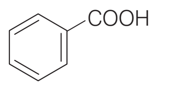
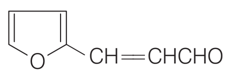


(a)  (b) 

(c)  (d) 

11. An aromatic compound '*A*' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound '*B*'. The compound '*B*' on reaction with molecular bromine and potassium hydroxide provides compound '*C*' having molecular formula C_6H_7N. The structure of '*A*' is **(2019 Main, 10 Jan II)**

(a)  (b) 

(c)  (d) 

12. The increasing basicity order of the following compounds is

(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2\underset{}{N}H$ with CH_2CH_3 on N

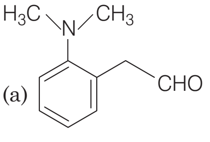
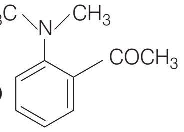
(C) $H_3C—N(CH_3)—CH_3$ (D) $Ph—N(CH_3)—H$

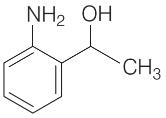
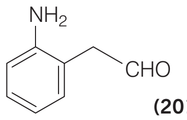
(a) $(D) < (C) < (B) < (A)$
(b) $(A) < (B) < (C) < (D)$
(c) $(A) < (B) < (D) < (C)$
(d) $(D) < (C) < (A) < (B)$ **(2019 Main, 9 Jan II)**

13. The tests performed on compound X and their inferences are :

	Test	Inference
(a)	2, 4- DNP test	Coloured precipitate
(b)	Iodoform test	Yellow precipitate
(c)	Azo-dye test	No dye formation

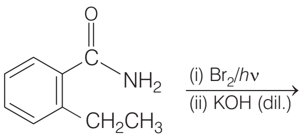
Compound 'X' is

(a)  (b) 

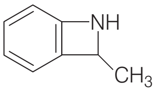
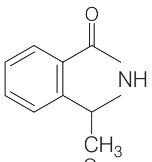
(c)  (d) 

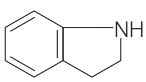
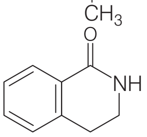
(2019 Main, 9 Jan II)

14. The major product of the following reaction is

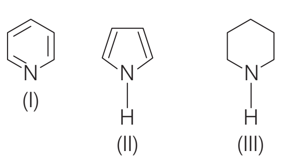


(2019 Main, 9 Jan II)

(a)  (b) 

(c)  (d) 

15. Arrange the following amines in the decreasing order of basicity: **(2019 Main, 9 Jan I)**



(a) I > II > III (b) III > II > I (c) I > III > II (d) III > I > II

16. The correct decreasing order for acid strength is **(2019 Main, 9 Jan I)**

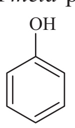
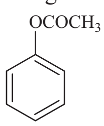
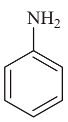
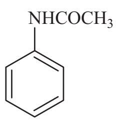
(a) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(b) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

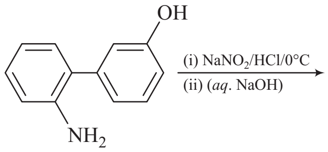
(c) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

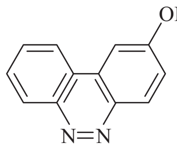
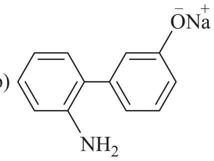
(d) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

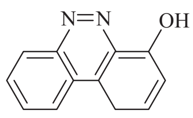
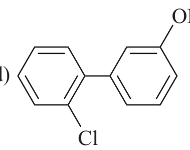
17. Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? **(2017 Main)**

(a)  (b)  (c)  (d) 

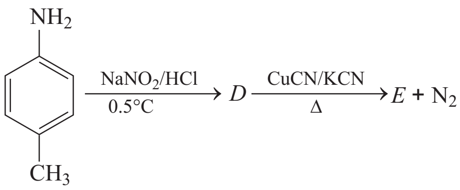
18. The major product of the following reaction is **(2017 Adv.)**



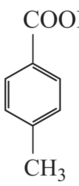
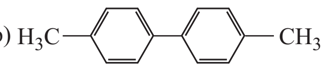
(a)  (b) 

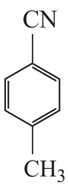
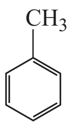
(c)  (d) 

19. In the reaction,

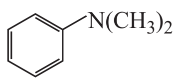
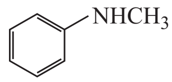


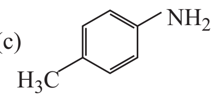
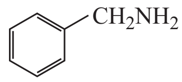
The product E is **(2015 Main)**

(a)  (b) 

(c)  (d) 

20. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(a)  (b) 

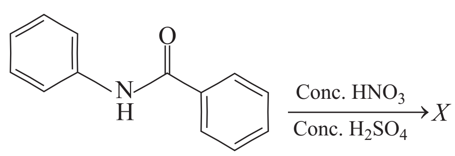
(c)  (d) 

(2011)

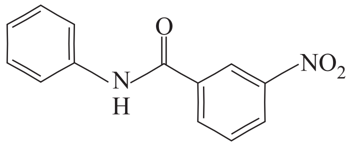
21. The species having pyramidal shape is **(2010)**

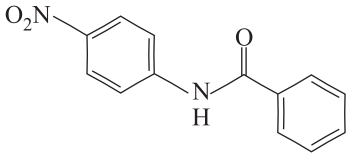
(a) SO_3 (b) BrF_3 (c) SiO_3^{2-} (d) OSF_2

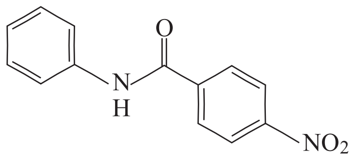
22. In the following reaction,

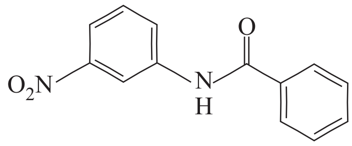


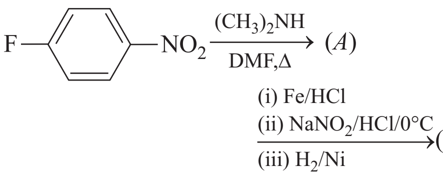
The structure of the major product X is **(2007, 3M)**

(a)


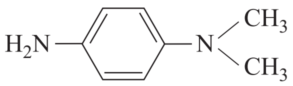
(b)


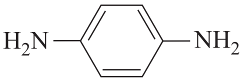
(c)


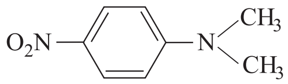
(d)


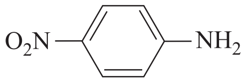
23.


(B), B is **(2003, 1 M)**

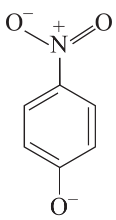
(a)


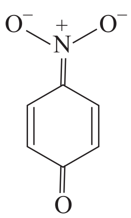
(b)


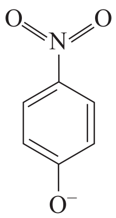
(c)


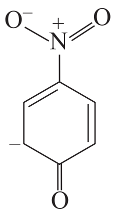
(d)


24. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is **(1999, 2M)**

(a)


(b)


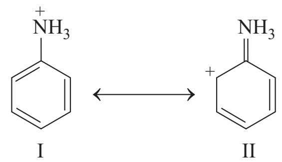
(c)


(d)


25. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives **(1998, 2M)**

(a) diphenyl ether (b) *p*-hydroxy azobenzene
(c) chlorobenzene (d) benzene

26. Examine the following two structures of anilinium ion and choose the correct statement from the ones given below : **(1993, 1M)**



(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
(b) II is not an acceptable canonical structure because it is non-aromatic
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
(d) II is an acceptable canonical structure

27. Chlorobenzene can be prepared by reacting aniline with **(1984, 1M)**

(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in the presence of anhyd $AlCl_3$
(d) nitrous acid followed by heating with cuprous chloride

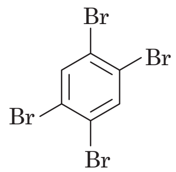
Objective Questions II

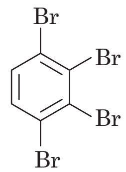
(One or more than one correct option)

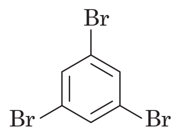
28. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%),Q (47%) and R (2%). The major product(s) of the following sequence is (are)

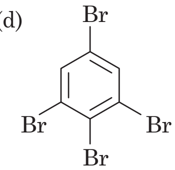
$$R \xrightarrow[\substack{(3)\ H_3O^+ \\ (4)\ NaNO_2,\ HCl/273\text{-}278\ K \\ (5)\ EtOH,\ \Delta}]{\substack{(1)\ Ac_2O,\ pyridine \\ (2)\ Br_2,\ CH_3CO_2H}} S \xrightarrow[\substack{(3)\ NaNO_2,\ HCl/273\text{-}278\ K \\ (4)\ H_3PO_2}]{\substack{(1)\ Sn/HCl \\ (2)\ Br_2/H_2O\ (excess)}}$$

Major product(s) **(2018 Adv.)**

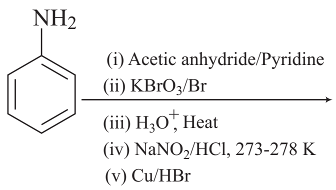
(a)


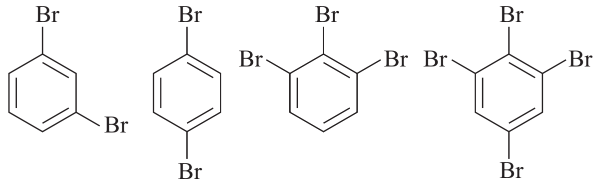
(b)


(c)


(d)


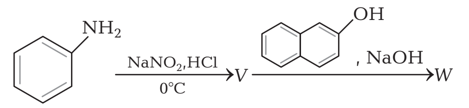
29. The product(s) of the following reaction sequence is (are) **(2017, Adv.)**

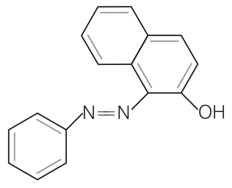
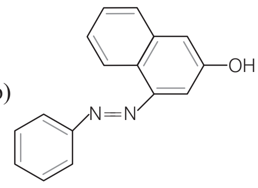


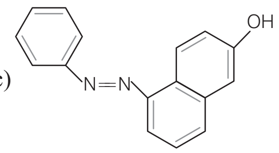
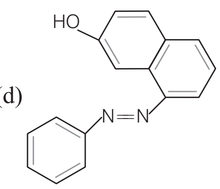


(a) (b) (c) (d)

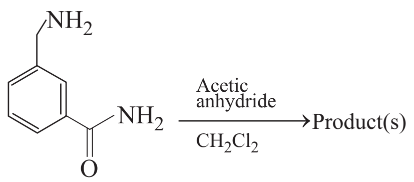
30. In the following reactions, the major product W is **(2015 Adv.)**

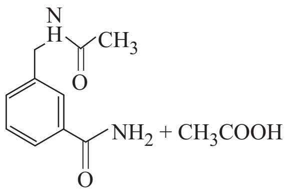


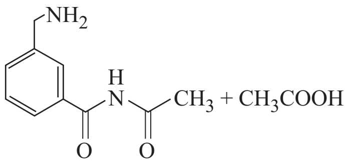
(a)  (b) 

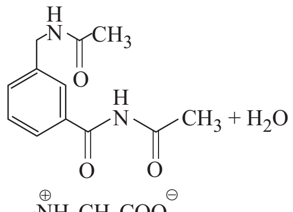
(c)  (d) 

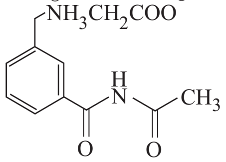
31. In the reaction shown below, the major product(s) formed is/are **(2014 Adv.)**



(a) 

(b) 

(c) 

(d) 

32. *p*-chloroaniline and anilinium hydrochloride can be distinguished by **(1998, 2M)**

(a) Sandmeyer reaction (b) $NaHCO_3$

(c) $AgNO_3$ (d) Carbylamine test

33. When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer, are **(1992, 1M)**

(a) the electron density on *meta* carbon is more than that on *ortho* and *para* positions

(b) the intermediate carbonium ion formed after initial attack of Br^+ at the *meta* position is less destabilised

(c) loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position

(d) easier loss of H^+ to regain aromaticity from *meta* position than from *ortho* and *para* positions

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.

(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.

(c) Statement I is correct; Statement II is incorrect.

(d) Statement I is incorrect; Statement II is correct.

34. **Statement I** Aniline on reaction with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

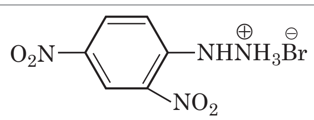
Statement II The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation **(2008, 3M)**

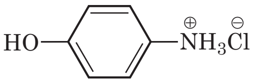
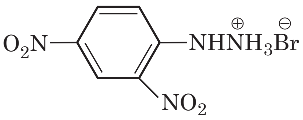
35. **Statement I** In strongly acidic solution, aniline becomes more reactive towards electrophilic reagents.

Statement II The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on nitrogen is no longer available for resonance. **(2001, 1M)**

Match the Column

36. Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. **(2008, 6M)**

	Column I		Column II
(A)	$H_2N—\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	(p)	Sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B)		(q)	Gives positive $FeCl_3$ test

	Column I		Column II
(C)		(r)	Gives white precipitate with $AgNO_3$
(D)		(s)	Reacts with aldehydes to form the corresponding hydrazone derivative

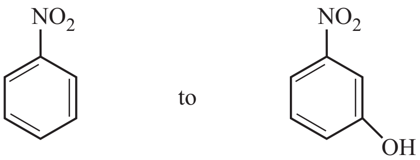
Fill in the Blanks

37. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its…… structure. **(1994, 1M)**

38. In an acidic medium, ……… behaves as the strongest base. (nitrobenzene, aniline, phenol) **(1981, 1M)**

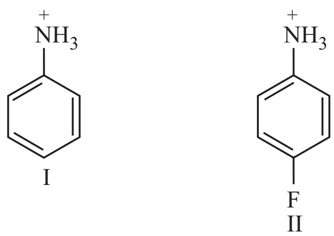
Subjective Questions

39. Convert



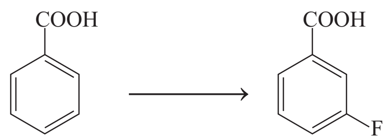
in not more than four steps. Also mention the reaction conditions and temperature. **(2004, 4M)**

40. Which of the following is more acidic and why?



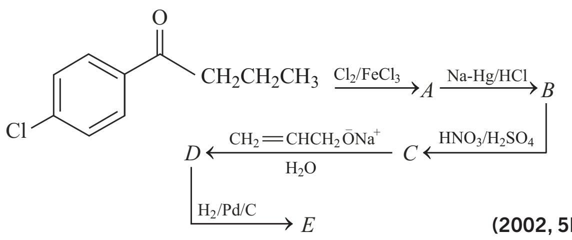
(2004, 2M)

41. Convert (in not more than 3 steps) : **(2003, 2M)**



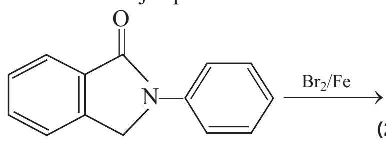
42. There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. **(2003, 4M)**

43. Write structures of the products *A*, *B*, *C*, *D* and *E* in the following scheme



(2002, 5M)

44. What would be the major product in the following reaction?

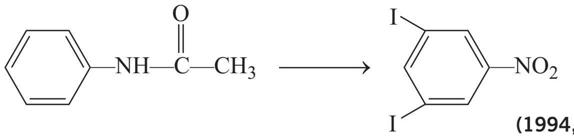


(2000, Main, 1M)

45. How would you bring about the following conversion (in 3 steps)?

Aniline $\longrightarrow$ Benzylamine **(2000, 3M)**

46. Complete the following reactions with appropriate reagents



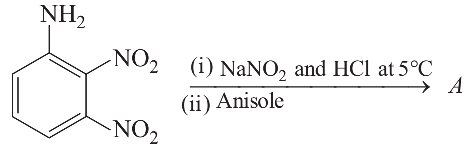
(1994, 4M)

47. Following reaction gives two products. Write the structures of the products.

$$CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$$ **(1998, 2M)**

48. Write the structure of foul smelling compound obtained when aniline is treated with chloroform in the presence of KOH. **(1996, 1M)**

49. Complete the following with appropriate structure:



(1995, 1M)

50. How will you bring about the following conversions?

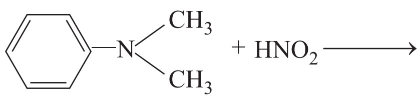
"Benzamide from nitrobenzene" **(1994, 2M)**

51. How will you bring about the following conversions?

"4-nitrobenzaldehyde from benzene" **(1994, 2M)**

52. Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. **(1993, 2M)**

53. Write the structure of the major organic product expected from the following reaction.

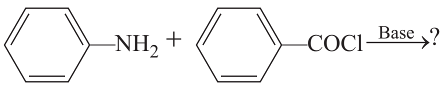


(1992, 1M)

54. How will you bring about the following conversion?

"4-nitro aniline to 1, 2, 3-tribromobenzene." **(1990, 2M)**

55. Complete the following with appropriate structures: **(1986, 1M)**



56. How would you convert aniline into chlorobenzene? **(1985, 1M)**

57. State the conditions under which the following preparation is carried out. "Aniline from benzene" **(1983, 1M)**

58. State the equation for the preparation of following compound.

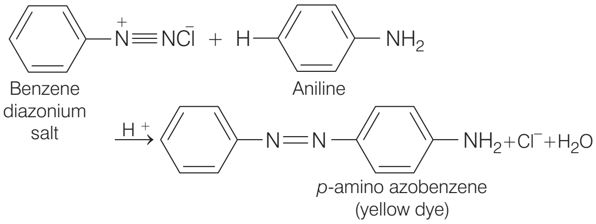
Chlorobenzene from aniline (in 2 steps). **(1982, 1M)**

Answers

1. (c)	**2.** (c)	**3.** (b)	**4.** (a)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (d)
5. (d)	**6.** (*)	**7.** (c)	**8.** (b)	**29.** (b)	**30.** (a)	**31.** (a)	**32.** (c,d)
9. (b)	**10.** (b)	**11.** (c)	**12.** (d)	**33.** (a,b)	**34.** (d)	**35.** (d)	
13. (b)	**14.** (a)	**15.** (d)	**16.** (c)	**36.** A → r, s B → p, q C → p, q, r D → p			
17. (c)	**18.** (a)	**19.** (c)	**20.** (c)	**37.** zwitter ionic	**38.** Aniline		
21. (d)	**22.** (b)	**23.** (a)	**24.** (c)				

Hints & Solutions

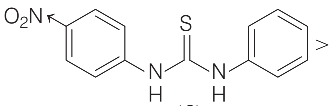
1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium salt to give *p*-amino azobenzene (yellow dye).



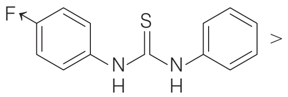
2. **Key Idea** pK_b value is defined as the minus lagarithm of K_b smallar the value of pK_b stronger is the base and *vice-versa*.

In the given options, $+R$ effect is shown by —CH_3 and —OCH_3 group (—OCH_3 > —CH_3). These group increases the electron density at *o* and *p*-positions. Groups such as —F and—NO_2 shows $-R$-effect (—NO_2 > —F). These group decreases the electron density at *o* and *p*- positions.

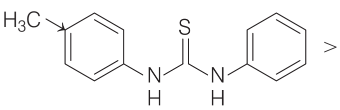
Increase in electron density at *p*-position makes the unshared electron pair of '*N*' more available and decrease in electron density at *p*-position makes the unshared electron pair of '*N*' less available. Compound containing —OCH_3 group act as strongest base and hence possess lowest value of pK_b. So, the correct increasing order of pK_b in the given compound is



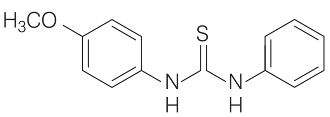
(*C*)



(*A*)

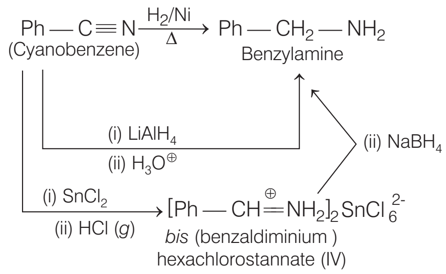


(*D*)



(*B*)

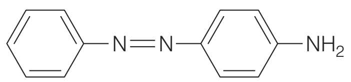
3. The preparation of benzylamine from cyanobenzene using given reagents are as follows :



$$\underset{}{PhCN} \xrightarrow[-NH_4Cl]{HCl,\,H_2O} \underset{\text{Benzoic acid}}{PhCOOH} \xrightarrow{NaBH_4} \underset{\text{Benzyl alcohol}}{PhCH_2OH}$$

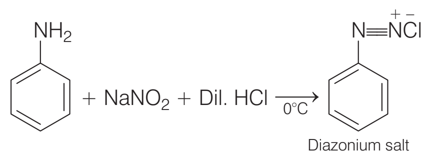
Thus, option (b) is incorrect.

4. Major product of the reaction is

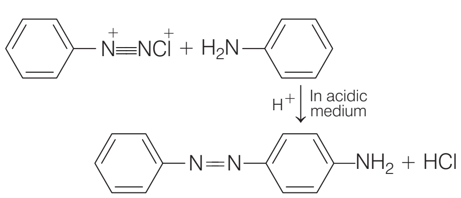


It is obtained by coupling reaction.

Reaction of aniline with dil. HCl and sodium nitrite at 0°C is shown below :

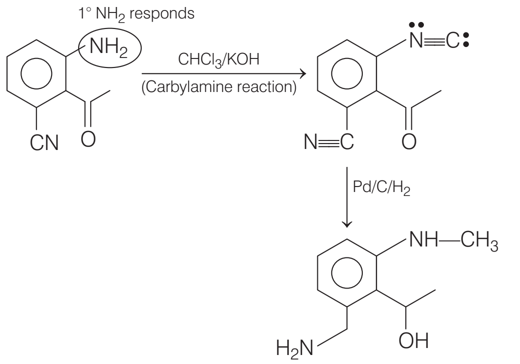


Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :



For an effective coupling, the solution must be so alkaline that the concentration of diazonium ion is too low. It must not be so acidic that the concentration of free amine or phenoxide ion is too low. That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

5.

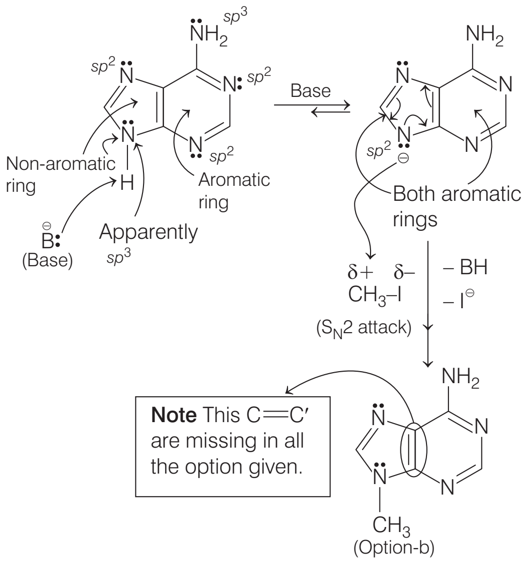


In step (i), 1° amine is converted into isocyanide, when reacts with $CHCl_3/KOH$. This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

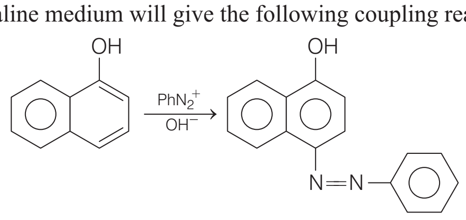
In step (ii), isocyanide is reduced to secondary amine and cyanide is reduced to primary amine, and carbonyl group to alcoholic group when treated with $Pd/C/H_2$.

6. N is more electronegative than '*C*'. So, H of $\overset{\delta-}{N}—\overset{\delta+}{H}$ bond is more acidic than that of C—H bond in the ring.

Again, sp^2-N is more electronegative ($s\% = 33.3$) than sp^3-N ($s\% = 25$) of the $—NH_2$ group.



7. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give the following coupling reaction.



In the presence of $\overset{-}{O}H$ ion, $Ar\overset{+}{N}_2$ exists in equilibrium with an unionised compound ($Ar — N = N — OH$) and salts $[ArN = N^+]^- —\overset{\ominus}{O}H$ derived from it, which do not couple.

$$[Ar — N \equiv N]^+ \overset{\ominus}{O}H \underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar — N = N — OH}$$

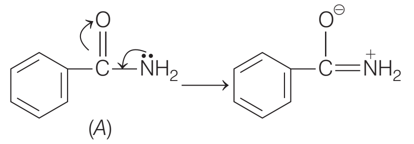
$$\underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar — N = N — \overset{-}{O}\overset{+}{Na}}$$

Following conditions are very useful for coupling reaction to take place.

(a) The solution must be so alkaline that the concentration of diazonium ion is too low.

(b) It must not be so acidic that the concentration of free phenoxide ion is too low.

8. The reaction of alkyl halide with amine or amides is a nucleophilic substitution reaction. More nucleophilic nitrogen is more reactive with alkyl halide. Compound (*A*) is benzamide and lone pair of 'N' of it, is not available in this compound.

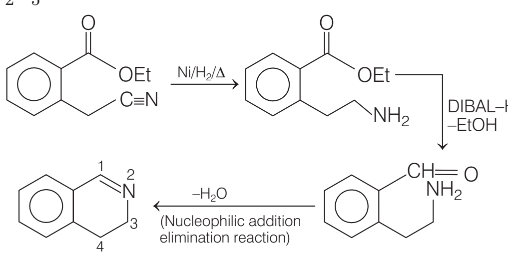


In compound (*D*), lone pair of 'N' are available but in compound (*C*), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group (—CN) attach to benzene ring.

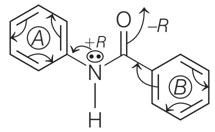
In compound (*B*), i.e. pthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them. Hence, the correct order is:

$$(B) < (A) < (C) < (D).$$

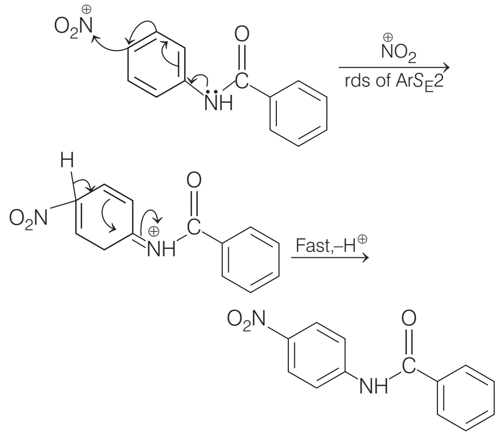
9. Ni/H_2 can reduce $—C \equiv N$ into $—CH_2—NH_2$ (1°-amine) but cannot reduce an ester group ($—CO_2Et$) whereas DIBAL-H, di-isobutylaluminium hydride, $[(CH_3)_2CH]_2AlH$ reduces the ester group ($—CO_2Et$) into —CHO (an aldehyde) and C_2H_5OH.



10. Here, in mononitration the electrophile produced from mixed acid (HNO_3 + conc. H_2SO_4) is $\overset{+}{N}O_2$.



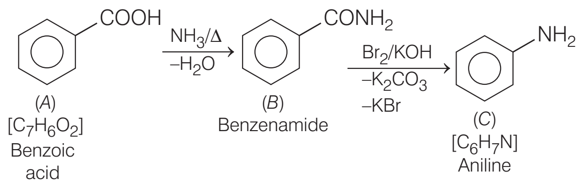
Ring-(*A*) is activated, i.e. becomes more nucleophilic by the $+R$ effect of the $—\ddot{N}H—$ group and it becomes o/p-directing towards the electrophile, NO_2^+ in the ArS_E2 reaction. For mononitration, $\overset{\oplus}{N}O_2$ will preferably come at *p*-position, whereas the ring-(B) gets deactivated by $-R$- effect of the $-\overset{O}{\overset{\|}{C}}-$ group,



11. Using retro-synthesis, to get the required compounds, A, B and C.

$$\underset{\substack{(C)\\ [1°\text{-amine}]\\ (\text{No. of C}=6\\ 1\text{ carbon less})}}{C_6H_7N} \xleftarrow[\substack{\text{KOH}\\ \text{Hoffmann}\\ \text{bromamide}\\ \text{reaction}\\ \text{(step down)}}]{Br_2} \underset{\substack{[\text{An amide}]\\ (\text{No.of C=7})}}{B} \xleftarrow{NH_3/\Delta} \underset{\substack{[\text{Carboxylic acid}\\ C_7H_6O_2\,]}}{A}$$

So, the reactions can be shown as:



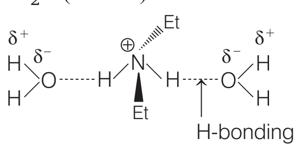
12. If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.

$$\underset{2°}{D} < \underset{1°}{A} < \underset{2°}{B} < \underset{3°}{C}$$

But, this order does not match with the options given. So, it has been asked on basicity of the amines in aqueous solution. When no phase is given, then basicity of amine is considered in aqueous solution as they are liquids. In aqueous solution, basicity of 2°-amines (aliphatic) is maximum because, of the thermodynamic stability of its conjugate acid.

$$\underset{(B)}{Et_2NH} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{Et_2\overset{\oplus}{N}H_2} + \overset{\ominus}{O}H$$

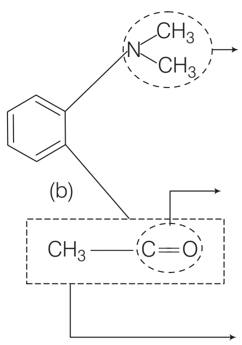
$Et_2\overset{\oplus}{N}H_2$ is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with H_2O (solvent) molecules.



Aromatic amines (D) are always weaker bases than aliphatic amines, because of the conjugation of lp of electrons of N (+ R-effect) with the benzene ring.

So, the correct order is (D) < (C) < (A) < (B).

13.



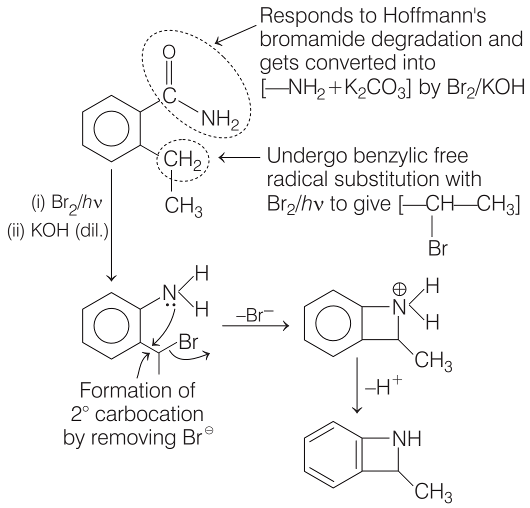
It is a 3°-amino group ($-NMe_2$) though aromatic which will not respond to diazotisation ($NaNO_2$ + dil. HCl/5°C). So, formation of diazonium ion and its further reaction with alkaline phenol or β-napthol at 5-10°C to produce a precipitate of azo-dye will not take place.

It is a keto group $>C=O$ and so it responds to 2, 4-DNP test with Brady's reagent (2, 4-dinitrophenyl hydrazine) to give a reddish orange precipitate.

It is a keto-methyl group $-\overset{O}{\overset{\|}{C}}-CH_3$ and hence, it responds to iodoform test to give a yellow precipitate of iodoform (CHI_3).

Compound (c) is an alcohol and does not give positive 2, 4-DNP test. Hence, eliminated (a) and (d) does not have $-CH_3CO$ group and does not give idoform test. Hence, eliminated.

14. In the given reaction,

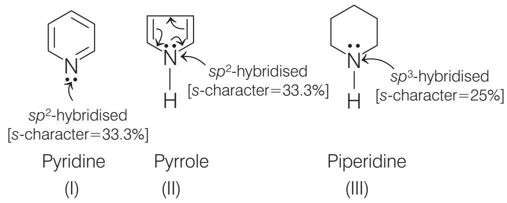


15. **Key Idea**

Basicity $\propto$ *Ease of donation of lone pair of electrons*

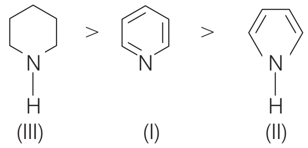
$$\propto \frac{1}{\%\ of\ s\text{-}character\ of\ N} \propto \frac{1}{Electronegativity\ of\ N}$$

The % of s-character in the given amines are as follows:



Therefore, piperidine (III) having minimum

% s-character is most basic. Among the rest, pyridine (I) and pyrrole (II) the lone pair of electrons of N in pyrrole (II) is involved in delocalisation and follows $(4n+2)\,\pi$ aromatic $(n=1)$ system. So, the N-atom of pyrrole (II) will show least basicity. Thus, the order of basicity is as follows:



16. All the given compounds are α-monosubstituted acetic acid derivatives and the α-substitutions have been made by strong $-I$ groups/atoms. More powerful the $-I$ group, stronger will be the acid.

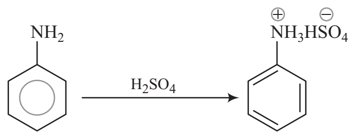
$-I$ power of different groups is as follows :

$$—NO_2 > —CN > —F > —Cl.$$

Thus, the correct decreasing order for acid strength is:

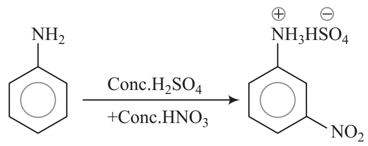
$$NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH.$$

17. Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significance amount ($\approx 47\%$) of meta-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.

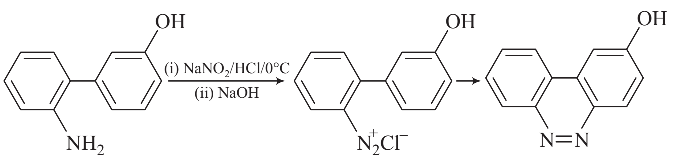


Aniline   Anilinium ion

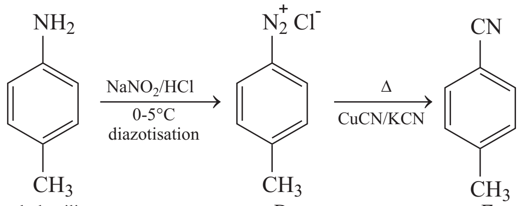
Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



18. *Diazo* coupling occur at *para*-position of phenol.

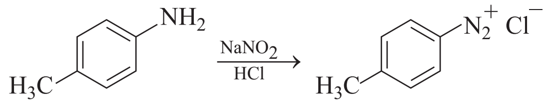


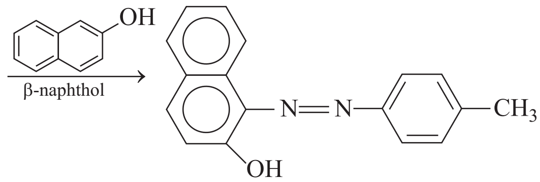
19.



4-methyl aniline   *D* 4-methyl diazonium chloride   *E* 4-methyl benzocyanide

20. As we know, benzenediazonium salt forms brilliant coloured dye with β-naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with $NaNO_2$ in dil. HCl forms the corresponding diazonium chloride salt.





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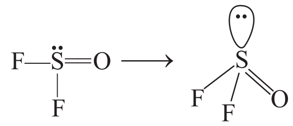
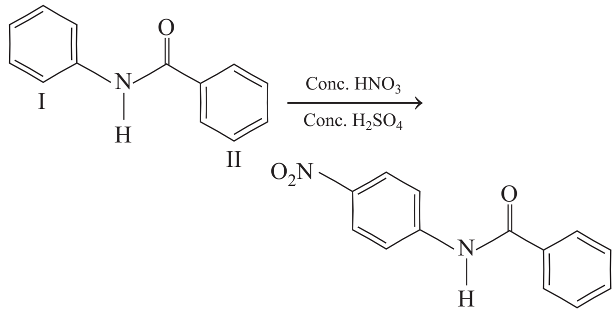


S is sp^3-hybridised   Pyramidal

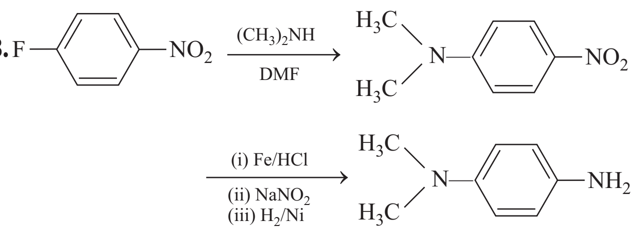
SO_3 is planar (S is sp^2-hybridised), BrF_3 is T-shaped and SiO_3^{2-} is planar (Si is sp^2-hybridised).

22.

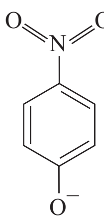


Ring-I is activated while ring-II is deactivated towards electrophilic aromatic substitution reaction.

23.

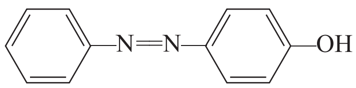


24.



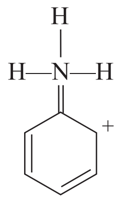
Nitrogen has five bonds and 10 valence electrons, not an acceptable resonance structure.

25. $C_6H_5\overset{+}{N_2}Cl^- + C_6H_5OH \longrightarrow$



p-hydroxy azobenzene

26. In structure II, nitrogen is associated with five bonds and 10 valence electrons, hence not acceptable.

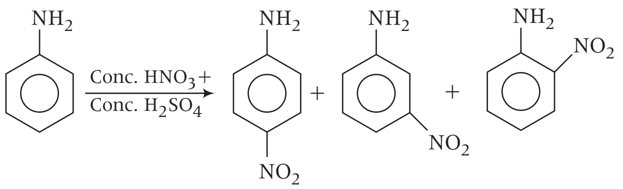


N-has five bonds and 10 valence electrons

27. $C_6H_5NH_2 + HNO_2 \longrightarrow C_6H_5N_2OH \xrightarrow{CuCl} C_6H_5—Cl$

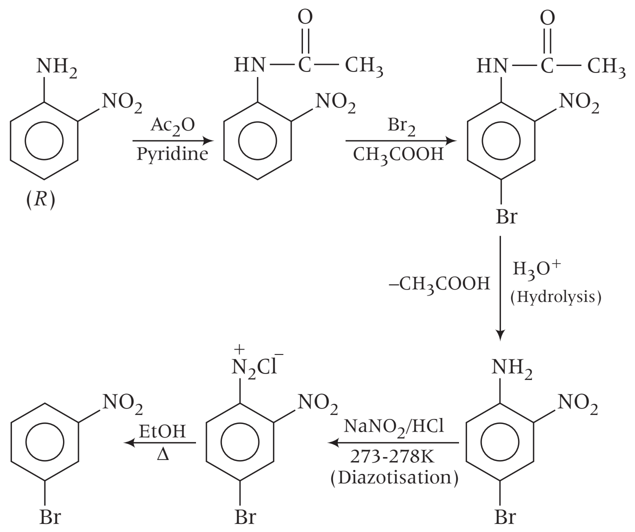
28. Given, Aniline $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3+} \underset{(51\%)}{P} + \underset{(47\%)}{Q} + \underset{(2\%)}{R}$

Then P, Q and R will be



P (51%) Q (47%) R (2%)

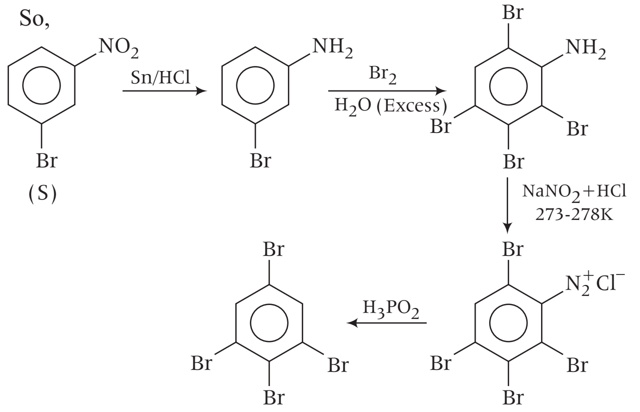
Its given $R \xrightarrow[\text{(iii) } H_3O^+ \text{ (iv) } NaNO_2, HCl/273\text{-}278\text{ K (v) EtOH, } \Delta]{\text{(i) } Ac_2O, \text{ Pyridine (ii) } Br_2, CH_3COOH} S$



Now from S to major products its given.

$S \xrightarrow[\text{(iii) } NaNO_2, HCl/273\text{-}278K \text{ (iv) } H_3PO_2]{\text{(i) Sn/ HCl (ii) } Br_2/H_2O \text{ (Excess)}} \text{Major product}$

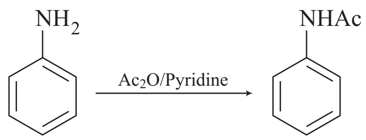
So,



Major product
1, 3, 4, 5-tetrabromobenzene

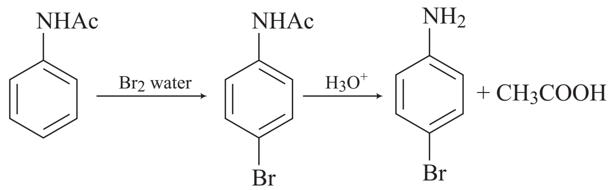
Hence, only (d) is the correct answer.

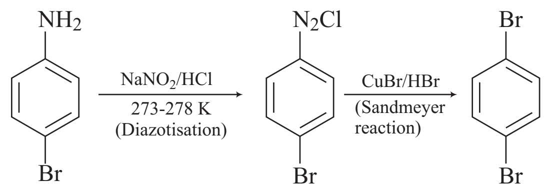
29.



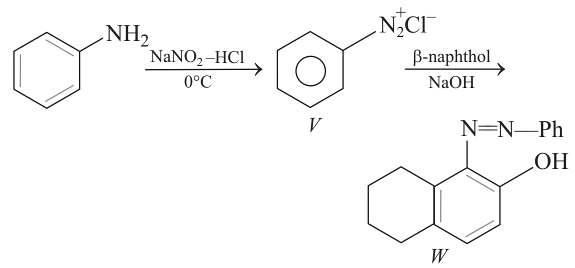
$KBrO_3 + HBr \longrightarrow Br_2$

Ac is CH_3CO (acetyl), it protects $—NH_2$ group from being oxidised.





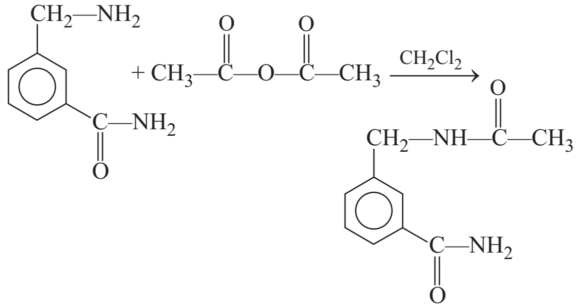
30.



31. **PLAN** This problem includes concept of acetylation reaction and regioselectivity of chemical reaction.

Regioselectivity means which group will react selectivity in the presence of two or more than two functional groups. Here, among two functional group $—NH_2$ and $—CONH_2$,

NH_2 is more nucleophilic, hence NH_2 group will undergo reaction faster than $CONH_2$.



$—CH_2—NH_2$ is more nucleophilic than $—\underset{\|}{\overset{}{C}}—NH_2$.
O

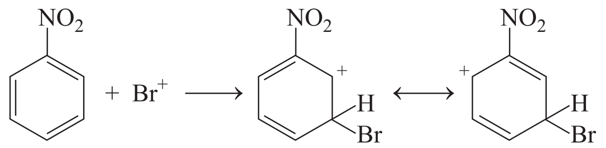
Hence, correct choice is (a).

32. $(C_6H_5\overset{+}{N}H_3Cl^-)$ + $AgNO_3 \longrightarrow AgCl\downarrow$
anilinium hydrochloride — precipitate

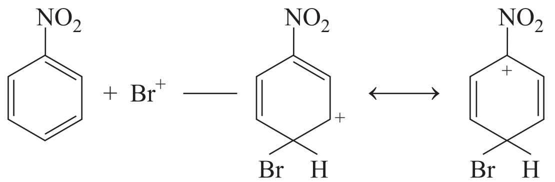
No such precipitate is formed with *p*-chloroaniline.

Also, carbylamine test will not be given by anilinium hydrochloride but *p*-chloroaniline give this test.

33. Nitro group withdraws electrons more from *ortho*/*para* position than from *meta* position. Also the σ-complex formed from *meta* attack is less destabilised than from *ortho*/*para* positions.



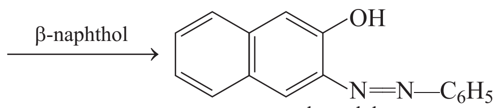
Nitro group not destabilising the positive charge by resonance.



Nitro group destabilises the positive charge directly by resonance, less stable σ-complex.

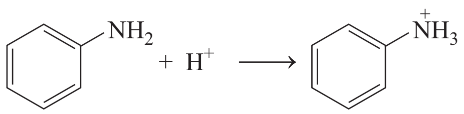
Similar phenomenon is observed with *ortho* attack.

34. $C_6H_5NH_2 + NaNO_2 / HCl \xrightarrow{0°C} C_6H_5N_2^+Cl^-$



coloured dye

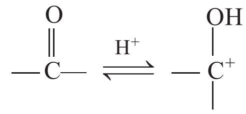
35. In strongly acidic medium, aniline is fully protonated, becomes deactivated for S_EAr reaction.



Lone pair on nitrogen is not available for resonance. Positive charge makes the group strongly electron withdrawing.

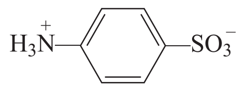
36. Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound. Phenolic group and salt of carboxylic acid gives $FeCl_3$ test.

Chloride salt gives white precipitate of AgCl on treatment with $AgNO_3$. Hydrazone formation occur effectively at pH = 4.5. The reaction proceeds in that condition only when H^+ concentration is just sufficient to activate the following enolisation.



As H^+ concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazinium ion which is not nucleophilic and reaction becomes impossible. Further low concentration of H^+ (in the case of 2,4-dinitrophenyl hydrazinium bromide) is not effective to proceed elimination.

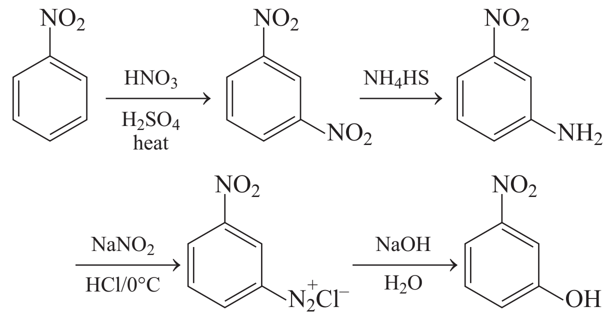
37. **Zwitter ionic**



sulphanilic acid

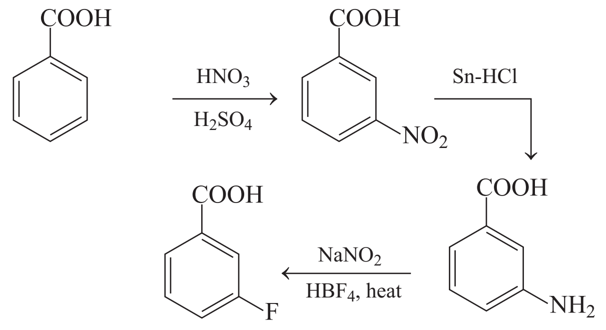
38. **Aniline** It is a stronger base than either phenol or nitrobenzene.

39.

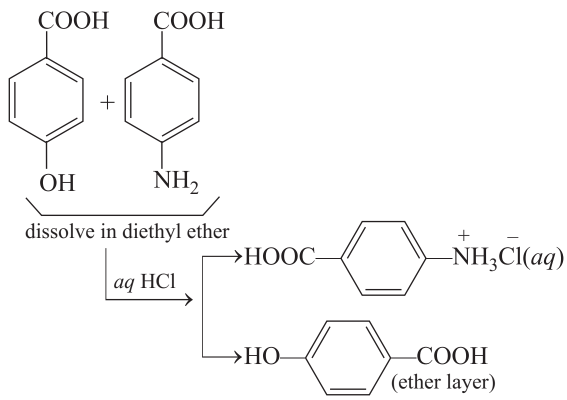


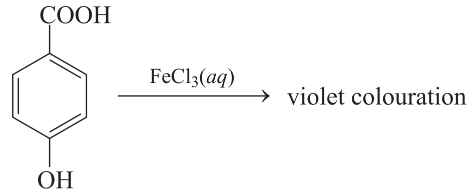
40. II is more acidic due to – *I* effect of F.

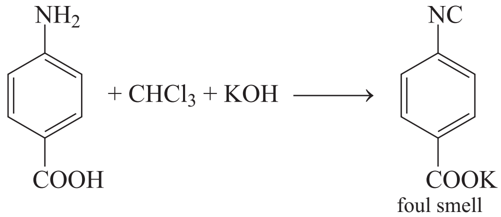
41.

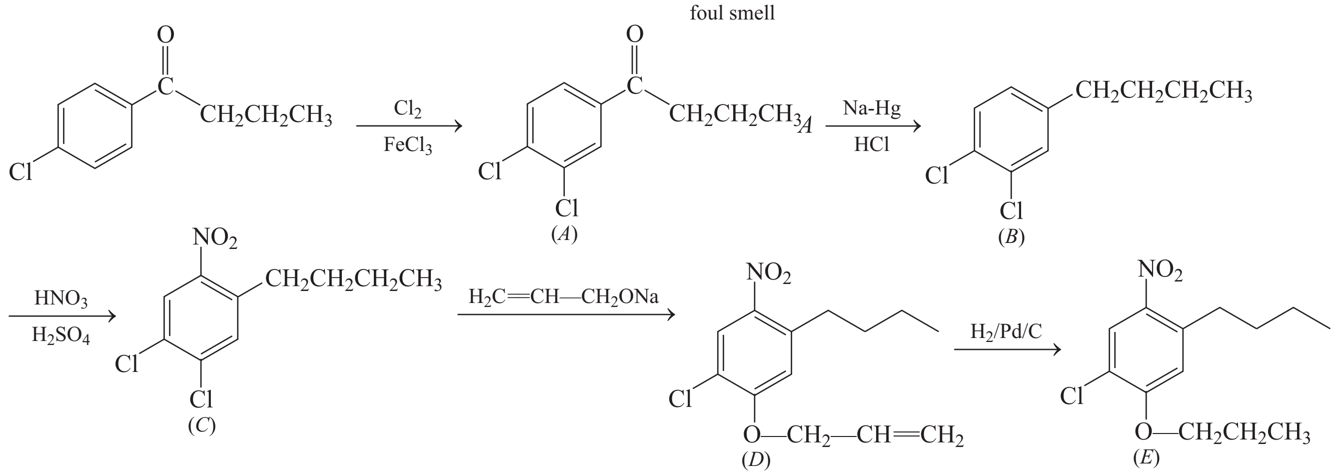


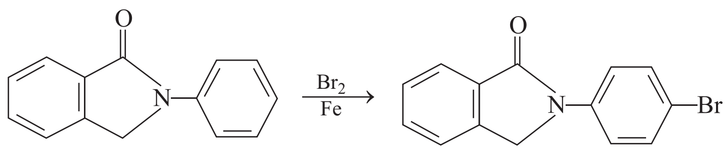
42.



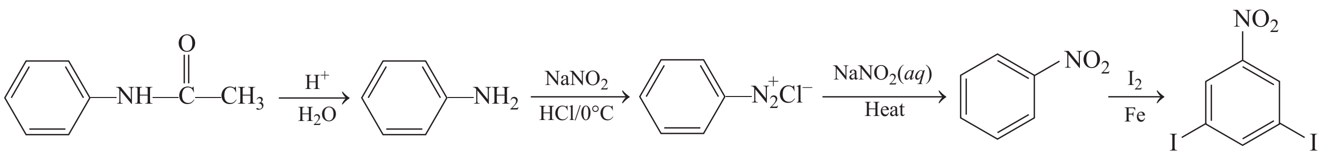


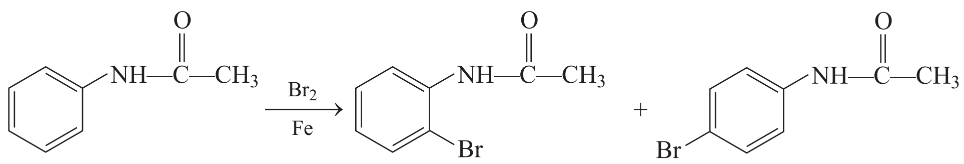


43. 

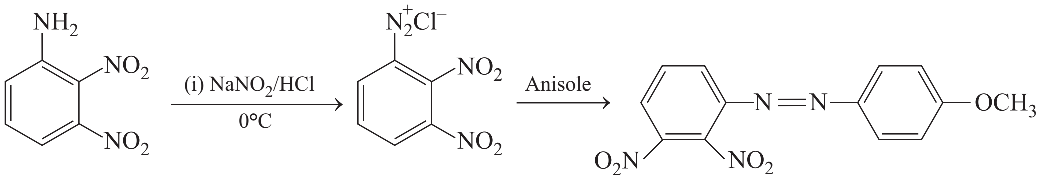
44. 

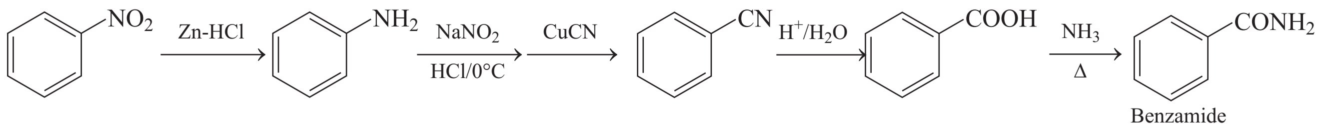
45. $C_6H_5NH_2 \xrightarrow[HCl/0°C]{NaNO_2} C_6H_5\overset{+}{N_2}Cl^- \xrightarrow{CuCN} C_6H_5—CN \xrightarrow{LiAlH_4} C_6H_5—CH_2NH_2$

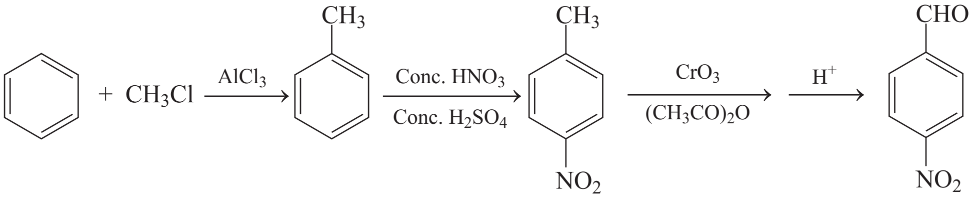
46. 

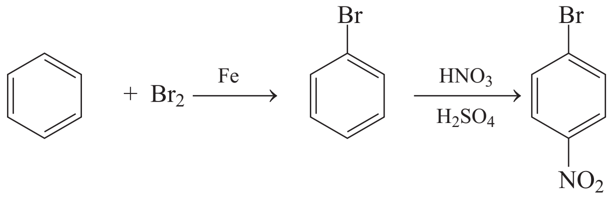
47. 

48. $C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{(foul smell)}}{\underset{\text{Isocyanide}}{C_6H_5NC}}$

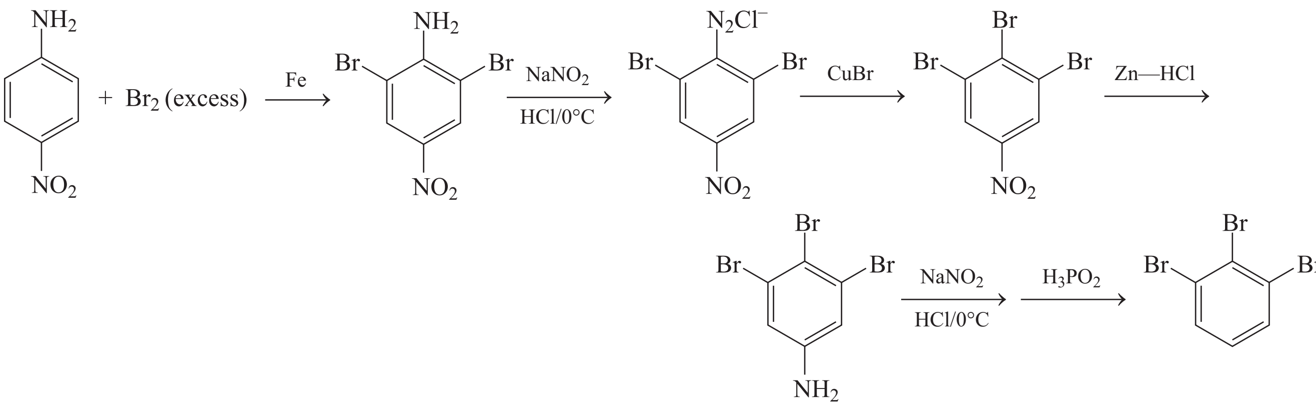
49. 

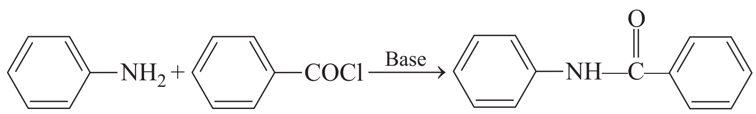
50. 

51. 

52. 

53. No reaction. Tertiary amine does not react with nitrous acid.

54. 

55. 

56. $C_6H_5\text{—}NH_2 \xrightarrow[0°C]{NaNO_2/HCl} C_6H_5N_2^+Cl^- \xrightarrow[Heat]{CuCl} C_6H_5\text{—}Cl$

57. $C_6H_6 + \text{Conc. } HNO_3 / \text{Conc. } H_2SO_4 \longrightarrow C_6H_5\text{—}NO_2 \xrightarrow{Zn-HCl} \underset{\text{Aniline}}{C_6H_5\text{—}NH_2}$

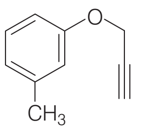
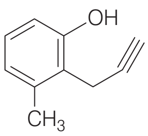
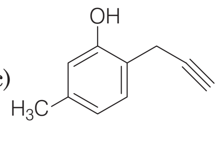
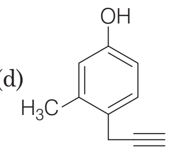
58. $C_6H_5NH_2 + NaNO_2 \xrightarrow[0°C]{HCl} C_6H_5N_2^+Cl^- \xrightarrow[Heat]{CuCl} C_6H_5\text{—}Cl$

Download Chapter Test
http://tinyurl.com/y437rg2e *or*

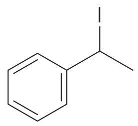
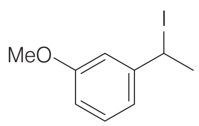
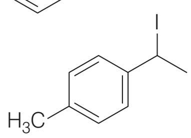
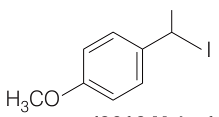
30
Aryl Halides and Phenols

Objective Questions I (Only one correct option)

1 What will be the major product when *m*-cresol is reacted with propargyl bromide ($HC\equiv C—CH_2Br$) in presence of K_2CO_3 in acetone? **(2019 Main, 12 April II)**

(a) 
(b) 
(c) 
(d) 

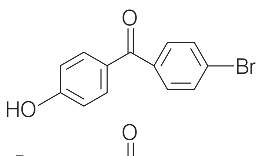
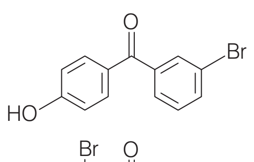
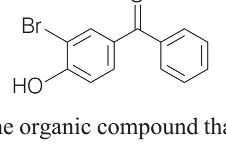
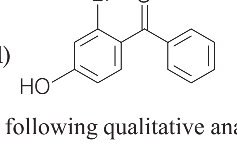
2. Increasing rate of S_N1 reaction in the following compounds is

(A) 
(B) 
(C) 
(D) 

(2019 Main, 10 April I)

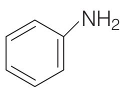
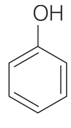
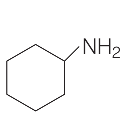
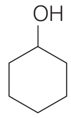
(a) (A) < (B) < (C) < (D)
(b) (B) < (A) < (C) < (D)
(c) (A) < (B) < (D) < (C)
(d) (B) < (A) < (D) < (C)

3. *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives **(2019 Main, 9 April II)**

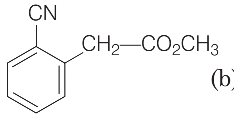
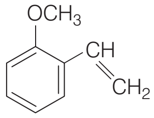
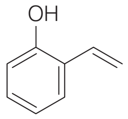
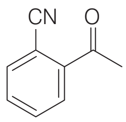
(a) 
(b) 
(c) 
(d) 

4. The organic compound that gives following qualitative analysis is **(2019 Main, 9 April I)**

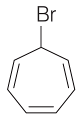
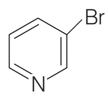
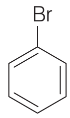
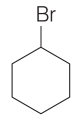
Test	Inference
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2 /water	Decolourisation

(a) 
(b) 
(c) 
(d) 

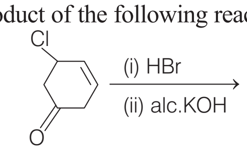
5. Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution **(2019 Main, 11 Jan II)**

(a) 
(b) 
(c) 
(d) 

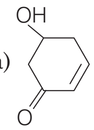
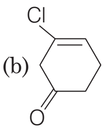
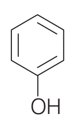
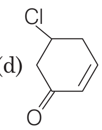
6. Which of the following compounds will produce a precipitate with $AgNO_3$? **(2019 Main, 11 Jan I)**

(a) 
(b) 
(c) 
(d) 

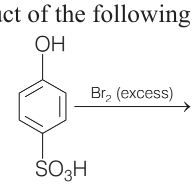
7. The major product of the following reaction is



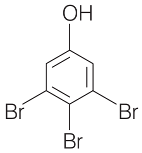
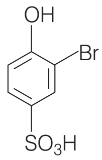
(2019 Main, 11 Jan I)

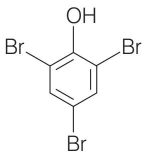
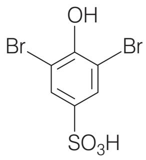
(a) 
(b) 
(c) 
(d) 

8. The major product of the following reaction is

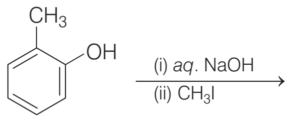


(2019 Main, 11 Jan I)

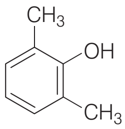
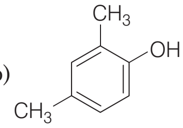
(a)  (b) 

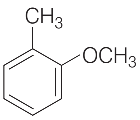
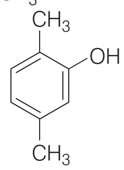
(c)  (d) 

9. The major product of the following reaction is

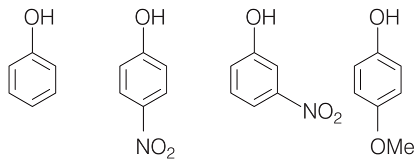


(2019 Main, 10 Jan II)

(a)  (b) 

(c)  (d) 

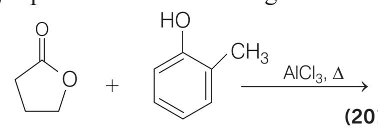
10. The increasing order of the pK_a values of the following compounds is (2019 Main, 10 Jan I)



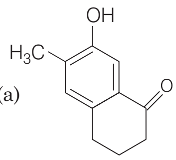
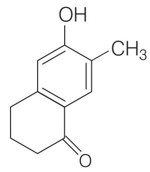
A *B* *C* *D*

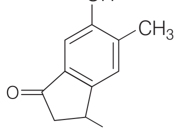
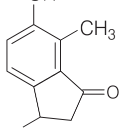
(a) $D < A < C < B$ (b) $B < C < A < D$
(c) $C < B < A < D$ (d) $B < C < D < A$

11. The major product of the following reaction is

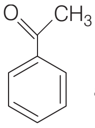
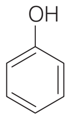
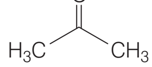


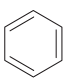
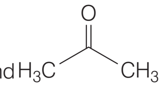
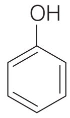
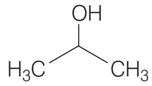
(2019 Main, 9 Jan II)

(a)  (b) 

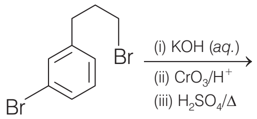
(c)  (d) 

12. The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are (2019 Main, 9 Jan II)

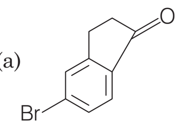
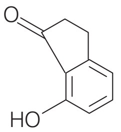
(a)  and CH_3—OH (b)  and 

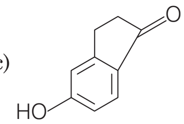
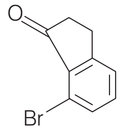
(c)  and  (d)  and 

13. The major product of the following reaction is

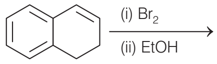


(2019 Main, 9 Jan I)

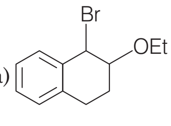
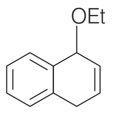
(a)  (b) 

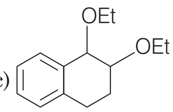
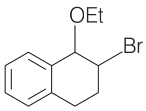
(c)  (d) 

14 The major product of the following reaction is

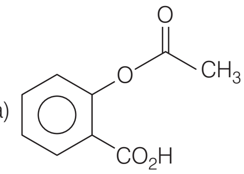
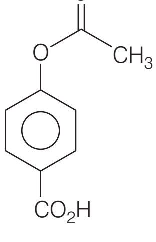


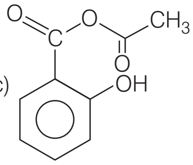
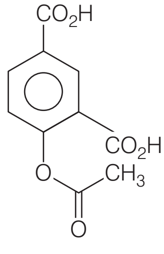
(2019 Main, 9 Jan I)

(a)  (b) 

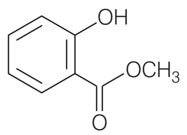
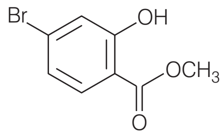
(c)  (d) 

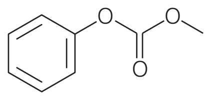
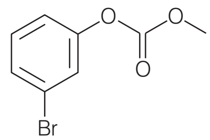
15. Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces: (2018 Main)

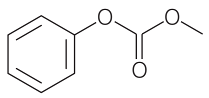
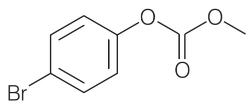
(a)  (b) 

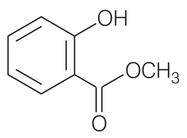
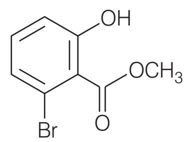
(c)  (d) 

16. Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively **(2018 Main)**

(a)  and 

(b)  and 

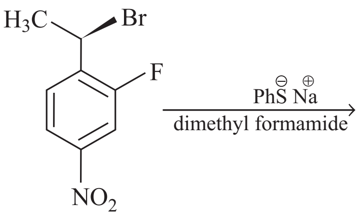
(c)  and 

(d)  and 

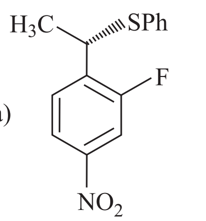
17. For the identification of β-naphthol using dye test, it is necessary to use **(2014 Adv.)**

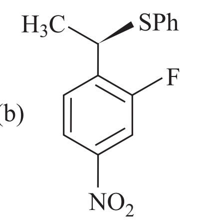
(a) dichloromethane solution of β-naphthol
(b) acidic solution of β-naphthol
(c) neutral solution of β -naphthol
(d) alkaline solution of β-naphthol

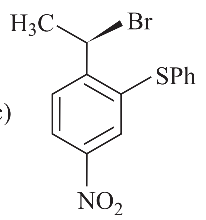
18. The major product of the following reaction is

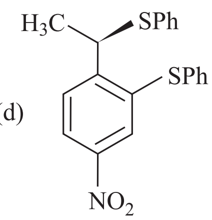


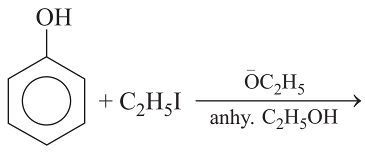
(2008, 3M)

(a) 

(b) 

(c) 

(d) 

19. 

(2003, 1M)

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

20. In the reaction of *p*-chlorotoluene with KNH_2 in liq. NH_3, the major product is **(1997, 1M)**

(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloroaniline

21. Phenol reacts with bromine in carbon disulphide at low temperature to give **(1988, 1M)**

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol
(c) *p*- bromophenol (d) 2, 4, 6-tribromophenol

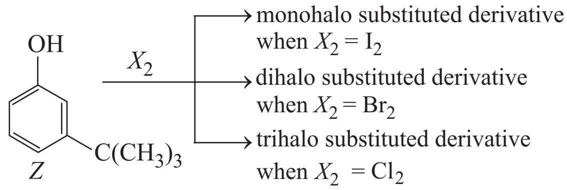
22. When phenol is treated with excess of bromine water, it gives **(1984, 1M)**

(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol

Objective Questions II

(One or more than one correct option)

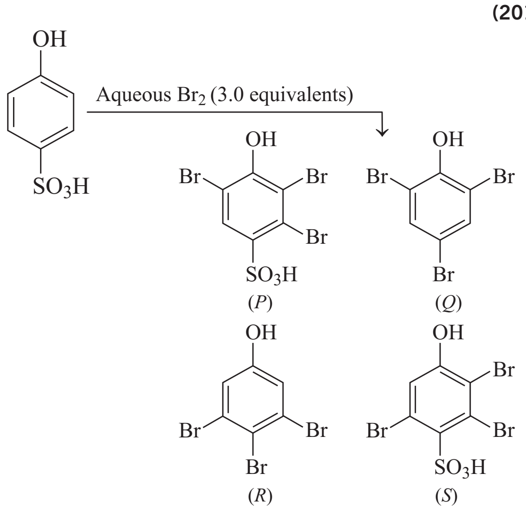
23. The reactivity of compound *Z* with different halogens under appropriate conditions is given below



The observed pattern of electrophilic substitution can be explain by

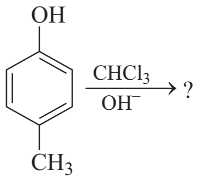
(a) the steric effect on the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group

24. The major product(s) of the following reaction is/are **(2013 Adv.)**

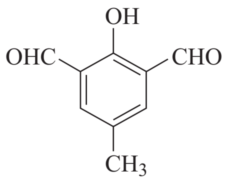


(a) *P* (b) *Q* (c) *R* (d) *S*

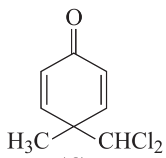
25. In the following reaction, the product (s) formed is/are



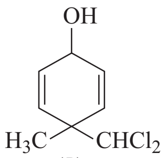
(2013 Adv.)



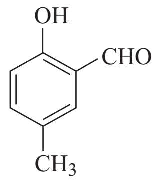
(*P*)



(*Q*)

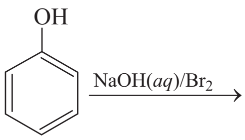


(*R*)

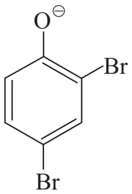


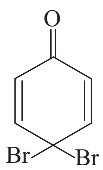
(*S*)

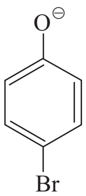
(a) *P* (major) (b) *Q* (minor) (c) *R* (minor) (d) *S* (major)

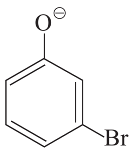
26. In the reaction, 

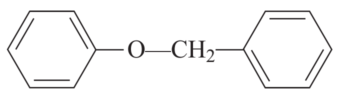
the intermediate(s) is/are **(2010)**

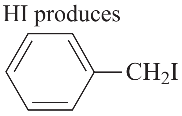
(a) 

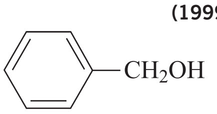
(b) 

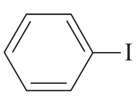
(c) 

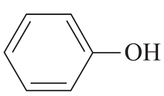
(d) 

27. The ether  ,when treated with HI produces **(1999, 3M)**

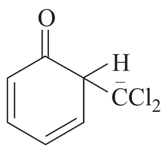
(a) 

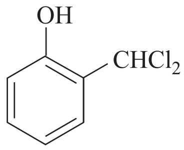
(b) 

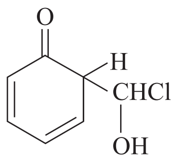
(c) 

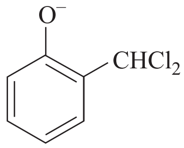
(d) 

28. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediates ? **(1995, 2M)**

(a) 

(b) 

(c) 

(d) 

29. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to **(1990, 1M)**

(a) the formation of less stable carbonium ion
(b) resonance stabilisation
(c) longer carbon halogen bond
(d) sp^2-hybridised carbon bonded to halogen

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

30. **Statement I** Bromobenzene, upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product.

Statement II In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **(2008, 3M)**

31. **Statement I** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Statement II In the case of phenol, the intermediate carbocation is more resonance stabilised. **(2000, M)**

32. **Statement I** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement II Cyanide (CN^-) is a strong nucleophile. **(1998, 2M)**

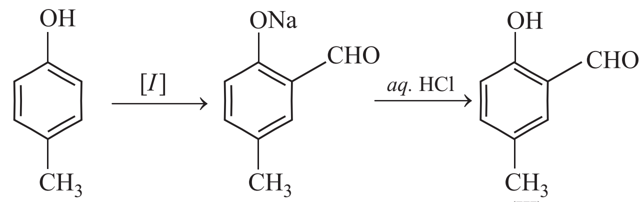
33. **Statement I** Aryl halides undergo nucleophilic substitution with ease.

Statement II The carbon halogen bond in aryl halides has partial double bond character. **(1991, 2M)**

Passage Based Problems

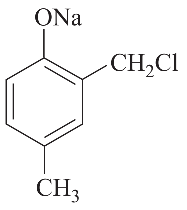
Passage 1

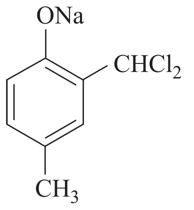
Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.

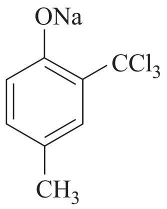


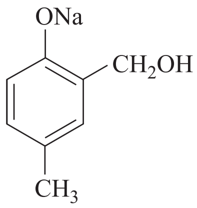
(I) (II) (III)

34. The structure of the intermediate I is

(a) 

(b) 

(c) 

(d) 

35. The electrophile in this reaction is

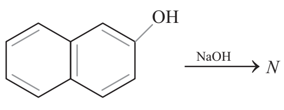
(a) $:CHCl$ (b) $^{+}CHCl_2$ (c) $:CCl_2$ (d) $^{\bullet}CCl_3$

36. Which one of the following reagents is used in the above reaction ?

(a) *aq* NaOH + CH_3Cl (b) *aq* NaOH + CH_2Cl_2
(c) *aq* NaOH + $CHCl_3$ (d) *aq* NaOH + CCl_4

Integer Type Questions

37. The number of resonance structures for N is **(2015, Adv.)**



Fill in the Blanks

38. Amongst the three isomers of nitrophenol, the one that is least soluble in water is ……… **(1992, 1M)**

39. Phenol is acidic due to resonance stabilisation of its conjugate base, namely …… **(1990, 1M)**

40. Formation of phenol from chlorobenzene is an example of ……… aromatic substitution. **(1989, 1M)**

41. The acidity of phenol is due to the ……… of its anion. **(1984, 1M)**

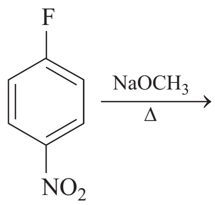
Subjective Questions

42. Carry out the following conversions.

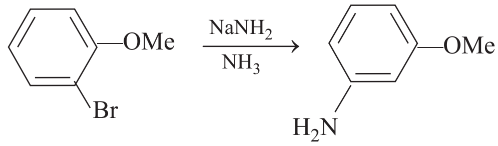
(i) Phenol to aspirin
(ii) Benzoic acid to *meta*-fluorobenzoic acid in not more than three steps. **(2003)**

43. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **(2001, 5M)**

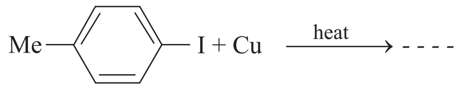
44. What would be the major product in the following reaction?



45. Explain briefly the formation of the products giving the structures of the intermediates.



46. Complete the following, giving the structures of the principal organic products

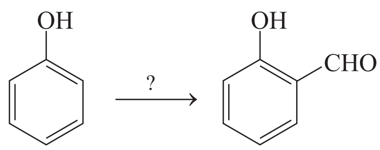


47. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps) ? **(1996, 2M)**

48. Explain the following in one or two sentences only :

"Phenol is an acid, but it does not react with sodium bicarbonate." **(1987, 1M)**

49. Complete the following with appropriate structures :



(1986, 1M)

50. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolve in dilute NaOH solution and gives a characteristic colour with $FeCl_3$. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound. **(1985, 2M)**

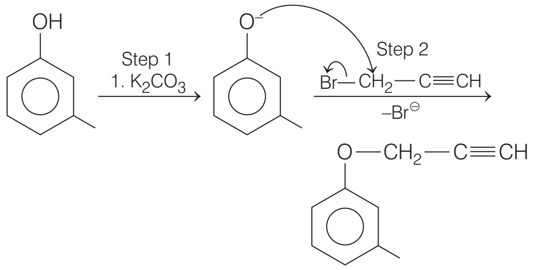
51. Give reason in one or two sentences for the following :
"*o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not." **(1985, 1M)**

Answers

1. (a)	**2.** (b)	**3.** (c)	**4.** (b)	**25.** (b,d)	**26.** (b,c)	**27.** (a, d)	**28.** (a,d)
5. (c)	**6.** (a)	**7.** (c)	**8.** (c)	**29.** (b,d)	**30.** (c)	**31.** (a)	**32.** (d)
9. (c)	**10.** (b)	**11.** (c)	**12.** (b)	**33.** (d)	**34.** (b)	**35.** (c)	**36.** (c)
13. (a)	**14.** (d)	**15.** (a)	**16.** (c)	**37.** (9)	**38.** *ortho*-nitrophenol		
17. (d)	**18.** (a)	**19.** (a)	**20.** (b)	**39.** phenoxide ion	**40.** nucleophilic	**41.** phenoxide ion	
21. (c)	**22.** (d)	**23.** (a,b,c)	**24.** (b)				

Hints & Solutions

1 The major product when *m*-cresol reacts with propargyl bromide ($HC \equiv C—CH_2Br$) in presence of K_2CO_3 in acetone is given in the following reaction:



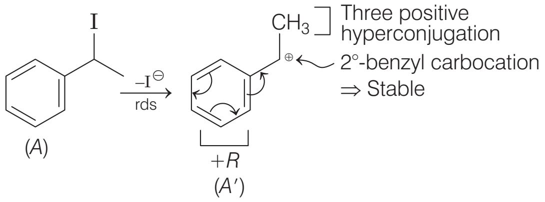
Major product

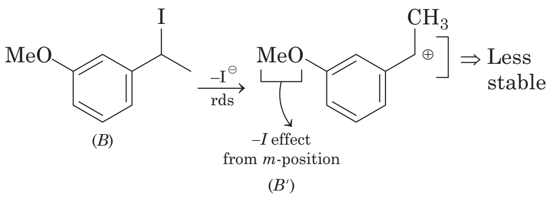
In **step 1** K_2CO_3 act as a base and abstract H-atom from —OH group. This leads to the formation of substituted phenoxide ion (highly stable).

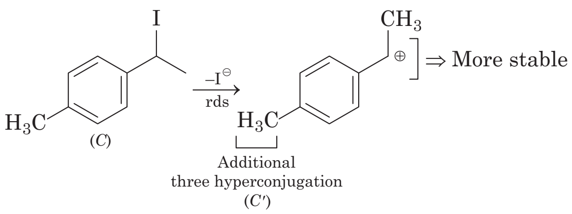
In **step 2** substituted phenoxide ion on reaction with $Br—CH_2—C \equiv CH$ gives the required product.

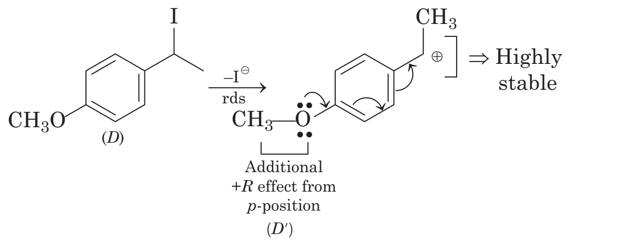
2. More stable the carbocation intermediate, higher will be the rate of S_N1 reaction.

The reaction involving carbocation intermediate formation for the given compounds are as follows:

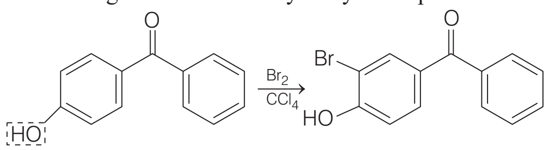




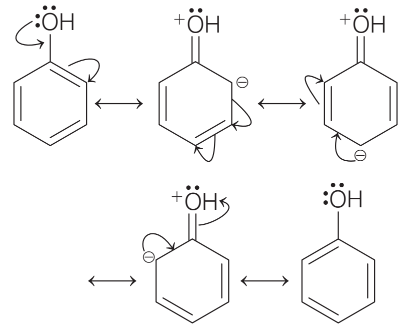




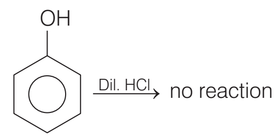
3. *p*-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.



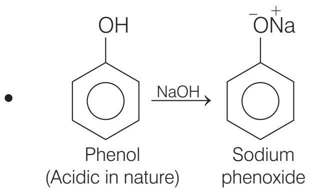
—OH group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions. —OH group also exhibit –I group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of —Br occur at *ortho* position. Resonating structures are as follows:

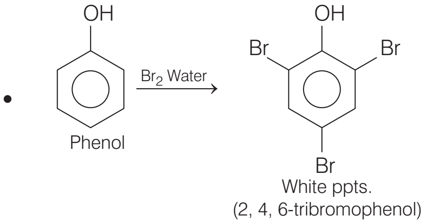


4. Phenol (ArOH) is insoluble in dil. HCl and readily soluble in NaOH solution. It reacts with Br_2/water to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of Br_2 water. Reactions involved are as follows :

• 

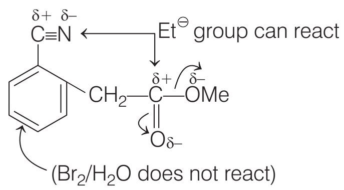
Phenol
(Acidic in nature)



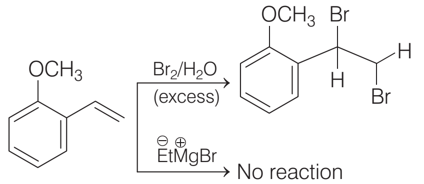


5. Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes $C_2H_5^-$ [$C_2H_5^-\overset{\oplus}{M}gBr$ in ether/aprotic medium] which can act as nucleophile as well as strong base. Bromine water (Br_2/H_2O, red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as $>C=C<$ is present outside the ring (aliphatic, not aromatic).

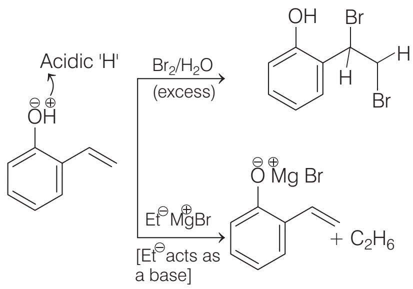
(a)



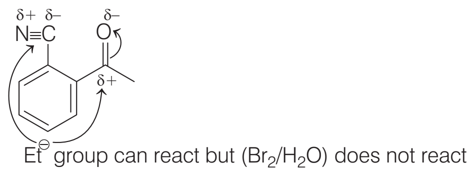
(b)



(c)

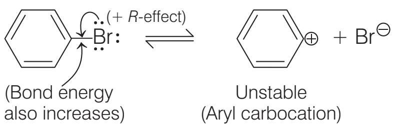


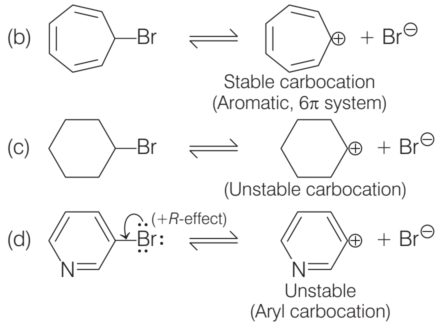
(d)

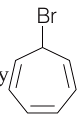


6. Only ionic halides (X^-) give precipitate of AgX with $AgNO_3$ solution. So, an organic bromide able to produce $R^{\oplus}$ (stable carbocation) and Br^- in aqueous solution will give precipitate of AgBr with $AgNO_3$.

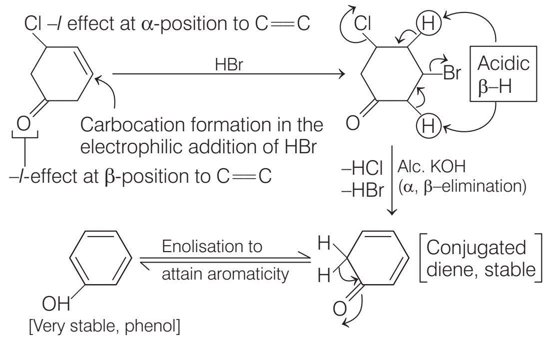
(a)

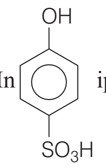


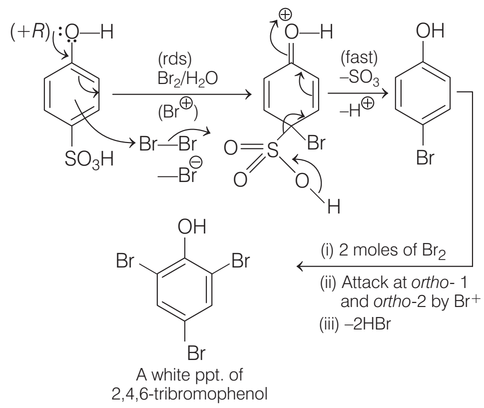


So, only  produces a precipitate of AgBr with $AgNO_3$ solution.

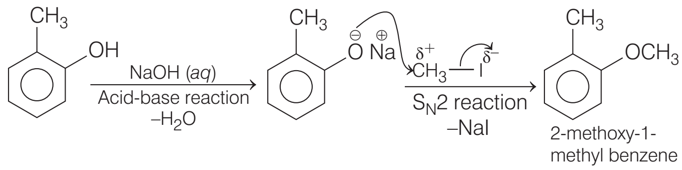
7. In presence of HBr, reactant containing $>C=C<$ undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc. KOH, α,β-elimination takes place that give corresponding diene. The diene undergoes enolisation to give stable product (phenol).



8. In  ipso-substitution takes place with the carbon bearing —SO_3H group. After the attack of the electrophilic Br^+ in the rate determining step (rds) of the ArS_E2 pathway desulphonation (—SO_3) takes place with a faster rate.



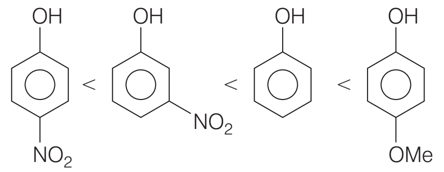
9. Substituted phenols react with *aq.*NaOH to form sodium phenoxides which on reaction with CH_3I undergoes S_N2 reaction to give 2-methoxy-1-methyl benzene.



10. Acidic strength is inversely proportional to pK_a value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol. Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol. Electron withdrawing groups ($-NO_2$) increases the acidic strength of phenol whereas electron donating group ($-OCH_3$) decreases the acidic strength of phenol. In case of $-NO_2$ group attached to phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

Thus, order of acidic strength of nitrophenol is:

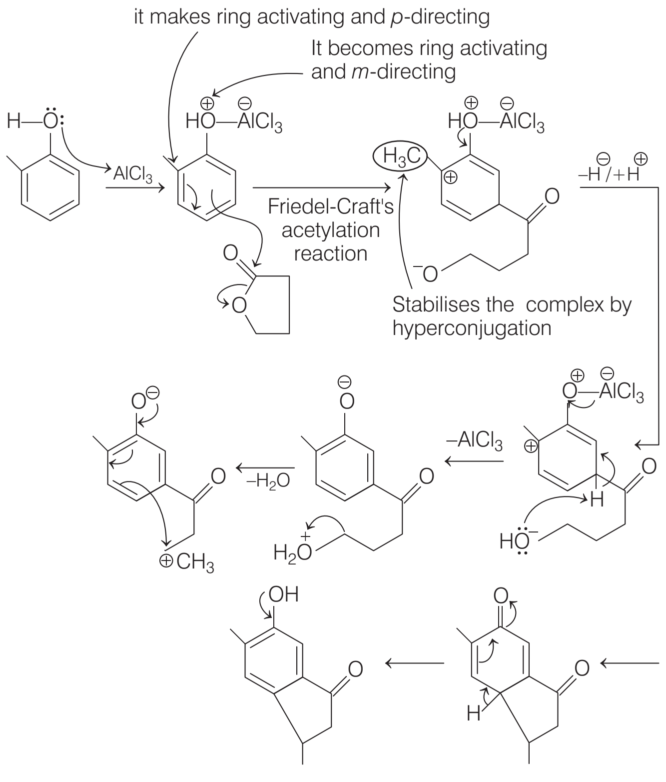
p-nitrophenol > *o*-nitrophenol and the correct order of the pK_a values of give option is



(*B*) (*C*) (*A*) (*D*)

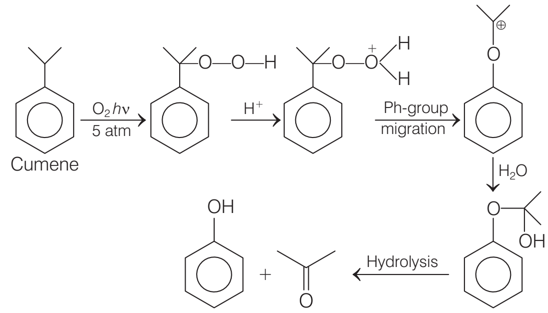
11. It is an aromatic electrophilic substitution reaction (ArS_E2).

The reaction follows $Ar\ S_E2$ (Aromatic electrophlic substitution pathway) as shown below :4



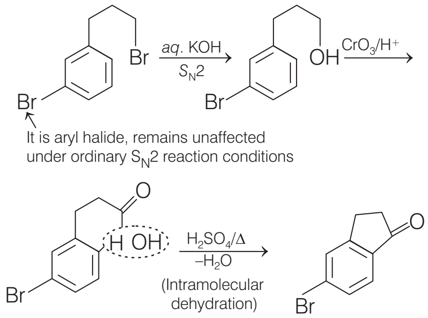
12 The given process is cumene process (Hock process) to synthesise phenol and acetone industrially.

In Hock p rocess, Ph — group migrate and release H_2O.

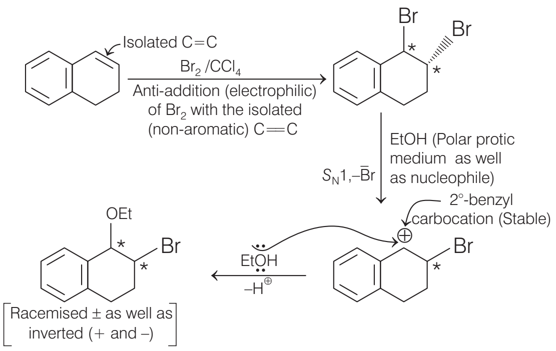


13. **Key Idea** The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step 1.

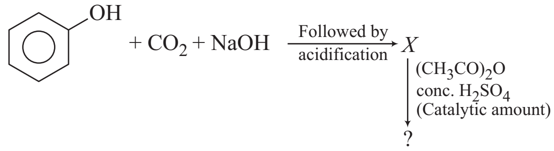
The road map of the given reaction is as follows:



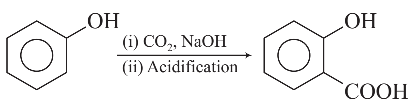
14 The road map of the given reaction is :



15.

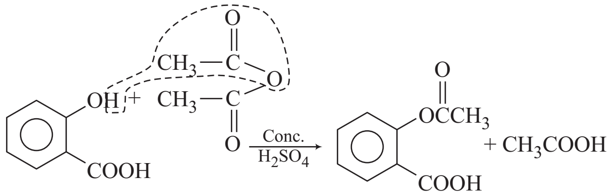


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as



Salicylic acid
(*X*)

The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as



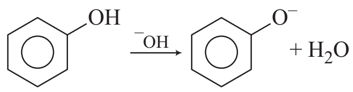
Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Pain killer).

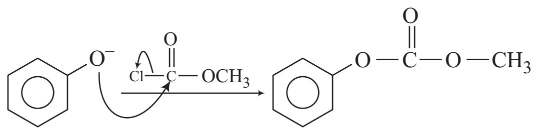
16. Given,

In the above road map, first reaction appears as acid base reaction followed by S_NAE (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

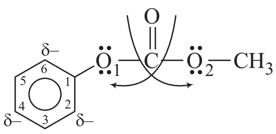
(i) **Acid base reaction**



(ii) **S_NAE**

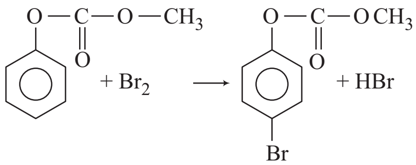


In the product of S_NAE the attached group is *ortho* and *para*-directing due to following cross conjugation



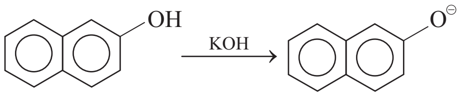
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group —O—C(=O)—O—CH_3 is bulky.

Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product i.e.

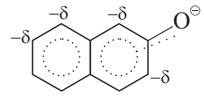


17. PLAN This problem can be solved by using the concept of synthesis of dye using electrophilic aromatic substitution reaction.

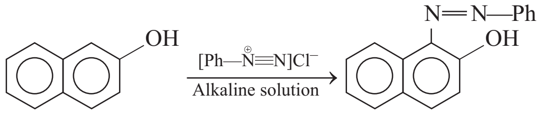
In basic (alkaline) solution naphthol exists as naphthoxide ion which is a strong *o*, *p*-directing group.



III

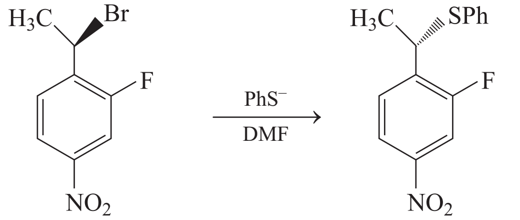


Thus, formation of dye can be shown as



Thus, (d) is the correct choice.

18.

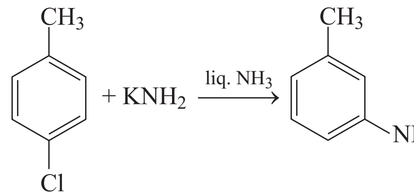


S_N2 reaction bring about inversion of configuration.

19. $C_6H_5OH + C_2H_5O^- \longrightarrow C_6H_5O^-$

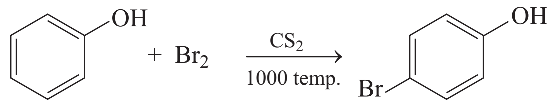
$$\xrightarrow{C_2H_5I} C_6H_5—OC_2H_5$$

20.



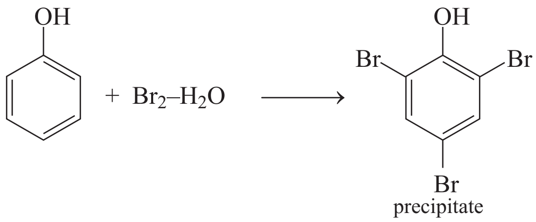
(Benzyne mechanism)

21.



In carbon disulphide, no phenoxide ion exist, therefore only monobromination takes place.

22.



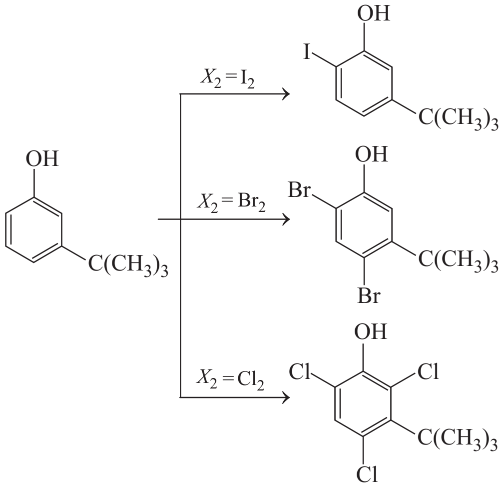
$$Br_2 + H_2O \longrightarrow HBrO + HBr$$

It is a reversible reaction, but equilibrium is significantly shifted to left, also indicated as $Br_2(aq)$.

23. PLAN This problem includes concept of effect of steric and electronic effect on reactivity of organic compounds.

Steric effect of halogens are as follows $Cl_2 < Br_2 < I_2$

Electronic effect of phenolic group directs the approaching electrophile towards *ortho* and *para* positions. Tertiary butyl group has large size so it causes steric effect around aromatic nucleus. On the basis of above factors the products of the given reactions are as follows:



Hence, orientation in electrophilic substitution reaction is decided by

(a) The steric effect of the halogen

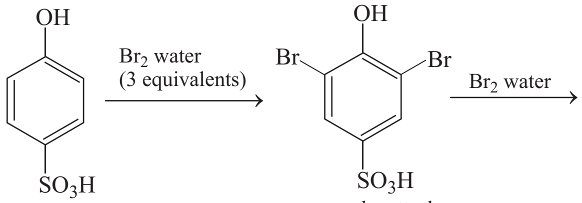
(b) The steric effect of the *tert*-butyl group

(c) The electronic effect of the phenolic group

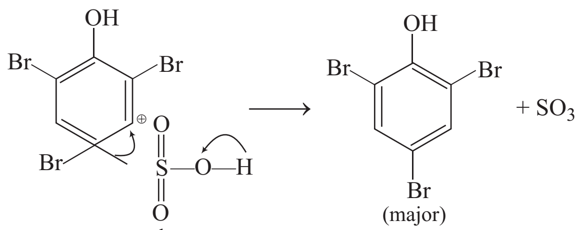
So, (a), (b) and (c) are correct choices.

24. PLAN —OH group is activating group and is *o*- and *p*-directing.

Also, —SO_3H is a better leaving group and is knocked out by Br^-.



ortho-attack

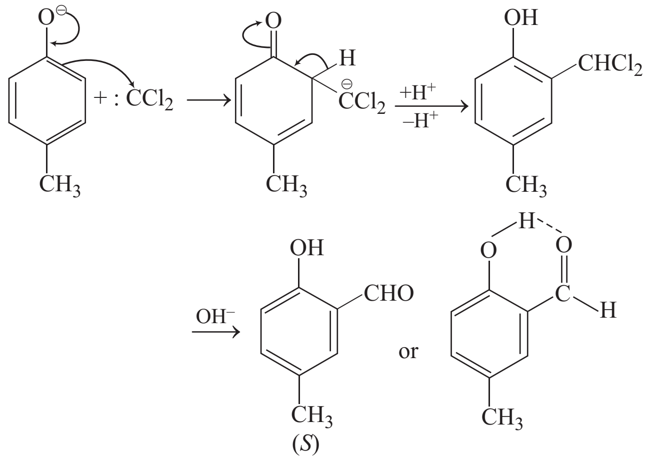


para-attack

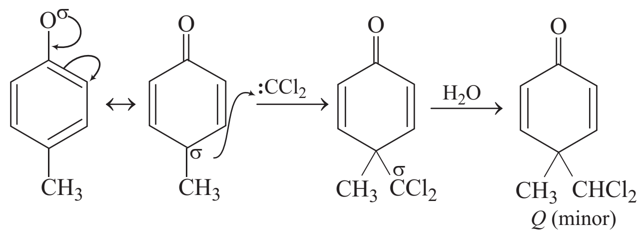
25. PLAN Phenolic compounds in alkaline solution react with chloroform ($CHCl_3$) at a temperature lower than that of $CHCl_3$ to form *ortho*-isomer as the major product (due to greater stability resulting from intramolecular hydrogen bonding).

$$\overset{-}{HO} + H{-}CCl_3 \rightleftharpoons H_2O - \overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^-} :CCl_2$$

dichloro carbene

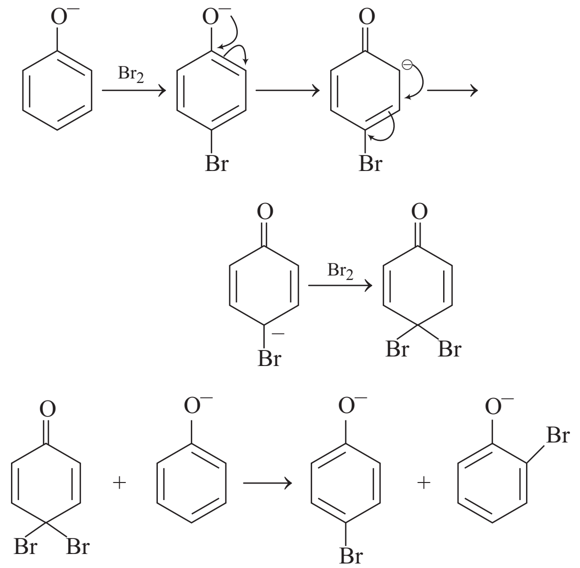


Major as stable due to intramolecular H-bonding.

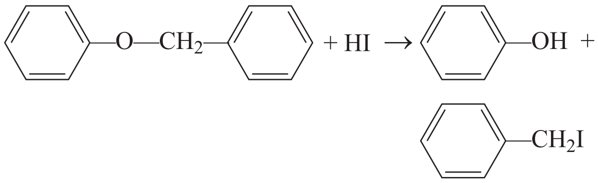


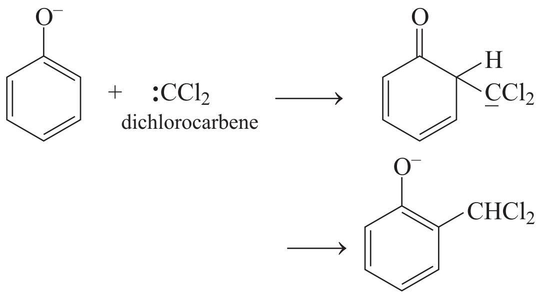
Thus, (b) and (d) are correct.

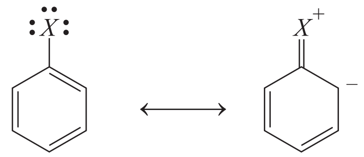
26. —OH in phenol is *ortho/para* directing group.



27.

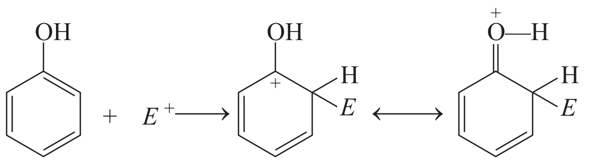


28. 

29. 

Above resonance makes X- a poor leaving group. Also, the carbon bearing X is sp^2- hybridised.

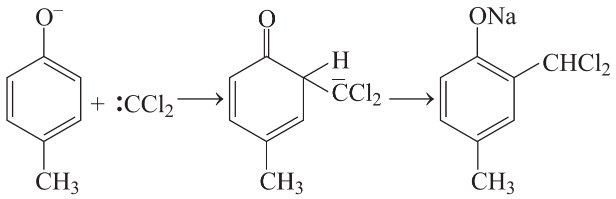
30. Bromo group is deactivating due to dominance of inductive effect over resonance effect. However, orientation is determined by mesomeric effet of —Br.

31. 

resonance stabilisation of intermediate carbocation

32. Statement I is incorrect, aryl halides do not undergo nucleophilic substitution reaction with ease. Cyanide ion (CN^-) is a strong nucleophile.

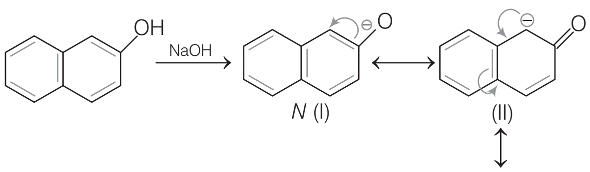
33. Statement I is incorrect, aryl halides do not usually undergo nucleophilic substitution with ease. Statement II is correct, resonance introduces partial double bond character to C—X bond.

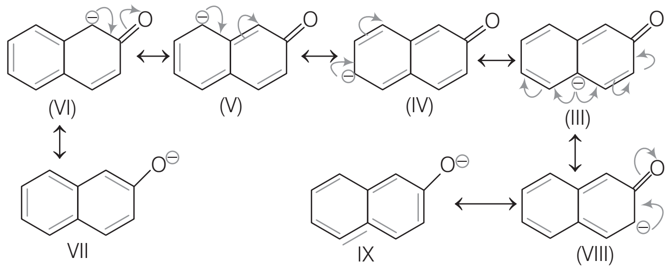
34. 

Intermediate

35. Dichlorocarbene is the electrophile as shown above.

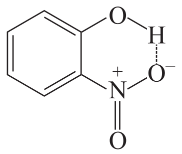
36. $CHCl_3 + NaOH \longrightarrow \underset{\text{electrophile}}{:CCl_2}$ (Dichlorocarbene)

37. 



All the above shown nine resonance structures are different.

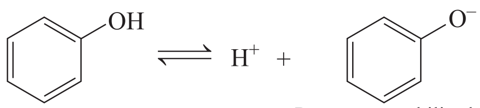
38. *Ortho*-nitrophenol : Due to intramolecular H-bonding.



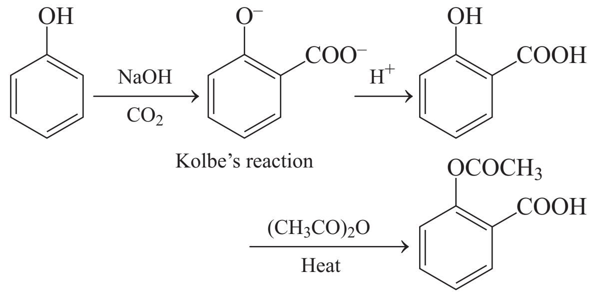
Intramolecular H-bonding in *ortho*-nitrophenol

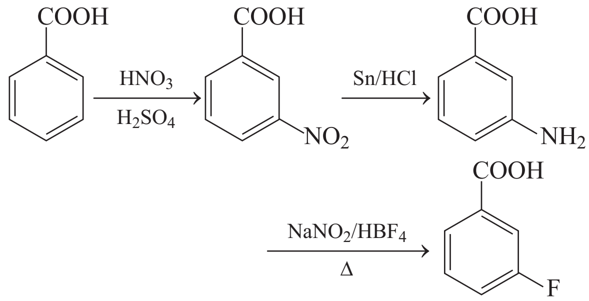
39. Phenoxide ion **40.** Nucleophilic

41. Phenoxide ion :

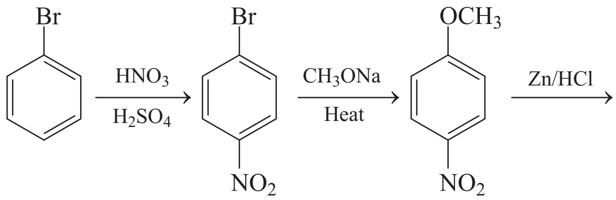


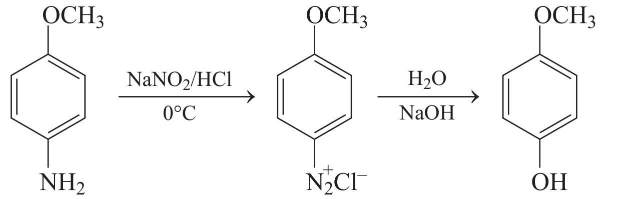
Resonance stabilised conjugate base

42. (i) 

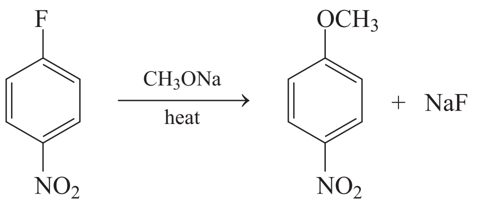
(ii) 

meta-fluorobenzoic acid

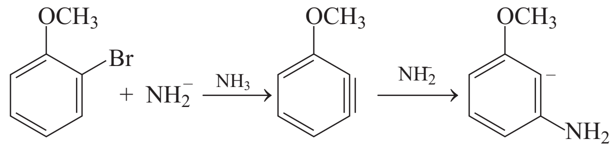
43. 



4-methoxyphenol

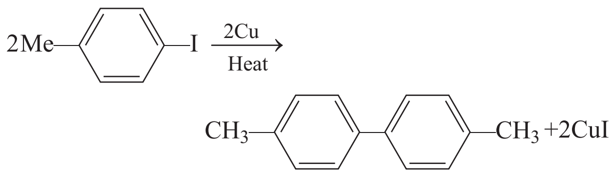
44. 

Nucleophilic aromatic substitution occur which is assisted by electron withdrawing —NO_2 group from *para* position.

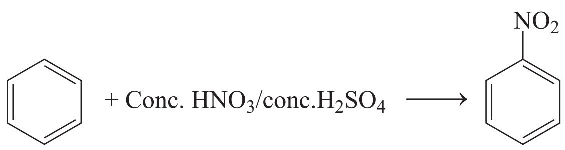
45. 

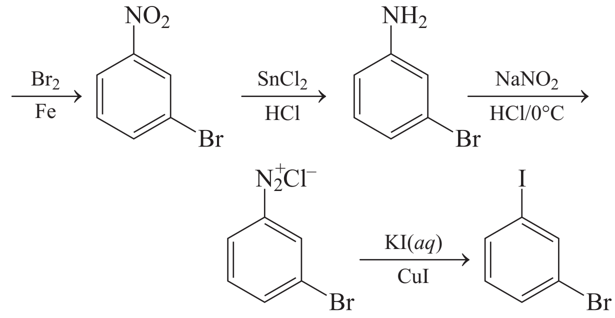
Benzyne

more stable carbanion is formed

46. 

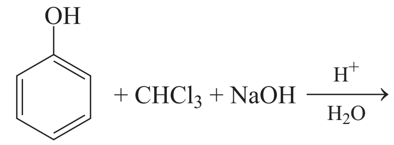
Ullmann's reaction

47. 



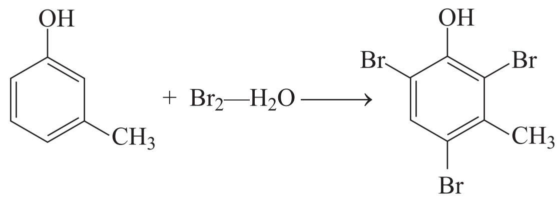
m-bromoiodo-benzene

48. Phenol is weaker acid than carbonic acid.

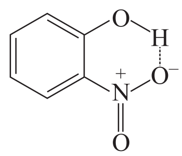
49. 

Reimer-Tiemann reaction

50. The compound must contain a hydroxy group on the ring with all three *ortho/para* positions vacant :



51. Intramolecular H-bonding in *ortho*-nitrophenol lowers its boiling point. No such intramolecular H-bonding is possible with *p*-nitrophenol and rather it is associated together by intermolecular H-bonding which increases the boiling point.



ortho-nitrophenol

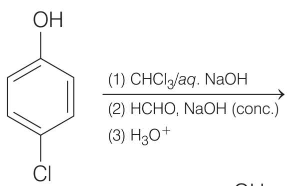
Download Chapter Test
http://tinyurl.com/y2xlovfc *or*

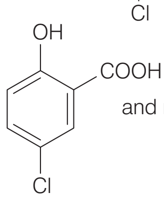
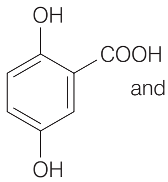
31

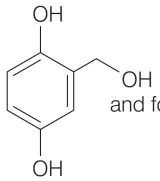
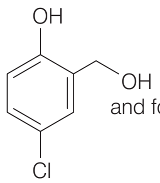
Aromatic Aldehydes, Ketones and Acids

Objective Questions I (Only one correct option)

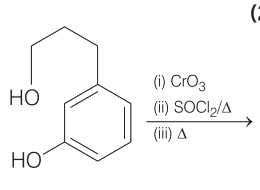
1. The major products of the following reaction are **(2019 Main, 12 April I)**

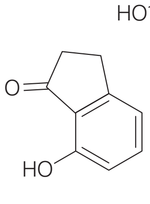
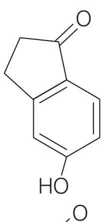


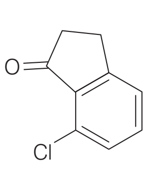
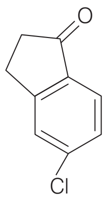
(a)  and methanol (b)  and methanol

(c)  and formic acid (d)  and formic acid

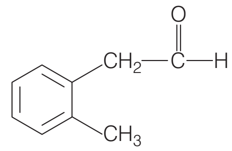
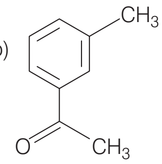
2. The major product of the following reaction is **(2019 Main, 12 April I)**

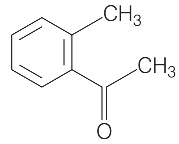
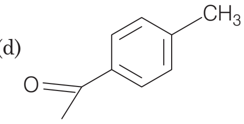


(a)  (b) 

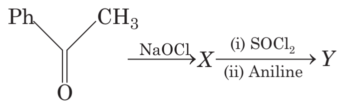
(c)  (d) 

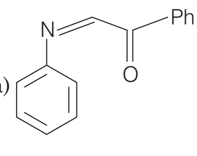
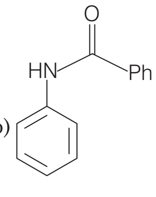
3. Compound $A(C_9H_{10}O)$ shows positive iodoform test. Oxidation of A with $KMnO_4/KOH$ gives acid $B(C_8H_6O_4)$. Anhydride of B is used for the preparation of phenolphthalein. Compound A is **(2019 Main, 10 April II)**

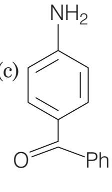
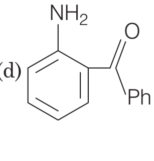
(a)  (b) 

(c)  (d) 

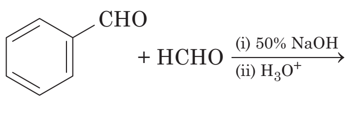
4. The major product Y in the following reaction is **(2019 Main, 10 April II)**



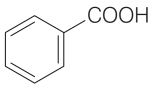
(a)  (b) 

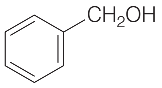
(c)  (d) 

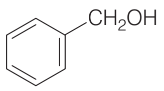
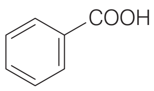
5. Major products of the following reaction are **(2019 Main, 10 April I)**



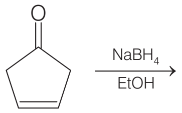
(a) CH_3OH and HCO_2H

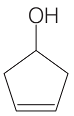
(b) CH_3OH and 

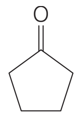
(c) HCOOH and 

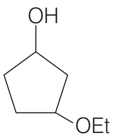
(d)  and 

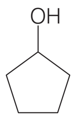
6. The major product of the following reaction is **(2019 Main, 12 Jan II)**



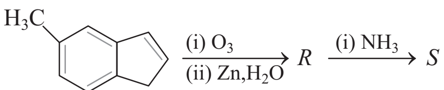
(a) 

(b) 

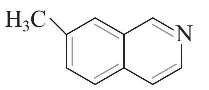
(c) 

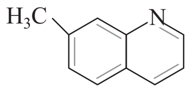
(d) 

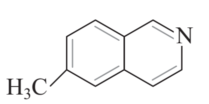
7. In the following reactions, the product S is

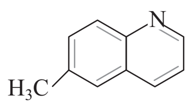


(2019 Main, 12 Jan I)

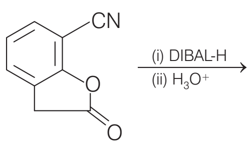
(a) 

(b) 

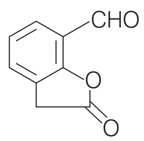
(c) 

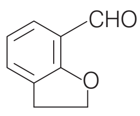
(d) 

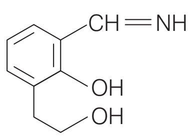
8. The major product of the following reaction is

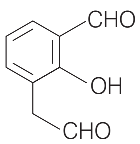


(2019 Main, 12 Jan I)

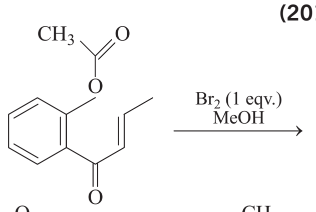
(a) 

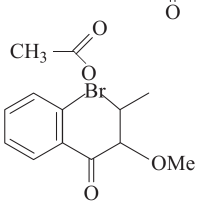
(b) 

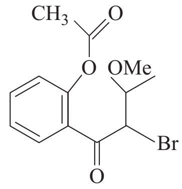
(c) 

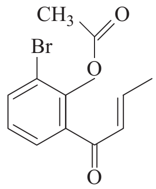
(d) 

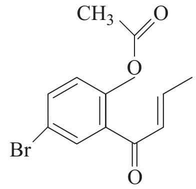
9. The major product obtained in the following conversion is **(2019 Main, 11 Jan II)**



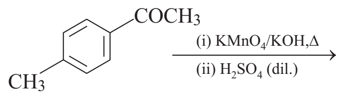
(a) 

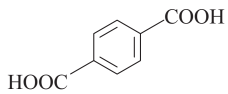
(b) 

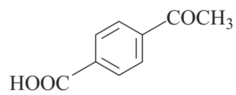
(c) 

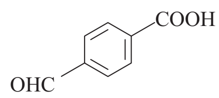
(d) 

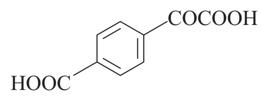
10. The major product of the following reaction is **(2019 Main, 11 Jan I)**



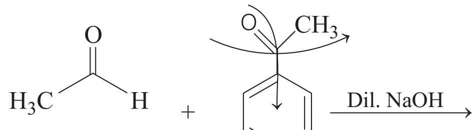
(a) 

(b) 

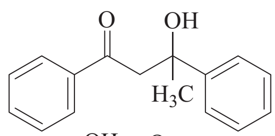
(c) 

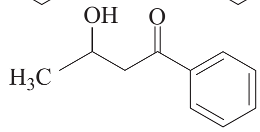
(d) 

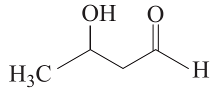
11. The major product formed in the following reaction is

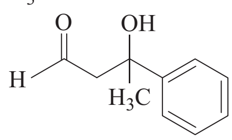


(2019 Main, 9 Jan II)

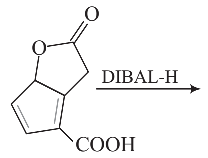
(a) 

(b) 

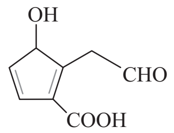
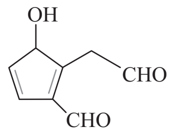
(c) 

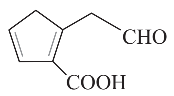
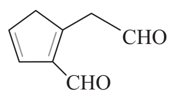
(d) 

12. The major product obtained in the following reaction is



(2017 Main)

(a)  (b) 

(c)  (d) 

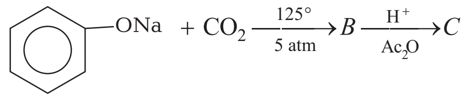
13. In the following sequence of reaction,

Toluene $\xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$ **(2015 Main)**

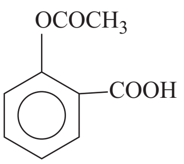
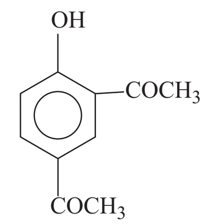
The product C is

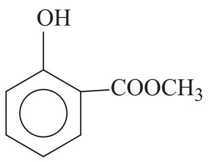
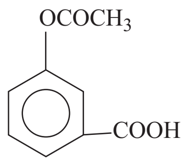
(a) C_6H_5COOH (b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

14. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.

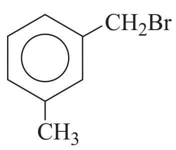
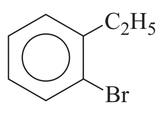


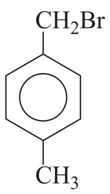
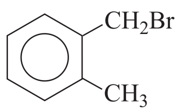
The major product C would be **(2014 Main)**

(a)  (b) 

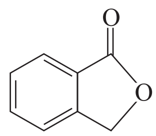
(c)  (d) 

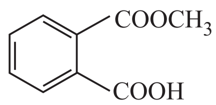
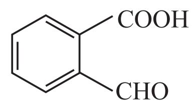
15. Compound (A), C_8H_9Br gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **(2013 Main)**

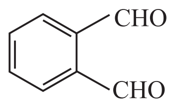
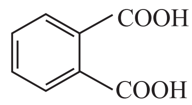
(a)  (b) 

(c)  (d) 

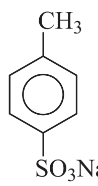
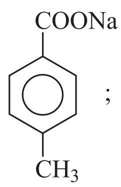
16. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the main product? **(2006, 5M)**

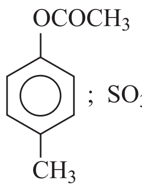
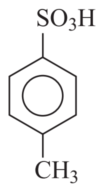


(a)  (b) 

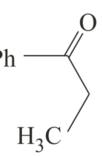
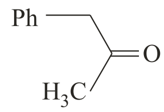
(c)  (d) 

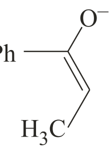
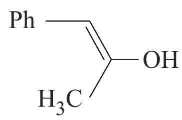
17. 4-methyl benzene sulphonic acid reacts with sodium acetate to give **(2005, 1M)**

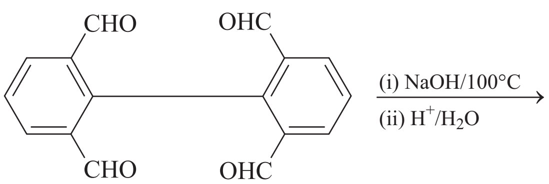
(a)  ; CH_3CO_2H (b)  ; SO_3

(c)  ; SO_3 (d)  ; NaOH

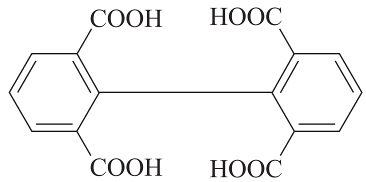
18. $Ph—C \equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$, A is **(2003, 1M)**

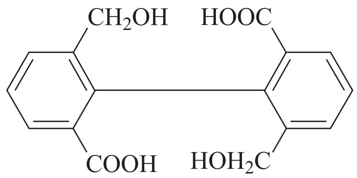
(a)  (b) 

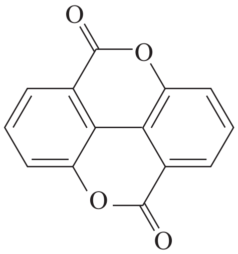
(c)  (d) 

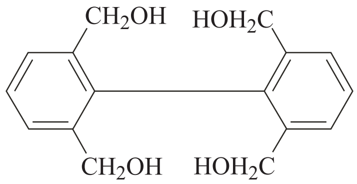
19. 

Major product **(2003, 1M)**

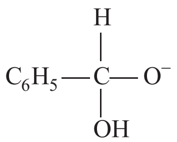
(a) 

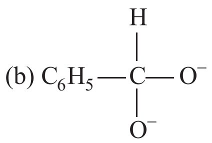
(b) 

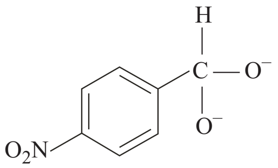
(c) 

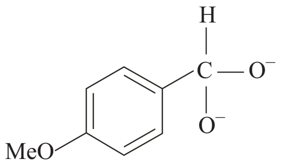
(d) 

20. In Cannizzaro's reaction, the intermediate which is the best hydride donor is **(1997)**

(a) 

(b) 

(c) 

(d) 

21. In the Cannizzaro's reaction given below :

$$2Ph—CHO \xrightarrow{KOH} Ph—CH_2OH + PhCO_2^-$$

The slowest step is **(1996, 1M)**

(a) the attack of —OH at the carbonyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of Ph—CH_2OH

22. *m*-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives **(1991, 1M)**

(a) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol
(b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde

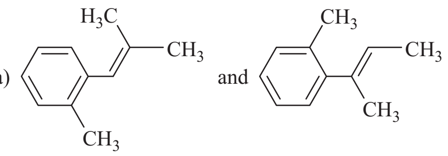
Objective Questions II

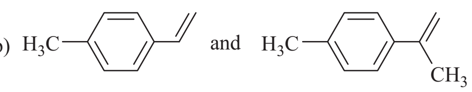
(One or more than one correct option)

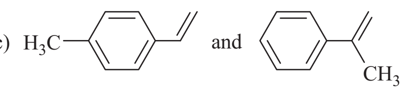
23. Compound *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is C_8H_8O. *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction. **(2017 Adv.)**

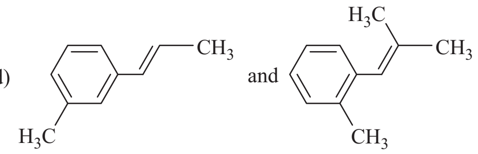
(i) $P \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{Q}$ (ii) $R \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{S}$

The option(s) with suitable combination of *P* and *R*, respectively, is(are)

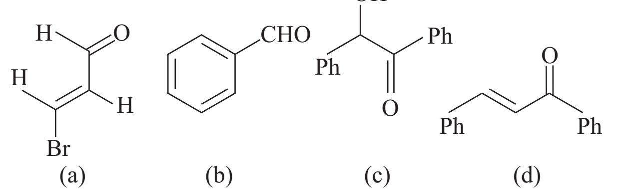
(a) 

(b) 

(c) 

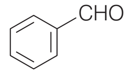
(d) 

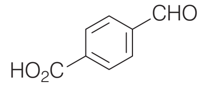
24. Positive Tollen's test is observed for

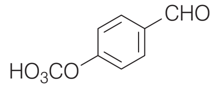


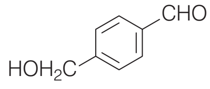
(a) (b) (c) (d)

25. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are **(2019 Main 12 Jan II)**

(a) 

(b) 

(c) 

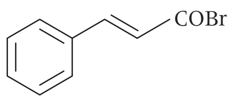
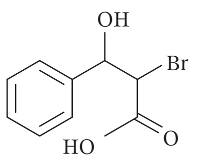
(d) 

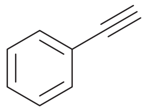
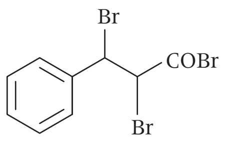
Passage Based Questions

Paragraph X

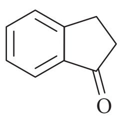
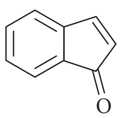
Treatment of benzene with CO / HCl in the presence of anhydrous $AlCl_3$ / CuCl followed by reaction with Ac_2O / NaOAc gives compound X as the major product. Compound X upon reaction with Br_2 / Na_2CO_3 followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2 / Pd - C, followed by H_3PO_4 treatment gives Z as the major product.

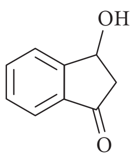
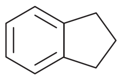
26. The compound Y is **(2018 Adv.)**

(a)  (b) 

(c)  (d) 

27. The compound Z is

(a)  (b) 

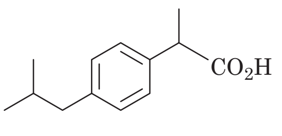
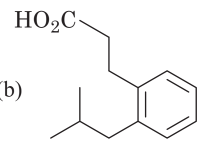
(c)  (d) 

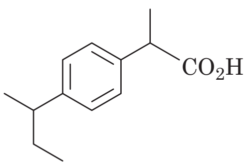
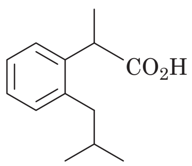
Paragraph A

An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidised to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S. **(2018 Adv.)**

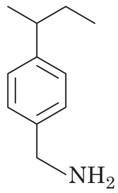
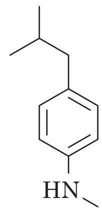
$$S \xleftarrow[\text{(4) } CHCl_3/KOH,\, \Delta \;\; \text{(5) } H_2/Pd\text{-}C]{\text{(1) } H_2/Pd\text{-}C \;\; \text{(2) } NH_3/\Delta \;\; \text{(3) } Br_2/NaOH} P \xrightarrow[\text{(3) MeMgBr, } CdCl_2 \;\; \text{(4) } NaBH_4]{\text{(1) } H_2/Pd\text{-}C \;\; \text{(2) } SOCl_2} Q \xrightarrow[\text{(3) } CO_2\text{(dry ice)} \;\; \text{(4) } H_3O^+]{\text{(1) HCl} \;\; \text{(2) Mg/}Et_2O} R$$

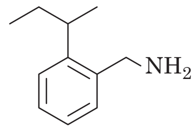
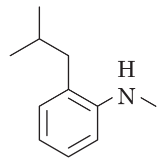
28. The Compound R is

(a)  (b) 

(c)  (d) 

29. The compound S is

(a)  (b) 

(c)  (d) 

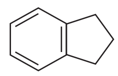
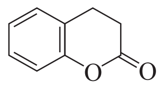
Passage

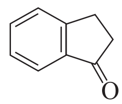
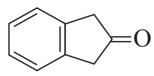
In the following reactions sequence, the compound J is an intermediate.

$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\text{(ii) } SOCl_2 \;\; \text{(iii) anhyd. } AlCl_3]{\text{(i) } H_2,\, Pd/C} K$$

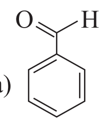
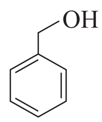
J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test. **(2012)**

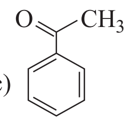
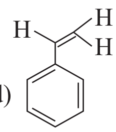
30. The compound K, is

(a)  (b) 

(c)  (d) 

31. The compound I, is

(a)  (b) 

(c)  (d) 

Fill in the Blanks

32. The structure of the intermediate product formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is …………… **(1992, 2M)**

True/False

33. Benzaldehyde undergoes aldol condensation in an alkaline medium. **(1982 , 1M)**

Subjective Questions

34. Five isomeric *para*-disubstituted aromatic compounds A to E with molecular formula $C_8H_8O_2$ were given for identification.
Based on the following observations, give structures of the compounds : **(2002, Main, 5M)**

(i) Both A and B form a silver mirror with Tollen's reagent; also, B gives a positive test with $FeCl_3$ solution.

(ii) C gives positive iodoform test .

(iii) D is readily extracted in aqueous $NaHCO_3$ solution.

(iv) E on acid hydrolysis gives 1, 4-dihydroxy benzene.

35. An organic compound A, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound B. The compound B on treatment with PCl_5, followed by reaction with $H_2/Pd/(BaSO_4)$ gives compound C, which on reaction with hydrazine gives a cyclised compound D ($C_{14}H_{10}N_2$). Identify A, B, C and D. Explain the formation of D from C. **(2000, 5M)**

36. Explain, why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid? **(1999, 2M)**

Matching Type Questions

Answer Q. 22, Q. 23 and Q. 24 by appropriately matching the information given in the three columns of the following table.
Column 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. **(2017 Adv.)**

	Column 1		Column 2		Column 3
(I)	Toluene	(i)	$NaOH/Br_2$	(P)	Condensation
(II)	Acetophenone	(ii)	$Br_2/h\nu$	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O/CH_3COOK$	(R)	Substitution
(IV)	Phenol	(iv)	$NaOH/CO_2$	(S)	Haloform

37. The only **CORRECT** combination in which the reaction proceeds through radical mechanism is

(a) (IV) (i) (Q) (b) (III) (ii) (P)
(c) (II) (iii) (R) (d) (I) (ii) (R)

38. For the synthesis of benzoic acid, the only CORRECT combination is

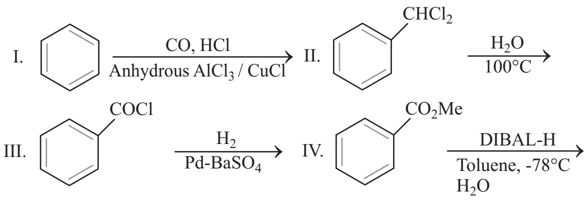
(a) (II) (i) (S) (b) (I) (iv) (Q)
(c) (IV) (ii) (P) (d) (III) (iv) (R)

30. The only **CORRECT** combination that gives two different carboxylic acids is

(a) (IV) (iii) (Q) (b) (II) (iv) (R)
(c) (I) (i) (S) (d) (III) (iii) (P)

Integer Type Questions

40. Among the following the number of reaction(s) that produce(s) benzaldehyde is **(2015 Adv.)**

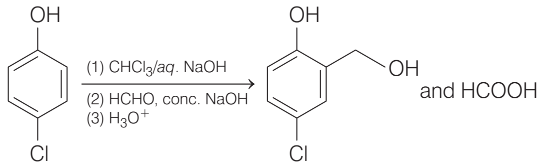


Answers

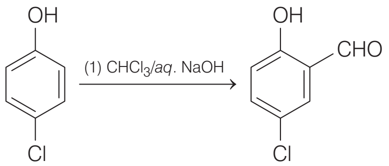
1. (d)	**2.** (b)	**3.** (c)	**4.** (b)	**21.** (b)	**22.** (a)	**23.** (b,c)	**24.** (a,b,c)
5. (c)	**6.** (a)	**7.** (a)	**8.** (d)	**25.** (b,d)	**26.** (c)	**27.** (a)	**28.** (a)
9. (b)	**10.** (a)	**11.** (c)	**12.** (a)	**29.** (b)	**30.** (c)	**31.** (a)	
13. (d)	**14.** (a)	**15.** (d)	**16.** (c)	**32.** $C_6H_5—CH(OAc)_2$		**33.** False	**37.** (a)
17. (a)	**18.** (a)	**19.** (b)	**20.** (d)	**38.** (d)	**39.** (b)	**40.** (4)	

Hints & Solutions

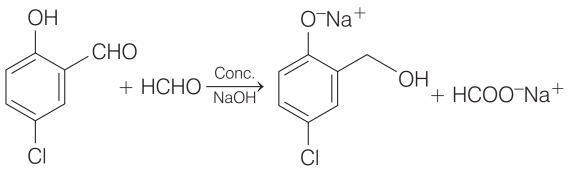
1. The major products of the given reaction are as follows:



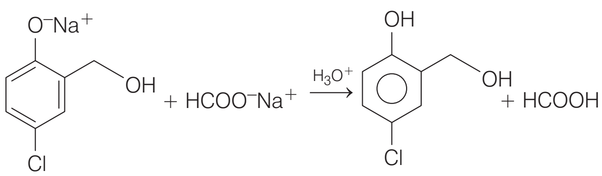
In step-I, substituted phenol undergoes Reimer-Tiemann reaction in presence of $CHCl_3$ / *aq.* NaOH



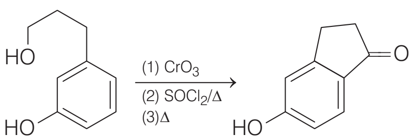
The aldehyde obtained in above equation does not possess α-hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



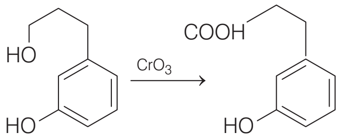
Upon hydrolysis, following reaction takes place



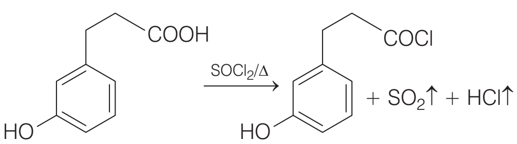
2. The major product formed in the reaction is as follows :



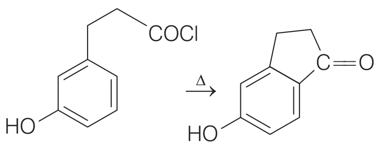
Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide (CrO_3) in acidic medium.



—OH group of carboxylic acid get substituted by —Cl in presence of $SOCl_2$ (Thionyl chloride).



Further, heating of product leads to intramolecular cyclisation.

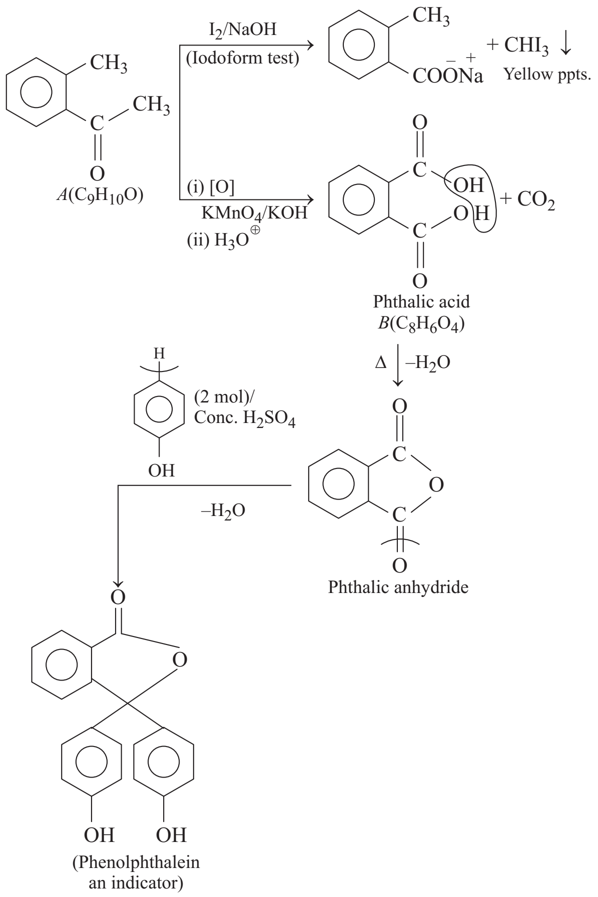


3. (i) $C_9H_{10}O$ shows positive iodoform test thus, $—\underset{\underset{O}{\|}}{C}—CH_3$ group is present.

(ii) $C_9H_{10}O$ on strong oxidation ($KMnO_4$ / KOH), gives acid ($C_8H_6O_4$), indicating it can be a dicarboxylic acid. So, '*A*' contains —$COCH_3$ and one —CH_3 group which get oxidised into —COOH and —COOH respectively.

(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, '*B*' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

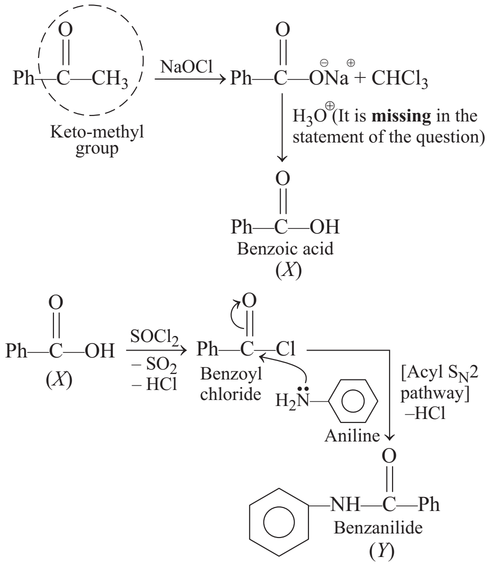
Thus, the reaction sequence is as follows :



4. NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

The given reaction takes place as follows :

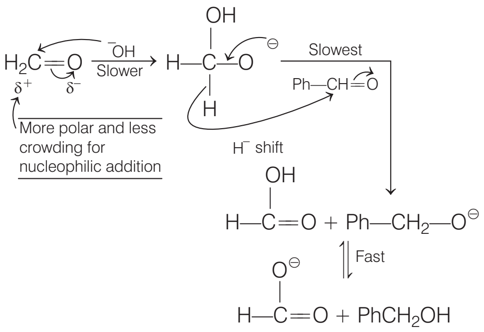


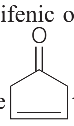
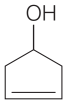
5. The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the —CHO groups of Ph—CHO and H—CHO are +1 and zero respectively. So, HCHO is the stronger reducing agent than PhCHO. As a result, HCHO is oxidised to HCOONa (by donation of hydride, H^-) and PhCHO (H^- acceptor) is reduced to $PhCH_2OH$.

$$Ph—\overset{+1}{C}HO + H\overset{0}{C}HO \xrightarrow{50\%\ NaOH} Ph—\overset{-1}{C}H_2OH + H\overset{+2}{C}O\overset{-}{O}\overset{+}{Na}$$

$$\xrightarrow{H_3O^+} \underset{\text{(Major products)}}{PhCH_2OH + HCOOH}$$

The reaction proceed *via* following mechanism.



6. Reducing agents like $LiAlH_4$, $NaBH_4$, i.e. complex hydrides usually does not affect olifenic or π-bonds. Thus, if $NaBH_4$ is applied to a compound like  then its $\rangle C=O$ bond will be reduced only and we get  as the final product.

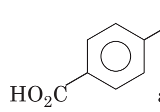
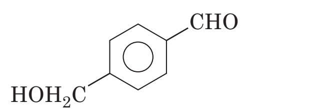
Thus, option (a) is correct answer.

7. **Key Idea** Grignard reagent usually attacks on $> C=O$ group as :

$$\rangle C=O + RMgX \longrightarrow \rangle C\langle^{OMgX}_{R} \text{ (Ionic salt)} \xrightarrow[-Mg(OH)X]{\text{Hydration}} \rangle C\langle^{OH}_{R}$$

The question is related to above reaction only with the condition that the consumption of $RMgX$ will be more than 1 equivalent in some of the given cases.

Among the given compounds B, i.e.

 and D, i.e. 

contain additional groups which can give active hydrogens. Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as:

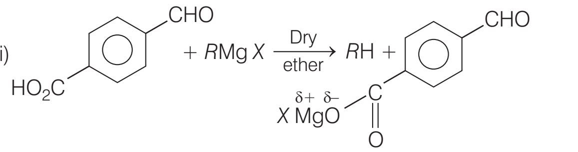
$$ROH + R'MgX \xrightarrow[\text{ether}]{\text{Dry}} R'H + Mg\langle^{OR}_{X}$$

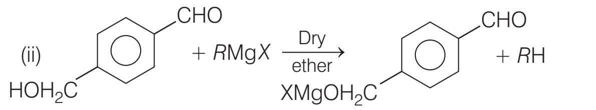
These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

(i) from the $>C=O$ group

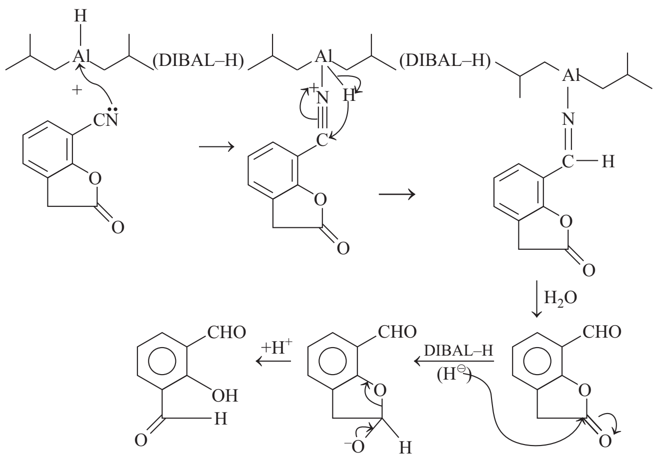
(ii) from the group which release active hydrogen

The additional reactions involved are:

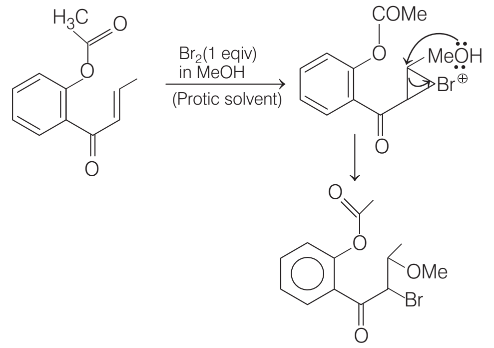
(i) 

(ii) 

8. DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula $[\lambda\text{-}Bu_2AlH]$. At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.

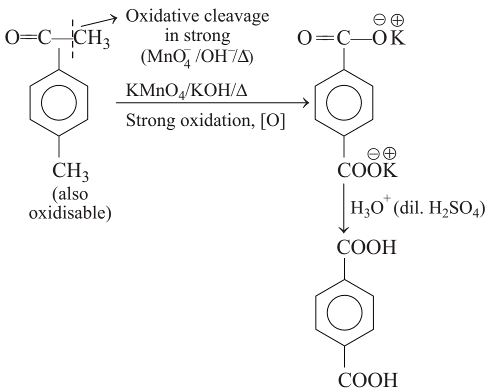


9. In presence of Br_2/EtOH, the reactant containing double bond undergoes electrophilic addition reaction *via* the formation of bromonium ion. On further attack of $-\ddot{\underset{\cdot\cdot}{O}}Me$ on bromonium ion gives the addition product.

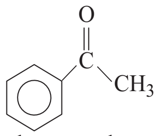


(Major)

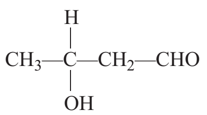
10. In presence of alkaline $KMnO_4$, vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.

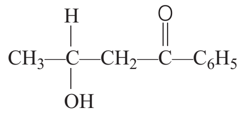


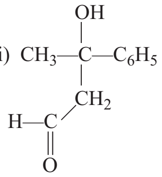
11. In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case CH_3CHO will lose

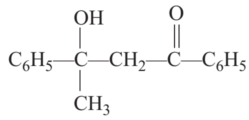
α-hydrogen faster than  due to one more reason, i.e. conjugation between benzene ring and $>C=O$ group. Along with sterically less hindered nucleophile of CH_3CHO will also add to the major product formation.

Following four products are possible in the reaction:

(i)  (Self Aldol condensation of CH_3CHO)

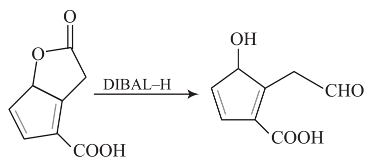
(ii)  (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which >C=O group of CH_3CHO is carbanion acceptor).

(iii)  (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which >C=O group of $C_6H_5COCH_3$ is carbanion acceptor).

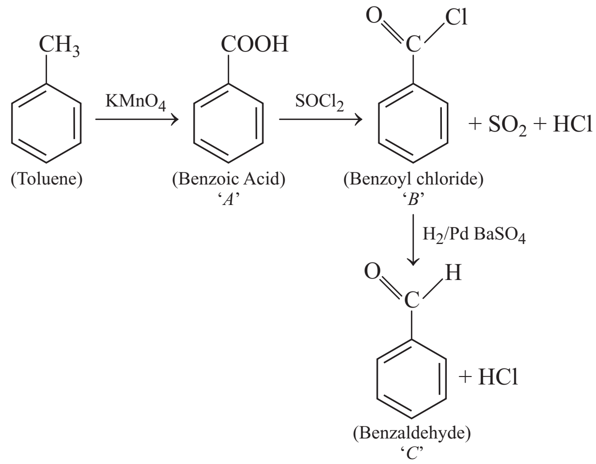
(iv)  (Self Aldol condensation product of $C_6H_5COCH_3$)

$\bar{O}H$ of base will prefer to attack on $-CH_3$ group of CH_3CHO for the formation of carbanion and as among the $>C=O$ groups available, the $>C=O$ group of CH_3CHO is the best carbanion acceptor. Hence, self condensation product of CH_3CHO will be the major product.

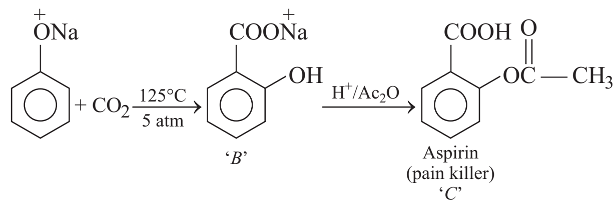
12. DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL —H, Lactones are reduced directly to aldehydes.



13. Toluene undergoes oxidation with $KMnO_4$, forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ($SOCl_2$) to give benzoyl chloride which upon reduction with H_2/Pd or $BaSO_4$ forms benzaldehyde (Rosenmund reduction) The conversion look like,

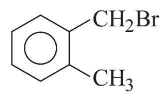


14. It is a Kolbe Schmidt reaction.

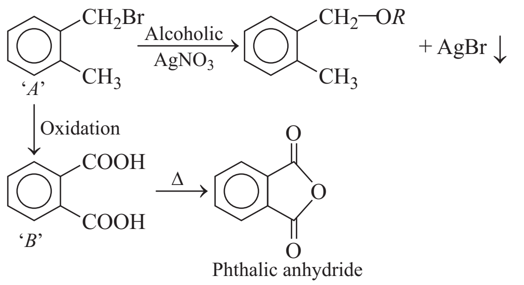


The second step of the reaction is an example of acetylation reaction.

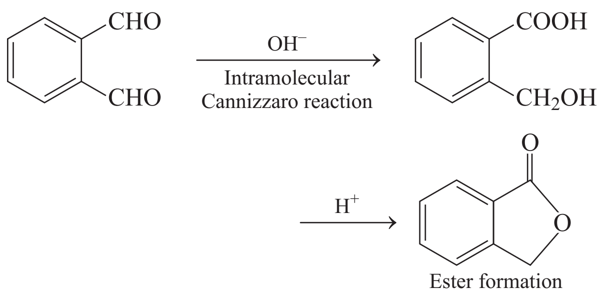
15. Compound A gives a precipitate with alcoholic $AgNO_3$, so it must contains Br in side chain. On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus. Since, compound B gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position. Thus, A must be



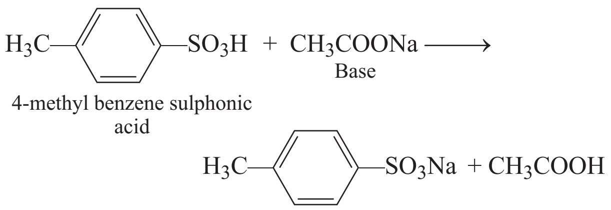
and the reactions are as follows :



16.



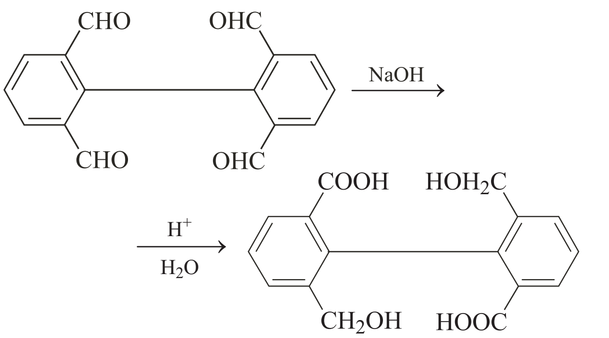
17.



18. $Ph-C\equiv C-CH_3 \xrightarrow{H^+} Ph-\overset{+}{C}=CH-CH_3$
Stable carbocation

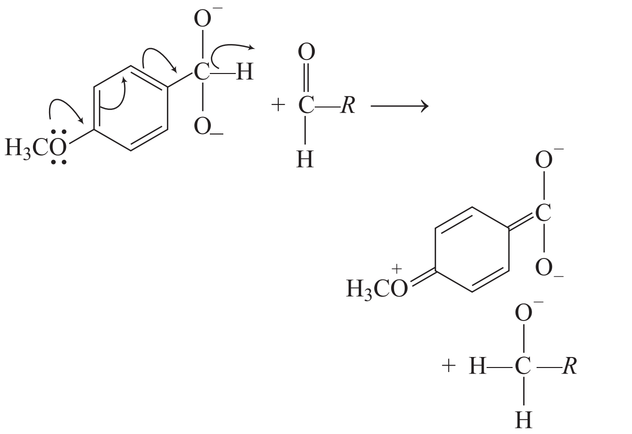
$\xrightarrow{H_2O} Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

19.

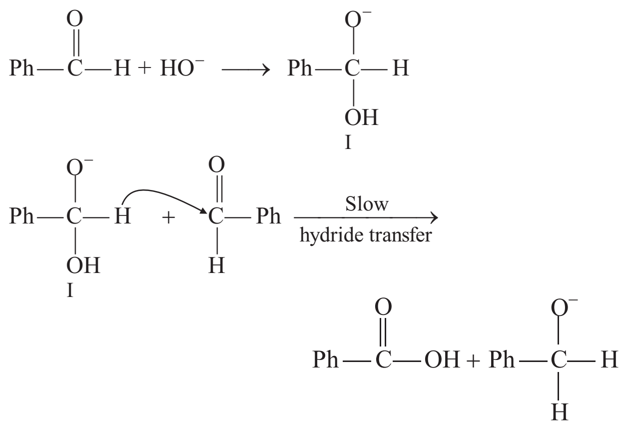


The above reaction is an example of intramolecular Cannizzaro reaction.

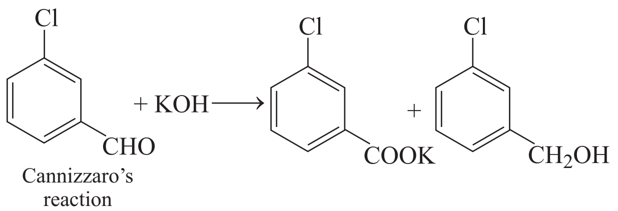
20. Dioxoanion is better hydride donor. Electron donating group at *ortho/para* position further promote H^- transfer.



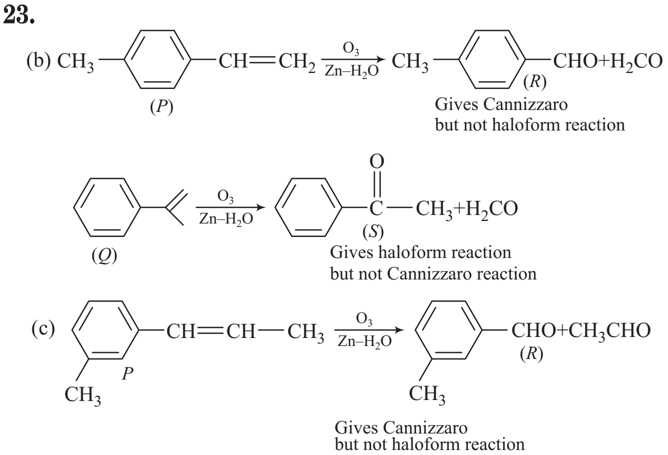
21.



22.

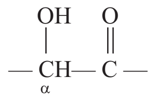


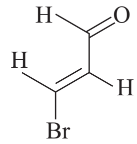
23.



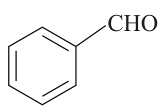
24. $\underset{\text{(Tollen's reagent)}}{RCHO + Ag_2O} \xrightarrow{OH^-} RCOOH + \underset{\text{Silver mirror}}{2Ag}$

Tollen's test is given by all aldehydes and all reducing sugars as glucose, fructose and α-hydroxy ketones.

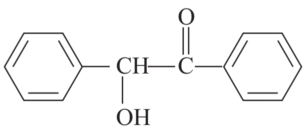




having an aldehyde group gives Tollen's test.

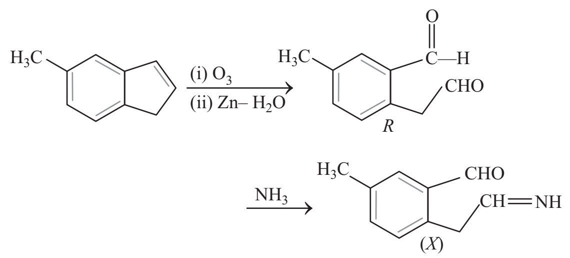


Aldehyde

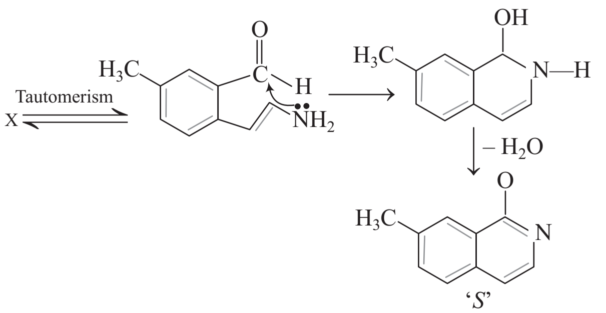
(c) 

α-hydroxy ketone give positive Tollen's test.

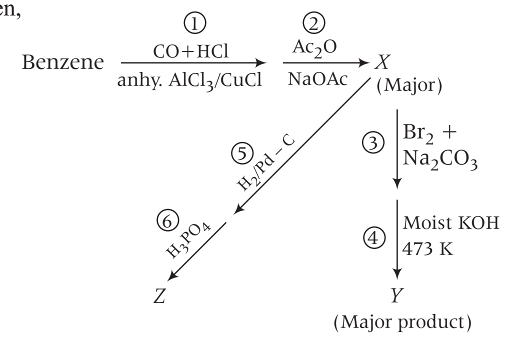
25.



In the above reaction, NH_3 prefer to attack at aliphatic aldehyde group than an less reactive aromatic aldehyde group.

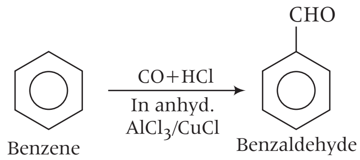


26. Given,



For this question we require only reaction 1 to 4 written above. Let us explore them one by one.

Reaction 1 It is called formylation or Gatterman Koch reaction. *A* — CHO group is introduced to benzene ring through this reaction as

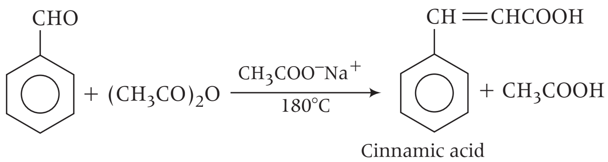


The attacking electrophile is $H—\overset{+}{C}{=}O$ which is generated as

(i) $CO + HCl \rightleftharpoons H—\underset{\underset{O}{\|}}{C}—Cl$

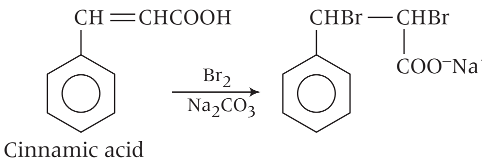
(ii) $H—\underset{\underset{O}{\|}}{C}—Cl + AlCl_3 \rightleftharpoons H—\underset{\underset{O}{\|}}{\overset{+}{C}} + AlCl_4^-$

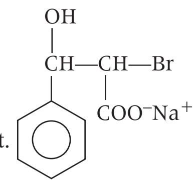
Reaction 2 It is Perkin condensation which results in α, β unsaturated acid as



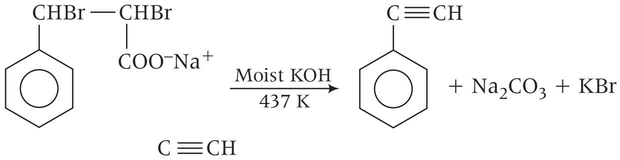
Note Besides $CH_3COO^-Na^+$, quinoline, pyridine, Na_2CO_3, triethylamine can also be used as bases in this reaction.

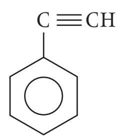
Reaction 3 It is simple addition of bromine to unsaturated acid formed through reaction 2.



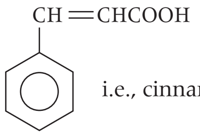
Na_2CO_3 works as a base in the reaction to trap H^+ to be released by — COOH of the reactant.  is also formed in the reaction as the minor product.

Reaction 4 It is decarboxylation and dehydrohalogenation of product produced by reaction 3 as



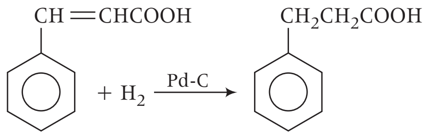
Hence, *Y* is  i.e., (c) is the correct answer.

27. **Reaction 5** The Perkin condensation product *X* is



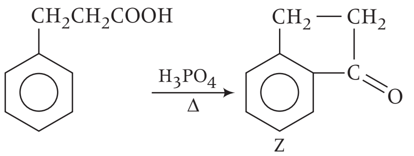
i.e., cinnamic acid (Ref. Q. 15)

This compound on hydrogenation with H_2 in the presence of Pd activated with charcoal (Pd – C) gives



3-Phenyl propanoic acid

Reaction 6 The product of reaction 5 on heating with H_3PO_4 dehydrates to give



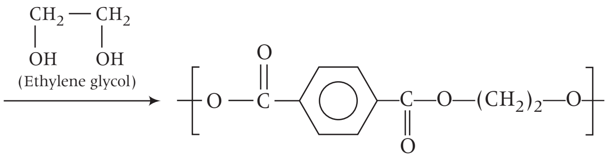
28. (a) Given,

(i) $C_{11}H_{12}O_2 \xrightarrow{\text{Oxidation}}$ Dibasic acid

(An organic acid '*P*')

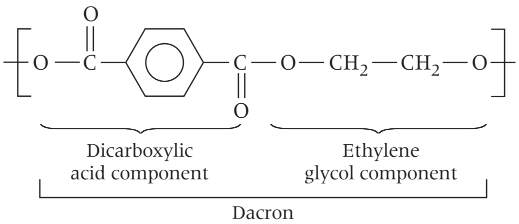
This indicates the presence of alkyl or alkenyl branch in *P* along with –COOH group.

(ii) Dibassic acid produced by oxidation of *P*



Dacron

This indicates presence of benzene ring in *P*; as concluded from the structure of dacron given below.

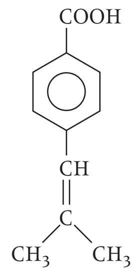


Attachment of —COO group in dacron also confirm the *para* position of branch with respect to —COOH group in *P*.

(iii) $P \xrightarrow{\text{Ozonolysis}}$ Aliphatic ketone + other oxidised products.

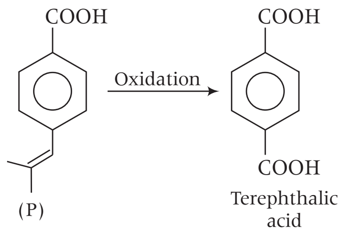
This reaction confirms the presence of multiple bonded branch i.e., alkenyl group in *P*.

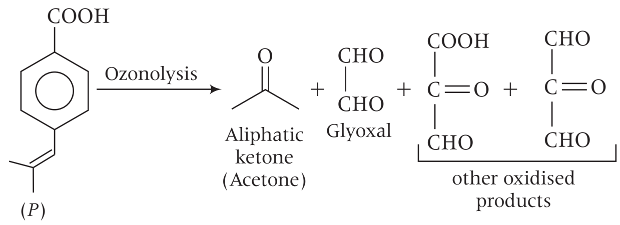
Thus *P* can be



IUPAC name : 4-(2-methyl) prop-l-enyl benzoic acid

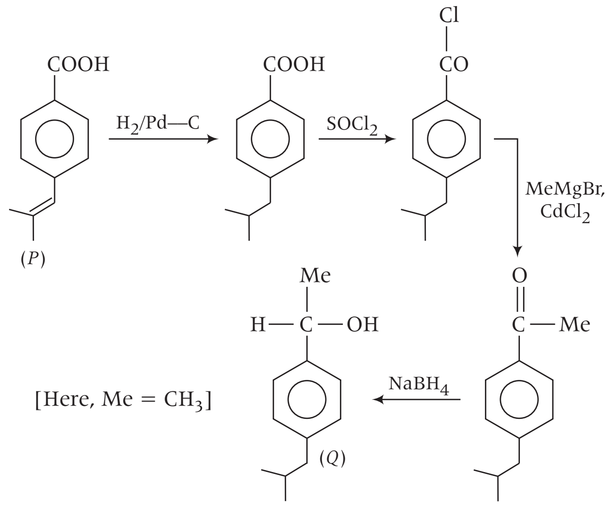
Now look for the reactions



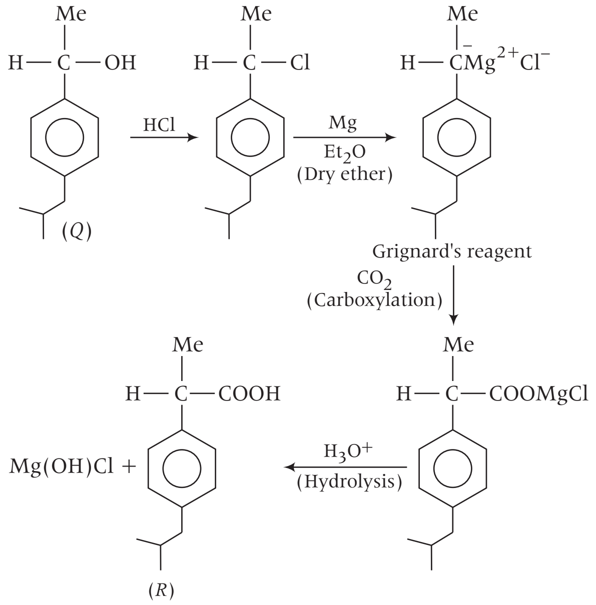


Given, $P \xrightarrow[\text{3. MeMgBr, CdCl}_2 \quad \text{4. NaBH}_4]{\text{1. H}_2\text{/Pd–C} \quad \text{2. SOCl}_2} Q$

So,



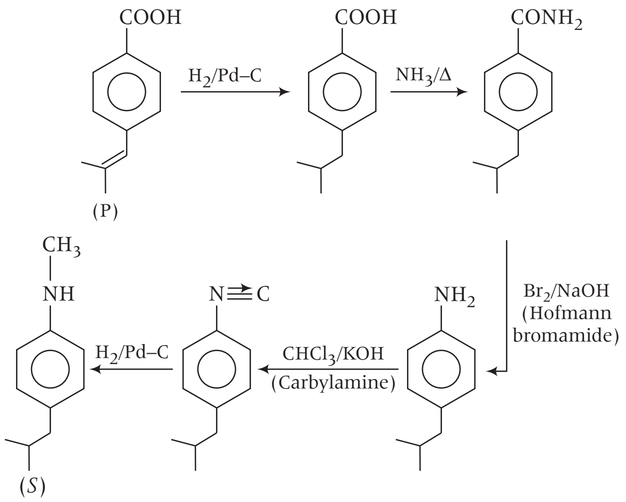
Further, $Q \xrightarrow[\text{3. CO}_2\text{ (Dry ice)} \quad \text{4. H}_3\text{O}^+]{\text{1. HCl} \quad \text{2. Mg/Et}_2\text{O}} R$



29. Given (In connection with Q. 17)

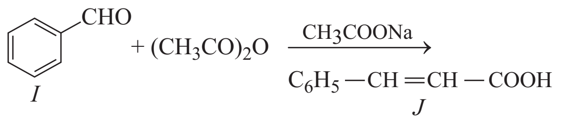
$$P \xrightarrow[\substack{4.\ CHCl_3/KOH,\Delta \\ 5.\ H_2/\ Pd-C}]{\substack{1.\ H_2/Pd-C \\ 2.\ NH_3/\Delta \\ 3.\ Br_2/NaOH}} S$$

So,



Passage

Sol for (Q. Nos. 30 to 31) The first step of reaction is Perkin's condensation.



J being a carboxylic acid gives effervescence with $NaHCO_3$. Also, J has olefinic bond, it will decolourise Baeyer's reagent.

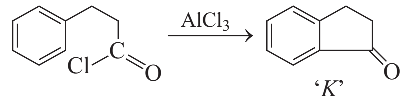
In the second step, J on treatment with H_2 / Pd / C undergo hydrogenation at olefinic bond only as :

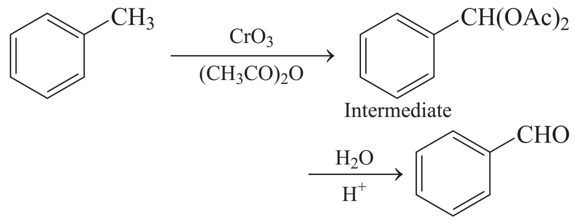
$$J + H_2 / Pd \longrightarrow C_6H_5—CH_2—CH_2—COOH$$

The hydrogenated acid, on treatment with $SOCl_2$ gives acid chloride.

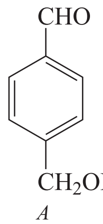
$$C_6H_5—CH_2—CH_2—COOH + SOCl_2 \longrightarrow C_6H_5—CH_2—CH_2—COCl + HCl + SO_2$$

In the final step, acid chloride formed above undergo intramolecular Friedel-Craft acylation as:

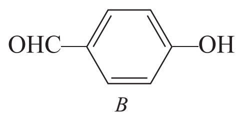


32. 

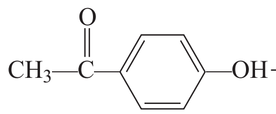
33. For aldol condensation, presence of at least one α-H is essential, which is not available to benzaldehyde.

34.  $\longrightarrow$ Gives positive Tollen's test but does not give $FeCl_3$ test.

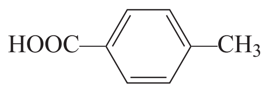
A

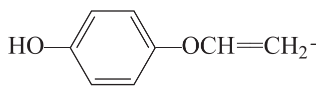
 $\longrightarrow$ Gives positive Tollen's test and $FeCl_3$ test.

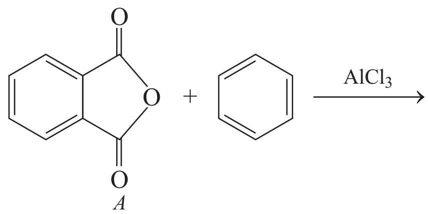
B

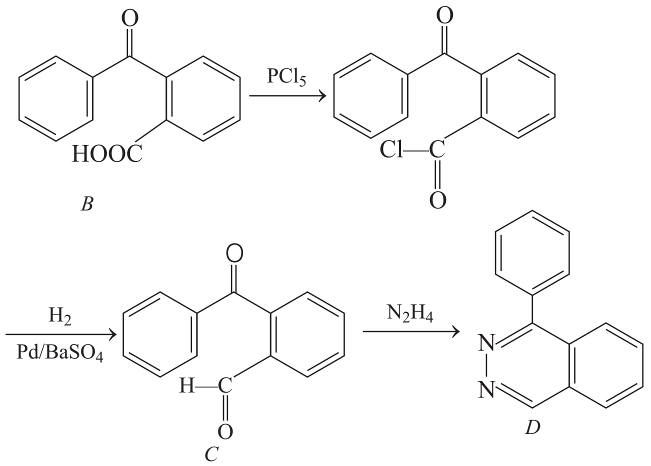
 $\longrightarrow$ Gives positive iodoform test.

C

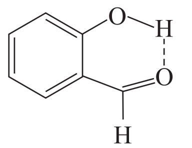
 $\longrightarrow$ Can be extracted with $NaHCO_3$.

 $\longrightarrow$ On hydrolysis give 1,4-dihydroxy benzene.

35. 



36. Intramolecular H-bonding in *ortho* hydroxy benzaldehyde is responsible for decrease in melting and boiling points.



Intramolecular H-bonding

p-hydroxy benzaldehyde molecules are associated by intermolecular H-bonding, has higher melting and boiling points.

37. $C_6H_5-CH_3 \xrightarrow[hv]{Br_2} C_6H_5-CH_2Br + HBr$ (Free radical bromination)

38. $C_6H_5-\overset{\overset{\Large O}{\|}}{C}-CH_3 \xrightarrow[(i)]{NaOH/Br_2} C_6H_5COONa + \underset{\text{Bromoform}}{CHBr_3}(P)$ (II)

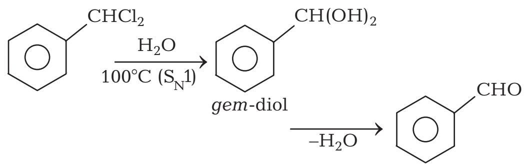
39. $C_6H_5CHO + CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

$\xrightarrow[\text{Perkin's condensation}]{CH_3COOK} C_6H_5-CH=CH-COOH$ (Cinnamic acid)

Cinnamic acid shows *cis-trans* isomerism.

40. I. Gattermann-Koch reaction.

II.



III. Rosenmund's reduction.

IV. Acid chloride, anhydride and ester undergo controlled reduction with di-iso-butylaluminium hydride (DIBAL-H) at – 78°C to give aldehydes.

Download Chapter Test
http://tinyurl.com/y4tw8a24 *or*

32

Biomolecules and Chemistry in Everyday Life

Topic 1 Biomolecules

Objective Questions I (Only one correct option)

1. Which of the given statements is incorrect about glycogen? **(2019 Main, 12 April II)**

(a) It is straight chain polymer similar to amylose
(b) Only α-linkages are present in the molecule
(c) It is present in animal cells
(d) It is present in some yeast and fungi

2. Which of the following statement is not true about RNA? **(2019 Main, 12 April I)**

(a) It controls the synthesis of protein
(b) It has always double stranded α-helix structure
(c) It usually does not replicate
(d) It is present in the nucleus of the cell

3. Number of stereo-centers present in linear and cyclic structures of glucose are respectively **(2019 Main, 10 April II)**

(a) 4 and 5 (b) 4 and 4
(c) 5 and 4 (d) 5 and 5

4. Amylopectin is composed of **(2019 Main, 10 April I)**

(a) β-D-glucose, C_1-C_4 and C_2-C_6 linkages
(b) α-D-glucose, C_1-C_4 and C_2-C_6 linkages
(c) β-D-glucose, C_1-C_4 and C_1-C_6 linkages
(d) α-D-glucose, C_1-C_4 and C_1 -C_6linkages

5. The peptide that gives positive ceric ammonium nitrate and carbylamine tests is **(2019 Main, 09 April II)**

(a) Lys-Asp (b) Ser-Lys
(c) Gln-Asp (d) Asp-Gln

6. Which of the following statement is not true about sucrose? **(2019 Main, 09 April I)**

(a) It is also named as invert sugar.
(b) The glycosidic linkage is present between C_1 of α-glucose and C_1 of β-fructose
(c) It is a non-reducing sugar
(d) On hydrolysis, it produces glucose and fructose

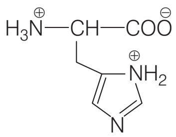
7. Fructose and glucose can be distinguished by **(2019 Main, 08 April II)**

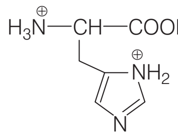
(a) Fehling's test (b) Barfoed's test
(c) Benedict's test (d) Seliwanoff's test

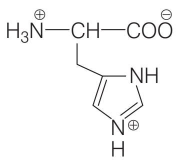
8. Maltose on treatment with dilute HCl gives **(2019 Main, 08 April I)**

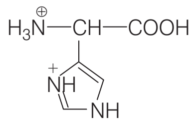
(a) D-glucose and D-fructose (b) D-fructose
(c) D-galactose (d) D-glucose

9. The correct structure of histidine in a strongly acidic solution (pH = 2) is **(2019 Main, 12 Jan II)**

(a) 

(b) 

(c) 

(d) 

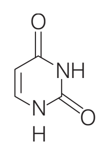
10. The correct match between Item I and Item II is

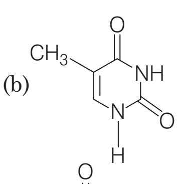
Item I	Item II
A. Ester test	P. Tyr
B. Carbylamine test	Q. Asp
C. Phthalein dye test	R. Ser
	S. Lys

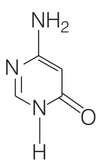
(2019 Main, 11 Jan II)

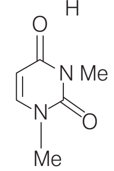
(a) $A \to Q; B \to S; C \to R$ (b) $A \to R, B \to Q; C \to P$
(c) $A \to R; B \to S; C \to Q$ (d) $A \to Q; B \to S; C \to P$

11 Among the following compounds, which one is found in RNA? **(2019 Main, 11 Jan I)**

(a) 

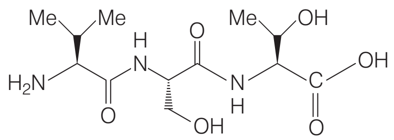
(b) 

(c) 

(d) 

12. Which of the following tests cannot be used for identifying amino acids ? **(2019 Main, 10 Jan II)**
(a) Barfoed test (b) Ninhydrin test
(c) Xanthoproteic test (d) Biuret test

13. The correct sequence of amino acids present in the tripeptide given below is **(2019 Main, 9 Jan II)**

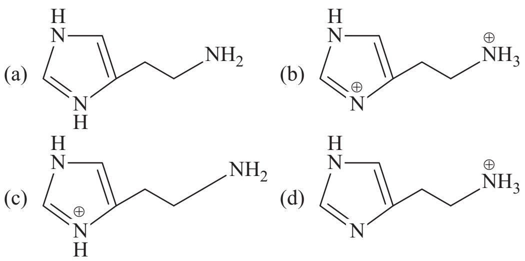


(a) Thr - Ser - Leu (b) Leu - Ser - Thr
(c) Val - Ser - Thr (d) Thr - Ser - Val

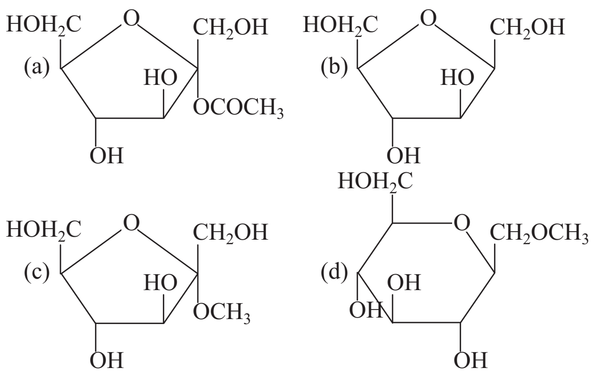
14 The increasing order of pK_a of the following amino acids in] aqueous solution is Gly, Asp, Lys, Arg **(2019 Main, 9 Jan I)**
(a) Asp < Gly < Arg < Lys (b) Arg < Lys < Gly < Asp
(c) Gly < Asp < Arg < Lys (d) Asp < Gly < Lys < Arg

15. Glucose on prolonged heating with HI gives **(2018 Main)**
(a) *n*-hexane (b) 1-hexene
(c) Hexanoic acid (d) 6-iodohexanal

16. The predominant form of histamine present in human blood is (pK_a, Histidine = 6.0) **(2018 Main)**



17. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? **(2017 Main)**



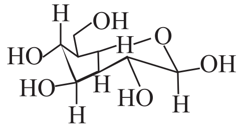
18. Thiol group is present in **(2016 Main)**
(a) cystine (b) cysteine
(c) methionine (d) cytosine

19. Which of the vitamins given below is water soluble? **(2015 Main)**
(a) Vitamin C (b) Vitamin D
(c) Vitamin E (d) Vitamin K

20. Which one of the following bases is not present in DNA? **(2014 Main)**
(a) Quinoline (b) Adenine
(c) Cytosine (d) Thymine

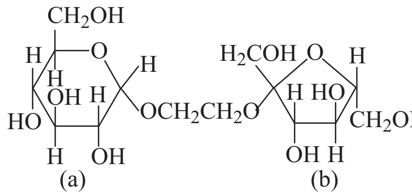
21. Synthesis of each molecule of glucose in photosynthesis involves **(2013 Main)**
(a) 18 molecules of ATP (b) 10 molecules of ATP
(c) 8 molecules of ATP (d) 6 molecules of ATP

22. The following carbohydrate is



(2011)
(a) a ketohexose (b) an aldohexose
(c) an α-furanose (d) an α-pyranose

23. The correct statement about the following disaccharide is



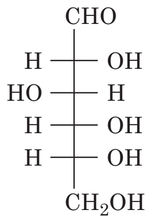
(2010)
(a) Ring (a) is pyranose with α-glycosidic link
(b) Ring (a) is furanose with α-glycosidic link
(c) Ring (b) is furanose with α-glycosidic link
(d) Ring (b) is pyranose with β-glycosidic link

24. Two forms of D-glucopyranose, are called **(2005, 1M)**
(a) enantiomers (b) anomers
(c) epimers (d) diastereomers

25. Which of the following pairs give positive Tollen's test ? **(2004, 1M)**
(a) Glucose, sucrose (b) Glucose, fructose
(c) Hexanal, acetophenone (d) Fructose, sucrose

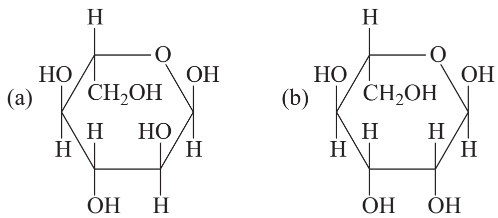
Objective Question II
(One or more than one correct option)

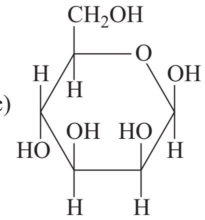
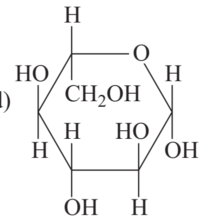
26. The Fischer presentation of D-glucose is given below.



D-glucose

The correct structure(s) of β-L-glucopyranose is (are) **(2018 Adv.)**



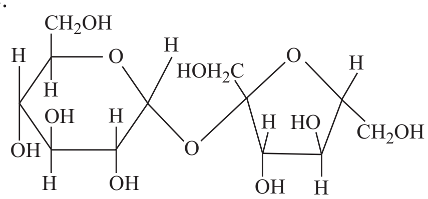
(c)  (d) 

27. For 'invert sugar', the correct statement(s) is (are)

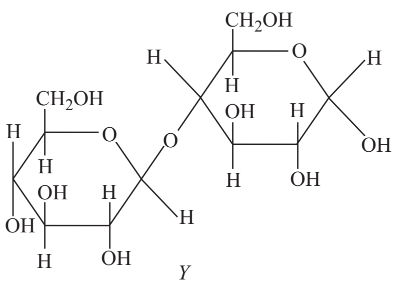
(Given: specific rotations of (+) - sucrose, (+) - maltose, L-(−)-glucose and L-(+)-fructose in aqueous solution are $+66°$, $+140°$, $-52°$ and $92°$, respectively) **(2016 Adv.)**

(a) Invert sugar is prepared by acid catalysed hydrolysis of maltose
(b) Invert sugar is an equimolar mixture of D-(+) -glucose and D-(–)- fructose
(c) Specific rotation of invert sugar is $-20°$
(d) On reaction with Br_2 water, invert sugar forms saccharic acid as one of the products

28. The correct statement(s) about the following sugars *X* and *Y* is/are: **(2009)**



X



Y

(a) *X* is a reducing sugar and *Y* is a non-reducing sugar
(b) *X* is a non-reducing sugar and *Y* is a reducing sugar
(c) The glucosidic linkages in *X* and *Y* are α and β, respectively
(d) The glucosidic linkages in *X* and *Y* are β and α, respectively

Assertion and Reason

Read the following questions and answer as per the direction given below :

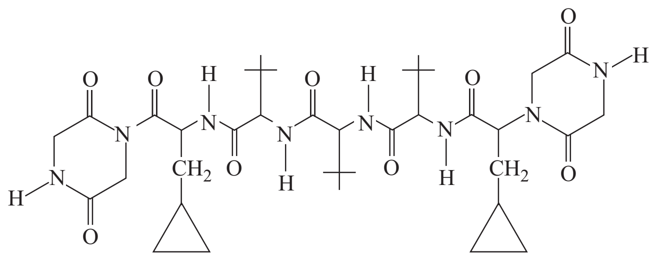
(a) Statement I is correct; Statement II is correct; Statement II is a correct explanation of Statement I.
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
(c) Statement I is correct; Statement II is incorrect.
(d) Statement I is incorrect; Statement II is correct.

29. Statement I Glucose gives a reddish-brown precipitate with Fehling's solution.

Statement II Reaction of glucose with Fehling's solution gives CuO and gluconic acid. **(2007, 3M)**

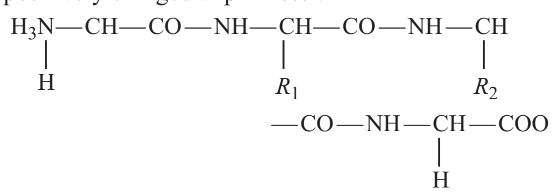
Integer Answer Type Questions

30. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is **(2014 Adv.)**



31. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with $—NH_2$ group attached to a chiral centre is **(2013 Adv.)**

32. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0 ? **(2012)**



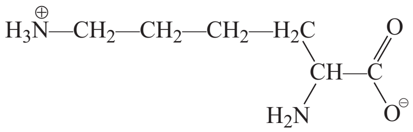
Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

33. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form, is **(2012)**

CHO
|
CH_2
|
CHOH
|
CHOH
|
CHOH
|
CH_2OH

34. A decapeptide (Molecular weight 796) on complete hydrolysis gives glycine (Molecular weight 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is **(2011)**

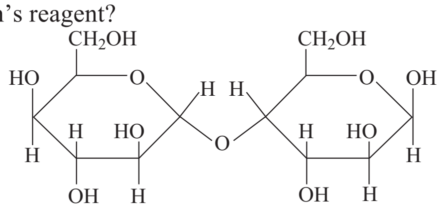
35. The total number of basic groups in the following form of lysine is **(2010)**



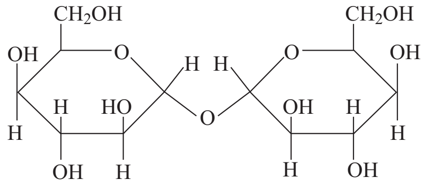
Subjective Questions

36. Which of the following disaccharide will not reduce Tollen's reagent? **(2005, 2M)**

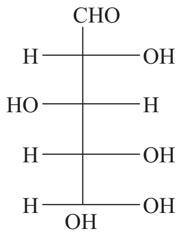
(a)



(b)



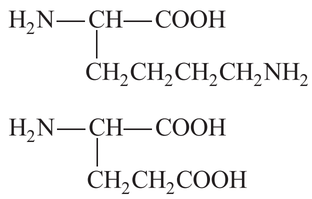
37. The structure of D-glucose is as follows :



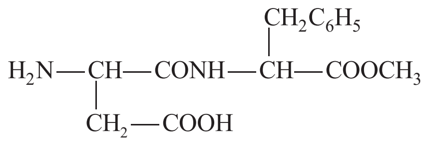
(i) Draw the structure of L-glucose.

(ii) Give the reaction of L-glucose with Tollen's reagent. **(2004, 2M)**

38. Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides? **(2003, 2M)**



39. Aspartame, an artificial sweetener, is a peptide and has the following structure



(i) Identify the four functional groups.

(ii) Write the Zwitter ionic structure.

(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.

(iv) Which of the two amino acids is more hydrophobic? **(2001, 5M)**

40. Give the structures of the products in the following reaction

$$\text{Sucrose} \xrightarrow{H^+} A + B$$ **(2000, 2M)**

41. Write the structure of alanine at pH = 2 and pH = 10. **(2000, 2M)**

Topic 2 Chemistry in Everyday Life

Objective Questions I (Only one correct option)

1. Which of the following is a thermosetting polymer? **(2019 Main, 12 April I)**

(a) Bakelite (b) Buna-N
(c) Nylon-6 (d) PVC

2. The correct match between **Item**-I and **Item**-II is

	Item-I		Item-II
A.	High density polythene	I.	Peroxide catalyst
B.	Polyacrylonitrile	II.	Condensation at high temperature and pressure
C.	Novolac	III.	Ziegler-Natta catalyst
D.	Nylon-6	IV.	Acid or base catalyst

(2019 Main, 10 April II)

Codes

	A	B	C	D		A	B	C	D
(a)	III	I	IV	II	(b)	IV	II	I	III
(c)	II	IV	I	III	(d)	III	I	II	IV

3. Which of the following is a condensation polymer? **(2019 Main, 10 April I)**

(a) Nylon-6, 6 (b) Neoprene
(c) Teflon (d) Buna - S

4. Noradrenaline is a/an

(a) antidepressant (b) antihistamine
(c) neurotransmitter (d) antacid

(2019 Main, 9 April II)

5. Which of the following compounds is a constituent of the polymer $\left[HN - \overset{\overset{\displaystyle O}{\|}}{C} - NH - CH_2 \right]_n$? **(2019 Main, 9 April II)**

(a) N-methyl urea
(b) Methylamine
(c) Ammonia
(d) Formaldehyde

6. The structure of nylon-6 is

(a) $\left[\!-(CH_2)_6-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\!\right]_n$ (b) $\left[\!-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}-\!\right]_n$

(c) $\left[\!-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\!\right]_n$ (d) $\left[\!-\overset{O}{\overset{\|}{C}}(CH_2)_6-\overset{H}{\overset{|}{N}}-\!\right]_n$

(2019 Main, 8 April II)

7. The two monomers for the synthesis of nylon 6, 6 are **(2019 Main, 12 Jan II)**

(a) $HOOC(CH_2)_4COOH, H_2N(CH_2)_4NH_2$
(b) $HOOC(CH_2)_6COOH, H_2N(CH_2)_4NH_2$
(c) $HOOC(CH_2)_4COOH, H_2N(CH_2)_6NH_2$
(d) $HOOC(CH_2)_6COOH, H_2N(CH_2)_6NH_2$

8. Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV) is a copolymer of ...... **(2019 Main, 12 Jan I)**

(a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid
(b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid
(c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid
(d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

9. The homopolymer formed from 4-hydroxybutanoic acid is

(a) $\left[-O\overset{O}{\overset{\|}{C}}(CH_2)_3-O-\right]_n$ (b) $\left[-\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}-\right]_n$

(c) $\left[-\overset{O}{\overset{\|}{C}}(CH_2)_3-O-\right]_n$ (d) $\left[-\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}-O-\right]_n$

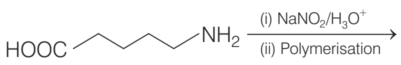
(2019 Main, 11 Jan II)

10. The correct match between Item I and Item II is

	Item I		Item II
A.	Allosteric effect	P.	Molecule binding to the active site of enzyme.
B.	Competitive inhibitor	Q.	Molecule crucial for communication in the body.
C.	Receptor	R.	Molecule binding to a site other than the active site of enzyme.
D.	Poison	S.	Molecule binding to the enzyme covalently.

(a) A → P; B → R; C → S; D → Q
(b) A → P, B → R; C → Q; D → S
(c) A → R; B → P; C → S; D → Q
(d) A → R; B → P; C → Q; D → S **(2019 Main, 11 Jan II)**

11. The polymer obtained from the following reaction is: **(2019 Main, 11 Jan I)**



(a) $\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{H}{\overset{|}{N}}-\right]_n$ (b) $\left[-O-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$

(c) $\left[-O\overset{O}{\overset{\|}{C}}(CH_2)_4O-\right]_n$ (d) $\left[-HN\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\right]_n$

12. The correct match between item (I) and item (II) is

	Item - I		Item - II
(A)	Norethindrone	(P)	Antibiotic
(B)	Ofloxacin	(Q)	Antifertility
(C)	Equanil	(R)	Hypertension
		(S)	Analgesics

(2019 Main, 11 Jan I)

(a) (A) → (Q); (B) → (R); (C) → (S)
(b) (A) → (Q); (B) → (P); (C) → (R)
(c) (A) → (R); (B) → (P); (C) → (S)
(d) (A) → (R); (B) → (P); (C) → (R)

13. The correct match between Item - I and Item - II is

	Item I (Drug)		Item II (Test)
A.	Chloroxylenol	P.	Carbylamine test
B.	Norethindrone	Q.	Sodium hydrogen carbonate test
C.	Sulphapyridine	R.	Ferric chloride test
D.	Penicillin	S.	Bayer's test

(2019 Main, 9 Jan I)

(a) A → R ; B → P ; C → S ; D → Q
(b) A → R ; B → S ; C → P ; D → Q
(c) A → Q ; B → P ; C → S ; D → R
(d) A → Q ; B → S ; C → P ; D → R

14. The formation of which of the following polymers involves hydrolysis reaction? **(2017 Main)**

(a) Nylon-6
(b) Bakelite
(c) Nylon-6, 6
(d) Terylene

15. Which of the following statements about low density polythene is false? **(2016 Main)**

(a) It is a poor conductor of electricity
(b) Its synthesis required dioxygen or a peroxide initiator as a catalyst
(c) It is used in the manufacture of buckets, dustbins etc.
(d) Its synthesis requires high pressure

16. Which of the following is an anionic detergent? **(2016 Main)**

(a) Sodium lauryl sulphate
(b) Cetyltrimethyl ammonium bromide
(c) Glyceryl oleate
(d) Sodium stearate

17. On complete hydrogenation, natural rubber produces **(2016 Adv.)**

(a) ethylene-propylene copolymer
(b) vulcanised rubber
(c) polypropylene
(d) polybutylene

18. Which polymer is used in the manufacture of paints and lacquers? **(2015 Main)**

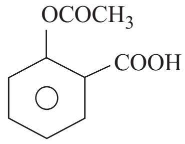
(a) Bakelite
(b) Glyptal
(c) Polypropene
(d) Polyvinyl chloride

19. Match the polymers in Column I with their main uses in Column II and choose the correct answer:

	Column I		Column II
(A)	Polystyrene	1.	Paints and lacquers
(B)	Glyptal	2.	Raincoats
(C)	Polyvinyl chloride	3.	Manufacture of toys
(D)	Bakelite	4.	Computer discs

Codes

	A	B	C	D		A	B	C	D
(a)	2	1	3	4	(b)	3	1	2	4
(c)	2	4	3	1	(d)	3	4	2	1

20. 

is used as

(a) Insecticide (b) Antihistamine
(c) Analgesic (d) Antacid

21. Which of the following is not an antacid? **(2015 Main)**

(a) Aluminium hydroxide (b) Cimetidine
(c) Phenelzine (d) Ranitidine

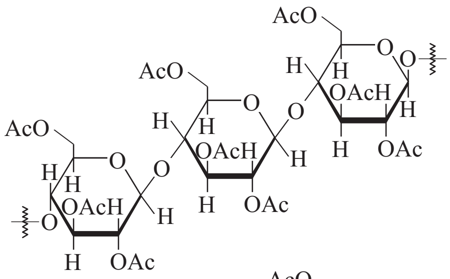
22. Which one is classified as a condensation polymer? **(2014 Main)**

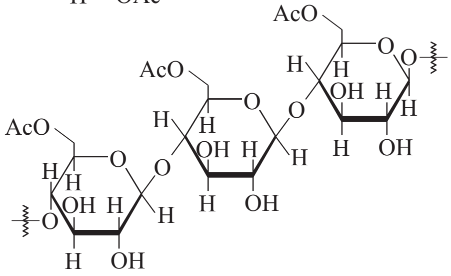
(a) Dacron (b) Neoprene
(c) Teflon (d) Acrylonitrile

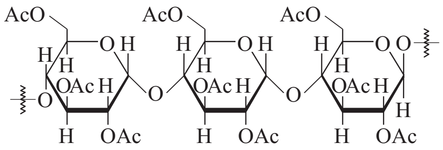
23. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is **(2009)**

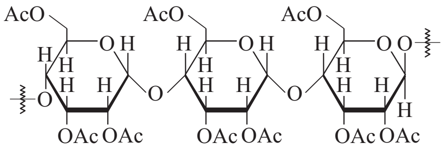
(a) nylon
(b) poly (vinyl chloride)
(c) cellulose
(d) natural rubber

24. Cellulose upon acetylation with excess acetic anhydride/H_2SO_4 (catalytic) gives cellulose triacetate whose structure is **(2008, 3M)**

(a) 

(b) 

(c) 

(d) 

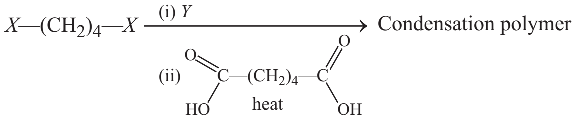
Objective Question II

(One or more than one correct option)

25. Under hydrolysis conditions, the compounds used for preparation of linear polymer and for chain termination, respectively are **(2012)**

(a) CH_3SiCl_3 and $Si(CH_3)_4$ (b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$
(c) $(CH_3)SiCl_2$ and CH_3SiCl_3 (d) $SiCl_4$ and $(CH_3)_3SiCl$

26. The correct functional group X and the reagent/reaction conditions Y in the following schemes are **(2011)**



(a) X = $COOCH_3$, Y = H_2/Ni/heat
(b) X = $CONH_2$, Y = H_2/Ni/heat
(c) X = $CONH_2$, Y = Br_2/NaOH
(d) X = CN, Y = H_2/Ni/heat

Match the Columns

27. Match the chemical substances in Column I with type of polymers/type of bond in Column II. **(2007, 6M)**

	Column I		Column II
A.	Cellulose	p.	Natural polymer
B.	Nylon-66	q.	Synthetic polymer
C.	Protein	r.	Amide linkage
D.	Sucrose	s.	Glycoside linkage

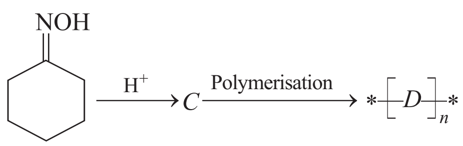
Subjective Questions

28. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH_3COCHO. **(2005)**

(a) Deduce the structure of A.
(b) Write the structure of 'all *cis*' – form of polymer of compound A.

29. Name the heterogeneous catalyst used in the polymerisation of ethylene. **(2003)**

30. Give the structures of the products in the following reaction. **(2000, 2M)**



Answers

Topic 1

1. (a)	**2.** (b)	**3.** (a)	**4.** (d)
5. (b)	**6.** (b)	**7.** (d)	**8.** (d)
9. (a)	**10.** (d)	**11.** (a)	**12.** (a)
13. (c)	**14.** (d)	**15.** (a)	**16.** (d)
17. (a)	**18.** (b)	**19.** (a)	**20.** (a)
21. (a)	**22.** (b)	**23.** (a)	**24.** (b)
25. (b)	**26.** (d)	**27.** (b,c)	**28.** (b,c)
29. (c)	**30.** (1)	**31.** (4)	**32.** (4)
33. (8)	**34.** (6)	**35.** (2)	

Topic 2

1. (a)	**2.** (a)	**3.** (a)	**4.** (c)
5. (d)	**6.** (b)	**7.** (c)	**8.** (d)
9. (c)	**10.** (d)	**11.** (b)	**12.** (b)
13. (b)	**14.** (a)	**15.** (c)	**16.** (a)
17. (a)	**18.** (b)	**19.** (b)	**20.** (c)
21. (c)	**22.** (a)	**23.** (d)	**24.** (a)
25. (b)	**26.** (a, b, c, d)		

27. $A \rightarrow p, s$; $B \rightarrow q, r$; $C \rightarrow p, r$; $D \rightarrow s$

Hints & Solutions

Topic 1 Biomolecules

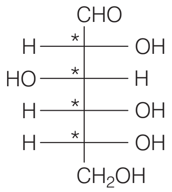
1. Statement (a) is incorrect. Glycogen is not a straight chain polymer similar to amylose. It is highly branched structure similar to amylopectin. It is known to be the storage material of animals. It is found in liver, muscles and brain. It breaks down to glucose by the action of enzymes when body needs a glucose. It is also found in yeast and fungi.

2. RNA does not have double stranded α-helix structure. Helixes present in RNA are single-stranded but sometimes they fold back on themselves to form a double helix structure. RNA usually does not replicate.

It is present in the nucleus of the cell. It controls the synthesis of protein. RNA molecules are of three types, i.e. messenger's RNA (*m*-RNA), ribosomal RNA (*r*RNA), transfer RNA (*t*-RNA).

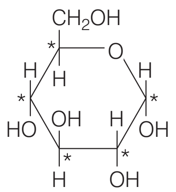
3. **Key Idea** Chiral centre is also called stereo-centre or stereogenic center.

Linear structure of glucose is as follows :

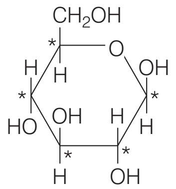


Fischer formula Number of stereo-centre (C^*) = 4.

Cyclic structure of glucose are as follows :



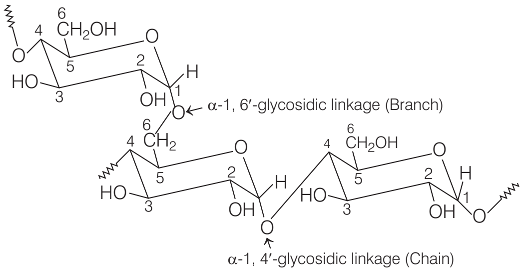
α-D-glucose



β-D-glucose

Haworth formula Number of stereo-centre (C^*) in each anomer = 5.

4. Amylopectin is the water-soluble component of starch. It is a branched-chain polymer of α-D-glucose. The main chain consists of an $\alpha-1, 4'$- glycosidic linkages between α-D-glucose units and the branches are connected to the main chain by α-1,6'- glycosidic linkages. Its structure can be represented as:

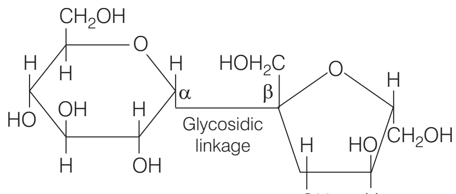


Structure of Amylopectin

5. The peptide that gives positive ceric ammonium nitrate and carbylamine tests is ser - lys. The structures of serine and lysine are,

$$\underset{\text{Serine}}{HO{-}CH_2{-}\underset{\underset{NH_2}{|}}{C}H{-}COOH} \quad \underset{\text{Lysine}}{H_2N{-}(CH_2)_4{-}\underset{\underset{NH_2}{|}}{C}H{-}COOH}$$

6. Statement-(b) is not true for sucrose. It is linked through a glycosidic linkage between C-1 of α-glucose and C-2 of β-fructose. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



α-D-glucose

β-D-fructose

On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(–)-fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{HCl} \underset{\text{D-(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-fructose}}{C_6H_{12}O_6}$$

7. Both fructose and glucose give following test positive.

(i) Fehling's test (red ppt. of Cu_2O is obtained).
(ii) Barfoed's test (red ppt. of Cu_2O is obtained)
(iii) Benedict's test (red ppt. of Cu_2O is obtained)

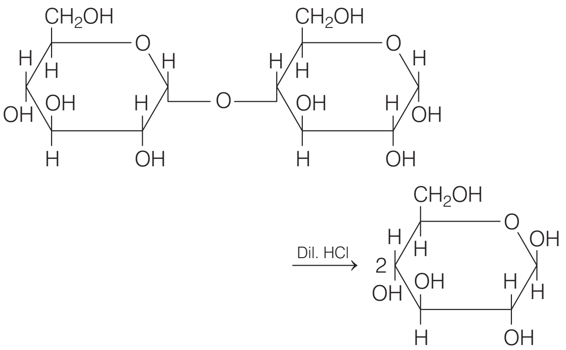
Fehling's solution : $CuSO_4$ + Na, K-tartrate (Rochelle salt)

Barfoed's reagent $\underset{(7\%)}{(CH_3COO)_2Cu} + \underset{(1\%)}{CH_3COOH} + \underset{(92\%)}{H_2O}$

Benedict's solution : $CuSO_4$ + Na-citrate + Na_2CO_3

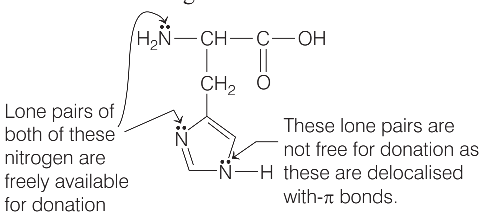
Seliwanoff's test is used to differentiate between ketose and aldose. The reagent is a solution of resorcinol in concentrated HCl. The reagent when heated along with a sugar will produce furfural or hydroxy-methylfurfural, which further reacts to give red color. Ketose (fructose) reacts more quickly than aldose (glucose).

8. Maltose on treatment with dil. HCl gives D-glucose. Hydrolysis of maltose yields two moles of α- D-glucose. Thus, it is composed of two α-D-glucose units in which C-1 of one glucose unit (I) is linked to C-4 of another glucose unit (II). The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties. So, it is a reducing sugar.



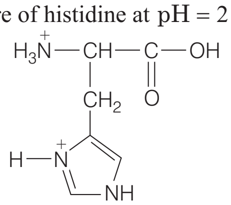
α-D-glucose

9. Histidine has following structure in



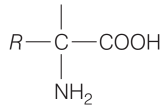
At highly acidic pH, i.e. 2 both the nitrogens with lone pairs will accept one H^+ each and $-\underset{\underset{O}{\|}}{C}-OH$ will not loose its H^+. Thus,

the final structure of histidine at pH = 2 will be



Thus, option (d) is the correct answer.

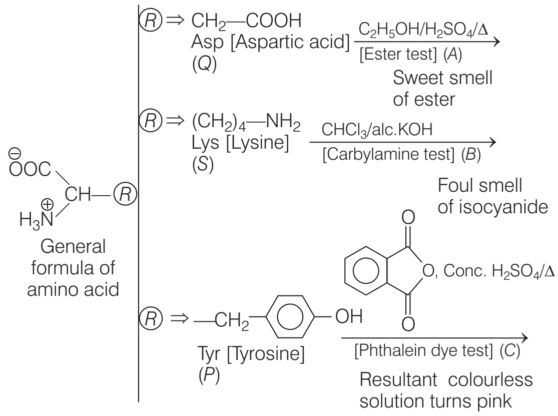
Note Amino acids have following generalise structure:



They have the tendency to loose H^+ of their $-COOH$ group at alkaline (higher) pH while the $-NH_2$ group present in them have the tendency to gain H^+ at acidic (lower) pH.

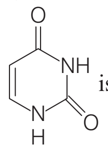
10. The correct match is :

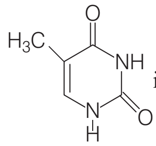
A $\rightarrow$ (Q); (B) $\rightarrow$ (S) (C) $\rightarrow$ (P)

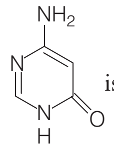


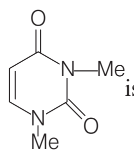
(A) Ester test confirms the presence of
$-COOH$ group.
(B) Carbylamine test confirms the presence of
$-NH_2$ group (1°).
(C) Phthalein dye test confirms the presence of phenolic
$-OH$ group.

11. RNA contains, adenine (A), guanine (G), cytosine (C) and uracil (U). In the given options,

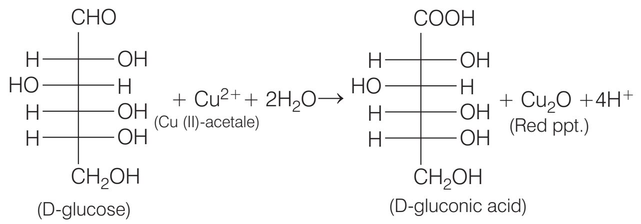
 is uracil (present in RNA only)

 is thymine (present in DNA)

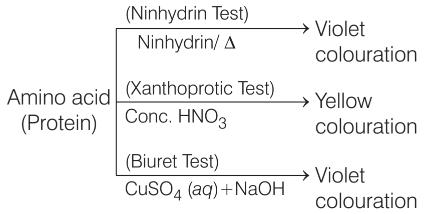
 is cytosine (present in both DNA and RNA)

 is not a pyrimidine base but a derivative of uracil.

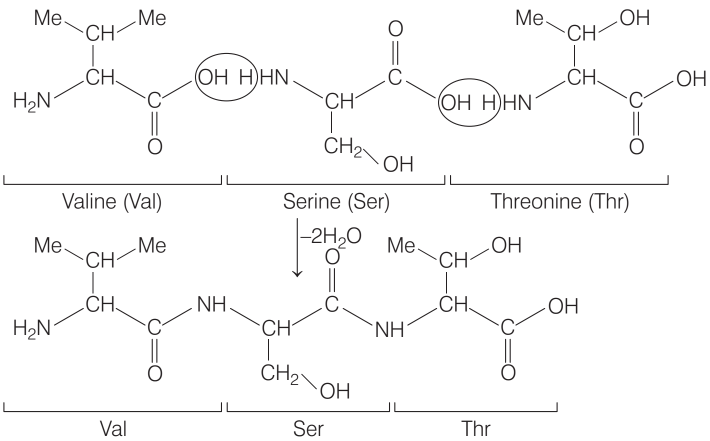
12. (i) Barfoed test is used for detecting the presence of monosaccharides like glucose, fructose etc. Barfoed reagents is Cu (II) acetate solution.



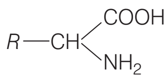
(ii)



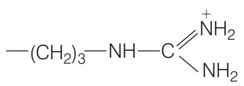
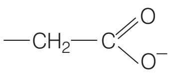
13. Formation of the tripeptide (Val-Ser-Thr) can be shown as:



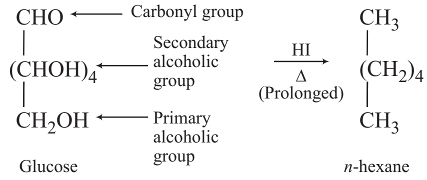
14 Amino acid molecules can be represented as,



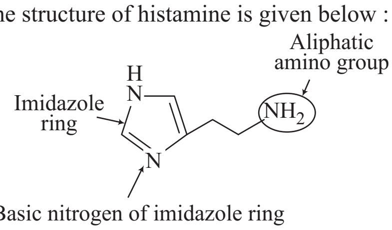
Nature of the 'R' group will determine the basicity (hence, pK_a) of an amino acid.

	'*R*' in the amino group	**Nature of *R***	**Nature of the amino acids**
1.	 (Arginine : Arg)	Basic	More basic (due to the presence of acetamidine group)
2.	 (Aspartic acid: Asp)	Acidic	Acidic
3.	—H (Glycine) : Gly	Neutral	Neutral
4.	$—(CH_2)_4—\overset{+}{N}H_3$ (Lysine : Lys)	Basic	Basic

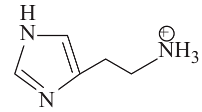
15. HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as



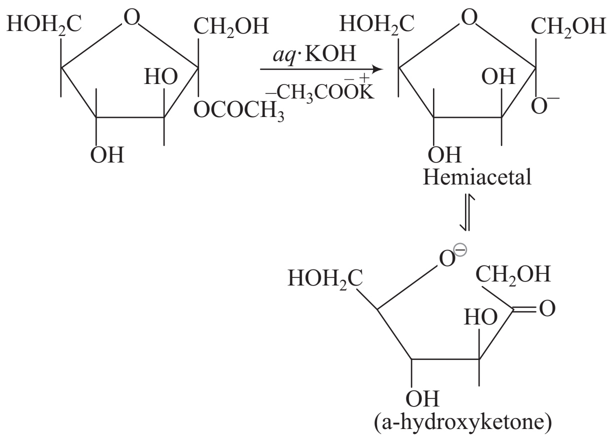
16. Our blood is slightly basic in nature with pH range from 7.35-7.4. The structure of histamine is given below :



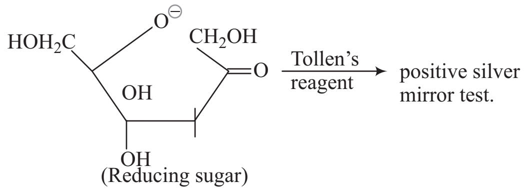
It is produced by decarboxylation of histidine having following structure. It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring. The aliphatic amino group has pK_a around 9.4. In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below



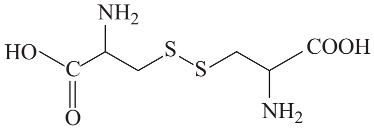
17. Sugars that have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.



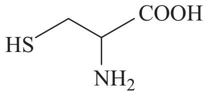
Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



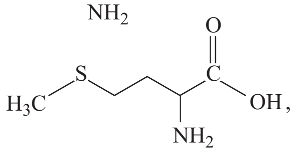
18. Cystine



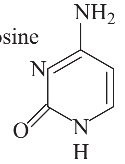
Cysteine



Methionine



Cytosine



Thiol group (SH) is present in cysteine.

19. Vitamin B and C are water soluble while vitamin A,D,E and K are fat soluble or water insoluble.

20. Quinoline is an alkaloid, it is not present in DNA. DNA has four nitrogen bases in adenine, guanine, cytosine and thymine.

21. 18 ATPs are involved in the formation of 1 glucose molecule as shown in the reaction below :

$$6CO_2 + 12NADPH + 18\ ATP \longrightarrow C_6H_{12}O_6 + 12NADP + 18\ ADP$$

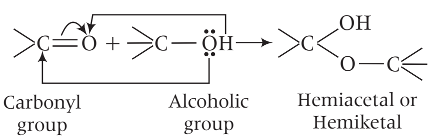
22. Here, the —OH of hemiacetal group is equatorial therefore, it is a β-pyranose of an aldohexose.

23. The six-membered cyclic ether is known as pyranose while the five membered cyclic ether is known as furanose. Hence, ring (a) is a pyranose and it has ether linkage at α-position that is known as α-glycosidic linkage in carbohydrate chemistry.

24. "α" and "β" cyclic hemiacetals of D-glucose having difference in configuration at C-1 only are called anomers.

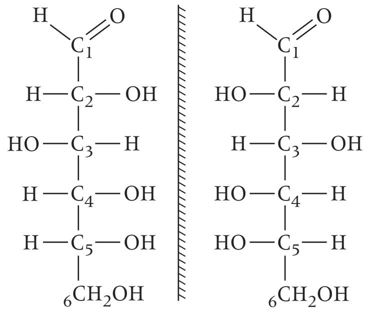
25. Both glucose and fructose are reducing sugars, reduces Tollen's reagent to metallic silver.

26. (d) A pyranose ring is a 6 membered ring having 5 carbon atoms and one oxygen atom. In glucose, it is formed by the reaction between >C=O group at position 1 and —OH group at 5th carbon atom. In general reaction between >C=O group and >C—OH looks like



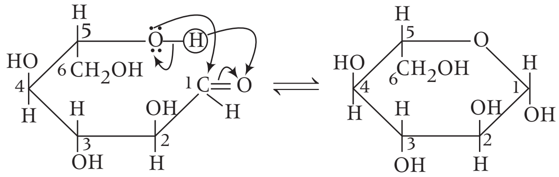
The product formed in called **hemiacetal**

(if>C=O group belongs to an aldehyde) or **hemiketal** (if >C=O group belongs to a ketone). L- glucose has the mirror image configuration of D-glucose i.e.,



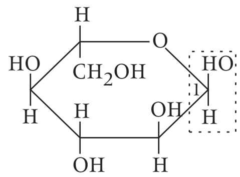
D-glucose L-glucose

So, β-L glucopyranose is formed as



β-L-glucopyranose

The α-L-glucopyranose has configurational change at C_1 only and looks like



α-L-glucopyranose

27. If there is inversion of specific rotation from (+) to (–), then invert sugar is formed.

(a) $\underset{\substack{(+)\text{Maltose} \\ 140°}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{D(+) \\ 52°}}{\text{Glucose}}$

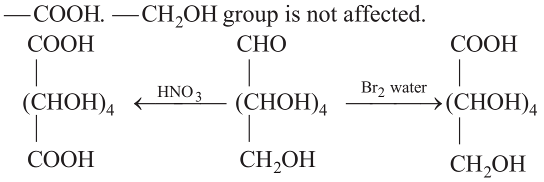
(b) $\underset{\substack{(+)\text{Sucrose} \\ +66°}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{D(+) \\ 52°}}{\text{Glucose}} + \underset{\substack{L(-) \\ -92°}}{\text{Fructose}}$

–40° for 2 moles mixture
–20° for 1 mole mixture

There is formation of invert sugar. Thus, correct.

(c) Specific rotation of invert sugar is –20° per mole. Thus, correct.

(d) Br_2 water is a weak oxidising agent. It oxidises —CHO to —COOH. —CH_2OH group is not affected.



Saccharic acid Gluconic acid (one of the products)

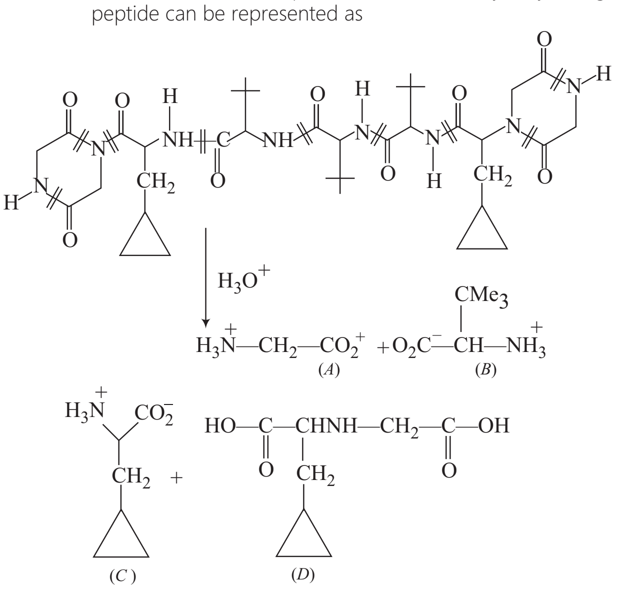
HNO_3 (a strong oxidising agent) oxidises invert sugar to saccharic acid. Thus, incorrect.

28. X is acetal, has no free hemiacetal, hence a non-reducing sugar while Y has a free hemiacetal group, it is reducing sugar. Also, glucosidic linkage of X is 'α' while that of Y is β-linkage.

29. **Statement I is correct** Presence of — CHO group in glucose is tested by Fehling's solution test where a reddish-brown precipitate of Cu_2O is formed.

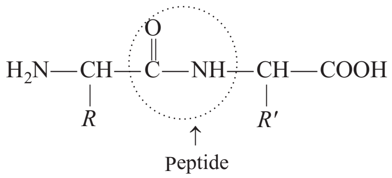
Hence, Statement II is incorrect.

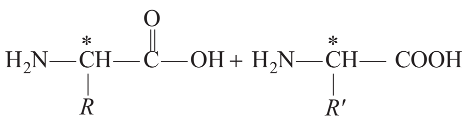
30. **PLAN** This problem can be solved by performing hydrolysis of peptide and deciding the nature of product.
Chemical reaction and product formed after hydrolysis of given peptide can be represented as



(A) is glycine which is only naturally occurring amino acid. While (B), (C) and (D) are not the naturally occurring amino acids. Hence, correct integer is (1).

31. **PLAN** A peptide linkage is hydrolysed to two free amino acids.





C^* is chiral carbon tetrapeptide has four amino acids joined by three peptide linkage.

— COOH group is on alanine part, thus it is at fixed C-terminal position in each combination.

Glycine is optically inactive thus it cannot be on the N— terminal side. Thus, possible combinations are

Phe-Gly-Val-Ala, Phe-Val-Gly-Ala,
Val-Gly-Phe-Ala, Val-Phe-Gly-Ala

Thus, in all **four combinations are possible.**

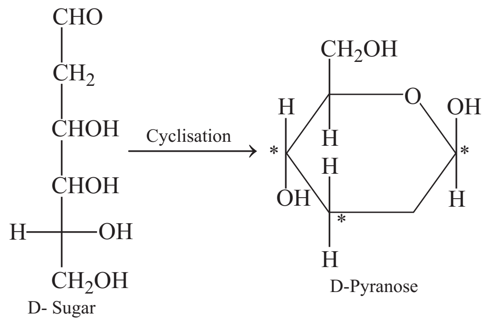
32. The amino acid remain completely in Zwitter ionic form at its isoelectric point. Amino acids with additional acidic group have their isoelectric pH less than 7.0 and increasing pH above isoelectric point makes them anionic.

On the other hand, amino acids with additional basic group have their isoelectric pH greater than 7.0 and decreasing pH below isoelectric point (by adding acid solution) makes them cationic. The given peptide with followings R_1 and R_2 are basic, will remain protonated (cationic) at pH = 7.0.

Peptide	R_1	R_2
IV	CH_2CONH_2	$(CH_2)_4NH_4$
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_4$
VIII	CH_2OH	$(CH_2)_4NH_4$
IX	$(CH_2)_4NH_2$	CH_3

Thus, 4 is the correct integer.

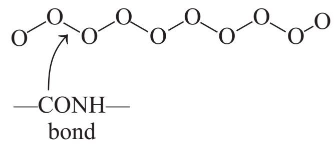
33. The D-form of given sugar is



Configurations at the three chiral carbons (starred) can be changed maintaining D-configuration. Hence, the total number of steroisomers of D-pyranose $= 2^3 = 8$

Thus, the correct integer is 8.

34. A decapeptide has nine peptide (amide) linkage as



Therefore, on hydrolysis, it will absorb nine water molecules.

Hence, total mass of hydrolysis product = 796 +18 × 9 = 958

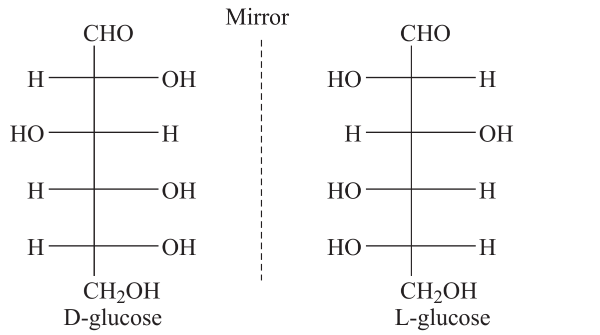
$\Rightarrow$ mass of glycine in hydrolysis product $= \dfrac{958 \times 47}{100} = 450$

$\Rightarrow$ number of glycine molecule in one molecule of decapeptide $= \dfrac{450}{75} = 6$

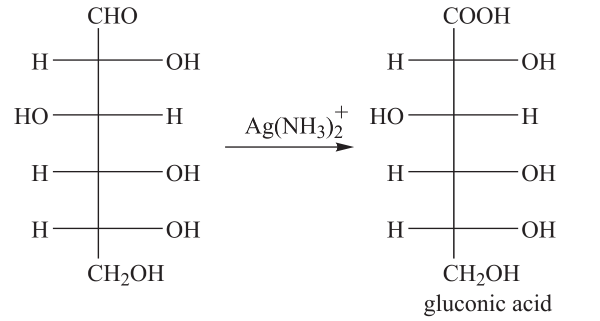
35. —OO^- and —NH_2 are two basic groups in lysine.

36. In structure (a), one ring has a free hemiacetal group, will hydrolyse into open chain in aqueous solution and therefore will reduce Tollen's reagent. Structure (b) has only acetal groups, will not hydrolyse in aqueous solution into open chain, will not reduce Tollen's reagent

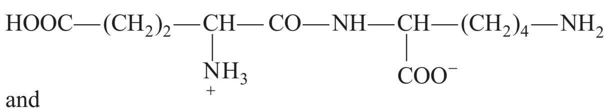
37. (i) D-glucose and L-glucose are enantiomers, hence



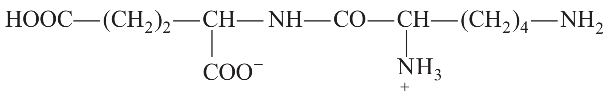
(ii)



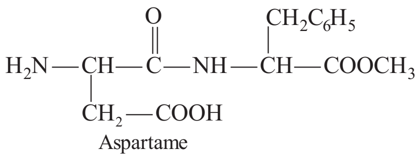
38. The dipeptides are



and

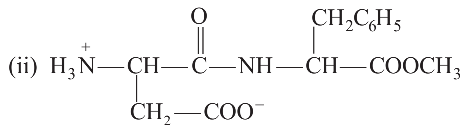


39.

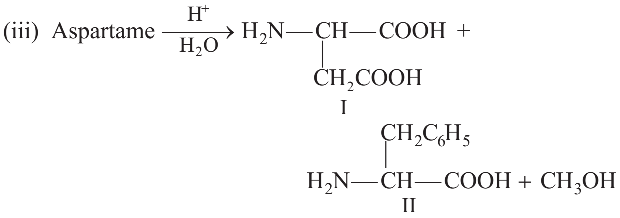


(i) Aspartame has amine, acid, amide and ester groups.

(ii)

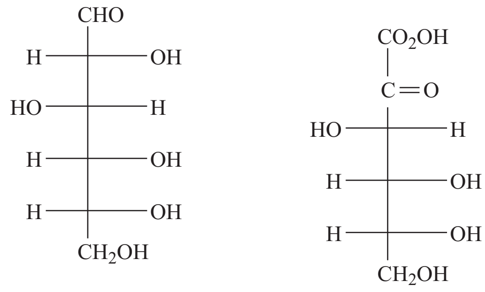


(iii)

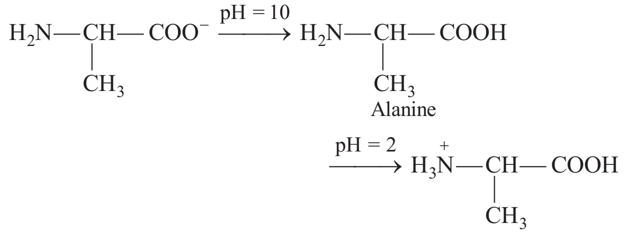


(iv) II is more hydrophobic due to the presence of phenyl group.

40. Sucrose $\xrightarrow[H_2O]{H^+}$ D-glucose + D-fructose



41.



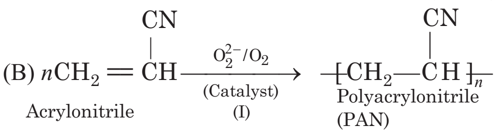
Topic 2 Chemistry in Everyday Life

1. Bakelite is a thermosetting polymer. These polymers are cross-linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. Once they get set, they cannot be reshaped and reused.

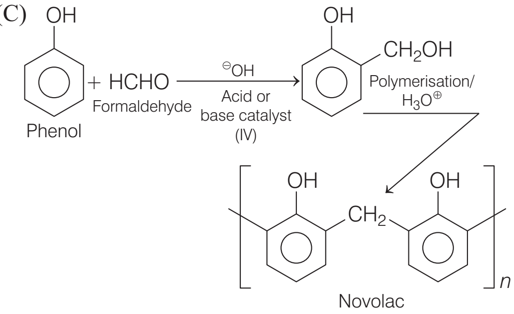
2. (A) $nCH_2{=}CH_2 \xrightarrow[\text{Ziegler-Natta catalyst (III)}]{[TiCl_4+(C_2H_5)_3Al]} \text{-}[CH_2]_n\text{-}$

Ethylene — High density polythene (HDPE)

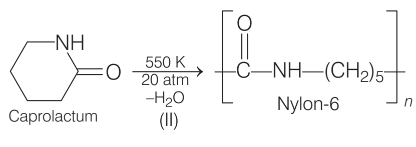
(B)



(C)



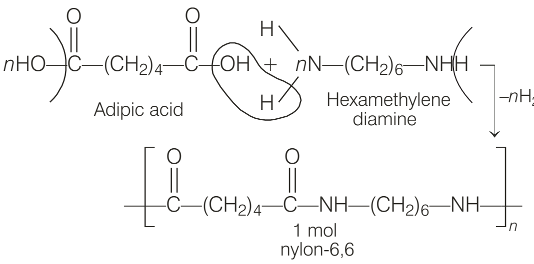
(D)



Thus, the correct match is as follows :

(A) → (III), (B) → (I), (C) → (IV), (D) → (II)

3. Nylon-6, 6 (an amide) is a condensation copolymer because it is obtained by condensation between adipic acid and hexamethylenediamine.



Neoprene, teflon and buna-S are addition polymers.

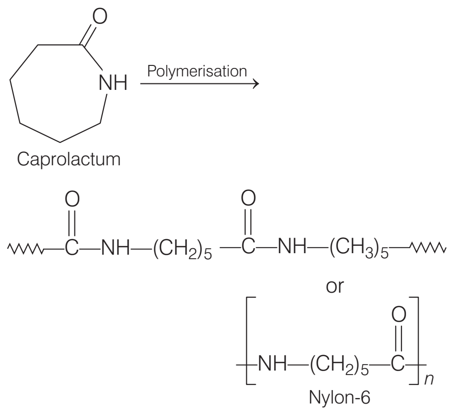
4. Noradrenaline is one of the example of neurotransmitters. It plays a major role in mood changes. If the level of noradrenaline is low for some reason, then signal-sending activity becomes low and the person suffers from depression.

5. Monomer of $-\!\!\left[NH-\overset{O}{\overset{\|}{C}}-NH-CH_2\right]_n\!\!-$ is formaldehyde. The polymer is also known as urea-formaldehyde resin. It is made from urea (NH_2CONH_2) and formaldehyde (HCHO).

$$\underset{\text{Urea}}{NH_2CONH_2} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{\text{Polymerisation}} \underset{\text{Urea-formaldehyde resin}}{-\!\!\left(NH-\overset{O}{\overset{\|}{C}}-NH-CH_2\right)_n\!\!-}$$

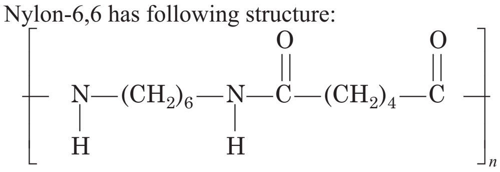
It is used for making unbreakable cups and laminated sheets.

6.



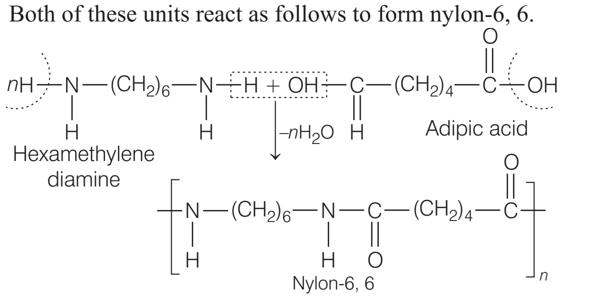
Nylon-6 is prepared by ring opening polymerisation of caprolactum. It is heated about 533 K in an inert atmospheric nitrogen about 4-5 hrs. Nylon-6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis.

7. Nylon-6,6 has following structure:

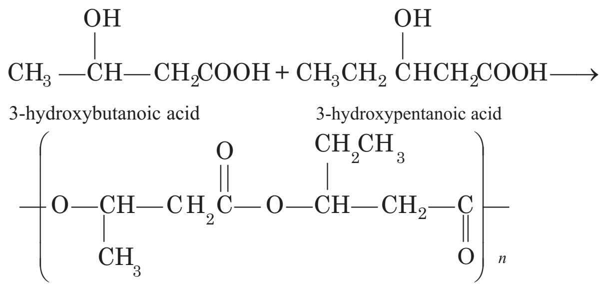


6 C-atoms 6 C-atoms

As it is a condensation polymer hence, each of its monomeric unit must contain 6 carbon atoms in them. Hence, a combination of adipic acid and hexamethylene diamine is the correct answer. Both of these units react as follows to form nylon-6, 6.

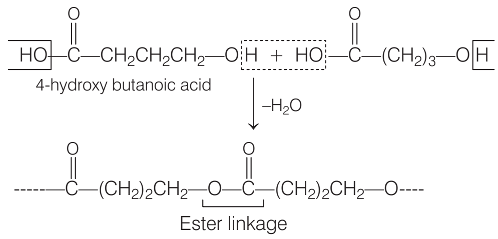


8. Poly-β-hydroxy butyrate Co-β-hydroxyvalerate (PHBV) is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. It is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment. The reaction involved is as follows :



(PHBV)

9. On polymerisation, 4-hydroxy butanoic acid will produce a condensation homopolymer by loss of H_2O molecules.



The homopolymer obtained can also be represented as $-\!\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_3\,O\right]_n\!\!-$

10. (A) Molecule binding to a site other than the active site of enzyme is called allosteric effect.

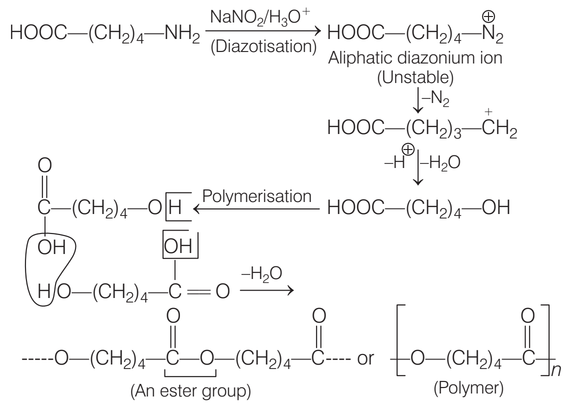
(B) Molecule binding to the active site of enzyme is called competitive inhibitor.

(C) Molecule crucial for communication in the body is called receptor.

(D) Molecule binding to the enzyme covalently is called poison.

Thus, the correct match is : A → R, B → P, C → Q, D → S

11. Given amino acid on reaction with $NaNO_2/H_3O^+$ gives diazotisation reaction which further evolves $-N_2$ gas along with formation of carbocation. On further reaction with water, it form $HOOC-(CH_2)-OH$ that undergoes polymerisation to give polymer.



12. The correct match is:

A → (Q) B → (P) C → (R)

(A) **Norethindrone** It is an antifertility drug(Q) containing synthetic progesterone derivative. [Other similar drug, is ethinylestradiol (novestrol)].

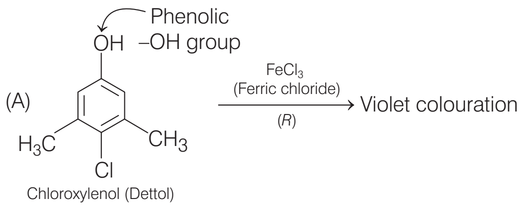
(B) **Ofloxacin** It is an antibiotic (P),

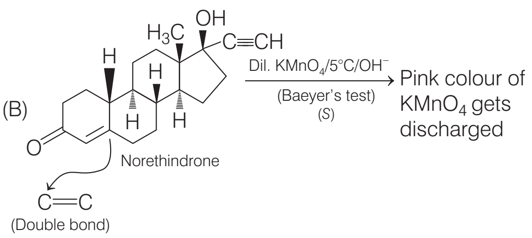
i.e produced wholly or partly by chemical synthesis with low concentration of microorganism.[Some other similar drugs : Penicillin, chloramphenicol, salvarsan etc.]

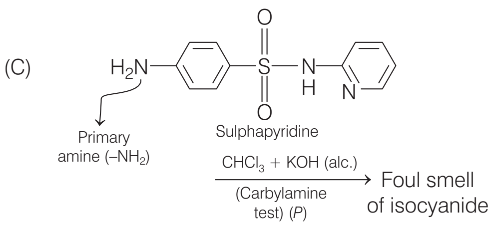
(C) **Equanil (meprobamate)** It is a mild tranquilizer for relieving hypertension. It relieve anxiety, stress, excitement by inducing a sense of well being.

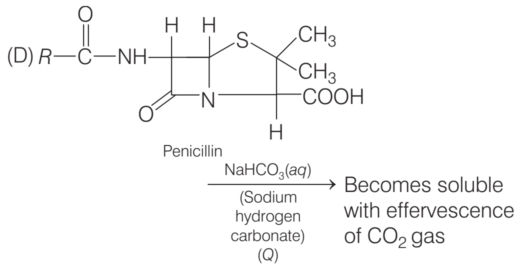
(Other similar drug is chlordiazepoxide.)

13



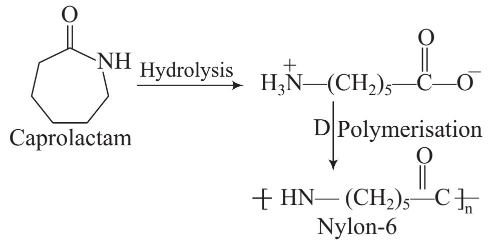






Thus, the correct match is: A → R; B → S; C → P; D → Q

14. Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



15. High density polythene is used in the manufacture of buckets, dustbins etc.

16. Sodium lauryl sulphate $[(CH_3(CH_2)_{10}CH_2OSO_3^-Na^+)]$ = Anionic detergent

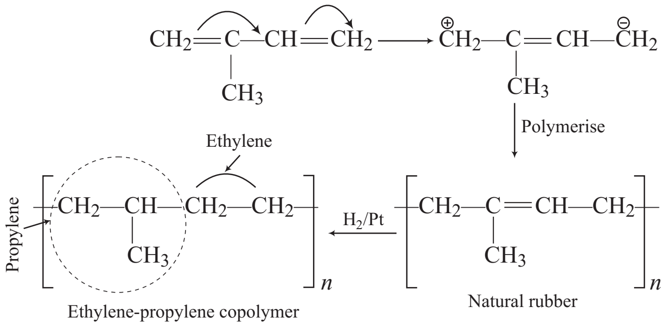
Cetyltrimethyl ammonium

$$\left[CH_3(CH_2)_{15}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]^+ Br^- = \text{Cationic detergent}$$

Glyceryl oleate $[(C_{17}\ H_{32}COO)_3C_3H_5]$ = Non-ionic detergent

Sodium stearate $[C_{17}\ H_{35}COO^-Na^+]$ = Anionic soap

17. Natural rubber is formed by polymerisation of isoprene.



This co-polymer is formed from propylene and ethylene.

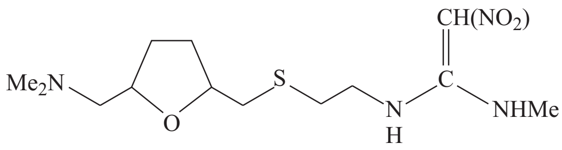
$$n\,CH_2=\underset{\underset{\large CH_3}{|}}{C}H + n\,CH_2=CH_2 \longrightarrow \left[CH_2-\underset{\underset{\large CH_3}{|}}{CH}-CH_2-CH_2\right]_n$$

18. (a) Bakelite is used for making gears, protective coating and electrical fittings.
(b) Glyptal is used in the manufacture of paints and lacquers.
(c) PP is used in the manufacture of textile, packaging materials etc.
(d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

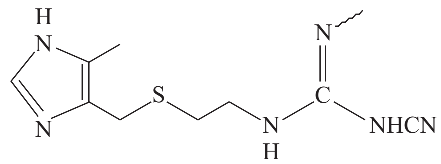
19. (a) Polystyreme- manufacturing toys (b) Glyptal- Paints and lacquers
(c) Polyvinyl chloride (PVC)- Raincoats (d) Bakelite- computer discs
Thus, the correct match is A $\rightarrow$ (1), B $\rightarrow$ (1), C $\rightarrow$ (2), D $\rightarrow$ (4)

20. The given structure is of aspirin which is used as analgesic.

21. Aluminium hydroxide $Al(OH)_3$, cimetidine and ranitidine are antacids while phenelzine is not.

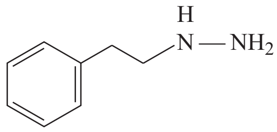


Ranitidine



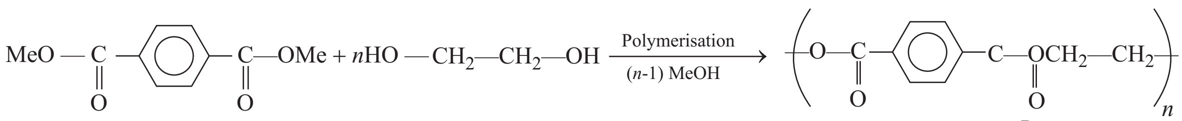
Cimetidine

Phenelzine is a tranquilizer, not an antacid.



Phenelzine is used as antidepressant drug.

22. Dacron is a condensation polymer of ethylene glycol and methyl terepthalate. Formation of dacron can be shown as

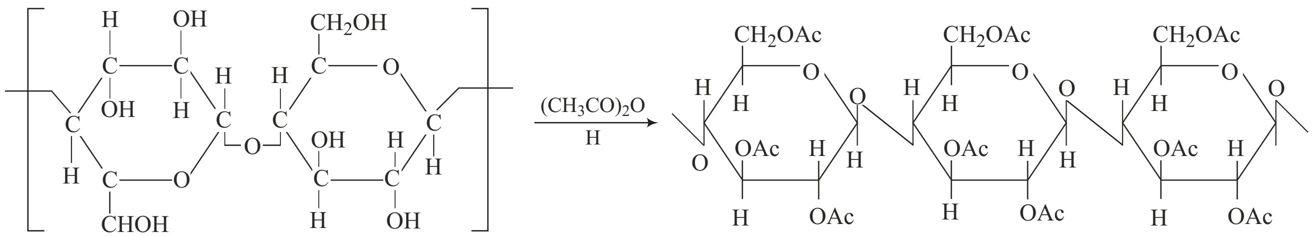


Dacron

Here, elimination of MeOH occurs as a by product. So, this reaction is known as condensation polymerisation.

23. Cellulose and nylons have H-bonding type of intermolecular attraction while poly (vinyl chloride) is polar. Natural rubber is hydrocarbon and has the weakest intermolecular force of attraction, i.e. van der Waals' force of attraction.

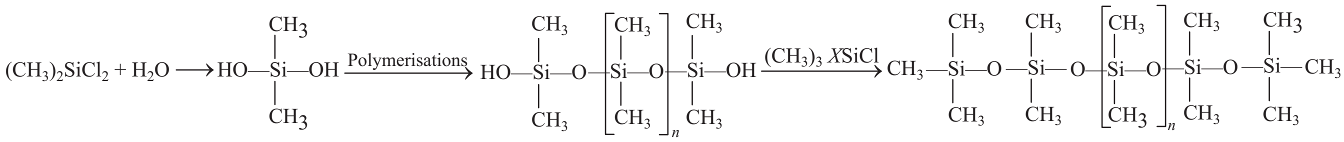
24.



Tri-acetylated cellulose

Tri-acetylated cellulose

25.



Linear chain polymer

Chain terminated linear chain silicone

26. (a) When $X = COOCH_3$

$$CH_3OOC-(CH_2)_4-COOCH_3 \xrightarrow[\text{Heat}]{H_2/Ni} HOCH_2-(CH_2)_4-CH_2OH + 2CH_3OH \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH}$$

$$\left[O-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right]_n$$

Ester, condensation polymer

(b) When $X = CONH_2$

$$H_2NOC-(CH_2)_4-CONH_2 \xrightarrow[\text{Heat}]{H_2/Ni} H_2N-(CH_2)_6-NH_2 \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH} \left[-HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Nylon, condensation polymer

(c) $$H_2NOC-(CH_2)_4-CONH_2 \xrightarrow[NaOH]{Br_2} \underset{\text{Hofmann's bromamide reaction}}{H_2N-(CH_2)_4-NH_2} \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH} \left[-HN-(CH_2)_4-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Nylon, condensation polymer

(d) When $X = CN$ $$NC-(CH_2)_4-CN \xrightarrow[\text{Heat}]{H_2/Ni} H_2N(CH_2)_6NH_2 \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH} \left[-HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Nylon, condensation polymer

In author's opinion (a) and (b) should also be the answer.

(a) $$HOCH_2-(CH_2)_4-CH_2OH + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Heat}} \left[-O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Polyester, a condensation polymer

(b) $$H_2N-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Heat}]{H_2/Ni} H_2NCH_2-(CH_2)_4-CH_2NH_2$$

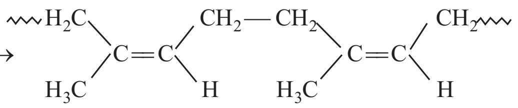
$$H_2NCH_2-(CH_2)_4-CH_2NH_2 + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Heat}} \left[-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Nylon, a condensation polymer

27. (A) Cellulose—a natural polymer of α-D-glucose, linked by glycoside linkage.
(B) Nylon-6, 6—a synthetic polymer of adipic acid and 1,6-diaminohexane. The diacid is linked with diamine through amide linkage.
(C) Protein—a natural polymer of α-amino acids where individual amino acid units are linked by amide linkage.
(D) Sucrose—has glycoside linkage, a disaccharide.

28. (a) $$\underset{\text{'}A\text{' Isoprene}}{H_2C=\overset{CH_3}{\overset{|}{C}}-CH=CH_2} \xrightarrow[Zn-H_2O]{O_3} 2HCHO + CH_3-\overset{O}{\overset{\|}{C}}-CHO$$

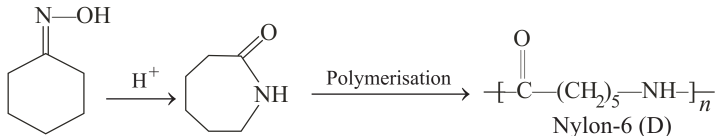
(b) Isoprene ⟶



natural rubber

29. *Zeigler-Natta* catalyst, which is a mixture of triethylaluminium '$(C_2H_5)_3Al$' and $TiCl_4$, is used as heterogeneous catalyst in polymerisation of ethylene.

30.



Caprolactum (C)

Nylon-6 (D)

33

Environmental Chemistry

Objective Questions I (Only one correct option)

1. The primary pollutant that leads to photochemical smog is **(2019 Main, 12 April II)**

(a) acrolein (b) nitrogen oxides
(c) ozone (d) sulphur dioxide

2. The correct set of species responsible for the photochemical smog is **(2019 Main, 12 April I)**

(a) N_2, NO_2 and hydrocarbons
(b) CO_2, NO_2, SO_2 and hydrocarbons
(c) NO, NO_2, O_3 and hydrocarbons
(d) N_2, O_2, O_3 and hydrocarbons

3. Air pollution that occurs in sunlight is **(2019 Main, 10 April II)**

(a) acid rain (b) oxidising smog
(c) fog (d) reducing smog

4. The regions of the atmosphere, where clouds form and where we live, respectively, are **(2019 Main, 10 April I)**

(a) stratosphere and stratosphere
(b) troposphere and troposphere
(c) troposphere and stratosphere
(d) stratosphere and troposphere

5. The layer of atmosphere between 10 km to 50 km above the sea level is called as **(2019 Main, 9 April II)**

(a) stratosphere (b) mesosphere
(c) thermosphere (d) troposphere

6. Excessive release of CO_2 into the atmosphere results in **(2019 Main, 9 April I)**

(a) formation of smog (b) depletion of ozone
(c) polar vortex (d) global warming

7. The maximum prescribed concentration of copper in drinking water is **(2019 Main, 8 April II)**

(a) 5 ppm (b) 0.5 ppm
(c) 0.05 ppm (d) 3 ppm

8. **Assertion** (A) Ozone is destroyed by CFCs in the upper stratosphere.

Reason (R) Ozone holes increase the amount of UV radiation reaching the earth. **(2019 Main, 8 April I)**

(a) Assertion and Reason are incorrect.
(b) Assertion and Reason are both correct and the Reason is the correct explanation for the Assertion.
(c) Assertion and Reason are correct, but the Reason is not the explanation for the Assertion.
(d) Assertion is false, but the Reason is correct.

9. Which is wrong with respect to our responsibility as a human being to protect our environment? **(2019 Main, 8 April I)**

(a) Restricting the use of vehicles
(b) Avoiding the use of floodlighted facilities
(c) Setting up compost tin in gardens
(d) Using plastic bags

10. The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of **(2019 Main, 12 Jan II)**

(a) 600 - 750 nm (b) 400 - 550 nm
(c) 0.8 - 1.5 nm (d) 200 - 315 nm

11. The compound that is not a common component of photochemical smog is **(2019 Main, 12 Jan II)**

(a) CF_2Cl_2 (b) $H_3C-\underset{\underset{O}{\|}}{C}-OONO_2$
(c) $CH_2 = CHCHO$ (d) O_3

12. Water samples with BOD values of 4 ppm and 18 ppm, respectively, are **(2019 Main, 12 Jan I)**

(a) clean and clean
(b) highly polluted and clean
(c) highly polluted and highly polluted
(d) clean and highly polluted

13. The molecule that has minimum/no role in the formation of photochemical smog, is **(2019 Main, 12 Jan I)**

(a) N_2 (b) $CH_2 = O$
(c) NO (d) O_3

14. Taj Mahal is being slowly disfigured and discoloured. This is primarily due to **(2019 Main, 11 Jan II)**

(a) water pollution (b) soil pollution
(c) global warming (d) acid rain

15. The higher concentration of which gas in air can cause stiffness of flower buds? **(2019 Main, 11 Jan II)**

(a) SO_2 (b) CO
(c) CO_2 (d) NO_2

16. Peroxyacetyl nitrate (PAN), an eye irritant is produced by **(2019 Main, 11 Jan I)**

(a) organic waste
(b) acid rain
(c) classical smog
(d) photochemical smog

17. The concentration of dissolved oxygen (DO) in cold water can go upto **(2019 Main, 11 Jan I)**

(a) 14 ppm (b) 10 ppm
(c) 8 ppm (d) 16 ppm

18. The reaction that is not involved in the ozone layer depletion mechanism in the stratosphere is **(2019 Main, 10 Jan II)**

(a) $CH_4 + 2O_3 \longrightarrow 3CH_2 = O + 3H_2O$

(b) $Cl\dot{O}(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$

(c) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + \dot{C}l(g)$

(d) $CF_2Cl_2(g) \xrightarrow{h\nu} \dot{C}l(g) + \dot{C}F_2Cl(g)$

19. Water filled in two glasses A and B have BOD values of 10 and 20, respectively. The correct statement regarding them, is **(2019 Main, 10 Jan I)**

(a) A is more polluted than B
(b) A is suitable for drinking, wherease B is not
(c) Both A and B are suitable for drinking
(d) B is more polluted than A

20. The pH of rain water, is approximately **(2019 Main, 9 Jan II)**

(a) 7.5 (b) 6.5
(c) 5.6 (d) 7.0

21. The condition for methemoglobinemia by drinking water is **(2019 Main, 9 Jan II)**

(a) > 50 ppm nitrate (b) > 50 ppm chloride
(c) > 50 ppm lead (d) > 100 ppm sulphate

22. A water sample has ppm level concentration of the following metals: $Fe = 0.2$; $Mn = 5.0$; $Cu = 3.0$; $Zn = 5.0$. The metal that makes the water sample unsuitable for drinking is **(2019 Main, 9 Jan I)**

(a) Cu (b) Fe
(c) Mn (d) Zn

Answers

1. (b)	**2.** (c)	**3.** (b)	**4.** (b)	**13.** (a)	**14.** (d)	**15.** (a)	**16.** (d)
5. (a)	**6.** (d)	**7.** (d)	**8.** (c)	**17.** (b)	**18.** (a)	**19.** (d)	**20.** (c)
9. (d)	**10.** (d)	**11.** (a)	**12.** (d)	**21.** (a)	**22.** (c)		

Hints & Solutions

1. The primary pollutant that leads to photochemical smog is nitrogen oxides. Burning of fossil fuels such as petrol and diesel in automobiles, reaction between nitrogen and oxygen and other such reactions result in a variety of pollutants, two main of which are hydrocarbons (unburnt fuel) and nitric oxide (NO).

$$N_2(g) + O_2(g) \xrightarrow[\text{diesel engines}]{\text{In petrol and}} 2NO(g)$$

When the concentration of these pollutants is sufficiently high, a chain reaction initiate because of the interaction of sunlight with oxides of nitrogen.

$$2NO(g) + O_2(g) \xrightarrow{\text{Sunlight}} 2NO_2(g)$$

$$NO_2(g) \xrightarrow{h\nu} NO(g) + \underset{\text{Nascent oxygen}}{[O]}$$

$$O_3(g) + NO(g) \longrightarrow \underset{\text{Brown gas}}{NO_2(g)} + O_2(g)$$

2. The correct set of species responsible for the photochemical smog is NO, NO_2, O_3 and hydrocarbons. Photochemical smog appears in warm, dry and sunny climate which are obtained by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Following reactions are involved during the formation of photochemical smog.

(i) $\underset{\text{(Originates from burning of fossil fuels)}}{N_2(g) + O_2(g)} \longrightarrow 2NO(g)$

(ii) $2NO(g) + O_2(g) \xrightarrow{\text{Sunlight}} 2NO_2(g)$

$NO_2(g) \xrightarrow{h\nu} NO(g) + \underset{\text{Nascent oxygen}}{[O]}$

(iii) $O(g) + O_2(g) \rightleftharpoons \underset{\text{Reacts rapidly with NO}}{O_3(g)}$

$$O_3(g) + NO(g) \longrightarrow \underset{\text{Brown gas (in high concentration form haze)}}{NO_2(g) + O_2(g)}$$

$$\underset{\text{(Unburnt hydrocarbon)}}{3CH_4(g)} + 2O_3(g) \longrightarrow \underset{\text{Formaldehyde}}{3CH_2{=}O(g)} + \underset{\text{Acrolein}}{CH_2{=}CHCH{=}O} + H_2O$$

3. In sunlight oxidising smog or photochemical smog or Los-Angeles smog is formed. This smog is brown in colour. It occurs in warm, dry and sunny climate. In presence of sunlight, NO_x (N-oxides), O_2 and unburnt hydrocarbons of air combine to produce photochemical smog which mainly contains peroxyacetyl nitrate (PAN). $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-NO_2$ (PAN)

4. The lowest region of atmosphere is troposphere which extends upto the height of 10 km (approx) from sea level. We live in the tropospheric region. It contains air, water vapour and dust which can form clouds with the help of strong air movement.
Above the troposphere, stratospheric region extends upto 50 km from sea level. It contains mainly N_2, O_2, O_3 and little water vapour. O_3 in the stratosphere absorbs 99.5% of the sun's harmful UV raditions and thus protects the lives on the earth.

5. The atmosphere between the heights 10 to 50 km above the sea level is stratosphere. Atmosphere is not of the same thickness at heights.

6. The effect of release of CO_2 gas into atmosphere is global warming.

7. According to W.H.O. and US environmental protection agency guidelines, maximum allowable concentration of metals in drinking water are as follows :

Metal	Maximum concentration (ppm or mg dm^{-3})
Cd	0.005
Mn	0.05 (option-c)
Al	0.2
Fe	0.2
Cu	3.0 (option-d)
Zn	5.0 (option-a)

8. Ozone is destroyed by CFCs in the upper stratosphere.

These compounds ultimately reach the stratosphere where they get broken down by powerful UV radiations and release chlorine free radical. The chlorine free radicals react with ozone and cause its depletion by converting it into chlorine monoxide radical and molecular oxygen.

$$CF_2Cl_2(g) \xrightarrow{h\nu} Cl(g) + \dot{C}F_2Cl(g)$$

$$CFCl_3(g) \xrightarrow{h\nu} CFCl_2(g) + \dot{C}l(g)$$

$$\dot{C}l(g) + O_3(g) \longrightarrow Cl\dot{O}(g) + O_2(g)$$

Ozone holes increase the amount of UV radiation reaching the earth. These radiations can cause skin cancer, sunburns, ageing of skin.

9. Using plastic bags is wrong with respect to responsibility as a human being to protect our environment. Plastic bags are non-biodegradable in nature. It remains in the environment as such and does not degraded by bacteria. If it is not disposed properly then it may lead serious threat to the environment. The activities that can be used to protect our environment are as follows:

- Restricting the use of vehicles.
- Avoiding the use of flood lighted facilities.
- Setting up compost tin in gardens.

10. Sun emits UV-radiations, which according to following EM categorisation have the wavelength range from 1 nm to 400 nm.

Type	Wavelength range
Radio wave	> 0.1 m
Microwave	0.1 m to 1 mm
Infrared wave	1 mm to 700 nm
Visible rays	700 nm to 400 nm
Ultraviolet rays	400 nm to 1 nm
X-rays	1 nm to 10^{-3} nm
Gamma rays	< 10^{-3} nm

Thus, option (d) with 200-315 nm range is the correct option.

11. Freons or CFCs or chlorofluoro carbons, i.e. CF_2Cl_2 is not the common component of photochemical smog. This smog is produced as the result of tropospheric pollution while freons are the components of stratospheric pollution. These are infact considered as the major cause of ozone layer depletion.

12. The amount of oxygen required by bacteria to break down the organic matter present in a certain value of a sample of water is called biochemical oxygen demand (BOD). The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5ppm whereas highly polluted water would have BOD value of 17 ppm or more.

BOD value of clean water = 4 ppm

BOD value of highly polluted water = 18 ppm

13. N_2 molecule has minimum role in the formation of photochemical smog. While $CH_2=O$, O_3 and NO has major role. When fossil fuels are burnt, a variety of pollutants are emitted. Two of them are hydrocarbons (unburnt) and NO. When these pollutants build upto high levels, a chain reaction occurs from their interaction with sunlight. The reactions involved in the formation of photochemical smog are as follows:

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$$

$$O(g) + O_2(g) \rightleftharpoons O_3(g)$$

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

O_3 reats with unburnt hydrocarbons to produce chemicals such as formaldehyde, acrolein and PAN.

$$3CH_4 + 2O_3 \longrightarrow 3CH_2=O + 3H_2O + CH_2=CCH=O + \underset{\text{(PAN)}}{CH_3\underset{\underset{O}{\|}}{C}OONO_2}$$

14. Acid rain (pH = 3.5 – 5.6) constitutes strong acids like HNO_3, H_2SO_4 and H_2SO_3 which slowly react with marble ($CaCO_3$) of Taj Mahal and make it disfigured and discoloured. Here, $CaCO_3$ (marble) gets dissolved in acids.

$$CaCO_3(s) \xrightarrow[\text{(Acid rain)}]{2\,H^{\oplus}(aq)} Ca^{2+}(aq) + H_2O(l) + CO_2(g)\uparrow$$

15. Organic pigments (colourents) present in flower buds retain their colour in the oxidised form of the pigment as their nature is itself oxidising in nature. When they comes in contact with moist SO_2 (acid rain) of higher concentration, they get decoloured and stiff.

$$SO_2 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$HSO_4^- \longrightarrow H^+ + SO_4^{2-}$$

Due to the release of H^+ ion (acid), the flower get decoloured and stiff.

As a result, flower eventually falls off from plants.

16. Molecular formula of peroxyacetyl nitrate (PAN) is $CH_3-\overset{\overset{O}{\|}}{C}-O-O-NO_2$. It is a secondary pollutant. It is present in photochemical smog (oxidising or Los Angeles smog). PAN is a powerful lachrymator or tear producer and it also causes breathing troubles.

17. Dissolved oxygen (DO) is the oxygen dissolved in water either from atmosphere or by photosynthesis. The lower the concentration of DO in a water sample, the more polluted is the water sample.

The concentration range of dissolved oxygen (DO) in cold water reaches upto 10 ppm, but that in normal water (at room temperature) is within 5 ppm.

18. CH_4 is not present in the stratosphere and also it cannot diffuse or escape into the stratosphere like freon-12 (CF_2Cl_2) from the atmosphere.

In the stratosphere, ozone layer depletion take place mainly by chlorofluorocarbons (CFCs) like CF_2Cl_2 and the mechanism of ozone layer depletion can be shown as:

(i) $CF_2Cl_2(g) \xrightarrow{h\nu} \dot{C}l(g) + \dot{C}F_2Cl(g)$ [Option, (d)]

(ii) $\dot{C}l(g) + O_3(g) \longrightarrow ClO^{\bullet}(g) + O_2$

(iii) $ClO^{\bullet}(g) + O(g) \longrightarrow Cl^{\bullet}(g) + O_2(g)$ [Option (b)]

(iv) $\dot{C}l(g) + \underset{\text{[Present in the stratosphere]}}{H_2O(g)} \longrightarrow HOCl(g) + H^{\bullet}(g)$

(v) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + Cl^{\bullet}(g)$ [Option (c)]

$\Rightarrow$ One $Cl^{\bullet}$ can destroy or deplete 10^5 O_3 molecules.

As (i) reaction is involved in the formation of photochemical smog, not in ozone layer depletion. So option (a) is correct.

19. BOD is defined as the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water. Clean water or drinking water has a BOD value < 5 ppm.

So, water filled with *A*, BOD = 10 ppm is polluted and water filled with *B*, BOD = 20 ppm, is also polluted. But, *B* is more polluted than *A*.

20. In clean air, rain water picks up some acidic oxides like CO_2 and SO_2 (obtained from volcanic eruptions). These substance make the rain slightly acidic (pH = 5.6 – 6).

21. According to EEC (European Environment Commission), excess of NO_3^- (> 50 ppm) in drinking water may lead to methemoglobinemia ('Blue baby syndrome'). It also may cause stomach-cancer.

22. For drinking water, the maximum recommended levels of some metals, set by European Environment Commission (EEC) is

Metal	Max. concentration in ppm
Zn	5
Mn	0.05
Fe	0.2
Cu	3

As the concentration of Mn in the given water sample is more than the recommended concentration. Thus, it makes water unsuitable for drinking.

JEE ADVANCED

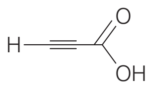
Solved Paper 2019

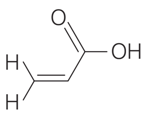
Paper 1

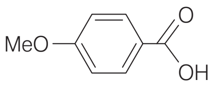
Section 1 (Maximum Marks : 12)

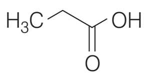
- This section contains **FOUR (04)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : **+3** If ONLY the correct options is chosen.
  Zero Marks : **0** If none of the options is chosen. (i.e. the question is unanswered)
  Negative Marks : **−1** In all other cases.

1. The correct order of acid strength of the following carboxylic acids is

I 

II 

III 

IV 

(a) III > II > I > IV
(b) I > II > III > IV
(c) II > I > IV > III
(d) I > III > II > IV

2. The green colour produced in the borax bead test of a chromium (III) salt is due to

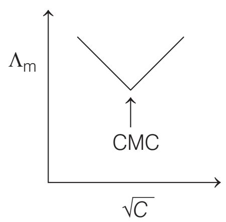
(a) Cr_2O_3 (b) CrB
(c) $Cr(BO_2)_3$ (d) $Cr_2(B_4O_7)_3$

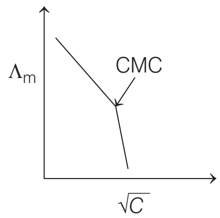
3. Calamine, malachite, magnetite and cryolite, respectively, are

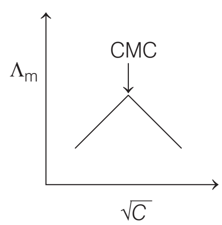
(a) $ZnCO_3$, $CuCO_3$, Fe_2O_3, Na_3AlF_6
(b) $ZnSO_4$, $CuCO_3$, Fe_2O_3, AlF_3
(c) $ZnSO_4$, $Cu(OH)_2$, Fe_3O_4, Na_3AlF_6
(d) $ZnCO_3$, $CuCO_3 \cdot Cu(OH)_2$, Fe_3O_4, Na_3AlF_6

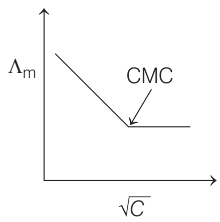
4. Molar conductivity (Λ_m) of aqueous solution of sodium stearate, which behaves as a strong electrolyte, is recorded at varying concentrations (C) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution?

(critical micelle concentration (CMC) is marked with an arrow in the figures)

(a) 

(b) 

(c) 

(d) 

Section 2 (Maximum Marks : 32)

- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options. **ONE OR MORE THAN ONE** of these four option(s) is (are) correct options(s).
- For each question, choose the options(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : **+4** If only (all) the correct option(s) is (are) chosen.
  Partial Marks : **+3** If all the four options are correct but ONLY three options are chosen.
  Partial Marks : **+2** If three or more options are correct but ONLY two options are chosen, both of which are correct and both of which are correct.
  Partial Marks : **+1** If two or more options are correct but ONLY one option is chosen and it is a correct option;
  Zero Marks : 0 If none of the option is chosen (i.e., the question is unanswered);
  Negative Marks : **−1** In all other cases.
- For example, in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then

  choosing ONLY (A), (B) and (D) will get + 4 marks
  choosing ONLY (A) and (B) will get + 2 marks
  choosing ONLY (A) and (D) will get + 2 marks
  choosing ONLY (B) and (D) will get + 2 marks
  choosing ONLY (A) will get + 1 marks
  choosing ONLY (B) will get + 1 marks
  choosing ONLY (D) will get + 1 marks
  choosing no option (i.e., the question is unanswered) will get 0 marks; and
  choosing any other combination of options will get – 1 mark.

---

5. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation.

(a) $2C(g) + 3H_2(g) \longrightarrow C_2H_6(g)$

(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(c) $\frac{3}{2}O_2(g) \longrightarrow O_3(g)$

(d) $\frac{1}{8}S_8(s) + O_2(g) \longrightarrow SO_2(g)$

6. A tin chloride Q undergoes the following reactions (not balanced)

$$Q + Cl^- \longrightarrow X$$
$$Q + Me_3N \longrightarrow Y$$
$$Q + CuCl_2 \longrightarrow Z + CuCl$$

X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.

Choose the correct option(s).

(a) There is a coordinate bond in Y

(b) The central atom in Z has one lone pair of electrons

(c) The oxidation state of the central atom in Z is + 2

(d) The central atom in X is sp^3 hybridised

7. In the decay sequence.

$$^{238}_{92}U \xrightarrow{-x_1} {}^{234}_{90}Th \xrightarrow{-x_2} {}^{234}_{91}Pa \xrightarrow{-x_3} {}^{234}Z \xrightarrow{-x_4} {}^{230}_{90}Th$$

x_1, x_2, x_3 and x_4 are particles/radiation emitted by the respective isotopes. The correct option(s) is(are)

(a) Z is an isotope of uranium

(b) x_2 is β^-

(c) x_1 will deflect towards negatively charged plate

(d) x_3 is γ-ray

8. Which of the following statement(s) is(are) correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (E_{av}) of a molecule in a gas at equilibrium?

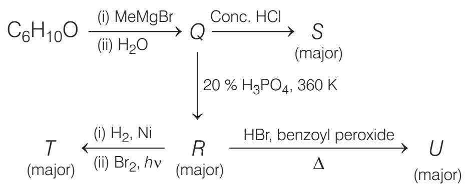
(a) U_{rms} is inversely proportional to the square root of its molecular mass

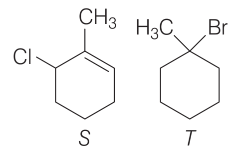
(b) U_{rms} is doubled when its temperature is increased four times

(c) E_{av} is doubled when its temperature is increased four times

(d) E_{av} at a given temperature does not depend on its molecular mass

9. Choose the correct option(s) for the following set of reactions.



(a)


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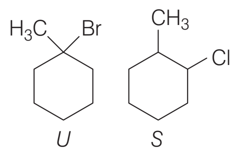
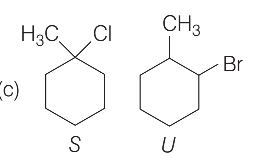
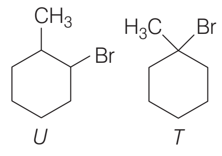


(c)


(d)


10. Which of the following statement(s) is(are) true?

(a) The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers
(b) Oxidation of glucose with bromine water gives glutamic acid
(c) Monosaccharides cannot be hydrolysed to given polyhydroxy aldehydes and ketones
(d) Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose

11. Fusion of MnO_2 with KOH in presence of O_2 produces a salt W. Alkaline solution of W upon electrolytic oxidation yields another salt X. The manganese containing ions present in W and X, respectively, are Y and Z. Correct statement(s) is (are)

(a) Both Y and Z are coloured and have tetrahedral shape
(b) Y is diamagnetic in nature while Z is paramagnetic
(c) In both Y and Z, π-bonding occurs between p-orbitals of oxygen and d-orbitals of manganese
(d) In aqueous acidic solution, Y undergoes disproportionation reaction to give Z and MnO_2

12. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules posses permanent dipole moment at room temperature.

(a) SO_2, C_6H_5Cl, H_2Se, BrF_5 (b) $BeCl_2$, CO_2, BCl_3, $CHCl_3$
(c) NO_2, NH_3, $POCl_3$, CH_3Cl (d) BF_3, O_3, SF_6, XeF_6

Section 3 (Maximum Marks : 18)

- This section contains **SIX (06)** questions. The answer to each question is a **NUMERICAL VALUE.**
- Four each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:
Full Marks : + 3 If ONLY the correct numerical value is entered.
Zero Marks : **0** In all other cases.

13. Among B_2H_6, $B_3N_3H_6$, N_2O, N_2O_4, $H_2S_2O_3$ and $H_2S_2O_8$, the total number of molecules containing covalent bond between two atoms of the same kind is ....

14. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapour pressure decreases from 650 mmHg to 640 mmHg. The depression of freezing point of benzene (in K) upon addition of the solute is .... (Given data : Molar mass and the molal freezing point depression constant of benzene are 78 g mol^{-1} and $5.12 \text{ K kg mol}^{-1}$, respectively).

15. Consider the kinetic data given in the following table for the reaction $A + B + C \longrightarrow$ Product

Experiment No.	$[A]$ (mol dm^{-3})	$[B]$ (mol dm^{-3})	$[C]$ (mol dm^{-3})	Rate of reaction (mol dm^{-3}s^{-1})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

The rate of the reaction for $[A] = 0.15 \text{ mol dm}^{-3}$, $[B] = 0.25 \text{ mol dm}^{-3}$ and $[C] = 0.15 \text{ mol dm}^{-3}$ is found to be $Y \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}$. The value of Y is ....

16. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}.

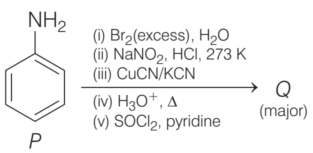
$$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$$

When equal volumes of $0.06 \text{ M } Fe^{2+}(aq)$ and $0.2 \text{ M } S^{2-}(aq)$ solutions are mixed, the equilibrium concentration of $Fe^{2+}(aq)$ is found by $Y \times 10^{-17}$ M. The value of Y is ....

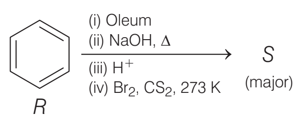
17. At 143 K, the reaction of XeF_4 with O_2F_2 produces a xenon compound Y. The total number of lone pair(s) of electrons present on the whole molecule of Y is ....

18. Schemes 1 and 2 describe the conversion of P to Q and R to S, respectively. Scheme 3 describes the synthesis of T from Q and S. The total number of Br atoms in a molecule of T is ....

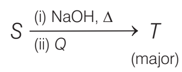
Scheme 1



Scheme 2



Scheme 3



Paper 2

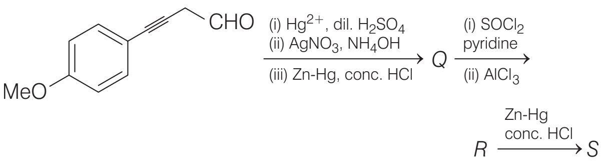
Section 1 (Maximum Marks : 32)

- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct options(s).
- For each question, choose the correct options(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

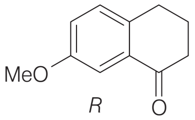
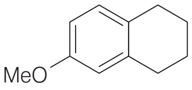
Full Marks : **+4** If only (all) the correct option(s) is (are) chosen.
Partial Marks : **+3** If all the four options are correct but ONLY three options are chosen.
Partial Marks : **+2** If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks : **+1** If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks : **0** If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : **−2** In all other cases.

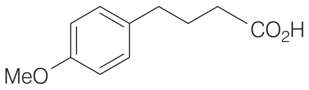
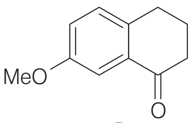
- **For example:** in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answer, then choosing ONLY (A), (B) and (D) will get +4 marks; choosing ONLY (A) and (B) will get +2 marks; choosing ONLY (A) and (D) will get +2 marks; choosing ONLY (B) and (D) will get +2 marks; choosing ONLY (A) will get +1 mark; choosing ONLY (B) will get +1 mark; choosing ONLY (D) will get +1 mark; choosing no option (i.e. the question is unanswered) will get 0 marks; and choosing any other combination of options will −1 mark.

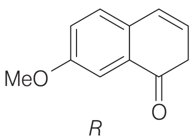
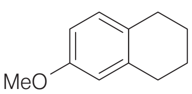
1. Choose the correct option(s) for the following reaction sequence

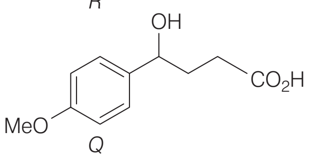
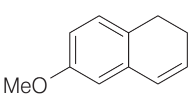


Consider *Q*, *R* and *S* as major products.

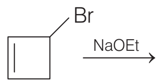
(a)  *R*  *S*

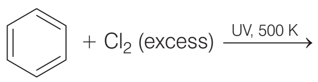
(b)  *Q*  *R*

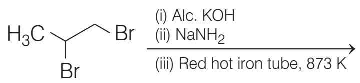
(c)  *R*  *S*

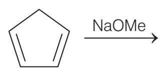
(d)  *Q*  *S*

2. Choose the correct option(s) that give(s) an aromatic compound as the major product.

(a) 

(b) 

(c) 

(d) 

3. The ground state energy of hydrogen atom is −13.6 eV. Consider an electronic state Ψ of He^+ whose energy, azimuthal quantum number and magnetic quantum number are −3.4 eV, 2 and 0, respectively. Which of the following statement(s) is(are) true for the state Ψ?

(a) It is a 4*d* state
(b) The nuclear charge experienced by the electron in this state is less than 2*e*, where *e* is the magnitude of the electronic charge
(c) It has 2 angular nodes
(d) It has 3 radial nodes

4. Consider the following reactions (unbalanced).

$$Zn + \text{Hot conc. } H_2SO_4 \longrightarrow G + R + X$$

$$Zn + \text{conc. NaOH} \longrightarrow T + Q$$

$$G + H_2S + NH_4OH \longrightarrow Z \text{ (a precipitate)} + X + Y$$

Choose the correct option(s).

(a) The oxidation state of Zn in T is +1
(b) R is a V-shaped molecule
(c) Bond order of Q is 1 in its ground state
(d) Z is dirty white in colour

5. With reference to *aqua-regia*, choose the correct option(s).

(a) *Aqua-regia* is prepared by mixing conc. HCl and conc. HNO_3 in 3 : 1 (v / v) ratio
(b) The yellow colour of *aqua-regia* is due to the presence of NOCl and Cl_2
(c) Reaction of gold with *aqua-regia* produces an anion having Au in +3 oxidation state
(d) Reaction of gold with *aqua regia* produces NO_2 in the absence of air

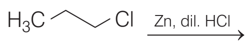
6. Choose the correct option(s) from the following.

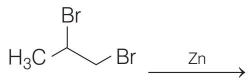
(a) Teflon is prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure
(b) Natural rubber is polyisoprene containing *trans* alkene units
(c) Cellulose has only α-D-glucose units that are joined by glycosidic linkages
(d) Nylon-6 has amide linkages

7. The cyanide process of gold extraction involves leaching out gold from its ore with CN^- in the presence of Q in water to form R. Subsequently, R is treated with T to obtain Au and Z. Choose the correct option(s).

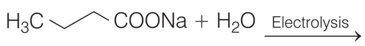
(a) Q is O_2
(b) Z is $[Zn(CN)_4]^{2-}$
(c) T is Zn
(d) R is $[Au(CN)_4]^-$

8. Which of the following reactions produce(s) propane as a major product?

(a) 

(b) 

(c) 

(d) 

Section 2 (Maximum Marks : 18)

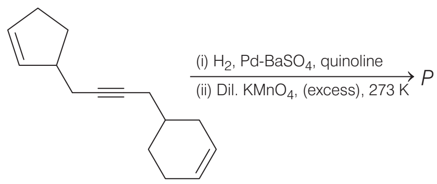
- This section contains **SIX (06)** questions. The answer to each question is a **NUMERICAL VALUE.**
- For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : **+3** If ONLY the correct numerical value is entered as answer.
Zero Marks : **0** In all other cases.

9. The decomposition reaction $2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$ is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After $Y \times 10^3$ s, the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is $5 \times 10^{-4}\ s^{-1}$, assuming ideal gas behaviour, the value of Y is ....

10. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is 1.2 g cm^{-3}, then molarity of urea solution is ...... (Given data : Molar masses of urea and water are 60 g mol^{-1} and 18 g mol^{-1}, respectively)

11. Total number of hydroxyl groups present in a molecule of the major product P is ....



12. Total number of *cis* N—Mn—Cl bond angles (that is Mn—N and Mn—Cl bonds in *cis* positions) present in a molecule of *cis* $[Mn(en)_2Cl_2]$ complex is ....
(en = $NH_2CH_2CH_2NH_2$)

13. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc. HNO_3 to a compound with the highest oxidation state of sulphur is ...... (Given data : Molar mass of water = 18 g mol^{-1})

14. Total number of isomers considering both structural and stereoisomers of cyclic ethers with the molecular formula C_4H_8O is ....

Section 3 (Maximum Marks : 12)

- This section contains **TWO (02)** List-Match sets.
- Each List-Match set has **TWO (02)** Multiple Choice Questions.
- Each List-Match set has two lists : List-I and List-II
- List-I has **Four** entries (I), (II), (III) and (IV) and **List-II** has **Six** entries (P), (Q), (R), (S), (T) and (U).
- **FOUR** options are given in each Multiple Choice Question based on **List-I** and **List-II** and **ONLY ONE** of these four options satisfies the condition asked in the Multiple Choice Questions.
- Answer to each question will be evaluated according to the following marking scheme :

Full Marks : **+3** If ONLY the option corresponding to the correct combination is chosen:
Zero Marks : **0** If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : **−1** In all other cases.

Answer the following by appropriately matching the lists based on the information given in the paragraph.

15. Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the *n*th orbit of the atom and List-II contains options showing how they depend on *n*.

	List-I		List-II
(I)	Radius of the *n* th orbit	(P)	$\propto n^{-2}$
(II)	Angular momentum of the electron in the *n*th orbit	(Q)	$\propto n^{-1}$
(III)	Kinetic energy of the electron in the *n*th orbit	(R)	$\propto n^{0}$
(IV)	Potential energy of the electron in the *n*th orbit	(S)	$\propto n^{1}$
		(T)	$\propto n^{2}$
		(U)	$\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II?

(a) (III), (P) (b) (III), (S)
(c) (IV), (U) (d) (IV), (Q)

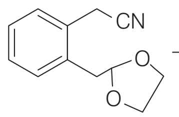
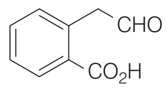
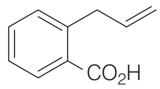
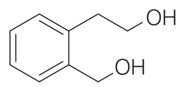
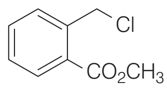
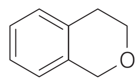
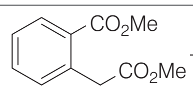
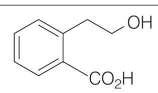
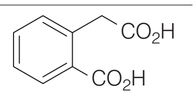
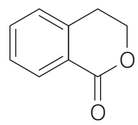
16. Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the *n*th orbit of the atom and List-II contains options showing how they depend on *n*.

	List-I		List-II
(I)	Radius of the *n*th orbit	(P)	$\propto n^{-2}$
(II)	Angular momentum of the electron in the *n*th orbit	(Q)	$\propto n^{-1}$
(III)	Kinetic energy of the electron in the *n*th orbit	(R)	$\propto n^{0}$
(IV)	Potential energy of the electron in the *n*th orbit	(S)	$\propto n^{1}$
		(T)	$\propto n^{2}$
		(U)	$\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II?

(a) (II), (R) (b) (I), (P)
(c) (I), (T) (d) (II), (Q)

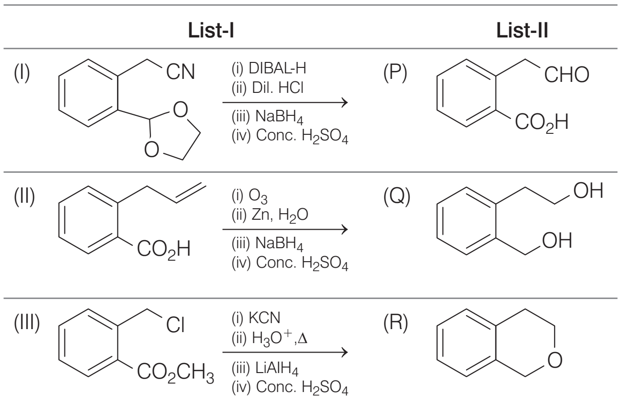
17. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.

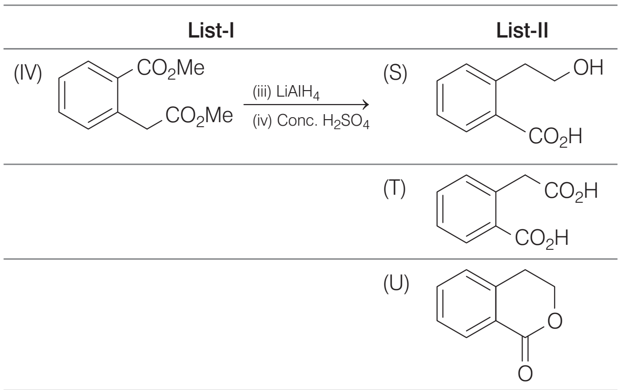
	List-I			List-II
(I)		(i) DIBAL-H (ii) Dil. HCl (iii) $NaBH_4$ (iv) Conc. H_2SO_4	(P)	
(II)		(i) O_3 (ii) Zn, H_2O (iii) $NaBH_4$ (iv) Conc. H_2SO_4	(Q)	
(III)		(i) KCN (ii) H_3O^+,Δ (iii) $LiAlH_4$ (iv) Conc. H_2SO_4	(R)	
(IV)		(iii) $LiAlH_4$ (iv) Conc. H_2SO_4	(S)	
			(T)	
			(U)	

Which of the following options has correct combination considering List-I and List-II?

(a) (III), (S), (R)
(b) (IV), (Q), (R)
(c) (III), (T), (U)
(d) (IV), (Q), (U)

18. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.





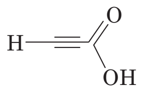
Which of the following options has correct combination considering List-I and List-II?

(a) (II), (P), (S), (U)
(b) (I), (Q), (T), (U)
(c) (II), (P), (S), (T)
(d) (I), (S), (Q), (R)

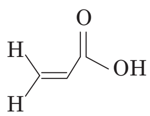
Answer *with* Explanations

Paper 1

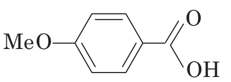
1. *(b)* Acidic nature depends upon nature of electron withdrawing group and electronegativity. Electronegativity further depends on % s character. Higher the s-character, greater will be the electronegativity and hence tendency to loose H increases thus acidic character also increases.

(I) 

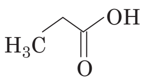
sp- hybridisation
(50% s character)
(pK_a = 1.86)

(II) 

sp^2 -hybridisation
(30-33% s character)
(pK_a = 4.3)

(III) 

sp^2 -hybridisation
(Resonance effect)
(pK_a = 4.5)

(IV) 

sp^3 -hybridisation
(25% s-character)
(pK_a = 4.8)

Hence, acidic order I > II > III > IV.

II is more acidic than III since electron donating group (—OCH_3) is attached to benzene ring in III which decreases the acidic character.

On the other hand, pK_a value also determined acidic nature, lower pK_a value gives maximum acidic character.

Hence, option (b) is correct.

2. *(c)* Borax bead test is performed only for coloured salt. Borax (sodium pyroborate), $Na_2B_4O_7 \cdot 10H_2O$ on heating gets fused and lose water of crystallisation. It swells up into fluffy white porous mass which melts into a colourless liquid which later form a clear transparent glassy bead consisting of boric anhydride and sodium metaborate.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O \uparrow$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{Boric anhydride}}{B_2O_3} + \underset{\text{Sodium metaborate}}{2NaBO_2}}_{\text{glassy bead}}$$

Boric anhydride is non-volalite. When it react with Cr(III) salt then deep green complex is formed.

$$2Cr^{3+} + 3B_2O_3 \longrightarrow \underset{\text{Deep green}}{2Cr(BO_2)_3}$$

Hence, option (c) is correct.

3. *(d)* $ZnCO_3$-Calamine (zinc ore)

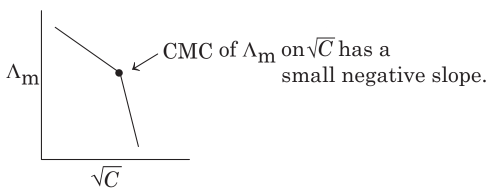
$CuCO_3 \cdot Cu(OH)_2$-Malachite (copper ore)

Fe_3O_4-Magnetite (iron ore)

Na_3AlF_6-Cryolite (aluminium ore)

Thus, option (d) is correct.

4. *(b)* ***Key Idea*** The aqueous solution of ionic surfactant, i.e. sodium stearate ($C_{17}H_{35}CO\bar{O}N\overset{+}{a}$) acts as a strong univalent type of electrolyte in the concentration range below the CMC and the linear function of dependence of Λ_m on $\sqrt{C}$ has a small negative slope.



At normal or low concentration, sodium stearate $[CH_3(CH_2)_{16}COO^-Na^+]$ behaves as strong electrolyte and for strong electrolyte, molar conductance (Λ_m) decreases with increase in concentration.

Above particular concentration, sodium stearate forms aggregates known as micelles. The concentration is called as CMC. Since, number of ions decreases and hence Λ_m also decreases.

Hence, option (b) is correct.

5. *(c, d)* The standard enthalpy of formation is defined as standard enthalpy change for formation of 1 mole of a substance from its elements, present in their most stable state of aggregation.

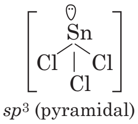
$$\frac{3}{2}O_2(g) \longrightarrow O_3(g);$$

$$\frac{1}{8}S_8(s) + O_2(g) \longrightarrow SO_2(g)$$

In the above two reactions standard enthalpy of reaction is equal to standard enthalpy of formation.

6. *(a, d)*

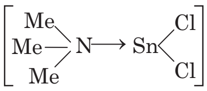
$$\underset{\substack{\text{Tin chloride}\\(Q)}}{SnCl_2} + Cl^- \longrightarrow \underset{(X)}{SnCl_3^-}$$



sp^3 (pyramidal)

$SnCl_3^-$ has ($3\sigma + 1lp$) and exist in pyramidal structure.

$$\underset{\substack{(3°\text{amine})\\(Q)}}{SnCl_2 + Me_3N} \longrightarrow \underset{(Y)}{SnCl_2 \cdot NMe_3}$$



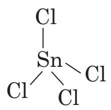
Y complex has coordinate bond in between nitrogen and Sn metal.

$$\underset{(Q)}{\overset{+2}{SnCl_2}} + \overset{+2}{2CuCl_2} \longrightarrow \underset{(Z)}{\overset{+4}{SnCl_4}} + \overset{+1}{2CuCl}$$

Reduction

Oxidation

Z is oxidised product and oxidation state of Sn is +4 in Z compound. Structure of $SnCl_4(Z)$ is



Thus, options (a, d) are correct.

7. *(a,b,c)* **Key Idea** The lose of one α-particle will decrease the mass number by 4 and atomic number by 2. On the other hand, loss of β-particle will increase the atomic number by 1.

In decay sequence,

$$_{92}U^{238} \longrightarrow {}_{90}Th^{234} + \underset{X_1 \text{ particle}}{_2He^4} \text{ (or } \alpha)$$

$$\downarrow$$

$$\underset{\substack{Z^{234}\text{ is isotope}\\ \text{of uranium}}}{_{92}U^{234}} + \underset{X_3\text{ particle}}{(\beta^- \text{ or } _{-1}e^0)} \longleftarrow {}_{91}Pa^{234} + \underset{X_2\text{ particle}}{(\beta^- \text{ or } _{-1}e^0)}$$

$$\longrightarrow {}_{90}Th^{230} + \underset{X_4\text{ particle}}{_2He^4} \text{ (or } \alpha)$$

X_1 particle will deflect towards negatively charged plate due to presence of positive charge on α- particles.

Hence, options (a, b, c) are correct.

8. *(a, b, d)* The explanation of given statements are as follows:

(a) U_{rms} is inversely proportional to the square root of its molecular mass.

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

Hence, option (a) is correct.

(b) When temperature is increased four times then U_{rms} become doubled.

$$U_{rms} = \sqrt{\frac{3R}{M} \times 4T}$$

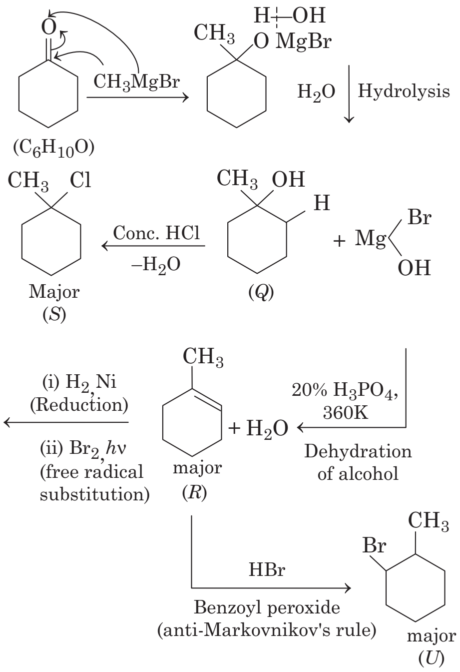
$$U_{rms} = 2 \times \sqrt{\frac{3RT}{M}}$$

Hence, option (b) is correct.

(c) and (d) E_{av} is directly proportional to temperature but does not depends on its molecular mass at a given temperature as $E_{av} = \frac{3}{2}KT$. If temperature raised four times than E_{av} becomes four time multiple.

Thus, option (c) is incorrect and option (d) is correct.

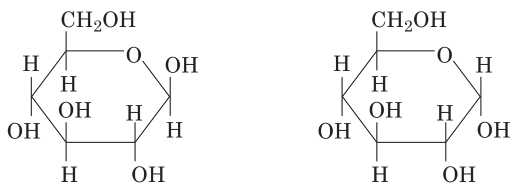
9. *(c, d)* The given road map problem is



Hence, options (c, d) are correct.

10. *(a, c, d)* The explanation of given statements are as follows:

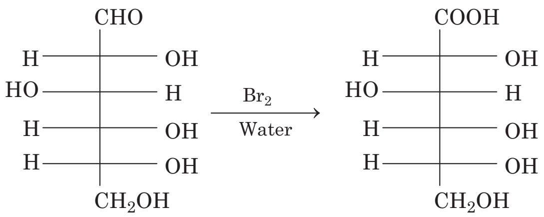
(a) Two six membered cyclic hemiacetal form of D-(+)- glucose are called anomers.



α-D(+)-glucopyranose $\qquad$ β-D(+)-glucopyranose

Both are anomers.

(b) Oxidation of glucose in presence of Br_2 water gives gluconic acid.



D-(+)-glucose   Gluconic acid

(c) Monosaccharides can not be hydrolysed into polyhydroxy aldehydes and ketones.

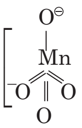
(d) Hydrolysis of sucrose gives D-glucose and L-fructose.

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\substack{\text{D-glucose}\\ \text{or dextrorotatory}}}{C_6H_{12}O_6} + \underset{\substack{\text{L-fructose}\\ \text{or laevorotatory}}}{C_6H_{12}O_6}$$

Hence, options (a, c, d) are correct.

11. *(a, c, d)* $MnO_2 + 2KOH + \frac{1}{2}O_2 \xrightarrow{\Delta} \underset{(W)\text{ potassium manganate}}{K_2MnO_4} + H_2O$

$$\underset{(W)}{K_2MnO_4\,(aq)} \rightleftharpoons 2K^+(aq) + \underset{(Y)}{MnO_4^{2-}(aq)}$$



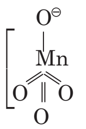
sp^3 hybridisation, tetrahedral (manganate ion)

Green coloured complex

MnO_4^{2-} ion has one unpaired electrons, therefore it gives *d-d* transition to form green colour. *Y* complex has paramagnetic nature due to presence of one unpaired electron. In aqueous solution,

$$\underset{(W)}{K_2MnO_4} + H_2O \xrightarrow{\text{Electrolytic oxidation}} H_2 + KOH + \underset{(X)}{KMnO_4}$$

$$KMnO_4(aq) \xrightarrow{\Delta} K^+ + \underset{(Z)}{MnO_4^-}$$



sp^3, tetrahedral (purple coloured complex ion)

MnO_4^- ions gives charge transfer spectrum in which a fraction of electronic charge is transferred between the molecular entities.

$$\because \quad \underset{(Y)}{MnO_4^{2-}} \xrightarrow[\text{oxidation}]{\text{Electrolytic}} \underset{(Z)}{MnO_4^-} + e^-$$

In acidic medium, *Y* undergoes disproportionation reaction.

$$\underset{(Y)}{3MnO_4^{2-}(aq)} + 4H^+ \longrightarrow \underset{(Z)}{2MnO_4^-} + MnO_2 + 2H_2O$$

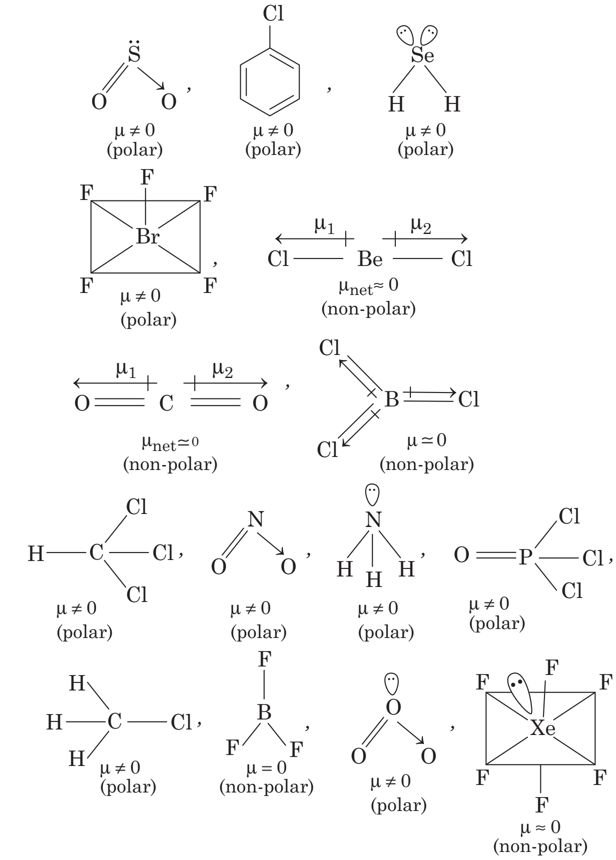
$\underset{(Y)}{MnO_4^{2-}}$ and $\underset{(Z)}{MnO_4^-}$ both ions form π-bonding between *p*-orbitals of oxygen and *d*-orbitals of manganese.

Thus, options (a, c, d) are correct.

12. *(a,c)*

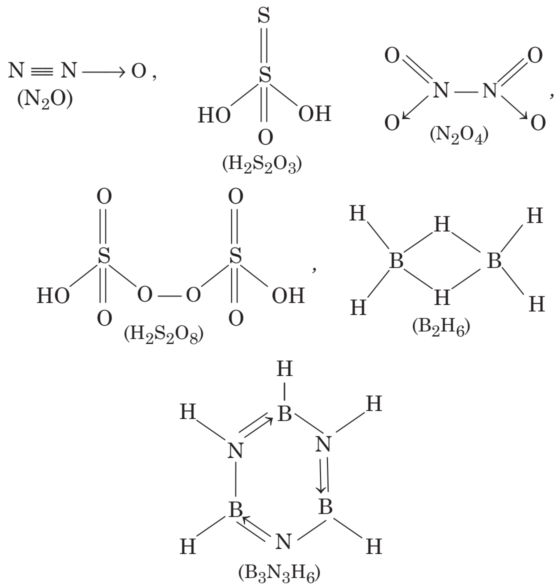
> ***Key Idea*** Dipole moment of a bond depends on the difference in the electronegativities of bonded atoms. More is the difference in the electronegativities, greater will be the dipole moment. Also,
> For symmetrical molecule, $\mu = 0$
> For unsymmetrical molecule, $\mu \neq 0$

The molecules which gives permanent dipole moment are polar in nature.



Thus, options (a, c) are correct.

13. *(4.00)* N_2O, N_2O_4, $H_2S_2O_3$ and $H_2S_2O_8$ molecules are containing covalent bond between two atoms.



B_2H_6 and $B_3N_3H_6$ have polar bond, but do not have same kind of atom.

14. *(1.02)* **Key Idea** First calculate, molar mass of solute using the formula, $\frac{p^\circ - p_s}{p^\circ} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$ and then calculate ΔT_f by applying the formula; $\Delta T_f = K_f \times m$.

When 0.5 g of non-volatile solute dissolve into 39 gm of benzene then relative lowering of vapour pressure occurs. Hence, vapour pressure decreases from 650 mmHg to 640 mmHg.

Given, vapour pressure of solvent (p°) = 650 mmHg

Vapour pressure of solution (p_s) = 640 mmHg

Weight of non-volatile solute = 0.5 g

Weight of solvent (benzene) = 39 g

From relative lowering of vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = x_{Solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$$

$$\frac{650 - 640}{650} = \frac{\frac{0.5}{\text{molar mass}}}{\frac{0.5}{\text{molar mass}} + \frac{39}{78}}$$

$$\frac{10}{650} = \frac{\frac{0.5}{\text{molar mass}}}{\frac{0.5}{\text{molar mass}} + 0.5}$$

$0.5 + 0.5 \times$ molar mass $= 65 \times 0.5$

$\therefore$ Molar mass of solute = 64 g

From molal depression of freezing point,

$$\Delta T_f = K_f \times \text{molality}$$

$$= \frac{K_f \times w_{solute}}{(MW)_{solute} \times w_{solvent}}$$

$$\Delta T_f = 5.12 \times \frac{0.5 \times 1000}{64 \times 39} \Rightarrow \Delta T_f = 1.02\text{K}$$

15. *(6.75)* Rate $= k[A]^x [B]^y [C]^z$

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{[0.2]^x\ [0.1]^y\ [0.1]^z}{[0.2]^x\ [0.2]^y\ [0.1]^z} = \frac{6 \times 10^{-5}}{6 \times 10^{-5}}$$

$\Rightarrow y = 0$

$$\frac{(\text{Rate})_1}{(\text{Rate})_3} = \frac{[0.2]^x\ [0.1]^y\ [0.1]^z}{[0.2]^x\ [0.1]^y\ [0.2]^z} = \frac{6 \times 10^{-5}}{1.2 \times 10^{-4}}$$

$\Rightarrow z = 1$

$$\frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{[0.2]^x\ [0.1]^y\ [0.1]^z}{[0.3]^x\ [0.1]^y\ [0.1]^2} = \frac{6 \times 10^{-5}}{9 \times 10^{-5}}$$

$\Rightarrow x = 1$

So, rate $= k[A]^1 [C]^1$

From exp-Ist,

$$\text{Rate} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$6.0 \times 10^{-5} = k[0.2]^1 [0.1]^1$$

$$k = 3 \times 10^{-3}$$

Given, $[A] = 0.15$ mol dm^{-3}

$[B] = 0.25$ mol dm^{-3}

$[C] = 0.15$ mol dm^{-3}

$\therefore$ Rate $= (3 \times 10^{-3}) \times [0.15]^1 [0.25]^0 [0.15]^1 = 3 \times 10^{-3} \times 0.15 \times 0.15$

Rate $= 6.75 \times 10^{-5}$ mol dm^{-3} s^{-1}

Thus, $Y = 6.75$

16. *(8.9)* Given, equilibrium constant (K_c) at 298 K $= 1.6 \times 10^{17}$

	$Fe^{2+}(aq)$ +	$S^{2-}(aq)$ $\rightleftharpoons$	$FeS(s)$
At initial concentration (Before mixing)	0.06 M	0.2 M	–
At initial concentration (After mixing)	0.03 M	0.1 M	–
At equilibrium	0.03-X	0.1 – 0.03 = 0.07	–

[Here, $K_c >> 10^3$, thus limiting reagent will be consumed almost completely, $0.03 - X = 0 \therefore X = 0.03$]

From equilibrium constant,

$$K_C = \frac{[\text{FeS}]}{[\text{Fe}^{2+}][\text{S}^{2-}]}$$

$$K_C = \frac{1}{X \times 0.07} \quad [\text{For } \underset{\text{(Pure solid)}}{\text{FeS(s)}} = 1 \text{ mol L}^{-1}]$$

$$1.6 \times 10^{17} = \frac{1}{X \times 0.07}$$

$$X = \frac{1}{1.6 \times 10^{17} \times 0.07} = 8.9 \times 10^{-17}$$

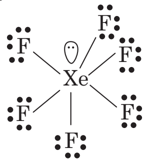
Given, $X = Y \times 10^{-17} = 8.9 \times 10^{-17}$

$\therefore$ $Y = 8.9$

17. *(19)* XeF_4 reacts with O_2F_2 to form $XeF_6 \cdot O_2F_2$ is fluoronating reagent.

$$XeF_4 + O_2F_2 \xrightarrow{143\text{ K}} \underset{(Y)}{XeF_6} + O_2$$

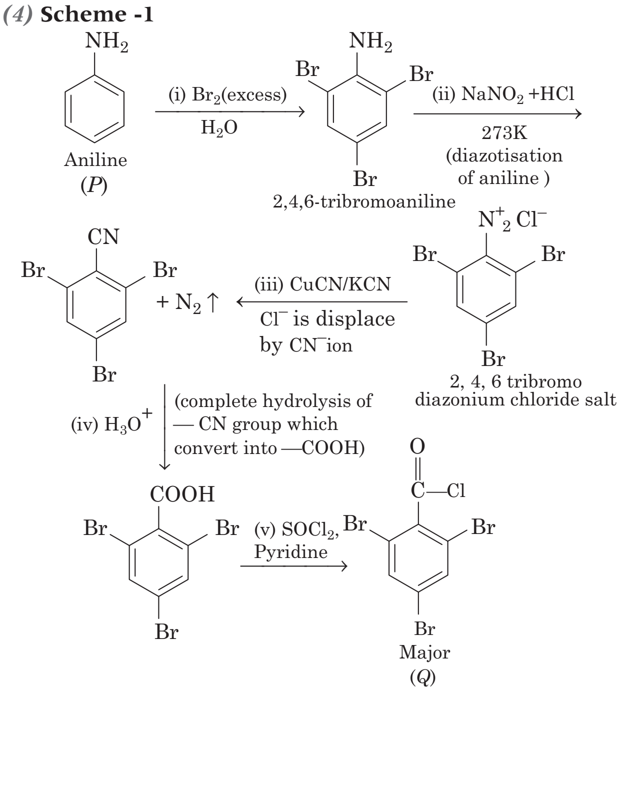
The structore of XeF_6 is



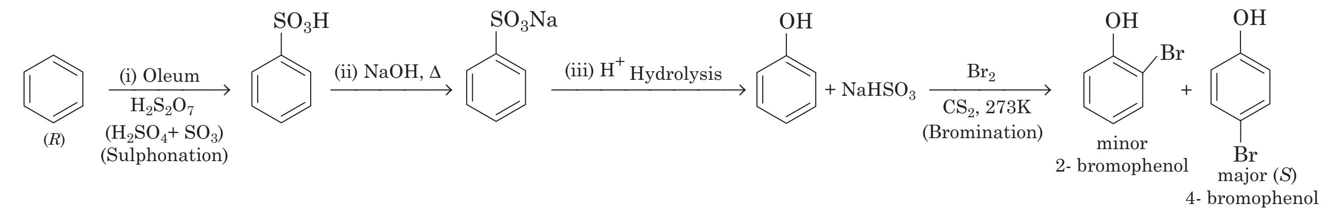
Y compound (XeF_6) has 3 lone pair in each fluorine and one lone pair in xenon.

Hence, total number of lone pairs electrons is 19.

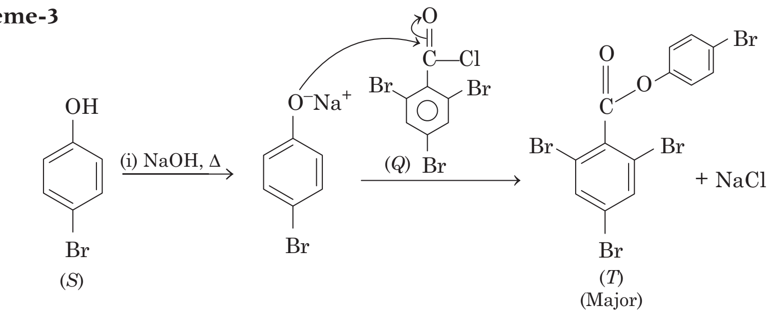
18. *(4)* **Scheme -1**



Scheme-2



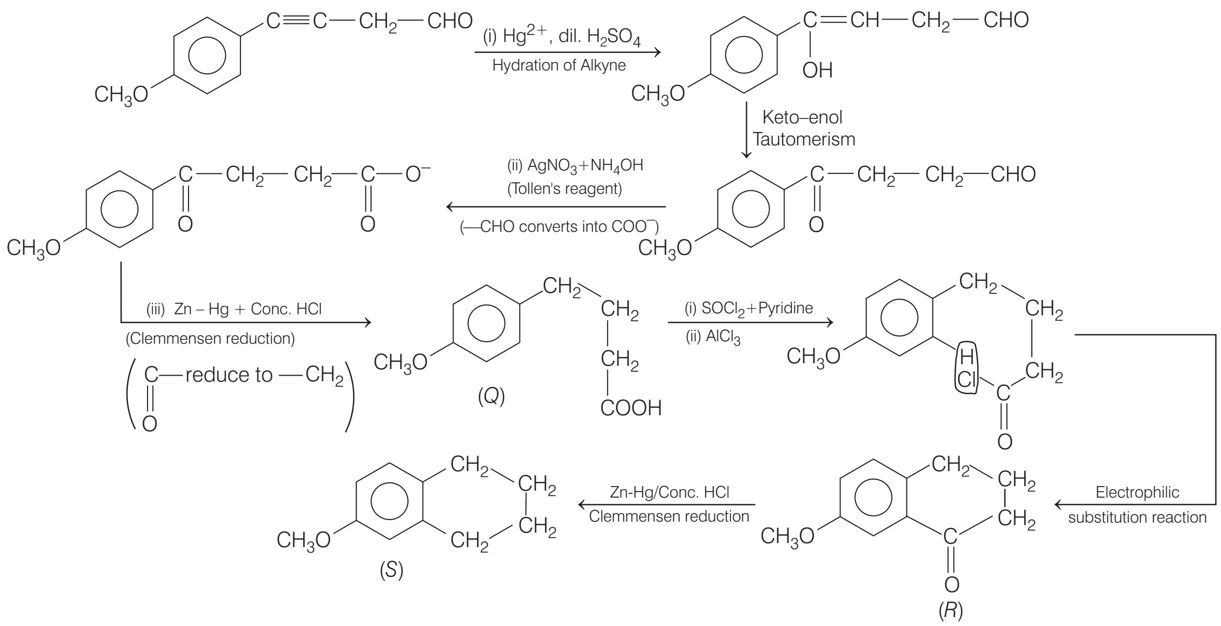
Scheme-3



T compound has total number of Br atom $=4$

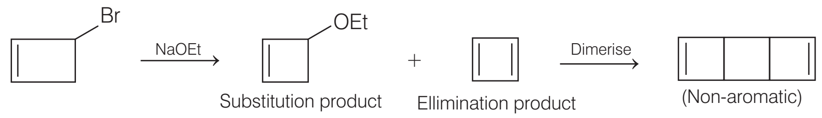
Paper 2

1. *(a, b)*

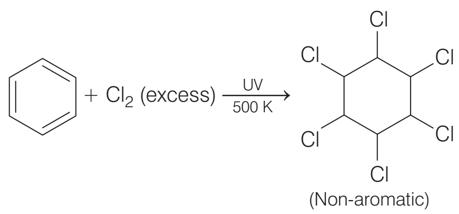


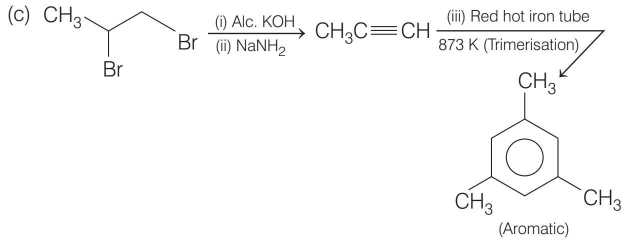
2. *(c, d)* **Key Idea** An aromatic compound must be cyclic and planar. It must follow $(4n+2)e^-$ rule and have the conjugated system in it.

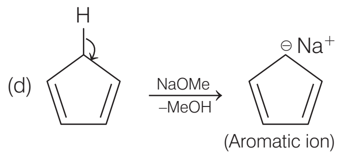
(a)



(b) Benzene react with Cl_2 (excess) in presence of UV light and 500 K of temperature to form benzene hexachloride (non-aromatic).







Thus, (c) and (d) options are correct.

3. ***(a, c)*** Given, ground state energy of hydrogen atom = – 13.6 eV

Energy of He^+ = – 3.4 eV, $Z = 2$

Energy of He^+, $E = -\dfrac{13.6 \times Z^2}{n^2}$ eV

$$-3.4 \text{ eV} = \frac{-13.6 \times (2)^2}{n^2} \Rightarrow n = \sqrt{\frac{13.6 \times 4}{3.4}} \Rightarrow n = 4$$

Given, azimuthal quantum number (l) = 2(d – subshell

Magnetic quantum number (m) = 0

$\therefore$ Angular nodes (l) = 2

Radial node = $n - l - 1 = 4 - 2 - 1 = 1$

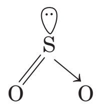
$nl = 4d$ state

Hence, options (a), (c) are correct.

4. ***(b, c, d)*** When Zn react with hot conc. H_2SO_4 then SO_2 is released and $ZnSO_4$ is obtained.

$$\underset{\text{(Hot + Conc.)}}{Zn + 2H_2SO_4} \longrightarrow \underset{(G)}{ZnSO_4} + \underset{(R)}{SO_2}\uparrow + \underset{(X)}{2H_2O}$$

$R(SO_2)$ molecule is V-Shaped



Thus, option (b) is correct.

When Zn is react with conc. NaOH then H_2 gas is evolved and Na_2ZnO_2 is obtained.

$$Zn + 2NaOH(\text{conc.}) \longrightarrow \underset{(T)}{Na_2ZnO_2} + \underset{(Q)}{H_2}\uparrow$$

In ground state, H—H (Q) (bond order = 1)

Thus, option (c) is correct.

The oxidation state of Zn in $T(Na_2ZnO_2)$ is +2

Thus, option (a) is incorrect.

$$\underset{(G)}{ZnSO_4} + H_2S + NH_4OH \longrightarrow \underset{(Z)}{ZnS}\downarrow + \underset{(X)}{2H_2O} + \underset{(Y)}{(NH_4)_2SO_4}$$

ZnS (Z) compound is dirty white coloured.

Thus, option (d) is correct.

5. ***(a, b, c)*** The explanation of given statements are as follows:

(a) *Aqua-regia* is prepared by mixing conc. HCl and conc. HNO_3 in 3:1 (v/v) ratio and is used in oxidation of gold and platinum. Hence, option (a) is correct.

(b) Yellow colour of *aqua-regia* is due to its decomposition into NOCl (orange yellow) and Cl_2 (greenish yellow). Hence, option (b) is correct.

(c) When gold reacts with *aqua-regia* then it produces $AuCl_4^-$ anion complex in which Au has +3 oxidation state.

$$\underbrace{\overset{0}{Au} + HNO_3 + 4HCl \longrightarrow \overset{+3}{Au}Cl_4^-}_{\text{Oxidation}} + H_3O^+ + NO + H_2O$$

Hence, option (c) is correct.

(d) Reaction of gold with *aqua-regia* produces NO gas in absence of air.

Hence, option (d) is incorrect.

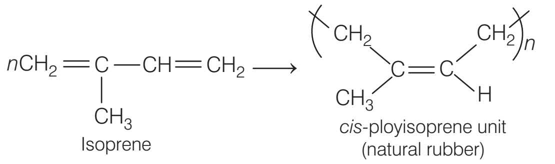
6. ***(a, d)*** The explanation of given statements are as follows:

(a) Teflon is prepared by heating tetrafluoroethene in presence of persulphate catalyst at higher pressure.

$$nCF_2{=}CF_2 \xrightarrow[\text{catalyst}]{\text{Persulphate}} \underset{\substack{\text{Thermoplastic Polymer}\\ \text{(PTFE)}}}{-\!\!\left(CF_2-CF_2\right)\!\!-}$$

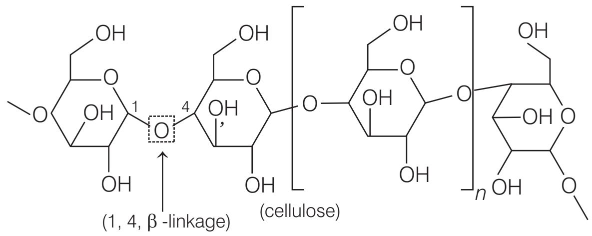
Thus, option (a) is correct.

(b) Natural rubber is polyisoprene containing *cis* alkene units.



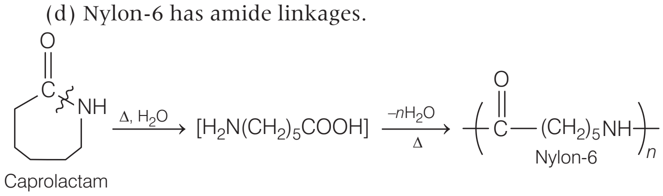
Thus, option (b) is incorrect.

(c) Cellulose has only β-D-glucose units that are joined together by glycosidic linkages as shown in the following structure:



Thus, option (c) is incorrect.

(d) Nylon-6 has amide linkages.



Thus, option (d) is correct.

7. ***(a, b, c)*** Cyanide process of gold extraction involves leaching out gold from its ore with CN^- in the presence of O_2 (Q) in water to form $[Au(CN)_2]^-$ (R).

When $[Au(CN)_2]^-$ reacts with Zn (T), it froms $[Zn(CN)_4]^{2-}$ (Z) and Au.

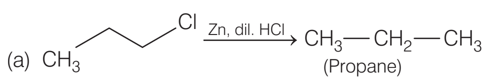
The corresponding reactions are as follows :

$$4Au(s) + 8CN^-(aq) \xrightarrow{H_2O + O_2(Q)} 4\underset{(R)}{[Au(CN)_2]^-} + 4OH^-(aq)$$

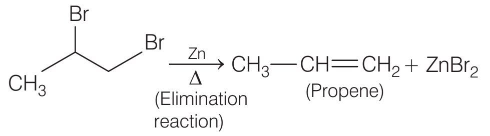
$$2\underset{(R)}{[Au(CN)_2]^-}(aq) + \underset{(T)}{Zn(s)} \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

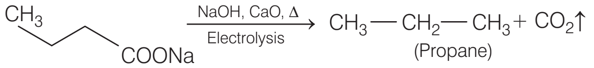
Hence, options (a, b, c) are correct.

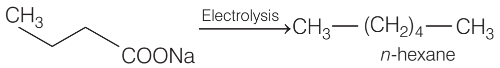
8. ***(a, c)*** The given reactions takes place as follows:



(1)

(b) 

(c) 

(d) 

Thus, options (a, c) are correct.

9. *(2.3)* At constant V, T

$$2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$$

At initial $t = 0$ 1   0   0

$t = Y \times 10^3$ sec $1 - 2p$ $2p$ p

$$p_{\text{Total}} = 1 - 2p + 2p + p$$
$$1.4 = 1 + p$$
$$p = 0.45 \text{ atm}$$

According to first order reaction,

$$k = \frac{2303}{t}\log\frac{p_i}{p_i - 2p}$$
$$p_i = 1\text{atm (given)}$$
$$2p = 2 \times 0.45 = 0.9 \text{ atm}$$

On substituting the values in above equation,

$$2k \cdot t = 2.303\log\frac{1}{1 - 0.9}$$
$$2 \times 5 \times 10^{-4} \times y \times 10^3 = 2.303\log\frac{1}{0.1}$$
$$y = 2.303 = 2.3$$

Note Unit of rate constant (k), i.e. s^{-1} represents that it is a first order reaction.

10. *(2.98 mole)*

> **Key Idea** Molarity $(M) = \dfrac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (in mL)}}$

Also, volume $= \dfrac{\text{Mass}}{\text{Density}}$

Given, mole fraction of urea $(\chi_{\text{urea}}) = 0.05$

Mass of water = 900 g

Density $= 1.2 \text{ g/cm}^3$

$$\chi_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \qquad \left[\because \text{Moles of water} = \frac{900}{18} = 50\right]$$

$$0.05 = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \Rightarrow 19n_{\text{urea}} = 50$$

$$n_{\text{urea}} = 2.6315 \text{ moles}$$
$$w_{\text{urea}} = n_{\text{urea}} \times (M \cdot wt)_{\text{urea}} = (2.6315 \times 60) \text{ g}$$

$$V = \frac{2.6315 \times 60 + 900}{1.2}\left[\because \text{Density} = \frac{\text{Mass of solution}}{\text{Volume of solution}}\right]$$

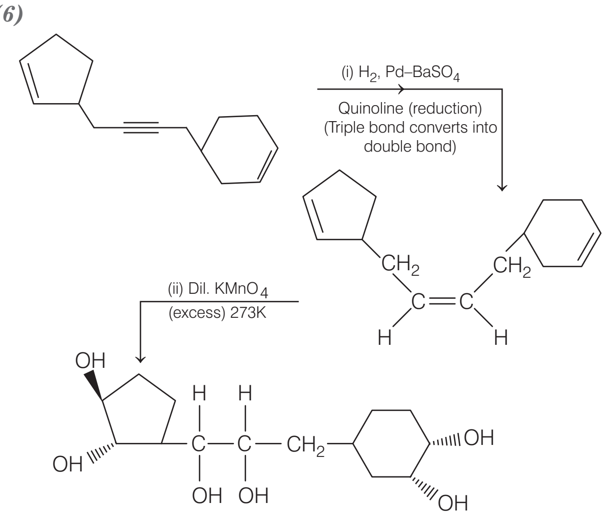
$= 881.57$ mL

Now, molarity

$$= \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution (mL)}}$$

$$= \frac{2.6315 \times 1000}{881.57} = 2.98 \text{ M}$$

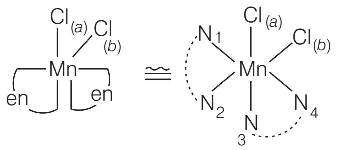
11. *(6)*



(P) (Major product)

Compound (P) has total number of hydroxyl groups = 6

12. *(6)* The structure of *cis*-$[Mn(en)_2Cl_2]$ complex is



Bond angles (Mn—N and Mn—Cl bond in *cis* positions)

Cl (a) —— Mn —— $N_{(1)}$

Cl (a) —— Mn —— $N_{(2)}$

Cl (a) —— Mn —— $N_{(4)}$

Cl (b) —— Mn —— N_1

Cl (b) —— Mn —— N_3

Cl (b) —— Mn —— N_4

Number of *cis* Cl—Mn—N = 6

13. *(288)*

> ***Key Idea*** Rhombic sulphur (S_8) gets oxidised into sulphuric acid and water, NO_2 gas is released on reaction with conc. HNO_3.

When rhombic sulphur (S_8) is oxidised by conc. HNO_3 then H_2SO_4 is obtained and NO_2 gas is released.

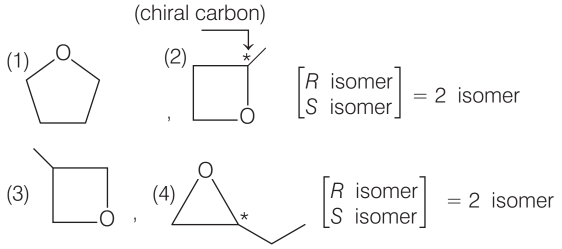
$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16\,H_2O$$

1 mole of rhombic sulphur produces = 16 moles of H_2O

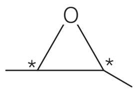
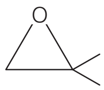
$\therefore$ Mass of water = 16×18 (molar mass of H_2O)

= 288 g

14. *(10.0)* The structure of cyclic ether with molecular formula, C_4H_8O are as follows:



(1-chiral carbon)

(5)  (6)  $\begin{bmatrix} R, R \text{ isomer} \\ R, S \text{ isomer} \\ S, S \text{ isomer} \end{bmatrix} = 3$ isomer

(2-chiral carbon)

Total number of isomers of cyclic ether with molecular formula, C_4H_8O are 10.

15. *(a)* (III) Kinetic energy of the electron in nth orbit,

$$\text{K.E.} = +13.6 \times \frac{Z^2}{n^2}$$

or $$\text{K.E.} \propto \frac{1}{n^2} \quad \text{or} \quad \text{K.E.} \propto n^{-2}$$

From list-II, correct match is (III P).

(IV) Potential energy of the electron in the nth orbit,

$$\text{P.E.} = -2 \times 13.6 \times \frac{Z^2}{n^2}$$

$$\text{P.E.} \propto \frac{1}{n^2}$$

$$\text{P.E.} \propto n^{-2}$$

From List II, correct match is (IV P).

Hence, correct matching from list-I and list-II on the basis of given option is (III, P).

16. *(c)* (I) Radius of the nth orbit,

$$r = 0.529 \times \frac{n^2}{Z}$$

Here, $$r \propto n^2$$

From list-II, correct match is (I, T)

(II) Angular momentum of the electron,

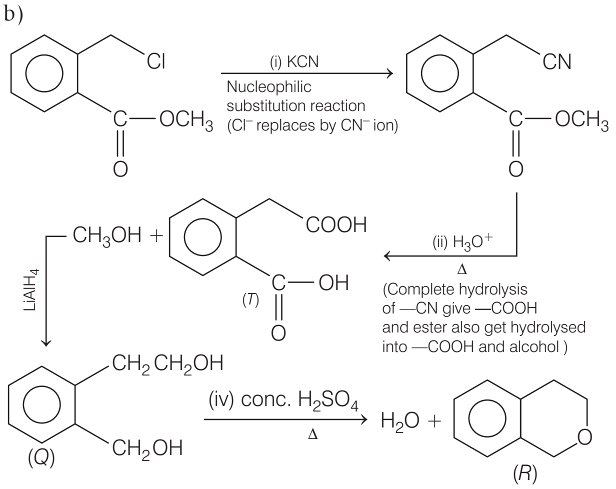
$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad mvr \propto n$$

From list-II, correct match (II, S)

Hence, correct matching from list-I and list-II on the basis of given option is (I, T).

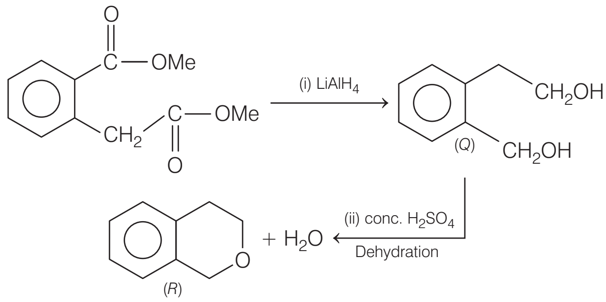
17. (b)

(III)



Hence, correct match of (III) are T, Q, R.

(IV)

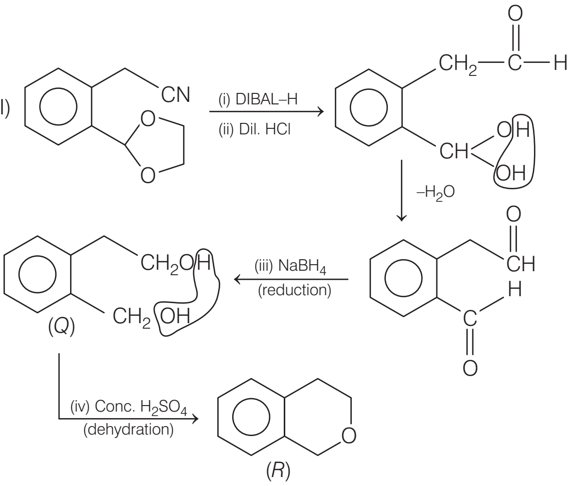


Hence, correct match of IV is Q, R.

Hence, correct matching from list-I and list II on the basis of given option is (IV), Q, R.

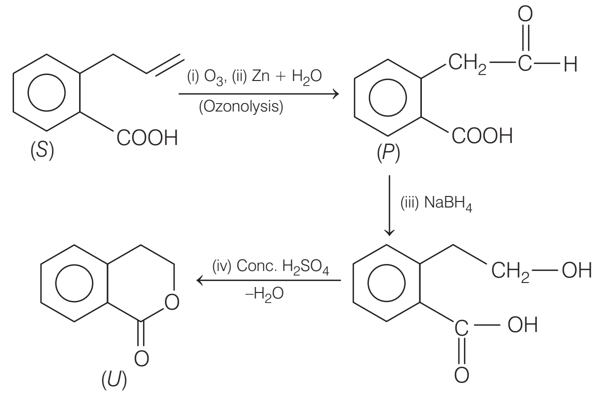
18. *(a)*

(I)



Hence, correct match of (I) are (Q, R)

(II)



Hence, correct match of II is (P,S,U).

Hence, correct matching from list-I and list-II on the basis of given option is (II), P, S, U.