CHEMISTRY (CODE – 043)

Chapter-wise Test: Haloalkanes and Haloarenes

(NCERT Class XII Chemistry, Unit 6: Haloalkanes and Haloarenes)

SOLUTIONS AND MARKING SCHEME

CLASS XII (2026-27)

Time: 1½ hours **Max. Marks: 35**

Step-by-step solutions with the distribution of marks. Marks for each step are shown in square brackets [ ]. Any other correct method or answer should be given full credit.

Quick answer key – Section A

Q.	1	2	3	4	5	6	7	8
Ans.	C	B	D	A	C	B	D	A

SECTION A

Questions 1 to 8 are multiple choice questions. Only one of the choices is correct. Select and write the correct choice as well as the answer to these questions. Each question carries 1 mark.

1	**Answer: C** The longest chain is propane. Numbering from the end that carries Br gives Br at C-1 and two methyl groups at C-2: **1-bromo-2,2-dimethylpropane**. (A is not possible, since C-2 of propane would then carry five bonds; B and D are different isomers of $C_5H_{11}Br$.)	1
2	**Answer: B** From the table, the bond length increases (139 → 214 pm) and the bond enthalpy decreases (452 → 234 kJ mol^{-1}) from C–F to C–I. The longest, weakest C–I bond breaks most easily, and I^- is the best leaving group, so R–I is the most reactive (R–I > R–Br > R–Cl >> R–F). A and D are the reverse of the data; C is wrong because the highest dipole moment in the table is that of CH_3Cl (1.860 D), since dipole moment depends on both charge and bond length.	1
3	**Answer: D** In each group the boiling point rises in the order RCl < RBr < RI (e.g. 249 K, 277 K, 316 K for CH_3X). As the size and mass of the halogen atom increase, the magnitude of the van der Waals forces increases, so more energy is needed to separate the molecules. The boiling point also *increases* with the size of the alkyl group (A is wrong), and C is wrong because mass and size of the halogen matter even though the C–I dipole moment is the smallest.	1
4	**Answer: A** The cyanide ion is an ambident nucleophile (it can attack through C or through N). AgCN is mainly covalent, so the nitrogen atom is free to donate its lone pair and the chief product is the isocyanide, CH_3CH_2NC. KCN, being predominantly ionic, attacks through carbon and gives the alkyl cyanide.	1
5	**Answer: C. $(CH_3)_3CBr$** In an S_N1 reaction the rate depends on the stability of the carbocation formed in the slow step. The tertiary carbocation $(CH_3)_3C^+$ is the most stable (+I effect and hyperconjugation of three methyl groups), so the tertiary halide reacts fastest: 3° > 2° > 1° > CH_3X.	1
6	**Answer: B** $ROH + SOCl_2 \rightarrow RCl + SO_2\uparrow + HCl\uparrow$. Both by-products are gases, so the alkyl chloride is obtained pure. This method cannot be used for phenols because the C–O bond in phenol has partial double bond character, and no catalyst is needed ($ZnCl_2$ is used with conc. HCl).	1
7	**Answer: D** $C_2H_5Br + NaI \rightarrow$(dry acetone) $C_2H_5I + NaBr\downarrow$. NaI dissolves in dry acetone but NaCl/NaBr does not; its precipitation removes a product from the equilibrium and, by Le Chatelier's principle, favours the forward reaction.	1

8	**Answer: A. Both A and R are true and R is the correct explanation of A.** In S_N2 the nucleophile approaches from the side opposite to the leaving group in a single step, so the configuration of the carbon is inverted like an umbrella turned inside out: (−)-2-bromooctane gives (+)-octan-2-ol. R correctly explains A.	1

SECTION B

Question Nos. 9 to 11 are very short answer questions carrying 2 marks each.

9	**(A)** (i) **n-C_3H_7Cl** (0.89 g mL^{-1}) is less dense than water and floats; all the others are heavier than water. [1] (ii) Density increases with the atomic mass of the halogen (Cl < Br < I: 0.89 → 1.335 → 1.747) and with the number of halogen atoms (CH_2Cl_2 < $CHCl_3$ < CCl_4). (It also increases with the number of carbon atoms.) [1] **(B)** (i) Chloromethane < bromomethane < dibromomethane < bromoform (the boiling point increases with the size and mass of the halogen and with the number of halogen atoms). [1] (ii) Isopropyl chloride < 1-chloropropane < 1-chlorobutane (branching lowers the boiling point; a longer chain raises it). [1]	1 + 1
10	**(A)** Ambident nucleophiles are nucleophiles with two nucleophilic centres, so they can attack through either centre (e.g. CN^- through C or N; NO_2^- through O or N). [1] KCN is ionic and the attack is through carbon: $C_2H_5Br + KCN \rightarrow C_2H_5CN$ (alkyl cyanide). AgCN is covalent and the attack is through nitrogen: $C_2H_5Br + AgCN \rightarrow C_2H_5NC$ (isocyanide). [1] **(B)** (i) Finkelstein reaction: $C_2H_5Br + NaI \rightarrow$(dry acetone) $C_2H_5I + NaBr\downarrow$ [1] (ii) Swarts reaction: $2CH_3Br + Hg_2F_2 \rightarrow 2CH_3F + Hg_2Br_2$ (or $CH_3Br + AgF \rightarrow CH_3F + AgBr$) [1]	1 + 1
11	**(A)** (i) **Pent-2-ene** (major) by β-elimination (dehydrohalogenation), following **Zaitsev's (Saytzeff's) rule**: the preferred alkene is the one with the greater number of alkyl groups on the doubly bonded carbons. [1] (ii) A mixture of **1,2-dichlorobenzene (ortho)** and **1,4-dichlorobenzene (para)** by electrophilic substitution (Cl is o,p-directing). [1] **(B)** Grignard reagents are highly reactive and react with any source of proton (water, alcohols, amines), so even traces of moisture must be avoided; the reaction is therefore carried out in dry ether. [1] $CH_3MgBr + H_2O \rightarrow CH_4 + Mg(OH)Br$ [1]	1 + 1

SECTION C

Question Nos. 12 to 15 are short answer questions carrying 3 marks each.

12	**(A)** (i) Reactivity decreases in the order CH_3Br > 1° > 2° > 3°. The S_N2 reaction needs the nucleophile to approach the carbon bearing the halogen; bulky alkyl groups on or near this carbon hinder the approach (steric hindrance). [1] (ii) The order is reversed: $(CH_3)_3CBr$ > $(CH_3)_2CHBr$ > CH_3CH_2Br > CH_3Br, because in S_N1 the rate depends on the stability of the carbocation formed in the slow step, and the 3° carbocation is the most stable. [1] (iii) **$(CH_3)_3CBr$** (S_N1: step I, slow ionisation to the carbocation $(CH_3)_3C^+$; step II, attack by the nucleophile). The intermediate is the **tertiary carbocation**. [1] **(B)** (i) **CH_3I**: iodide is a better leaving group (larger size, weaker C–I bond). [1] (ii) **CH_3Cl**: a methyl halide has only three small H atoms, while the tertiary halide is sterically hindered. [1] (iii) **1-Bromobutane**: it is a primary halide with less steric hindrance than the secondary 2-bromobutane. [1]	1 + 1 + 1
13	**(A)** (i) **I is S_N2** (single step, one transition state, no intermediate); **II is S_N1** (two steps, with an intermediate between two transition states; the first step is slow and rate-determining). [1] (ii) **Y** is the transition state of the S_N2 reaction, in which carbon is simultaneously bonded to the incoming nucleophile and the outgoing halide; such a structure is unstable and cannot be isolated. **X** is the carbocation intermediate (planar, sp^2 hybridised) of the S_N1 reaction. [1] (iii) I (S_N2): inversion of configuration. II (S_N1): racemisation, because the planar carbocation can be attacked by the nucleophile from either side, giving a 50:50 mixture of both configurations. [1] **(B)** (i) Enantiomers are stereoisomers that are non-superimposable mirror images of each other (equal and opposite rotation of plane-polarised light). [1] (ii) A racemic mixture contains two enantiomers in equal proportions, written (±) or *dl*. It is optically inactive because the rotation due to one enantiomer is cancelled by that of the other. [1] (iii) Retention of configuration is the preservation of the spatial arrangement of bonds at an asymmetric centre during a reaction, when no bond to the stereocentre is broken. [1]	1 + 1 + 1
14	**(A)** (i) **P and R are chiral**: the central carbon carries four different groups (CH_3, C_2H_5, Cl, H in P; Br, I, Cl, H in R), so the mirror image is non-superimposable. **Q is achiral**: it carries two identical CH_3 groups and is superimposable on its mirror image. [1] (ii) P is **2-chlorobutane** (CH_3–C*HCl–CH_2CH_3); the carbon bonded to Cl (C-2) is the asymmetric carbon (stereocentre). [1] (iii) Zero (the rotations cancel). Such a mixture is a **racemic mixture** (racemic modification), written (±). [1] **(B)** (i) $2C_2H_5Br + 2Na \rightarrow$(dry ether) C_2H_5–C_2H_5 (butane) + 2NaBr [1] (ii) $2C_6H_5Cl + 2Na \rightarrow$(dry ether) C_6H_5–C_6H_5 (biphenyl) + 2NaCl [1] (iii) $C_6H_5Cl + CH_3Br + 2Na \rightarrow$(dry ether) $C_6H_5CH_3$ (toluene) + NaCl + NaBr [1]	1 + 1 + 1

15	**(A)** (i) $CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$ [1] (ii) $C_6H_5NH_2 \rightarrow (NaNO_2 + HCl,\ 273–278\ K)\ C_6H_5N_2^+Cl^- \rightarrow (Cu_2Cl_2)\ C_6H_5Cl + N_2$ (Sandmeyer reaction) [1] (iii) $CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$ (Markovnikov addition) [1] **(B)** (i) Chloroform is slowly oxidised by air in the presence of light to the extremely poisonous gas carbonyl chloride (phosgene): $2CHCl_3 + O_2 \rightarrow (light)\ 2COCl_2 + 2HCl$. It is stored in dark bottles filled completely so that air is excluded. [1] (ii) DDT is chemically very stable and not metabolised rapidly; being fat soluble it is stored in fatty tissues and builds up in animals over time. It is also highly toxic to fish, and many insects have developed resistance to it. [1] (iii) Freons are very stable and diffuse unchanged into the stratosphere, where they initiate radical chain reactions that upset the natural ozone balance (ozone depletion). [1]	1 + 1 + 1

SECTION D

Question No. 16 is a case-based/data-based question carrying 4 marks.

16	(i) Reactivity increases with the number of $–NO_2$ groups at the ortho/para positions (the conditions become milder: 623 K at 300 atm → 443 K → 368 K → warm water). The nitro group withdraws electron density from the ring and so facilitates attack by the nucleophile; the negative charge of the intermediate carbanion is stabilised by resonance by the $–NO_2$ group at the ortho and para positions. [1] (ii) A $–NO_2$ group at the meta position has **no effect** on the reactivity: none of the resonating structures of the intermediate carbanion bears the negative charge on the carbon atom carrying the $–NO_2$ group, so the negative charge is not stabilised. [1] (iii) **(A)** Any two (1 mark each): (a) Resonance: the lone pair on Cl is in conjugation with the π electrons of the ring, giving the C–Cl bond partial double bond character, which makes it difficult to break. (b) Hybridisation: the carbon in C–Cl is sp^2 in chlorobenzene (greater s-character, more electronegative, shorter C–Cl bond: 169 pm against 177 pm in haloalkane) and sp^3 in chloroethane. (c) The phenyl cation formed by self-ionisation is not stabilised by resonance, so S_N1 is ruled out. (d) The electron rich nucleophile is repelled by the electron rich ring. [2] **(B)** Through the inductive effect, Cl withdraws electrons and destabilises the carbocation intermediate, thereby deactivating the ring (this effect is stronger and controls the reactivity). Through resonance, the lone pairs of Cl increase the electron density at the ortho and para positions and stabilise the intermediate for attack at these positions, so the resonance effect controls the orientation. [2]	1 + 1 + 2

SECTION E		
Question No. 17 is a long answer question carrying 5 marks.		
17	**(A)** (i) S_N1: 3° > 2° > 1° > CH_3X (more stable carbocation); S_N2: CH_3X > 1° > 2° > 3° (less steric hindrance). For the same alkyl group, R–I > R–Br > R–Cl >> R–F in both. [1] (ii) Step I (slow, rate determining, reversible): $(CH_3)_3C–Br \rightleftharpoons (CH_3)_3C^+ + Br^-$. Step II (fast): $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3C–OH$. The rate depends only on the concentration of the halide, so the reaction is **first order** (S_N1). [2: ½ + ½ for steps, ½ for the slow step, ½ for the order] (iii) This is an S_N1 reaction. The carbocation formed in the slow step is sp^2 hybridised and planar (achiral); OH^- can attack from either side with equal probability, giving equal amounts of the two enantiomers, a racemic mixture (±), which is optically inactive. [1] (iv) S_N2 mechanism; **inversion of configuration**, since the OH^- attacks from the side opposite to the leaving Br^-. [1] **(B)** (1 mark each) (i) $CH_3CH_2CH_2Cl + KOH(aq) \rightarrow CH_3CH_2CH_2OH + KCl$ [1] (ii) $CH_3CH_2CH_2Cl + KOH(alc)$, heat $\rightarrow CH_3CH{=}CH_2 + KCl + H_2O$ [1] (iii) $CH_3CH_2CH_2Cl + KCN \rightarrow CH_3CH_2CH_2CN + KCl$ [1] (iv) $2CH_3CH_2CH_2Cl + 2Na \rightarrow$(dry ether) $CH_3(CH_2)_4CH_3 + 2NaCl$ (Wurtz reaction) [1] (v) $CH_3CH_2CH_2Cl + Mg \rightarrow$(dry ether) $CH_3CH_2CH_2MgCl$; $CH_3CH_2CH_2MgCl + H_2O \rightarrow CH_3CH_2CH_3 + Mg(OH)Cl$ [1]	5

Topic coverage of the paper

Topic (NCERT section)	Questions
Classification and nomenclature (6.1, 6.2)	Q1
Nature of C–X bond (6.3)	Q2 (table)
Methods of preparation of haloalkanes and haloarenes (6.4, 6.5)	Q6, Q7, Q10 (B), Q11 (A), Q15 (A), Q17 (B)
Physical properties: boiling point, density, solubility (6.6)	Q3 (figure), Q9 (table)
Nucleophilic substitution S_N1 and S_N2, ambident nucleophiles (6.7.1)	Q4, Q5, Q10 (A), Q12 (table), Q13 (figure), Q17
Stereochemistry: chirality, inversion, racemisation (6.7.1c)	Q8, Q13, Q14 (figure), Q17 (A)
Elimination reactions and reactions with metals (6.7.1)	Q11, Q14 (B), Q17 (B)
Reactions of haloarenes (6.7.2)	Q11 (A), Q16 (table)
Polyhalogen compounds (6.8)	Q15 (B)

Figure/table-based questions (7): Q2, Q3, Q9, Q12, Q13, Q14 and Q16.