CHEMISTRY (CODE – 043)

Chapter-wise Test: Amines

(NCERT Class XII Chemistry, Unit 9: Amines)

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.	D	A	C	B	D	A	B	C

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: D** The longest chain attached to nitrogen (ethyl) is the parent, ethanamine. The other two groups on nitrogen are named with the locant N and written alphabetically: **N-ethyl-N-methylethanamine**. (“Triethylamine” is a different compound and is a common name.)	1
2	**Answer: A. Row 1** Aniline reacts with $NaNO_2$ and HCl at 273–278 K to form **benzenediazonium chloride** (diazotisation), not phenol. Phenol is obtained only if the diazonium salt solution is allowed to warm to about 283 K. Rows 2, 3 and 4 are correct: Fe/HCl reduces the nitro group; benzamide undergoes Hoffmann bromamide degradation to aniline; a primary amine gives an isocyanide (carbylamine reaction).	1
3	**Answer: C** All three amines have the same molar mass (73), so (A) is wrong. A primary amine has two N–H bonds, a secondary amine has one, and a tertiary amine has none, so the extent of intermolecular hydrogen bonding falls in the order 1° > 2° > 3°, and so does the boiling point (350.8 K > 329.3 K > 310.5 K).	1
4	**Answer: B. Benzenamine** The Gabriel synthesis is used only for **primary aliphatic amines**. It needs a nucleophilic substitution of a halide by the phthalimide anion, and aryl halides do not undergo nucleophilic substitution with this anion, so aromatic primary amines cannot be made. Phenylmethanamine is prepared from benzyl halide, which is reactive.	1
5	**Answer: D. ethanamine** This is the Hoffmann bromamide degradation. The amide loses its carbonyl carbon (as carbonate), so the primary amine formed has **one carbon atom less** than the amide: $CH_3CH_2CONH_2 + Br_2 + 4NaOH \rightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$.	1
6	**Answer: A. $C_6H_5CH_2NH_2$** The carbylamine reaction is given only by **primary** amines (aliphatic or aromatic), which have an $–NH_2$ group: $C_6H_5CH_2NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5CH_2NC + 3KCl + 3H_2O$. B is a secondary amine, and C and D are tertiary amines, so they do not respond.	1
7	**Answer: B. 2,4,6-tribromoaniline** The $–NH_2$ group is a powerful activating, ortho- and para-directing group. Bromine water therefore substitutes all three ortho and para positions at once, giving a **white precipitate of 2,4,6-tribromoaniline**.	1

8	**Answer: C. A is true but R is false** A is true: aniline does not undergo Friedel–Crafts alkylation or acylation. R is false: $-NH_2$ is an electron-*donating* (activating) group by resonance. The real reason is that aniline, a Lewis base, forms a salt with the Lewis-acid catalyst $AlCl_3$; nitrogen then acquires a positive charge and becomes a strong deactivating group.	1

SECTION B

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

9	**(A)** (i) A smaller pK_b means a stronger base, so the order is $(CH_3)_2NH$ (3.27) > CH_3NH_2 (3.38) > $(CH_3)_3N$ (4.22) > NH_3 (4.75) > $C_6H_5NH_2$ (9.38). [1] (ii) In aniline the lone pair on nitrogen is delocalised into the benzene ring (five resonance structures), so it is less available for protonation. The anilinium ion has only two resonance structures and is less stable, so aniline is a weaker base. In methanamine the +I effect of CH_3 increases the electron density on N. [1] **(B)** (i) $(C_2H_5)_2NH$ > $C_2H_5NH_2$ > NH_3 > $C_6H_5NH_2$. [1] (ii) In water, basic strength depends on the +I effect, on **solvation** of the substituted ammonium cation by hydrogen bonding (more N–H bonds, so greater stabilisation), and on steric hindrance. In the trimethylammonium ion there is only one N–H for hydrogen bonding, so it is less stabilised than the dimethylammonium ion, and $(CH_3)_3N$ is a weaker base than $(CH_3)_2NH$ in water. [1]	1 + 1
10	**(A)** (i) $C_6H_5CONH_2 + Br_2 + 4NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$ (Hoffmann bromamide degradation). [1] (ii) The amine has **one carbon atom less** than the amide (benzamide C_7 gives aniline C_6). [1] **(B)** (i) Phthalimide + ethanolic KOH → potassium salt of phthalimide; this is heated with bromoethane (C_2H_5Br) to give N-ethylphthalimide; alkaline hydrolysis (aq. NaOH) then gives ethanamine and the sodium salt of phthalic acid. [1] (ii) The phthalimide anion has only one N–H to replace, so it gives only a primary amine on hydrolysis; the product is a primary aliphatic amine only. [1]	1 + 1
11	**(A)** (i) Carbylamine test: methanamine (primary) on warming with $CHCl_3$ and alcoholic KOH gives the foul-smelling methyl isocyanide; N,N-dimethylmethanamine (tertiary) does not. [1] (ii) Carbylamine test: aniline (primary) gives the foul-smelling phenyl isocyanide; N-methylaniline (secondary) does not. (The Hinsberg test also works.) [1] **(B)** (i) Aniline, a Lewis base, forms a salt with anhydrous $AlCl_3$. The nitrogen then carries a positive charge and strongly deactivates the ring, so the reaction does not take place. [1] (ii) Ethanamine forms hydrogen bonds with water; the small alkyl group is hydrophobic only to a small extent. In aniline the large hydrophobic C_6H_5 part outweighs the hydrogen bonding of $-NH_2$, so it is insoluble. [1]	1 + 1

SECTION C

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

12	**(A)** (i) X = **primary** amine (positive carbylamine test; its sulphonamide has an N–H and dissolves in alkali). Y = **secondary** amine (sulphonamide has no acidic hydrogen, so it is insoluble in alkali). Z = **tertiary** amine (does not react). [1½] (ii) The sulphonamide of a primary amine, $RNHSO_2C_6H_5$, still has a hydrogen on nitrogen; this hydrogen is strongly acidic because of the strongly electron-withdrawing sulphonyl group, so it dissolves in alkali as a salt. [1] (iii) Z is C_3H_9N and tertiary: $(CH_3)_3N$, **N,N-dimethylmethanamine**. [½] **(B)** Step 1: aniline + $(CH_3CO)_2O$ (or CH_3COCl, pyridine) → acetanilide. The $–NH_2$ group is protected by acetylation because it is too strongly activating and would give 2,4,6-tribromoaniline. [1] Step 2: acetanilide + Br_2 (in ethanoic acid) → *p*-bromoacetanilide (major product, since $–NHCOCH_3$ is a weaker activator). [1] Step 3: hydrolysis (H_3O^+/OH^-) of the amide → *p*-bromoaniline. [1]	3
13	**(A)** (i) A = **aniline** ($C_6H_5NH_2$, reduction of the $–NO_2$ group by Fe/HCl); B = **benzenediazonium chloride** ($C_6H_5N_2^+Cl^-$, diazotisation at 273–278 K). [1] (ii) C = **chlorobenzene** (C_6H_5Cl), by the **Sandmeyer reaction** (Cu(I) chloride); D = **iodobenzene** (C_6H_5I). [1] (iii) E = **phenol** (C_6H_5OH): the diazonium salt is hydrolysed when the temperature of the solution is allowed to rise to 283 K. [1] **(B)** (i) $C_6H_5N_2^+Cl^- + HBF_4 \rightarrow C_6H_5N_2^+BF_4^- \downarrow + HCl$; on heating, $C_6H_5N_2^+BF_4^- \rightarrow C_6H_5F + BF_3 + N_2$. Reagent: fluoroboric acid (HBF_4). [1½] (ii) $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$. Reagent: hypophosphorous acid (or ethanol). [1½]	3
14	**(A)** (i) A **coupling reaction**: the diazonium group is retained (it is an electrophilic substitution in which the diazonium ion attacks the para position). [1] (ii) P = **p-hydroxyazobenzene** (4-(phenylazo)phenol); Q = **p-aminoazobenzene**. [1] (iii) The products have an extended conjugated system with both aromatic rings joined through the –N=N– (azo) group; such azo compounds are coloured and are used as dyes. [1] **(B)** (i) In aniline the lone pair on N is delocalised over the benzene ring, so it is less available for protonation; aniline is a weaker base (larger pK_b). [1] (ii) Methylamine is basic and ionises in water to give OH^- ions: $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$. These OH^- ions precipitate Fe^{3+} as hydrated ferric oxide ($FeCl_3 + 3OH^- \rightarrow Fe(OH)_3\downarrow$ ($Fe_2O_3 \cdot xH_2O$) + $3Cl^-$). [1] (iii) The stability of the arenediazonium ion is due to resonance (delocalisation of the positive charge over the benzene ring), which is not possible in alkyldiazonium ions. [1]	3

15	**(A)** (i) $C_6H_5NH_2 + CH_3COCl \rightarrow C_6H_5NHCOCH_3$ (N-phenylethanamide, acetanilide) + HCl. [1] (ii) Pyridine is a base stronger than the amine; it removes the HCl formed and shifts the equilibrium to the right. [1] (iii) Direct nitration gives tarry oxidation products and, in the strongly acidic medium, aniline is protonated to the anilinium ion, which is meta-directing, so a significant amount of the meta isomer forms. After acetylation the activating effect is controlled and the *p*-nitro derivative is the major product. [1] **(B)** (i) Anilinium hydrogensulphate forms first and on heating gives **sulphanilic acid** (*p*-aminobenzenesulphonic acid). [1] (ii) Exhaustive methylation: the final product is the quaternary salt, **N,N,N-trimethylbenzenaminium (phenyltrimethylammonium) iodide**, $C_6H_5N^+(CH_3)_3I^-$. [1] (iii) $CH_3CH_2NH_2 + HNO_2 \rightarrow [CH_3CH_2N_2^+Cl^-] \rightarrow CH_3CH_2OH + N_2\uparrow + HCl$; the unstable aliphatic diazonium salt gives ethanol and nitrogen gas. [1]	3

SECTION D

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

16	(i) **$(CH_3)_2NH$** (pK_b = 3.27, the smallest value); it is a **secondary** amine. [1] (ii) In benzylamine the $-NH_2$ is attached to a CH_2 group, not to the ring, so the lone pair on N is not delocalised into the benzene ring and is available for protonation. In aniline the lone pair is delocalised (resonance), so aniline is far less basic. [1] (iii) Gas phase: $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$ (only the +I effect operates). In water the ammonium ions are also stabilised by solvation through hydrogen bonding, which decreases with more alkyl groups (fewer N–H bonds), and steric hindrance also acts; hence the order in water is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$. [1] **OR** (iii) *p*-Methylaniline is the stronger base: electron-releasing groups increase basic strength and electron-withdrawing groups ($-NO_2$) decrease it. The $-CH_3$ group is electron releasing and increases the electron density on N, whereas the $-NO_2$ group withdraws electrons and lowers it, so *p*-nitroaniline is the weaker base. [1] (iv) N-methylaniline (pK_b 9.30 is smaller than 9.38), so it has the larger K_b: the +I effect of the CH_3 group increases the electron density on nitrogen. [1]	1 + 1 + 1 + 1

SECTION E		
Question No. 17 is a long answer question carrying 5 marks.		
17	**(A)** (i) A = C_6H_5COOH, **benzoic acid** (benzenecarboxylic acid). B = $C_6H_5CONH_2$, **benzamide** (benzenecarboxamide). C = $C_6H_5NH_2$, **aniline** (benzenamine). [1½] (C_6H_7N is one carbon less than B, the Hoffmann bromamide degradation, so B is an amide; $C_7H_6O_2$ with a benzene ring and a carboxylic acid group is benzoic acid.) [½] (ii) $C_6H_5CONH_2 + Br_2 + 4NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$. [1] (iii) D = **benzenediazonium chloride**, $C_6H_5N_2^+Cl^-$. E = **p-hydroxyazobenzene** (coupling reaction at the para position of phenol). [1] (iv) Carbylamine test: $C_6H_5NH_2 + CHCl_3 + 3KOH$ (alc., heat) $\rightarrow C_6H_5NC + 3KCl + 3H_2O$; foul-smelling phenyl isocyanide. [1] **(B)** (i) $CH_3CH_2Br + KCN$ (alcoholic) $\rightarrow CH_3CH_2CN$ (propanenitrile) [1]; $CH_3CH_2CN + 4[H]$ ($LiAlH_4$, or H_2/Ni, Na/C_2H_5OH) $\rightarrow CH_3CH_2CH_2NH_2$ (propan-1-amine). [1] (ii) Step 1: $C_6H_5NH_2 + 3Br_2$ (bromine water) → 2,4,6-tribromoaniline (white ppt.) + 3HBr. [1] Step 2: 2,4,6-tribromoaniline + $NaNO_2$ + HCl (273–278 K) → 2,4,6-tribromobenzenediazonium chloride. [1] Step 3: H_3PO_2 (or CH_3CH_2OH) + $H_2O \rightarrow$ 1,3,5-tribromobenzene + N_2. [1]	5

Topic coverage of the paper

Topic (NCERT section)	Questions
Structure, classification and nomenclature of amines (9.1–9.3)	Q1
Preparation: nitro reduction, nitriles, Gabriel, Hoffmann bromamide (9.4)	Q2 (table), Q4, Q5, Q10, Q17
Physical properties: boiling point, solubility, hydrogen bonding (9.5)	Q3 (figure), Q11 (B)
Basic character and pK_b data, Table 9.3 (9.6)	Q9 (table), Q16 (table)
Chemical reactions: carbylamine, acylation, alkylation, Hinsberg, HNO_2 (9.6)	Q6, Q8, Q11, Q12 (table), Q15
Electrophilic substitution of aniline (9.6)	Q7, Q8, Q12 (B), Q15
Diazonium salts: preparation, Sandmeyer, replacement and coupling (9.7–9.10)	Q13 (figure), Q14 (figure), Q17

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