Collegedunia NCERT Formula Sheet

The Ultimate Formula Reference for Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 9: Amines

Classification · Nomenclature · Preparations · Basicity · Chemical Reactions · Diazonium Salts · Azo Coupling · JEE & NEET

Quick Reference — Amine Classes, Symbols & Key Data

Symbol / Class	Type	General formula & key feature
R–NH_2	1° (primary) amine	One H of NH_3 replaced by R/Ar; e.g. CH_3NH_2, $C_6H_5NH_2$
R_2NH	2° (secondary) amine	Two H of NH_3 replaced; simple if R = R′, mixed otherwise
R_3N	3° (tertiary) amine	All three H of NH_3 replaced; no N–H bond
$R_4N^+X^-$	Quaternary ammonium salt	All four valences of N as N–C; ionic salt; e.g. $(CH_3)_4N^+I^-$
Ar–NH_2	Aryl (aromatic) amine	–NH_2 on benzene ring; e.g. aniline $C_6H_5NH_2$
C–N–C bond angle	$\approx 108°$ $(CH_3)_3N$	N is sp^3, pyramidal; one lone pair on N (Fig. 9.1)
pK_b (NH_3)	4.75	Reference base; in water at 298 K
pK_b (CH_3NH_2)	3.38	Stronger base than NH_3 (+I of –CH_3)
pK_b ($(CH_3)_2NH$)	3.27	Strongest among methylamines in water
pK_b ($(CH_3)_3N$)	4.22	Weaker than 2° in water (solvation $>$ +I effect)
pK_b ($C_6H_5NH_2$)	9.38	Much weaker than NH_3 — lone pair delocalised into ring
pK_b ($(C_6H_5)_2NH$)	13.21	Two aryl groups; almost neutral
pK_b ($C_6H_5NHCH_3$)	9.30	N-methylaniline; slightly stronger than aniline
b.p. CH_3NH_2	266.8 K	1° amine; N–H$\cdots$N H-bonding
b.p. $(CH_3)_3N$	276 K	3° amine; no N–H, only dipole-dipole
Aniline	b.p. 457 K	Colourless oil $\rightarrow$ brown on air oxidation; slightly soluble in H_2O
HNO_2 source	$NaNO_2$ + HCl, 273–278 K	Generates HNO_2 *in situ*; used for amine differentiation
Diazonium salt	Ar–$N_2^+X^-$	Stable below 278 K; loses N_2 readily; drawn as Ar–N$\equiv$N$^+$ X^-

1 Structure & Classification of Amines (9.1)

NCERT Section 9.1 derives every amine as an N-alkyl or N-aryl substituted ammonia. The N atom is sp^3-hybridised with one lone pair, so amines are pyramidal (Fig. 9.1) and act both as Lewis bases (donate lone pair) and as Brønsted bases (accept H^+).

Classification (9.1.1)

Replace 1, 2 or 3 H atoms of NH_3 by R/Ar to get:

- **Primary (1°):** R–NH_2 (e.g. CH_3NH_2, $C_6H_5NH_2$).
- **Secondary (2°):** R_2NH or RR′NH (e.g. $(CH_3)_2NH$, $C_6H_5NHCH_3$).
- **Tertiary (3°):** R_3N or RR′R″N (e.g. $(CH_3)_3N$).

- **Quaternary ammonium salt:** $R_4N^+X^-$ (e.g. $(CH_3)_4N^+I^-$).

Simple amines have identical R groups, **mixed** amines have different R groups. Counting rule: *number of H atoms of NH_3 replaced by R/Ar = degree of the amine.*

Structure of the N atom in amines (9.1.2, Fig. 9.1)

N is sp^3-hybridised: three σ-bonds (to H/C) plus one lone pair occupy a roughly tetrahedral arrangement, so amines are **pyramidal**.

Bond-angle data: NH_3 $\angle$H–N–H $= 107°$; $(CH_3)_3N$ $\angle$C–N–C $\approx 108°$; aniline C–N–H plane ≈ 108–$112°$ — close to tetrahedral $109.5°$ but compressed by lone-pair repulsion.

In aniline, the N–H plane is sometimes drawn *flatter* than in alkylamines because the lone pair is partially in a p-type orbital that conjugates into the ring. The lone pair makes amines **nucleophilic and basic** — the central fact that drives the entire chapter.

Why pyramidal, not planar

A planar N would mean sp^2 + the lone pair in a pure p-orbital. The sp^3 pyramidal geometry is energetically preferred because (a) all four electron pairs are kept farthest apart, and (b) lone pair in sp^3 has more s-character (≈25%) so it sits closer to N. **Inversion** of the pyramid is fast at room temperature — like an umbrella flipping — so chiral amines (3 different R + lone pair) cannot be resolved.

2 Nomenclature of Amines (9.2)

NCERT Section 9.2 sets out both *common* (alkyl + amine) and IUPAC (*N*-substituent prefix + parent alkanamine / benzenamine) systems. Mastering both is critical for naming/identification questions.

Common system (9.2)

Rule: list R groups in alphabetical order + word "amine" (one word for 1°).

- $CH_3NH_2 \rightarrow$ methylamine; $(CH_3)_2NH \rightarrow$ dimethylamine; $(CH_3)_3N \rightarrow$ trimethylamine.
- $CH_3NHC_2H_5 \rightarrow$ ethylmethylamine.
- $C_6H_5NH_2 \rightarrow$ aniline (retained IUPAC + common).

Use *di-, tri-* for identical R groups; for unequal R groups, alphabetical order with no multiplier.

IUPAC system (Table 9.1)

Aliphatic 1°: parent alkane $\rightarrow$ alkan-**amine** (locant inserted before -amine).

- $CH_3CH_2CH_2NH_2 \rightarrow$ propan-1-amine.
- $(CH_3)_2CHNH_2 \rightarrow$ propan-2-amine.

Aromatic 1°: benzenamine (= aniline).

2° & 3°: *N*-(smaller chain)-*N*-(...)-(parent chain)-amine.

- $CH_3NHC_2H_5 \rightarrow$ *N*-methylethan-1-amine (parent = ethane, larger).
- $(CH_3)_2NC_2H_5 \rightarrow$ *N*,*N*-dimethylethanamine.
- $C_6H_5NHCH_3 \rightarrow$ *N*-methylbenzenamine ($\equiv$ *N*-methylaniline).

Choose the longest carbon chain as the parent; the *smaller* R group(s) on N go as *N*-prefix. Locant of $-NH_2$ on parent gets the lowest number.

Don't confuse *N*-methylaniline with *p*-toluidine

N-methylaniline = C_6H_5–NH–CH_3 (–CH_3 on N, 2° amine). *p*-Toluidine = 4-CH_3–C_6H_4–NH_2 (–CH_3 on ring, 1° amine). Position of the methyl group decides the class.

3 Preparation of Amines (9.3)

Section 9.3 lists six standard routes. Each starts from a readily available functional group (–NO_2, –CN, –$CONH_2$, R–X) and ends at an amine. Memorise the reagent + degree of amine produced.

Reduction of nitro compounds (9.3.1)

General:

$R\text{–}NO_2 \longrightarrow [H_2/\text{Pd or Pt or Ni; or Sn/HCl; or Fe/HCl}]\ R\text{–}NH_2$

$C_6H_5NO_2 \longrightarrow [\text{Sn + conc. HCl}]\ C_6H_5NH_3^+Cl^- \longrightarrow [\text{NaOH}]\ C_6H_5NH_2$

Two common ways: catalytic H_2 over Pd/Pt/Ni in alcohol (gives free amine directly) or metal/acid (gives the ammonium salt; basify with NaOH to release amine). **Fe/HCl** is industrial — $FeCl_2$ regenerates HCl, making it catalytic in HCl.

Reduction of nitriles (9.3.2) — Mendius reduction

$R\text{–}C{\equiv}N \longrightarrow [H_2/\text{Ni or Na/}C_2H_5OH\text{ or }LiAlH_4]\ R\text{–}CH_2\text{–}NH_2$

Adds two H_2 across C≡N. **Carbon count goes up by 1** (R–X → R–CN → R–CH_2NH_2) — this is the standard *ascent of series* for converting RX into the next-higher 1° amine. Gives only **1° amine**, never 2° or 3°.

Reduction of amides (9.3.3)

$R\text{–}CONH_2 \longrightarrow [LiAlH_4,\ \text{then } H_2O]\ R\text{–}CH_2NH_2$

Distinct from Hoffmann bromamide: in amide reduction the C of –$CONH_2$ is reduced from C=O to CH_2, so the **same number of carbons** are retained between starting amide and product amine. $LiAlH_4$ is the only common reagent. Gives 1° amine.

Ammonolysis of alkyl halides (9.3.4)

$R\text{–}X \longrightarrow [NH_3\text{ (excess), sealed tube, heat}]\ R\text{–}NH_3^+X^- \longrightarrow [\text{NaOH}]\ R\text{–}NH_2$

Successive alkylation chain:

$NH_3 \longrightarrow [R\text{–}X]\ R\text{–}NH_2 \longrightarrow [R\text{–}X]\ R_2NH \longrightarrow [R\text{–}X]\ R_3N \longrightarrow [R\text{–}X]\ R_4N^+X^-$

Reactivity of R–X: R–I > R–Br > R–Cl.

Mechanism = S_N2 by NH_3 on R–X. Each amine product is itself nucleophilic and competes for more R–X, so the reaction gives a **mixture of 1°, 2°, 3° amines and quaternary salt**. Using a large excess of NH_3 favours the 1° amine.

Gabriel phthalimide synthesis (9.3.5) — pure 1° amine

Three steps:

(1) Phthalimide + KOH ⟶ [ ] K^+ phthalimide$^-$ (potassium phthalimide).

(2) K-phthalimide + R–X $\longrightarrow$ $[\Delta]$ N-alkylphthalimide + KX.

(3) N-alkylphthalimide $\longrightarrow$ $[\text{NaOH/H}_2\text{O or H}_3\text{O}^+,\ \Delta]$ R–NH_2 + phthalate.

Phthalimide N–H is acidic (two adjacent C=O); KOH deprotonates it to a soft nucleophile that does S_N2 once on R–X. Hydrolysis releases the pure 1° amine. **Restriction: aromatic amines (Ar–NH_2) cannot be made this way** — aryl halides do not undergo S_N2 in step (2).

Hoffmann bromamide degradation (9.3.6)

$\text{R–CONH}_2 + \text{Br}_2 + 4\,\text{NaOH} \longrightarrow [\,]\ \text{R–NH}_2 + \text{Na}_2\text{CO}_3 + 2\,\text{NaBr} + 2\,\text{H}_2\text{O}$

Carbon count drops by 1 (amide R–CONH_2 has $n+1$ C, product amine R–NH_2 has n C). The reaction proceeds via an N-bromoamide $\rightarrow$ nitrene-like intermediate $\rightarrow$ **isocyanate (R–N=C=O)** $\rightarrow$ hydrolysis to R–NH_2. Works for both alkyl and aryl amides; gives **only 1° amine**.

JEE/NEET Extension — distinguishing carbon-count rules

- Ammonolysis, amide reduction, Gabriel: *same* carbon count.
- Nitrile reduction (Mendius): carbon count goes *up* by 1 (R–X $\rightarrow$ R–CH_2NH_2).
- Hoffmann bromamide: carbon count goes *down* by 1 (R–CONH_2 $\rightarrow$ R–NH_2).

Use this to spot the right method in JEE multi-step synthesis questions.

"GAS-HAN" — the six amine prep methods

Gabriel phthalimide, **A**mmonolysis of R–X, **S**n/HCl — reduction of nitro, **H**offmann bromamide, **A**mide reduction (LiAlH_4), **N**itrile reduction (Mendius). Six routes — learn one carbon-count change per pair.

4 Physical Properties — Boiling Points & Solubility (9.4)

Section 9.4 explains how N–H bonds drive amine boiling points and water solubility: 1° has two N–H, 2° has one, 3° has none. Hence the b.p. order **1°** $>$ **2°** $>$ **3°** for equal carbon count.

Boiling-point trend (9.4)

For amines of similar molecular mass:
R–NH_2 (1°) $>$ R_2NH (2°) $>$ R_3N (3°).

Example (M.W. $\approx$ 59):
n-propylamine (b.p. 322 K) $>$ ethyl(methyl)amine (310 K) $>$ trimethylamine (276 K).

Comparison with neighbours:
alkane $<$ ether $<$ amine $<$ alcohol $<$ carboxylic acid.

Strength of intermolecular H-bonding rises with number of N–H bonds. Tertiary amines have *no* N–H so they only exchange dipole-dipole forces — their b.p. falls below comparable alcohols and even some 2° amines.

Water solubility

- Lower amines (C_1–C_3) of all three classes are **miscible** with water — they form N$\cdots$H–O and O$\cdots$H–N bonds.
- Solubility **decreases as the carbon chain grows** (hydrophobic R dominates).
- Aniline and higher aromatic amines are only slightly soluble in water but freely soluble in organic solvents (alcohol, ether, benzene).

Smell: lower amines smell of fish/ammonia; many higher amines have foul odours — putrescine ($NH_2(CH_2)_4NH_2$) and cadaverine ($NH_2(CH_2)_5NH_2$) are formed in decaying protein.

5 Basic Character of Amines (9.5)

Section 9.5 is the most heavily tested topic in this chapter. Amines accept H^+ via their lone pair: stronger lone-pair availability $\Rightarrow$ stronger base $\Rightarrow$ larger K_b / smaller pK_b.

Basicity in water — K_b & pK_b (9.5.1)

$$R\text{–}NH_2 + H_2O \rightleftharpoons R\text{–}NH_3^+ + OH^-$$

$$K_b = \frac{[R\text{–}NH_3^+][OH^-]}{[R\text{–}NH_2]} \qquad pK_b = -\log_{10} K_b$$

Conjugate-acid pK_a data (methylamines, 298 K):

- $CH_3NH_3^+$: $pK_a = 10.62$
- $(CH_3)_2NH_2^+$: $pK_a = 10.77$
- $(CH_3)_3NH^+$: $pK_a = 9.80$
- NH_4^+: $pK_a = 9.25$

Stronger base $\Rightarrow$ larger K_b $\Rightarrow$ **smaller** pK_b. Conjugate-acid relation: $pK_a(RNH_3^+) + pK_b(RNH_2) = 14$ at 298 K — so the conjugate-acid pK_a order matches the basicity order.

Basicity order in water (9.5.1, Table 9.3)

Aliphatic amines (methyl series, in water):

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

(pK_b: 3.27 3.38 4.22 4.75)

Ethyl series in water:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

Aromatic vs aliphatic:

$CH_3NH_2 > NH_3 \gg C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$.

Aryl amines are far weaker bases than aliphatic amines or even NH_3 because the N lone pair is delocalised into the ring (Fig. 9.3, five resonance structures), so it is less available for H^+.

Three structural factors (9.5.1)

The basicity of an amine in aqueous solution is a balance of:

(1) Inductive (+I) effect: alkyl R groups push electron density onto N $\Rightarrow$ *increase* basicity. So 3° should be most basic in gas phase: $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$.

(2) Solvation (H-bonding) of conjugate acid: R–NH_3^+ (3 N–H) > $R_2NH_2^+$ (2 N–H) > R_3NH^+ (1 N–H) in stabilisation by water. More H-bonds ⇒ more stable cation ⇒ stronger base.
(3) Steric hindrance: bulky R groups around N hinder protonation, reducing basicity in 3° amines.

In water the three effects oppose each other. Net order for methylamines: **$(CH_3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > NH_3.**

Why aryl amines are weak bases

Aniline ⇌ five resonance structures (Fig. 9.3): in two of them the N lone pair sits on the *ortho* or *para* ring carbon, so it is **not available** to grab H^+.

Energy comparison:
- Aniline: 5 resonance structures (lone-pair delocalised).
- Anilinium ($PhNH_3^+$): only 2 (Kekulé) resonance structures.

Loss of resonance stabilisation on protonation makes aniline much weaker than CH_3NH_2.

Ring substituent effect (anilines, p-substituted):
- *p*-CH_3 (+I, weak +H): **more basic** than aniline (*p*-toluidine $p\,K_b \approx 8.92$).
- *p*-OCH_3 (+M dominates): **more basic** than aniline.
- *p*-NH_2 (strong +M): clearly more basic than aniline.
- *p*-Cl, *p*-Br (–I dominates over weak +M): **less basic** than aniline.
- *p*-NO_2, *p*-CN (strong –M / –I): **much less basic** (*p*-nitroaniline $p\,K_b = 13.0$, almost neutral).

Gas phase vs solution

In the gas phase (no solvation), **pure +I effect** determines basicity:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.
In water, solvation reshuffles the order so that 2° often beats 3°. NCERT presents only the aqueous order — but JEE often asks for the gas-phase order, so remember both.

6 Chemical Reactions of Amines (9.6)

Section 9.6 collects the reactions of the lone-pair on N (alkylation, acylation, with HNO_2, carbylamine) and the ring reactions of arylamines (electrophilic substitution). All of these are NCERT-exam staples.

Salt formation with mineral acids (9.6)

$R\text{–}NH_2 + HX \longrightarrow [\,]\ R\text{–}NH_3^+X^-$ (e.g. $R\text{–}NH_3^+Cl^-$, $R\text{–}NH_3^+HSO_4^-$)

$C_6H_5NH_2 + HCl \longrightarrow [\,]\ C_6H_5NH_3^+Cl^-$ (anilinium chloride)

Every amine (1°, 2°, 3°) is protonated by HCl, H_2SO_4, HNO_3 etc. to give a water-soluble ammonium salt. **Adding NaOH regenerates the free amine** — exploited in extraction (basify → amine separates as oil/solid; acidify → salt dissolves back).

Alkylation (9.6.1)

$R\text{–}NH_2 \longrightarrow [R\text{–}X]\ R_2NH \longrightarrow [R\text{–}X]\ R_3N \longrightarrow [R\text{–}X]\ R_4N^+X^-$

Each amine is more nucleophilic than the last, so the reaction does not stop — always gives a **mixture**. Same logic as in ammonolysis (Section 9.3.4).

Acylation (9.6.2)

$R\text{–}NH_2 + R'COCl \longrightarrow [\text{base (pyridine)}]\ R\text{–}NHCOR' + HCl$

$R\text{–}NH_2 + (R'CO)_2O \longrightarrow [\ ]\ R\text{–}NHCOR' + R'COOH$

$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow [\ ]\ C_6H_5NHCOCH_3$ (acetanilide)

1° and 2° amines give substituted amides; 3° amines (no N–H) **do not acylate**. Pyridine traps the HCl byproduct; acetanilide is itself a substrate-protector in aniline ring chemistry.

Carbylamine test (9.6.3) — 1° amine only

$R\text{–}NH_2 + CHCl_3 + 3\,KOH \longrightarrow [\Delta]\ R\text{–}N{\equiv}C + 3\,KCl + 3\,H_2O$

Foul-smelling **isocyanide (R–NC)** is the test for any 1° amine (alkyl or aryl). 2° and 3° amines give no isocyanide. The carbylamine reaction is a classical distinguishing test.

Reaction with HNO_2 (nitrous acid) (9.6.4)

1° aliphatic amine:

$R\text{–}NH_2 + HNO_2 \longrightarrow [\ ]\ R\text{–}N_2^+\,Cl^- \longrightarrow [-N_2]\ R\text{–}OH$ (+ alkenes, R–X)

1° aromatic amine (273–278 K):

$Ar\text{–}NH_2 + HNO_2 + HCl \longrightarrow [\ ]\ Ar\text{–}N_2^+Cl^- + 2\,H_2O$ (*stable diazonium salt*)

2° amine (alkyl or aryl): $R_2NH + HNO_2 \rightarrow R_2N\text{–}N{=}O$ (yellow *N*-nitrosamine).

3° amine: $R_3N + HNO_2 \rightarrow R_3NH^+NO_2^-$ (no reaction beyond salt formation).

HNO_2 is the master distinguishing reagent — 1° aliphatic effervesces N_2, 1° aromatic gives stable diazonium, 2° gives yellow oil, 3° just neutralises. Always written with $NaNO_2$ + HCl at 273–278 K.

Hinsberg test (9.6.5) — benzenesulphonyl chloride

$C_6H_5SO_2Cl$ (*Hinsberg reagent*) reacts with:

- **1° amine:** gives *N*-alkyl benzenesulphonamide — soluble in KOH (N–H is acidic due to two adjacent $–SO_2$).
- **2° amine:** gives *N*,*N*-dialkyl benzenesulphonamide — insoluble in KOH (no N–H).
- **3° amine:** no reaction (no N–H to lose).

Tests in one tube: dissolve all three; treat with $PhSO_2Cl$ + KOH. 1° dissolves clear; 2° floats as a solid; 3° remains as a separate liquid layer.

Electrophilic substitution on arylamine (9.6.6)

$–NH_2$ is **strongly activating** and **ortho/para directing**.

Bromination of aniline:

$C_6H_5NH_2 + 3\,Br_2 \longrightarrow [H_2O]$ 2,4,6-tribromoaniline + 3 HBr
(White ppt, no catalyst needed.)

Nitration:
$C_6H_5NH_2 \longrightarrow [\text{conc. } HNO_3/H_2SO_4]$ 47% m-nitroaniline + 51% p- + 2% o-
(In strong acid, $-NH_2$ becomes $-NH_3^+$ which is **meta-directing** — hence m-isomer forms.)

To make pure p-nitroaniline, protect $-NH_2$ as acetanilide:
$C_6H_5NH_2 \longrightarrow [(CH_3CO)_2O]$ $C_6H_5NHCOCH_3 \longrightarrow [HNO_3/H_2SO_4]$ p-O_2N–$C_6H_4NHCOCH_3 \longrightarrow [H_3O^+]$ p-nitroaniline

Sulphonation:
$C_6H_5NH_2 \longrightarrow [\text{conc. } H_2SO_4,\ 453\text{–}473\ K]$ sulphanilic acid (p-aminobenzenesulphonic acid, zwitterion).

Friedel-Crafts (alkylation/acylation) **fails on aniline** — the basic $-NH_2$ complexes with $AlCl_3$, deactivating the ring. Acylate first (acetanilide) to do F–C reactions cleanly.

$-NH_2$ becomes meta-directing in strong acid

In conc. HNO_3/H_2SO_4 aniline is protonated to the anilinium ion ($-NH_3^+$). The cation is electron-withdrawing (–I), so it **deactivates and meta-directs**. That is why direct nitration of aniline gives 47% *meta* isomer, not the expected *ortho/para*. Protecting $-NH_2$ as acetanilide preserves the +M activating, *p*-directing character.

7 Diazonium Salts — Preparation & Properties (9.7)

Section 9.7 introduces the diazonium salt Ar–$N_2^+X^-$ — the most synthetically useful organic intermediate in benzene chemistry. It is made cold from a 1° aromatic amine and acts as a placeholder for almost any other functional group on the ring.

Preparation — Diazotisation (9.7.1)

$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow [273\text{–}278\ K]$ $C_6H_5N_2^+Cl^- + NaCl + 2\,H_2O$

Generates HNO_2 *in situ* ($NaNO_2$ + HCl). Below 278 K (0–5 °C) the diazonium ion is stable; above 283 K it decomposes to phenol + N_2. **Only 1° aromatic amines** give stable diazonium salts; 1° aliphatic amines give unstable R–N_2^+ that decomposes immediately.

Structure & stability

Ar–$N_2^+Cl^-$ drawn as Ar–N≡N^+ Cl^-.

Stability comes from **resonance delocalisation** of the positive charge into the benzene ring: positive charge spreads from N to the *ortho* and *para* ring carbons, with N=N shifting to N–N along the way.

Solid Ar–$N_2^+X^-$ is **explosive when dry**; always handle as the cold aqueous solution. Aliphatic R–N_2^+ has no such ring resonance, hence decomposes immediately.

8 Reactions of Diazonium Salts — Loss of N_2 (9.8)

Section 9.8 lists the substitution reactions of Ar–N_2^+, where N_2 is the leaving group. Almost every common aromatic functional group (–Cl, –Br, –I, –CN, –F, –OH, –H) can be installed via this route — this is why diazonium chemistry is central to aromatic synthesis.

Sandmeyer reactions — Cl, Br, CN (9.8.1)

$Ar\text{–}N_2^+Cl^- \longrightarrow [CuCl/HCl]\ Ar\text{–}Cl + N_2$

$Ar\text{–}N_2^+Cl^- \longrightarrow [CuBr/HBr]\ Ar\text{–}Br + N_2$

$Ar\text{–}N_2^+Cl^- \longrightarrow [CuCN/KCN]\ Ar\text{–}CN + N_2$

Catalysed by Cu(I) salts; mechanism is radical. The Cu salt provides the nucleophile (Cl^-/Br^-/CN^-). Yields are generally 70–90%. Note: Ar–CN can be hydrolysed to Ar–COOH (carbon count goes up by 1 from starting Ar–NH_2).

Gattermann reaction — Cu/HX (9.8.1)

$Ar\text{–}N_2^+Cl^- \longrightarrow [Cu\ (powder)/HCl]\ Ar\text{–}Cl + N_2$

$Ar\text{–}N_2^+Cl^- \longrightarrow [Cu/HBr]\ Ar\text{–}Br + N_2$

Same outcome as Sandmeyer but uses **copper metal (Cu^0) in halogen acid** instead of Cu(I) salt. Gives slightly lower yields and is simpler to set up; Sandmeyer is generally preferred at industrial scale.

Replacement by I and F (9.8.1)

Iodination (no catalyst needed):

$Ar\text{–}N_2^+Cl^- + KI \longrightarrow [\ ]\ Ar\text{–}I + N_2 + KCl$

Balz–Schiemann fluorination:

$Ar\text{–}N_2^+Cl^- + HBF_4 \longrightarrow [\ ]\ Ar\text{–}N_2^+BF_4^- \longrightarrow [\Delta]\ Ar\text{–}F + N_2 + BF_3$

Direct halogenation of benzene gives only Cl/Br products via electrophilic substitution; **the Ar–F and Ar–I aromatics are only conveniently prepared via the diazonium route**.

Replacement by –OH & –H

Hydroxylation (Ar–OH):

$Ar\text{–}N_2^+Cl^- + H_2O \longrightarrow [warm,\ dil.\ H_2SO_4]\ Ar\text{–}OH + N_2 + HCl$

Reduction (Ar–H):

$Ar\text{–}N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow [\ ]\ Ar\text{–}H + N_2 + H_3PO_3 + HCl$

or, alternatively, $Ar\text{–}N_2^+Cl^- \longrightarrow [C_2H_5OH]\ Ar\text{–}H + N_2 + CH_3CHO + HCl.$

Hydrolysis to phenol works on warming (above 283 K). Reduction to Ar–H is the only way to **remove an –NH_2/–NO_2 group from a benzene ring** (used as a directing handle that is then deleted).

JEE/NEET Extension — diazonium retrosynthesis

Whenever a target arene has Ar–F, Ar–I, Ar–CN, or a specific substitution pattern that direct E.A.S. can't deliver, **work backwards through the diazonium salt**: target $\Leftarrow$ Ar–N_2^+ $\Leftarrow$ Ar–NH_2

$\Leftarrow$ Ar–NO_2 $\Leftarrow$ benzene (HNO_3/H_2SO_4). This is the standard 5-step JEE problem.

9 Diazonium Coupling & Azo Dyes (9.8.2)

Section 9.8.2 covers reactions where Ar–N_2^+ keeps the N_2 unit and adds it to another aromatic ring as –N=N–. These *azo* compounds are the basis of dye chemistry — bright yellow/orange/red colours from extended N=N–C=C conjugation.

Coupling with phenol (alkaline pH 9–10)

$C_6H_5N_2^+Cl^- + C_6H_5OH \longrightarrow$ [NaOH, dilute] p-HO–C_6H_4–N=N–C_6H_5 + HCl

(*p-hydroxyazobenzene*, orange dye)

Couples preferentially at the *para* position; coupling at *ortho* occurs if *para* is blocked. Alkaline conditions deprotonate phenol to PhO^-, the more reactive coupling component.

Coupling with aniline (mildly acidic pH 4–5)

$C_6H_5N_2^+Cl^- + C_6H_5NH_2 \longrightarrow$ [pH 4–5] p-H_2N–C_6H_4–N=N–C_6H_5 + HCl

(*p-aminoazobenzene*, yellow dye)

Slightly acidic conditions: too acidic protonates –NH_2 to –NH_3^+ (ring deactivated, no coupling); too basic destroys Ar–N_2^+. The optimum pH window is 4–5.

Why azo compounds are coloured

The –N=N– bridge connects two aromatic rings into a conjugated π-system. The extended chromophore absorbs in the visible region (350–550 nm), so transmitted light appears **yellow** $\rightarrow$ **orange** $\rightarrow$ **red** depending on the substituents on the rings. Pushing electron-donor groups (–NH_2, –OH) deeper into the conjugation shifts absorption to longer wavelengths (bathochromic shift).

Diazonium as a synthetic "hub"

From a single Ar–NH_2 (made from Ar–NO_2) you can build:

- Ar–Cl, Ar–Br (Sandmeyer/Gattermann);
- Ar–I (KI), Ar–F (HBF_4/Δ);
- Ar–CN $\rightarrow$ Ar–COOH (hydrolysis);
- Ar–OH (H_2O/Δ);
- Ar–H (H_3PO_2);
- Ar–N=N–Ar′ azo dyes (coupling).

The diazonium ion is the most versatile synthetic handle in aromatic chemistry — almost any group can be installed in two steps via Ar–N_2^+. This is why NCERT devotes a separate section to it.

JEE/NEET Extension — selective *para* bromination of aniline

To make pure *p*-bromoaniline, **acetylate first** to acetanilide — this lowers the activating power of –NH_2 from very-strong to moderate, so monobromination gives selectively *p*-Br. Hydrolyse

back to amine:
$PhNH_2 \longrightarrow [(CH_3CO)_2O]$ $PhNHCOCH_3 \longrightarrow [Br_2/CH_3COOH]$ p-Br–$C_6H_4NHCOCH_3 \longrightarrow [H_3O^+]$ p-Br–$C_6H_4NH_2$.

10 Quick Recap — Distinguishing Tests

A condensed lookup for the most-asked NCERT distinguishing tests on amines.

Test / reagent	1°	2° & 3° behaviour
HNO_2 ($NaNO_2$ + HCl, 273–278 K)	R–NH_2 $\rightarrow$ $N_2\uparrow$ + R–OH (alkyl); Ar–N_2^+ stable (aryl)	2°: yellow oil R_2N–NO; 3°: only salt formation
Carbylamine ($CHCl_3$ + KOH/Δ)	Foul-smelling R–NC (positive)	No reaction
Hinsberg ($PhSO_2Cl$ + KOH)	$PhSO_2NHR$ — soluble in KOH	2°: $PhSO_2NR_2$ insoluble in KOH; 3°: no reaction
Acylation (R′COCl, pyridine)	R–NHCOR′ (amide)	2°: R_2NCOR'; 3°: no reaction
Acid/base solubility	All amines soluble in dilute HCl	3° amine $\rightarrow$ $R_3NH^+Cl^-$, regenerated on adding NaOH
Br_2/H_2O on aniline	White ppt of 2,4,6-tribromoaniline (only Ar–NH_2)	No ppt for aliphatic 1° amines

Ascent vs descent of series

Ascent (+1 C): R–X $\rightarrow$ R–CN $\rightarrow$ R–CH_2NH_2 (Mendius reduction).
Descent (–1 C): R–$CONH_2$ $\rightarrow$ R–NH_2 (Hoffmann bromamide).
Same C count: amide reduction ($LiAlH_4$) and Gabriel synthesis.