CLASS 12 CHEMISTRY — FORMULA SHEET

Chapter 9 : Amines (NCERT)

9.1 Classification & Structure

Concept	Detail
Amine	Derivative of ammonia (NH_3) ; one+ H replaced by alkyl/aryl
Primary (1°)	$R–NH_2$ (one carbon on N)
Secondary (2°)	R_2NH (two carbons on N)
Tertiary (3°)	R_3N (three carbons on N)
Aliphatic amine	N bonded to alkyl group(s)
Aromatic amine	N bonded directly to aromatic ring (e.g. aniline)
Shape	Pyramidal (sp^3 N with lone pair)

9.2 Methods of Preparation

Method	Reaction
Reduction of nitro compounds	$R–NO_2 + H_2/Ni$ (or Sn/HCl) → $R–NH_2$
Ammonolysis of haloalkanes	$R–X + NH_3 \rightarrow R–NH_2$ (gives a mixture)
Reduction of nitriles	$RCN + H_2/Ni$ (or $LiAlH_4$) → $R–CH_2–NH_2$
Reduction of amides	$RCONH_2 + LiAlH_4 \rightarrow R–CH_2–NH_2$
Gabriel phthalimide synthesis	Gives pure 1° amine (not for aryl amines)
Hoffmann bromamide degradation	$RCONH_2 + Br_2/KOH \rightarrow R–NH_2$ (one C less)

9.3 Basic Strength of Amines

Concept	Detail
Basicity reason	Lone pair on N accepts a proton (Lewis base)
In gas phase	3° > 2° > 1° > NH_3 (inductive effect)
In aqueous (aliphatic)	2° > 1° > 3° > NH_3 (balance of +I, solvation, steric)
Aromatic amines	Weaker bases than ammonia (lone pair delocalised into ring)
Aniline vs alkyl amine	Aniline is much weaker (resonance stabilises lone pair)
Electron-withdrawing groups	Decrease basicity (e.g. nitroaniline)
Electron-donating groups	Increase basicity (e.g. toluidine)

9.4 Chemical Reactions

Reaction	Detail
With acids	Form salts ($R–NH_2 + HCl \rightarrow R–NH_3^+Cl^-$)
Acylation	Amine + acyl chloride → amide

Reaction	Detail
Carbylamine reaction	1° amine + $CHCl_3$ + KOH → isocyanide (foul smell ; test for 1° amine)
Hinsberg test	Distinguishes 1°, 2°, 3° amines (with benzenesulphonyl chloride)
Reaction with HNO_2 (1° aliphatic)	→ alcohol + N_2 gas
Reaction with HNO_2 (1° aromatic)	→ diazonium salt (at 0-5°C)
Bromination of aniline	→ 2,4,6-tribromoaniline (white ppt) with Br_2 water

9.5 Diazonium Salts

Reaction	Product
Formation	Aniline + $NaNO_2$/HCl (0-5°C) → benzenediazonium chloride
Sandmeyer (–Cl, –Br)	With CuCl/CuBr → chloro/bromo benzene
Sandmeyer (–CN)	With CuCN → benzonitrile
Replacement by –I	With KI → iodobenzene
Replacement by –OH	Warm with water → phenol
Replacement by –H	With H_3PO_2 → benzene
Coupling reaction	With phenol/aniline → azo dye (coloured)

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Basicity (aqueous)	Aliphatic amines: 2° > 1° > 3° > NH_3. Aromatic amines are weaker than NH_3.
Why aniline weak	Lone pair delocalised into the ring → less available for protonation.
Carbylamine test	Only 1° amines give foul-smelling isocyanide (with $CHCl_3$/KOH).
Hinsberg test	Distinguishes 1°/2°/3° amines using benzenesulphonyl chloride.
Gabriel synthesis	Gives PURE 1° amine ; fails for aromatic amines.
Hoffmann degradation	Amide → amine with ONE carbon less (Br_2/KOH).
Diazonium key	Made at 0-5°C ; gateway to many aromatic compounds (Sandmeyer etc.).
Coupling → dyes	Diazonium + phenol/aniline → coloured azo dyes.