Amines

9.1 Structure of Amines

- Amines are derivatives of ammonia (NH_3) where one or more H atoms are replaced by alkyl/aryl groups
- Nitrogen in amines is sp^3 hybridised with a lone pair of electrons
- Shape is pyramidal, bond angle slightly less than 109.5° (e.g., 108° in trimethylamine)
- The lone pair makes amines behave as Lewis bases and nucleophiles

9.2 Classification

- **Primary (1°):** One H of NH_3 replaced → RNH_2 (e.g., CH_3NH_2)
- **Secondary (2°):** Two H replaced → R_2NH (e.g., $(CH_3)_2NH$)
- **Tertiary (3°):** All three H replaced → R_3N (e.g., $(CH_3)_3N$)
- Simple amines: all groups same; Mixed amines: groups different

9.3 Nomenclature

- **Common:** Alkyl group name + amine (e.g., methylamine, diethylamine)
- **IUPAC:** Replace 'e' of alkane with 'amine' → alkanamine (e.g., CH_3NH_2 = methanamine)
- For 2° and 3° amines, use locant **N** for groups on nitrogen (e.g., $CH_3NHCH_2CH_3$ = N-methylethanamine)
- $C_6H_5NH_2$ = Aniline (common) = Benzenamine (IUPAC)

9.4 Preparation of Amines

1. Reduction of nitro compounds:

- $ArNO_2 \rightarrow ArNH_2$ (using H_2/Pd or Sn+HCl or Fe+HCl)
- $C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

2. Ammonolysis of alkyl halides:

- $RX + NH_3 \rightarrow RNH_2$ (1°) $\rightarrow R_2NH$ (2°) $\rightarrow R_3N$ (3°) $\rightarrow R_4N^+X^-$ (quaternary salt)
- Disadvantage: gives mixture of 1°, 2°, 3° amines and quaternary salt
- Use excess NH_3 to get mainly primary amine
- Reactivity: RI > RBr > RCl

3. Reduction of nitriles:

- $R–C≡N + 2H_2 \rightarrow RCH_2NH_2$ (using $LiAlH_4$ or H_2/Ni)
- Used for ascending the amine series (product has one more carbon)

4. Reduction of amides:

- $RCONH_2 + LiAlH_4 \rightarrow RCH_2NH_2$

5. Gabriel phthalimide synthesis:

- Phthalimide + KOH → potassium phthalimide + RX → N-alkylphthalimide → hydrolysis → RNH_2 (primary amine)
- Only gives primary amines; cannot prepare aromatic primary amines (aryl halides don't undergo nucleophilic substitution)

6. Hoffmann bromamide degradation:

- $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
- Product amine has one carbon less than the starting amide

- Gives only primary amines

9.5 Physical Properties

- Lower aliphatic amines are gases with fishy smell; higher ones are liquid/solid
- Aniline is colourless but turns dark on exposure to air (oxidation)
- Lower amines are soluble in water (H-bonding with water); solubility decreases with increasing molecular mass
- Boiling point order: Primary > Secondary > Tertiary (for isomeric amines, due to extent of H-bonding)
- Alcohols have higher boiling points than amines of comparable molecular mass (O is more electronegative than N, stronger H-bonds)

9.6 Chemical Reactions

1. Basic character of amines

- Amines react with acids to form salts: $RNH_2 + HCl \rightarrow RNH_3^+Cl^-$
- Basicity measured by Kb (larger Kb = stronger base) or pKb (smaller pKb = stronger base)

Aliphatic amines vs Ammonia:

- Alkyl groups have +I effect → increase electron density on N → stronger base than NH_3
- In gaseous phase: 3° > 2° > 1° > NH_3
- In aqueous phase: order is irregular due to interplay of +I effect, solvation, and steric hindrance
  - For methyl: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
  - For ethyl: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

Aromatic amines vs Ammonia:

- Aniline is a weaker base than NH_3 (pKb = 9.38 vs 4.75)
- Reason: lone pair on N is delocalized into benzene ring (resonance) → less available for protonation
- Electron-releasing groups ($–CH_3$, $–OCH_3$) on ring increase basicity
- Electron-withdrawing groups ($–NO_2$, –X, –COOH) decrease basicity

2. Alkylation

- Amines + RX → higher substituted amines (nucleophilic substitution)

3. Acylation

- 1° and 2° amines react with acid chlorides/anhydrides → amides
- $C_2H_5NH_2 + CH_3COCl \rightarrow CH_3CONHC_2H_5$ (N-Ethylethanamide) + HCl
- $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3$ (Acetanilide) + CH_3COOH
- Benzoylation: $RNH_2 + C_6H_5COCl \rightarrow RNHCOC_6H_5 + HCl$

4. Carbylamine reaction (Isocyanide test)

- Only primary amines give this reaction
- $RNH_2 + CHCl_3 + 3KOH \rightarrow R–NC$ (isocyanide, foul smell) + 3KCl + $3H_2O$
- Used as a test for primary amines

5. Reaction with nitrous acid ($NaNO_2$ + HCl)

- **1° aliphatic amine:** $RNH_2 + HNO_2 \rightarrow ROH + N_2\uparrow + H_2O$ (unstable diazonium salt decomposes)
- **1° aromatic amine:** $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$ (at 273-278K → stable diazonium salt)

6. Reaction with arylsulphonyl chloride (Hinsberg's reagent)

- **1° amine:** gives sulphonamide → soluble in alkali (has acidic H on N)
- **2° amine:** gives sulphonamide → insoluble in alkali (no H on N)
- **3° amine:** does not react
- Used to distinguish 1°, 2°, 3° amines

7. Electrophilic substitution (Aniline)

- $–NH_2$ is ortho/para directing and strongly activating

(a) Bromination:

- Aniline + $3Br_2(aq)$ → 2,4,6-Tribromoaniline (white ppt) + 3HBr
- To get mono-substituted product: protect $–NH_2$ by acetylation → brominate → hydrolyse → p-bromoaniline

(b) Nitration:

- Direct nitration gives o-, p- and m-nitroaniline (m- due to protonation in acidic medium → anilinium ion is meta directing)
- Controlled nitration: acetylate → nitrate → hydrolyse → p-nitroaniline

(c) Sulphonation:

- Aniline + conc. H_2SO_4 → anilinium hydrogensulphate → heat at 453-473K → sulphanilic acid (p-aminobenzenesulphonic acid)

Note: Aniline does NOT undergo Friedel-Crafts reaction (forms salt with $AlCl_3$, N becomes positively charged → deactivates ring)

9.7 Diazonium Salts — Preparation

- General formula: $ArN_2^+X^-$
- **Diazotisation:** $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$ (at 273-278K)
- Aromatic diazonium salts are stable at low temperature; aliphatic ones are highly unstable
- Stability due to resonance of diazonium ion with benzene ring

9.9 Reactions of Diazonium Salts

A. Reactions involving displacement of N_2

Reaction	Reagent	Product
Sandmeyer	Cu_2Cl_2/HCl	$ArCl + N_2$
Sandmeyer	Cu_2Br_2/HBr	$ArBr + N_2$
Sandmeyer	CuCN/KCN	$ArCN + N_2$
Gattermann	Cu/HCl	$ArCl + N_2$
Gattermann	Cu/HBr	$ArBr + N_2$
Iodide replacement	KI	$ArI + N_2$
Fluoride replacement	HBF_4 then heat	$ArF + N_2$
Replacement by H	H_3PO_2 or C_2H_5OH	$ArH + N_2$
Replacement by OH	Warm with H_2O	$ArOH + N_2$
Replacement by NO_2	$NaNO_2$/Cu (with HBF_4)	$ArNO_2 + N_2$

B. Coupling reactions (retention of diazo group)

- $C_6H_5N_2^+Cl^- + C_6H_5OH$ → p-Hydroxyazobenzene (orange dye) + HCl
- $C_6H_5N_2^+Cl^- + C_6H_5NH_2$ → p-Aminoazobenzene (yellow dye) + HCl
- These are electrophilic substitution reactions
- Products are azo dyes (coloured, contain –N=N– bond)

9.10 Importance of Diazonium Salts

- They serve as intermediates for introducing groups like –F, –Cl, –Br, –I, –CN, –OH, $–NO_2$ into the aromatic ring
- Aryl fluorides and iodides cannot be made by direct halogenation but can be made via diazonium salts
- –CN group can be introduced via diazonium salt (not possible by direct nucleophilic substitution on chlorobenzene)

Key Equations to Remember

Reaction	Equation
Reduction of nitrobenzene	$C_6H_5NO_2 + Sn/HCl \rightarrow C_6H_5NH_2$
Ammonolysis	$RX + NH_3 \rightarrow RNH_2 + HX$
Reduction of nitrile	$RCN + 2H_2 \rightarrow RCH_2NH_2$
Hoffmann degradation	$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3$
Carbylamine reaction	$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$
Diazotisation	$C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^-$ (273-278K)
Coupling with phenol	$C_6H_5N_2^+Cl^- + C_6H_5OH \rightarrow p\text{-}HOC_6H_4N{=}NC_6H_5$
Sandmeyer (Cl)	$ArN_2^+Cl^- + Cu_2Cl_2/HCl \rightarrow ArCl + N_2$