

CLASS 12

CHEMISTRY

REVISION NOTES

Class 12 Chemistry Chapter 9 Amines – Revision Notes

Quick revision notes for Class 12 Chemistry Chapter 9 – Amines, covering classification, basicity trends, key name reactions, and diazonium salt chemistry. Ideal for last-minute board exam revision.

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Quick revision notes for **Class 12 Chemistry Chapter 9 – Amines**, covering classification, basicity trends, key name reactions, and diazonium salt chemistry. Ideal for last-minute board exam revision.

Classification and Structure

Amines ($R-NH_2$, R_2NH , R_3N) are classified as **primary, secondary or tertiary** based on the number of carbon groups attached to nitrogen — unlike alcohols/halides, this classification is based on substitution at N, not at a carbon. Nitrogen is sp^3 hybridised with a pyramidal shape and one lone pair, which is responsible for both its basicity and its nucleophilicity.

Basicity Trends

In **aqueous solution**, basicity of simple alkyl amines follows: **secondary > primary > tertiary > NH_3** — a balance between the electron-donating (+I) effect of alkyl groups (favouring more substitution) and steric hindrance to solvation of the ammonium ion (penalising the bulky tertiary amine). In the **gas phase** (no solvation effects), basicity increases steadily with alkyl substitution: tertiary > secondary > primary > NH_3 .

Aromatic amines are weaker bases than both aliphatic amines and ammonia, since the nitrogen lone pair is delocalised into the ring by resonance; electron-withdrawing ring substituents ($-NO_2$) weaken this basicity further, while electron-donating groups ($-CH_3$) strengthen it.

Key Name Reactions

Hofmann's bromamide degradation: $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$ — the product amine has **one carbon fewer** than the starting amide. **Gabriel phthalimide synthesis:** potassium phthalimide + 1° alkyl halide (S_N2) $\rightarrow$ N-alkylphthalimide $\rightarrow$ (hydrolysis) $\rightarrow$ pure primary amine; **fails for aromatic amines** since aryl halides cannot undergo S_N2 . **Carbylamine reaction:** a primary amine + $CHCl_3$ + alc. KOH, heat $\rightarrow$ a foul-smelling isocyanide — positive only for 1° amines. **Diazotisation:** $ArNH_2 + NaNO_2 + 2HCl$ at 273–278K $\rightarrow$ $ArN_2Cl + NaCl + 2H_2O$; stable for aromatic amines, but aliphatic diazonium salts decompose instantly even in the cold.

Diazonium Salt Reactions

Displacement of N_2 (ring retained): Sandmeyer reaction ($Cu_2Cl_2/Cu_2Br_2/CuCN \rightarrow Ar-Cl/Ar-Br/Ar-CN$), Gattermann reaction (Cu powder + HX, similar products without a cuprous salt), KI (direct iodination, no catalyst), Balz–Schiemann (HBF_4 , then heat $\rightarrow Ar-F$), H_3PO_2/H_2O (reduction to $Ar-H$), hydrolysis ($H_2O/\Delta \rightarrow Ar-OH$). **Retention of N_2 (coupling reactions):** with phenols (mildly alkaline medium) or aromatic amines (mildly acidic medium), giving brightly coloured azo compounds — the basis of azo dyes; coupling occurs mainly para to the activating group (ortho if para is blocked).

Identification and Distinguishing Tests

Hinsberg's test (benzenesulfonyl chloride): 1° amine $\rightarrow$ sulfonamide soluble in KOH (has an acidic N–H); 2° amine $\rightarrow$ sulfonamide insoluble in KOH (no acidic N–H); 3° amine $\rightarrow$ no reaction, separates unreacted.

Carbylamine test: positive only for 1° amines. **Bromine water test:** aniline gives an instant white precipitate of 2,4,6-tribromoaniline; benzylamine (whose $-NH_2$ is not conjugated to a ring) does not.

Reaction with HNO_2 : aliphatic 1° amines give brisk N_2 effervescence; aromatic 1° amines give a stable diazonium salt; 2° amines give a yellow oily N-nitrosamine; 3° amines simply form a salt.

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