ChapterNotes

chapternotes.in · free NEET & JEE prep

CHAPTER NOTES

Amines Class 12 Notes — CBSE Chemistry Chapter 13

- ✓ Chapter-wise notes & important questions
- ✓ Free gamified practice app — streaks, levels, revision
- ✓ Free mock & prediction papers with answer keys

Source: https://chapternotes.in/cbse/class-12-chemistry/amines-class-12-notes/

Scan to practice this chapter free in the app

Amines Class 12 Notes — CBSE Chemistry Chapter 13

Chapter 13 — **Amines** — introduces nitrogen-containing organic compounds that are derivatives of ammonia. From the adrenaline in your body to the aniline used in dyes, amines are biologically and industrially vital. This chapter carries **5-7 marks** in Board exams. Focus on basicity comparison, diazonium salt reactions, and distinction tests.

Key Concepts

Classification

Type	Structure	Example
Primary (1°)	$R–NH_2$	CH_3NH_2 (methylamine), $C_6H_5NH_2$ (aniline)
Secondary (2°)	R_2NH	$(CH_3)_2NH$ (dimethylamine)
Tertiary (3°)	R_3N	$(CH_3)_3N$ (trimethylamine)

Preparation

1. Hofmann Ammonolysis: $RX + NH_3 \rightarrow RNH_2 + R_2NH + R_3N + R_4N^+X^-$ (mixture!)
(Excess NH_3 → mainly 1° amine)

2. Gabriel Phthalimide Synthesis (1° amine only):
Phthalimide + KOH → potassium phthalimide + RX → N-alkylphthalimide →(N_2H_4) RNH_2 + phthalhydrazide

3. Reduction of Nitro Compounds:
$RNO_2 + 3H_2/Ni \rightarrow RNH_2$ (catalytic reduction)
$ArNO_2 + Sn/HCl \rightarrow ArNH_2$ (aniline — standard lab method)

4. Hoffmann Bromamide Degradation:
$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
(Amide → amine with ONE LESS carbon — very useful!)

Gabriel synthesis: Only gives **primary amines**. Cannot be used for aromatic amines ($ArNH_2$) because aryl halides don't undergo SN2 with potassium phthalimide.

Basicity of Amines

In aqueous solution (pKb values):

$(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3 > C_6H_5NH_2$

In gas phase (no solvation):

$3° > 2° > 1° > NH_3$ (purely inductive effect)

Why aniline is a weak base: The lone pair on N is delocalised into the benzene ring (resonance), making it less available for protonation. Hence aniline is much weaker than aliphatic amines.

Effect of Substituents on Basicity

- **Electron-donating groups ($–CH_3$, $–OCH_3$) on ring:** Increase basicity of aromatic amines
- **Electron-withdrawing groups ($–NO_2$, –Cl) on ring:** Decrease basicity
- p-Toluidine ($p\text{-}CH_3C_6H_4NH_2$) > aniline > p-nitroanilline

Reactions of Amines

Distinction Tests (Hinsberg Test)

Hinsberg Reagent = $C_6H_5SO_2Cl$ (benzenesulphonyl chloride)

1° amine → sulphonamide (dissolves in NaOH — acidic H on N)

2° amine → sulphonamide (insoluble in NaOH — no acidic H)

3° amine → no reaction with Hinsberg reagent

Carbylamine Test (for 1° amines only)

$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC$ (isocyanide, foul smell!) $+ 3KCl + 3H_2O$

Only 1° amines (aliphatic and aromatic) give this test.

Reaction with Nitrous Acid ($NaNO_2$ + HCl)

Amine Type	Reaction	Product
1° aliphatic	$RNH_2 + HNO_2$	$ROH + N_2\uparrow + H_2O$ (unstable diazonium → alcohol)
1° aromatic	$ArNH_2 + HNO_2$ (0-5°C)	$ArN_2^+Cl^-$ (diazonium salt — stable at 0-5°C!)
2° (both)	$R_2NH + HNO_2$	$R_2N–N=O$ (nitrosoamine — yellow oily liquid)
3° aliphatic	$R_3N + HNO_2$	$R_3N^+H \cdot NO_2^-$ (salt)
3° aromatic	$Ar_3N + HNO_2$	p-nitroso compound (electrophilic substitution on ring)

Diazonium Salts — The Most Versatile Intermediate!

Preparation: $ArNH_2 + NaNO_2 + 2HCl \xrightarrow{(0\text{-}5°C)} ArN_2^+Cl^- + NaCl + 2H_2O$ (diazotisation)

Reactions replacing N_2:

$ArN_2^+Cl^- + CuCl/HCl \rightarrow ArCl + N_2$ (Sandmeyer — chloride)

$ArN_2^+Cl^- + CuBr/HBr \rightarrow ArBr + N_2$ (Sandmeyer — bromide)

$ArN_2^+Cl^- + CuCN/KCN \rightarrow ArCN + N_2$ (Sandmeyer — cyanide)

$ArN_2^+Cl^- + KI \rightarrow ArI + N_2 + KCl$ (no Cu catalyst needed!)

$ArN_2^+Cl^- + H_3PO_2 + H_2O \rightarrow ArH + N_2$ (replace NH_2 with H)

$ArN_2^+Cl^- + HBF_4 \rightarrow ArF + N_2 + BF_3$ (Balz-Schiemann — fluoride)

$ArN_2^+Cl^- + H_2O \xrightarrow{(warm)} ArOH + N_2 + HCl$ (phenol)

Coupling reactions (N_2 retained):

$ArN_2^+ + C_6H_5OH \rightarrow Ar–N=N–C_6H_4OH$ (azo dye — coloured!)

$ArN_2^+ + C_6H_5NH_2 \rightarrow Ar–N=N–C_6H_4NH_2$ (azo dye)

Why diazonium salts are so important: They allow introduction of groups (–F, –Cl, –Br, –I, –CN, –OH, –H) that cannot be directly introduced onto a benzene ring! They are the key intermediate for aromatic synthesis.

Important Definitions

Term	Definition
Amine	Organic derivative of ammonia where H atoms are replaced by alkyl/aryl groups
Diazotisation	Conversion of 1° aromatic amine to diazonium salt using $NaNO_2$ + HCl at 0-5°C
Coupling Reaction	Reaction of diazonium salt with activated aromatic compound to form azo dye
Carbylamine Reaction	Test for 1° amine using $CHCl_3$ + KOH → foul-smelling isocyanide
Hofmann Degradation	Conversion of amide to amine with one less carbon using Br_2/NaOH

Solved Examples — NCERT Based

Example 1: Basicity Comparison

Q: Arrange in increasing order of basicity: $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Solution:

$C_6H_5NH_2$ is weakest (lone pair delocalised into ring). NH_3 is next. Among aliphatic: 2° > 1° in aqueous solution (balance of inductive and solvation effects).

$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

Example 2: Conversion via Diazonium Salt

Q: Convert aniline to chlorobenzene.

Solution:

Step 1: $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow_{(0\text{-}5°C)} C_6H_5N_2^+Cl^-$ (diazonium salt)

Step 2: $C_6H_5N_2^+Cl^- + CuCl/HCl \rightarrow \mathbf{C_6H_5Cl} + N_2$ (Sandmeyer reaction)

Example 3: Hinsberg Test

Q: How can you distinguish between ethylamine, diethylamine, and triethylamine using Hinsberg reagent?

Solution:

Treat each with $C_6H_5SO_2Cl$ (Hinsberg reagent):

Ethylamine (1°): Forms sulphonamide → dissolves in NaOH (due to acidic –NH)

Diethylamine (2°): Forms sulphonamide → does NOT dissolve in NaOH (no acidic H on N)

Triethylamine (3°): No reaction with Hinsberg reagent

Example 4: Gabriel Synthesis

Q: Prepare propan-1-amine using Gabriel synthesis.

Solution:

Phthalimide + KOH → potassium phthalimide

Potassium phthalimide + $CH_3CH_2CH_2Br$ → N-propylphthalimide

N-propylphthalimide + N_2H_4 (hydrazine) → **$CH_3CH_2CH_2NH_2$** (propan-1-amine) + phthalhydrazide

Important Questions for Board Exams

1 Mark Questions

1. Why is aniline a weaker base than methylamine?
2. What is the carbylamine reaction?
3. What is diazotisation?
4. Name the reagent used in Hinsberg test.

2 Mark Questions

1. How do primary, secondary and tertiary amines react with nitrous acid?
2. Explain why $(CH_3)_3N$ is a weaker base than $(CH_3)_2NH$ in aqueous solution.
3. Write the Gabriel phthalimide synthesis reaction for methylamine.
4. Give the Hofmann bromamide degradation reaction.

3 Mark Questions

1. What are diazonium salts? How are they prepared? Write any 4 reactions.
2. How will you distinguish between 1°, 2° and 3° amines using Hinsberg test?
3. Compare the basicity of methylamine, dimethylamine, aniline and ammonia with reasons.

5 Mark Questions

1. What are amines? Discuss their classification and preparation (any 3 methods). Compare their basic character.
2. Describe the chemistry of diazonium salts: preparation, Sandmeyer reaction, coupling reactions, and importance in synthesis.

Quick Revision Points

- Amines: 1° (RNH_2), 2° (R_2NH), 3° (R_3N)
- Gabriel synthesis: only 1° amines, not aromatic amines
- Hofmann degradation: amide → amine (1 less C)
- Basicity (aq): 2° > 1° > 3° > NH_3 >> aniline
- Aniline weak base: lone pair delocalised into ring
- Carbylamine test: 1° amines only → foul smell of isocyanide
- Hinsberg: 1° dissolves in NaOH, 2° doesn't, 3° no reaction
- Diazonium salt: $ArNH_2$ + $NaNO_2$ + HCl at 0-5°C
- Sandmeyer: ArN_2^+ + CuX/HX → ArX (Cl, Br, CN)
- Coupling: diazonium + phenol/amine → azo dye

← Previous: Aldehydes, Ketones and Carboxylic Acids

Next: Biomolecules →