Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH₃ molecule by alkyl/aryl group(s).

In the IUPAC system, the amines are regarded as alkanamines, e.g.,

Structure

The nitrogen atom in amine is sp³-hybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.

Methods of Preparation of Amines
Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking large excess of NH₃.

Order of reactivity of halides ‘with amines is RI > RBr > RCI.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

(iv) Schmidt reaction
(v) Reduction of amides

\[ R-C\text{-}NH}_2 \xrightarrow{(i) \text{LiAlH}_4} R\text{-}CH}_2\text{NH}_2 \]

It only produces 1° amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(viii) Hofmann bromamide degradation reaction

\[ R-C\text{-}NH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O} \]

In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAlH\(_4\)/ether.

Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell.
2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
3. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
4. Boiling points order primary > secondary > tertiary
5. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

**Basic Strength of Amines**

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the $K_b$ (dissociation constant of base), higher is the basicity of amines.

Lesser the $pK_b$, higher is the basicity of amines.

Aliphatic amines ($\text{CH}_3\text{NH}_2$) are stronger bases than $\text{NH}_3$ due to the electron releasing $+/-$ effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows

$$\text{(C}_2\text{H}_5\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$$

$$\text{(CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$$

Aromatic amines are weaker bases than aliphatic amines and $\text{NH}_3$, due to the fact that the electron pair on the nitrogen atom is involved in resonance with the $\pi$-electron pairs of the ring.

Electron releasing groups (e.g., $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$ etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like $-\text{NO}_2$, $-\text{X}$, $-\text{CN}$ etc.) tend to decrease the same.

o-substituted aromatic amines are usually weaker bases than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to steric and electronic factors.

**Chemical Properties of Amines**

(i) **Alkylation** All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.

\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{C}_2\text{H}_5\text{Br} \xrightarrow{-\text{HBr}} (\text{C}_2\text{H}_5)_2\text{NH} \xrightarrow{-\text{HBr}} (\text{C}_2\text{H}_5)_3\text{N} \xrightarrow{+ \text{C}_2\text{H}_5\text{Br}} (\text{C}_2\text{H}_5)_4\text{NB}r
\]

Aromatic amines also undergo alkylation as given below.

[Visit www.ncerthelp.com](http://www.ncerthelp.com) (Visit for all ncert solutions in text and videos, CBSE syllabus, note and many more)
(ii) Acylation
\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{CH}_3\text{COCl} \xrightarrow{\text{Base}} \text{C}_2\text{H}_5\text{N} - \text{C} - \text{CH}_3 + \text{HCl}
\]
\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{CH}_3\text{C} = \text{O} \rightarrow \text{C}_2\text{H}_5\text{N} - \text{C} - \text{CH}_3 + \text{CH}_3\text{COOH}
\]

(iii) Benzoylation
\[
\text{CH}_3\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{Pyridine}} \text{CH}_3\text{NHCOC}_6\text{H}_5 + \text{HCl}
\]
Benzoylation of aniline is known as Schotten Baumann reaction.

(iv) Carbylamine reaction [only by 1° amines]
\[
\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{Heat}} \text{R-N} \equiv \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}
\]
isoxyanide
(a bad smelling compound)

MIC or methyl isocyanate gas (CH₃-N=C=O) was responsible for Bhopal gas tragedy in December 1984.

(v) Reaction with nitrous acid
\[
\text{RNH}_2 + \text{HNO}_2 \xrightarrow{\text{NaNO}_2 + \text{HCl}} [\text{RN}_2\text{Cl}] \xrightarrow{\text{H}_2\text{O}} \text{ROH} + \text{N}_2 + \text{HCl}
\]
Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.
\[
\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{NaNO}_2 + 2\text{HCl}} 273-278 \text{K} \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}
\]
benezene diazonium chloride
But secondary and tertiary amines react with nitrous acid in different manner.

Methyl amine give dimethyl ether with HNO₂.

**(vi) Reaction with aryl sulphonyl chloride** [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.

![Reaction with aryl sulphonyl chloride](image)

Tertiary amines does not react with benzenesulphonyl chloride.

**(vii) Reaction with aldehydes** Schiff base is obtained.

![Reaction with aldehydes](image)

**(viii) Electrophilic substitution reactions** Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and para-positions.

![Electrophilic substitution reactions](image)
To prepare monosubstituted derivative, activating effect of \(-\text{NH}_2\) group must be controlled. It can be done by protecting the \(-\text{NH}_2\) group by acetylation with acetic anhydride.

\[
\begin{align*}
\text{NH}_2 & \quad \text{H-N-C-CH}_3 \\
& \quad \text{Br}_2 \quad \text{CH}_3\text{COOH} \\
& \quad \text{NH}_2 \\
& \quad \text{Br} \\
& \quad \text{OH}^- \quad \text{or H}^+ \\
& \quad \text{(p-bromoaniline)}
\end{align*}
\]

(b) Nitration Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.

\[
\begin{align*}
\text{NH}_2 & \quad \text{H-N-C-CH}_3 \\
& \quad \text{HNO}_3, \text{H}_2\text{SO}_4, \text{288 K} \\
& \quad \text{NHCOCH}_3 \\
& \quad \text{OH}^- \quad \text{or H}^+ \\
& \quad \text{(p-nitroaniline)}
\end{align*}
\]

In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.
(d) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence behave like a strong deactivating group for further chemical reaction.

(ix) **Oxidation** Use of different oxidising agents gives different products.

**e.g.,**

<table>
<thead>
<tr>
<th>Oxidising agent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidified KMnO₄ (or Na₂C₂O₇ + CuSO₄ + dil acid)</td>
<td>Aniline black (a dye)</td>
</tr>
<tr>
<td>Chronic acid (Na₂C₂O₇ + Conc. H₂SO₄)</td>
<td>p-benzoquinone</td>
</tr>
<tr>
<td>Caro's acid (H₂SO₃)</td>
<td>Nitrobenzene and nitrosobenzene</td>
</tr>
<tr>
<td>Conc. nitric acid</td>
<td>Decomposes</td>
</tr>
</tbody>
</table>

**Separation of Mixture of Amines** (1°, 2° and 3°)

(a) Fractional distillation This method is based on the boiling points of amines and is used satisfactorily in Industry.

(b) Hofmann’s method Diethyloxalate is called Hofmann’s reagent with which mixture of amines is treated.
1° amine forms solid dialkyl oxamide \((\text{CONHR})_2\)

2° amine forms liquid dialkyl oxamic ester \((\text{CONR}_2\text{COOC}_2\text{H}_5)\)

3° amines do not react

(c) Hinsberg’s method see chemical reactions.

**Benzene Diazonium Chloride** \((\text{C}_6\text{H}_5\text{N}_2^+;\text{Cl}^-)\)

**Preparation** (Diazotisation reaction)

\[
\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273-278 \text{K}} \text{C}_6\text{H}_5\text{N}==\text{N}==\text{Cl} + \text{NaCl} + 2\text{H}_2\text{O}
\]

The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

**Properties**

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

**Stability of Arenediazonium salts**

It is relatively more stable than the alkyl diazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:
Various resonating structures of arenediazonium ion

**Chemical Reactions**

\[ \text{Cu}^+, \text{H}_3\text{PO}_4/\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_3\text{PO}_3 + \text{HCl} \]  
(Hypophosphorous acid)

\[ \text{C}_6\text{H}_4\text{N}_3^+\text{Cl}^- \rightarrow \text{C}_8\text{H}_6 + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO} \text{ (Deamination)} \]

\[ \text{CuBr} / \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{N}_2 \]  
(bromobenzene)
Alkyl Cyanides’

These compound have formula RCN. These are the derivatives of RCN.

According to IUPAC system, cyanides are named as ‘alkane nitrile’, e.g.,

\[
\text{C}_2\text{H}_5\text{CN}, \quad \text{C}_6\text{H}_5\text{CN}
\]

butanenitrile benzenenitrile
Methods of Preparation

(i) From alkyl halides

\[ RX + KCN(alc) \xrightarrow{100^\circ C} RCN + RNC \]

(ii) From acid amides

\[ RCONH_2 \xrightarrow{P_2O_5, \Delta \text{ or } -H_2O} RC\equiv N \]

Physical properties

1. These are neutral compound with pleasant odour, similar to bitter almonds.
2. These are soluble in water as well as organic solvents.
3. These are poisonous but less than HCN.

Chemical Properties

(i) Hydrolysis

\[ RCN \xrightarrow{\text{Alk} \text{ H}_2\text{O}_2} RCONH_2 \xrightarrow{\text{H}_2\text{O}} RCOOH + NH_3 \]

(ii) Reduction

\[ RCN + 4 [H] \xrightarrow{Na+CsH_6OH} RCH_2NH_2 \]
\[ RCN + 4 [H] \xrightarrow{LiAlH_4} RCH_2NH_2 \]

Alkyl isocyanides (RNC)

According to IUPAC system, these are named as ‘alkane isonitrile’

e.g., CH\(_3\)NC methyl isonitrile
C₆H₅NC benzene isonitrile

Methods of Preparation

(a) From alkyl halides

\[ R-X + AgCN \xrightarrow{C_2H_5OH, \Delta} RNC + RCN \]

(b) Carbylamine reaction

\[ RNH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} RNC + 3KCl + 3H_2O \]

(c) From N-alkyl formamide

\[ R-NH-C-H \xrightarrow{POCl_3, Pyridine} R-N=\overset{=}C + H_2O \]

Physical Properties

1. These are colourless unpleasant smelling liquids.
2. These are soluble in organic solvents but insoluble in water.

Chemical Properties

(i) Hydrolysis

\[ R-N=\overset{=}C + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH \]

(ii) Reduction

\[ RN=\overset{=}C + 4[H] \xrightarrow{Na/C_2H_5OH or Ni or Pt} RNHCH₃ \]

(iii) Addition reaction Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.

\[ RNC + S \rightarrow RNCS \]
\[ RNC+HgO \rightarrow RNCO + Hg \]
\[ RNC+O_3 \rightarrow RNCO \]

(iv) Isomerisation At 250°C, it isomerises to nitrile.

\[ RNC \xrightarrow{\Delta} RCN \]
Nitro Compounds

These are obtained by replacing one H of hydrocarbon by -NO₂ group.

These are named according to IUPAC system as ‘nitro alkane’.

Methods of Preparation

(i) From alkyl halides

\[ RX + AgNO_2 \xrightarrow{\Delta} RNO_2 + AgX \]

(ii) Nitration Nitrating mixture is conc HNO₃ + conc H₂SO₄.

Physical Properties

1. These are colourless pleasant smelling liquids.
2. Their boiling point are much higher than isomeric alkyl nitriles.
3. These are less soluble in water but readily soluble in organic solvents.

Chemical Properties

(i) Reduction With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.
Nitrobenzene gives different products with different reagents and in different mediums.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Reagent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Sn/HCl</td>
<td>aniline</td>
</tr>
<tr>
<td>Neutral</td>
<td>Zn/NH₄Cl</td>
<td>N-phenyl hydroxylamine</td>
</tr>
<tr>
<td>Alkaline</td>
<td>Na₂AsO₄/NaOH</td>
<td>azoxybenzene ( (C₆H₅N ≡ NC₆H₅) )</td>
</tr>
<tr>
<td>Alkaline</td>
<td>Zn/NaOH, CH₃OH</td>
<td>azobenzene</td>
</tr>
<tr>
<td>Alkaline</td>
<td>Zn/NaOH, C₂H₅OH</td>
<td>hydrazobenzene</td>
</tr>
<tr>
<td>Metallic hydride</td>
<td>LiAlH₄</td>
<td>aniline</td>
</tr>
<tr>
<td>Metallic hydride</td>
<td>dil H₂SO₄</td>
<td>( ρ )-aminophenol</td>
</tr>
</tbody>
</table>

(ii) Action of HNO₂

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

\[
RCH₂NH₂ + HNO₂ \xrightarrow{\text{H}_2\text{O}} RCH(\text{NO}_2) + \text{HNO}_3 \quad \text{nitrolic acid}
\]

\[
\xrightarrow{\text{NaOH}} RCH(\text{NO}_2) \rightarrow RCH(\text{NO}_2)_2 \quad \text{(red)}
\]

2° nitroalkanes give pseudonitroil with HNO₂.

\[
R₂CH(\text{NO}_2) + HNO₂ \xrightarrow{\text{H}_2\text{O}} R₂C\text{NO}_2 \quad \text{pseudonitroil}
\]
3° nitroalkanes does not react with HNO₂

(iii) Nef carbonyl synthesis Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H₂SO₄ at room temperature. This reaction is called Nef carbonyl synthesis.

(iv) Electrophilic substitution On nitration, nitrobenzene gives m-dinitrobenzene (as -NO₂ is a m-directing group and strongly deactivating).

(v) Nucleophilic substitution reaction -NO₂ group activates the ring towards nucleophilic substitution.