SYLLABUS

1. Structure of amino groups (primary, secondary and tertiary)
2. Nomenclature
3. Important methods of preparation
4. Physical properties – Basic character of amines
5. Chemical reactions
6. Separation of primary, secondary and tertiary amines
7. Some commercially important compounds

1 General Introduction

Amines may be regarded as amino derivatives of hydrocarbons. They may also be regarded as derivatives of
ammonia in which one or more H-atoms have been replaced by alkyl or aryl groups. Depending upon whether
one, two or all the three H-atoms of ammonia have been replaced by alkyl or aryl groups, amines are classified as
primary (1°), secondary (2°) and tertiary (3°) respectively.

\[
\begin{align*}
\text{H} & \quad \text{Primary amine (1° Amine)} \\
\text{R – N – H} & \\
\text{R} & \quad \text{Secondary amine (2° Amine)} \\
\text{R – N – R} & \\
\text{R} & \quad \text{Tertiary amine (3° Amine)} \\
\text{R} & \quad \text{(where R may be alkyl or aryl group)}
\end{align*}
\]

Thus, the characteristic or the functional group for primary, secondary and tertiary amines are – NH\(_2\) (amino) >
NH (imino) and > N – (tertiary nitrogen atom) respectively.

Amines are further divided into two categories:

1. Aliphatic amines: Amines in which the nitrogen atom is directly linked to one, two or three (same or different)
alkyl groups are called aliphatic amines. These may be primary, secondary or tertiary. For example,

\[
\begin{align*}
\text{C}_2\text{H}_5\text{NH}_2 & \quad \text{Diethylamine (2°)} \\
\text{C}_2\text{H}_5 & \quad \text{Aniline (1°)} \\
\text{C}_6\text{H}_{5}\text{N} & \quad \text{Diphenylamine (2°)} \\
\text{C}_2\text{H}_5 & \quad \text{Triethylamine (3°)}
\end{align*}
\]

2. Aromatic amines: These are of two types:

(a) Arylamines or nucleus substituted amines: Amines in which the nitrogen atom is directly linked to one,
two or three (same or different) aromatic rings or aryl groups are called arylamines. Like aliphatic amines,
arylamines can also be primary, secondary or tertiary. For example,

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{N} & \quad \text{Triphenylamine (3°)}
\end{align*}
\]
(b) **Aralkylamines or side chain substituted amines**: Amines in which the nitrogen atom is attached to the side chain/s of one, two or three (same or different) aromatic rings are called *aralkylamines*. These can also be primary, secondary and tertiary. For example,

\[
\begin{align*}
\text{Benzylamine (1°)} & \quad \text{(C}_6\text{H}_5\text{CH}_2\text{)}_2\text{NH} \\
\text{Dibenzylamine (2°)} & \quad \text{(C}_6\text{H}_5\text{H}_2\text{)}_2\text{N} \\
\text{Tribenzylamine (3°)} & \quad \text{(C}_6\text{H}_5\text{CH}_2\text{)}_3\text{N}
\end{align*}
\]

**Simple and mixed amines**: Secondary and tertiary amines are further classified as simple and mixed amines respectively according as all the alkyl or aryl groups attached to the nitrogen atom are same or at least two are different.

**Simple amines**:

\[
\begin{align*}
\text{Dimethylamine (Secondary)} & \quad (\text{CH}_3)_2\text{NH} \\
\text{Triethylamine (Tertiary)} & \quad (\text{CH}_3\text{CH}_2)_3\text{N} \\
\text{Diphenylamine (Secondary)} & \quad (\text{C}_6\text{H}_5\text{H}_2)_2\text{NH} \\
\text{Tribenzylamine (Tertiary)} & \quad (\text{C}_6\text{H}_5\text{CH}_2)_3\text{N}
\end{align*}
\]

**Mixed amines**:

\[
\begin{align*}
\text{Ethylmethylamine (Secondary)} & \quad \text{CH}_3\text{CH}_2\text{H} = \text{N} \\
\text{Ethylmethyl} – n – \text{propylamine (Tertiary)} & \quad \text{CH}_3\text{CHCHCH}_3 = \text{N}
\end{align*}
\]

**Quaternary ammonium compounds**: Apart from three types of amines, there is another class of compounds called *quaternary ammonium compounds*. These compounds may be regarded as derivatives of ammonium salts in which all the four H-atoms of the ammonium ion have been replaced by alkyl or aryl groups. For example,

\[
\begin{align*}
\text{Tetramethylammoniumiodide} & \quad [(\text{CH}_3)_4\text{N}]^+\text{I}^- \\
\text{Tetraethylammoniumhydroxide} & \quad [(\text{CH}_3\text{CH}_2)_4\text{N}]^+\text{OH}^- \\
\text{Trimethylphenylammoniumbromide} & \quad \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Br}^-
\end{align*}
\]

### 2. Electronic Structure of the Amino Group

The ground state of N-atom has five electrons in the valence shell and thus needs three more electrons to complete its octet. These three electrons are acquired by mutual sharing of electrons with monovalent atoms/groups. In 1° amines, N-atom shares its three electrons, one each with the carbon atom of the alkyl (or aryl) group and two H-atoms; in 2° amines with carbon atoms of two alkyl (or aryl) groups and one hydrogen while in 3° amines with carbon atoms of three alkyl (or aryl) groups. In all these, the remaining two electrons are present as a lone pair of electrons. Thus, the electronic structures of 1°, 2° and 3° amines are shown below:

\[
\begin{align*}
\text{1° Amines} & \quad \text{R} \cdots \text{N} \cdots \text{H} \\
\text{2° Amines} & \quad \text{R} \cdots \text{N} \cdots \text{R} \\
\text{3° Amines} & \quad \text{R} \cdots \text{N} \cdots \text{H}
\end{align*}
\]

In terms of orbitals, the ground state electronic configuration of N is
$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. The 2 $s$-orbital and three 2 $p$-orbitals hybridize to form four $sp^3$-hybridized orbitals; three of these orbitals contain one electron each while the fourth contains a lone pair of electrons. In 1° amines, one of the three half filled $sp^3$-orbitals overlaps with $sp^3$-hybridized orbital of the carbon atom of the alkyl group (or $sp^2$-hybridized orbital of the carbon atom of the alkyl group) and the remaining two overlap with $s$-orbitals of hydrogen atoms thereby forming one C–N and two N–H $\sigma$-bonds.

In 2° amines, two of the three $sp^3$-hybridized orbitals of N overlap with $sp^3$-hybridized orbitals of the carbon of two alkyl groups (or $sp^2$-hybridized orbitals of carbon atoms of the aryl groups) and one with $s$-orbital of the H-atom thereby forming two C–N and one N–H, $\sigma$-bonds.

In 3° amines, all the three $sp^3$-hybridized orbitals of N overlap with $sp^3$-hybridized orbitals of carbon atoms of three alkyl groups (or $sp^2$-hybridized orbitals of the carbon atoms of the aryl groups). In all these three amines, the fourth $sp^3$-orbital contains the lone pair of electrons as shown in Fig. 15.2.1.

Since lone-pair-lone pair repulsions are much greater than bond pair-bond pair repulsions, therefore, the bond angle between any two adjacent H-atoms or alkyl groups decreases from the tetrahedral angle of 109°28′ to 107° in 1° and 2° amines. However, in case of 3° amines, due to steric hindrance between the three bulky alkyl groups, the bond angle increases from 107° in ammonia to 108° in trimethylamine. Thus, all the three amines (1°, 2° or 3°) like NH$_3$ have pyramidal shape.

3 Nomenclature

1. **Aliphatic amines:** In the common system, aliphatic amines are named by the following two methods.

   (i) According to one method, aliphatic amines are called **alkylamines**. The common names of aliphatic primary amines are then obtained by adding the suffix amine to the name of the alkyl group attached to the nitrogen atom. In case of mixed secondary and tertiary amines, the names of the alkyl groups are arranged in alphabetical order and the suffix amine is then added. However for simple secondary and tertiary amines respectively, the prefixes di and tri are used before the name of the alkyl group.

   Similarly, the names of **aralkylamines** are derived by adding the suffix amine to the name of the aralkyl group (or groups arranged in alphabetical order).

   (ii) According to the second system, aliphatic amines are called **aminoalkanes**. In this system, the primary amines are named by adding the prefix amino to the name of the parent alkane corresponding to the longest possible straight chain. The position of the amino group and that of the substituents, if any are indicated by the arabic numerals with the carbon atom bearing the amino group getting the lowest possible number.

   Secondary and tertiary amines are named respectively as **N-alkylaminoalkanes** and **N-alkyl N-alkylaminoalkanes** (or N, N-dialkylaminoalkanes in case the two substituent alkyl groups are the same). The largest alkyl group forms a part of the aminoalkane while the smaller alkyl groups are considered as substituents. The prefixes N-and N, N-simply mean that the alkyl groups are attached to the nitrogen atom rather than to a carbon atom.

   In case of aralkylamines, the position of the aryl group is indicated by a suitable number.

   In the IUPAC system, aliphatic amines are called **alkanamines**. These names are obtained by removing the final ‘e’ from the name of the corresponding alkane and adding the suffix amine.

   It may be noted here that regardless of the system of nomenclature, the complete name of an amine is always written as one word.
The common and IUPAC names of some aliphatic amines are given below:

<table>
<thead>
<tr>
<th>AMINE</th>
<th>COMMON NAME</th>
<th>IUPAC NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NH}_2 )</td>
<td>Methylamine or Aminomethane</td>
<td>Methanamine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{NH}_2 )</td>
<td>Ethylamine or Aminoethane</td>
<td>Ethanamine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{NH}_2 )</td>
<td>( n )-Propylamine or 1-Aminopropane</td>
<td>1-Propanamine or Propan-1-amine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{CH}_2\text{NH}_2 )</td>
<td>Isopropylamine or 2-Aminopropane</td>
<td>Propan-2-amine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{NH} )</td>
<td>Dimethylamine or N-Methylaminomethane</td>
<td>N-Methylmethanamine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{NH} )</td>
<td>Ethylmethylamine or N-Methylethananmine</td>
<td>N-Methylethanamine</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{NH} )</td>
<td>Trimethylamine or N, N Dimethylaminomethane</td>
<td>N, N-Dimethylaminomethane</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}_2\text{H}_2\text{NH} )</td>
<td>Deithylmethylamine or N-Ethyl-N-methylaminoethane</td>
<td>N-Ethyl-N-methylaminoethane</td>
</tr>
</tbody>
</table>

2. **Aromatic amines.** In the common system, aromatic amines are called **arylamines**. The name of an individual amine is then obtained by adding the suffix **amine** to the name of the aryl group. More often they are named as derivatives of the simplest aromatic amine called **aniline**.

In the IUPAC system, the simplest aromatic amine is called **benzenamine** and other amines are named as derivatives of this amine.

It may be noted here again that the complete name of an amine is always written as one word.

The common and IUPAC names of some arylamines are given below:
For sake of further illustration, the common and IUPAC names of some complex aliphatic and aromatic amines are given below:

Common: 2–Methyl–3–aminopentanes
IUPAC : 2–Methyl–3–pentanamine

\[
\begin{align*}
\text{CH}_3 - \text{NH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
&\text{\textit{Common:} 2–(N–Methylamino)–4–methylpentane} \\
&\text{\textit{IUPAC:} N,4–Dimethylpentan–2–amine}
\end{align*}
\]

Common : N–Ethyl–N–methylaniline
IUPAC : N–Ethyl–N–methylbenzenamine

\[
\begin{align*}
\text{CH}_3 - \text{NH} - \text{CH} - \text{CH}_3 \\
\text{Common : 1–Phenylaminoethane} \\
\text{IUPAC : 1–Phenylethananmine}
\end{align*}
\]
In case of polyfunctional compounds, the amino group is considered to be a substituent. For example,
\[
\begin{align*}
2 & \quad H_2N\text{–CH}_2\text{CH}_2\text{–OH} \\
1 & \quad 2\text{–Aminoethanol}
\end{align*}
\[
\begin{align*}
4 & \quad NH_2\text{–C}_2\text{H}_2\text{C}_2\text{H}_2\text{–COOH} \\
3 & \quad 4\text{–Aminobutanoic acid}
\end{align*}
\]
Since amines are better known by their common names, therefore, in this unit, we shall be using common names more frequently though here and there some IUPAC names have also been given.

4 Isomerism in Amines

Amines show the following four types of isomerism:

1. **Chain isomerism**: Aliphatic amines containing four or more carbon atoms show chain isomerism. For example,

\[
\begin{align*}
\text{CH}_3\text{–CH}–\text{CH}_2–\text{CH}_2–\text{NH}_2 & \quad \text{Butan–1–amine} \\
\text{CH}_3\text{–CH}–\text{CH}_2–\text{CH}_2–\text{NH}_2 & \quad \text{Butan–2–amine}
\end{align*}
\]

2. **Metamerism**: Aliphatic amines having the same molecular formula but different alkyl groups on either side of the nitrogen atom show metamerism. For example,

\[
\begin{align*}
\text{CH}_3\text{CH}_2–\text{NH}–\text{CH}_2\text{CH}_3 & \quad \text{Diethylamine} \\
\text{CH}_3\text{–NH}–\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{Methyl n–propylamine} \\
\text{CH}_3\text{–NH}–\text{CH(CH}_3)_2 & \quad \text{Isopropylmethylamine}
\end{align*}
\]

are metamers.

3. **Position isomerism**: Aliphatic amines containing three or more carbon atoms show position isomerism due to difference in position of the amino group. For example,

\[
\begin{align*}
\text{(i) CH}_3\text{CH}_2\text{CH}_2\text{–NH}_2 & \quad \text{Propan–1–amine} \\
\text{Propan–2–amine} \\
\text{(ii) CH}_3\text{CH}_2\text{CH}_2\text{–NH}_2 & \quad \text{Butan–1–amine} \\
\text{Butan–2–amine}
\end{align*}
\]

Similarly aromatic amines also show position isomerism. For example,

\[
\begin{align*}
o\text{-Toluidine} & \quad m\text{-Toluidine} \\
p\text{-Toluidine}
\end{align*}
\]

4. **Functional isomerism**: Primary, secondary and tertiary amines having the same molecular formula show functional isomerism among themselves. For example,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2–\text{NH}_2 & \quad \text{Propylamine (1°)} \\
\text{CH}_3\text{CH}_2–\text{NH}–\text{CH}_3 & \quad \text{Ethylmethylamine (2°)} \\
(CH)_3\text{N} & \quad \text{Trimethylamine (3°)}
\end{align*}
\]

are functional isomers.
5 Methods of Preparation

Amines are generally prepared by the following methods:

1. **From alkyl halides and ammonia or amines (Hofmann's ammonolysis Method).** Amines are produced when an alcoholic solution of ammonia (or an amine) and an alkyl halide is heated in a sealed tube at 373 K. This reaction is called ammonolysis and usually gives a mixture of primary, secondary and tertiary amines along with some quaternary ammonium salts as illustrated below:

   ![Diagram of ammonolysis reaction]

   This reaction is a typical example of a nucleophilic substitution reaction in which ammonia (or the amine) acts as a nucleophile due to the presence of a lone pair of electrons on the nitrogen atom. The ammonia molecule first attacks an alkyl halide molecule to form a primary amine salt which then further reacts with ammonia to give the corresponding free primary amine and the ammonium halide (reaction i).

   The primary amine thus formed being almost as nucleophilic and basic as ammonia attacks another molecule of alkyl halide to form a secondary amine (reaction ii) which, in turn, reacts with another molecule of alkyl halide to form a tertiary amine (reaction iii) and finally quaternary ammonium salt (reaction iv).

   The actual composition of the reaction mixture depends upon the ratio of the alkyl halide and ammonia used. If excess of alcoholic ammonia is used, primary amine is the main product. However, the mixtures obtained are very complex and difficult to separate. Therefore, this method is used in the manufacture of amines and not as a laboratory preparation.

   **Limitation:** This method cannot be used for the preparation of arylamines since arylhalides are much less reactive than alkyl halides towards nucleophilic substitution reactions.

2. **Reduction of nitro compounds:** Both aliphatic and aromatic primary amines can be easily prepared by the reduction of the corresponding nitro compounds. This reduction can be achieved in a number of ways as discussed below:

   (i) **Catalytically with hydrogen in the presence of Raney Ni, Pt or Pd as catalyst at room temperature.**

   $$\text{R – NO}_2 \text{ or } \text{Ar – NO}_2 + 3\text{H}_2 \xrightarrow{\text{Room temp.}} \text{R – NH}_2 \text{ or } \text{Ar – NH}_2 + 2\text{H}_2\text{O}$$
For example,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NO}_2 + 3\text{H}_2 & \overset{\text{Raney Ni or Pt}}{\text{\longrightarrow}} \text{CH}_3\text{CH}_2\text{-NH}_2 + 2\text{H}_2\text{O} \\
\text{Nitroethane} & \text{Ethylamine}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_4\text{-NO}_2 + 3\text{H}_2 & \overset{\text{Raney Ni or Pt}}{\text{\longrightarrow}} \text{C}_6\text{H}_5\text{-NH}_2 + 2\text{H}_2\text{O} \\
\text{Nitrobenzene} & \text{Aniline}
\end{align*}
\]

(ii) With an active metal such as, Fe, Sn, Zn etc. and conc. hydrochloric acid. For example,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{-NO}_2 + 6[\text{H}] & \overset{\text{Sn/HCl}}{\text{\longrightarrow}} \text{CH}_3\text{CH}_2\text{-NH}_2 + 2\text{H}_2\text{O} \\
\text{Nitroethane} & \text{Ethylamine}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_4\text{-NO}_2 + 6[\text{H}] & \overset{\text{Fe/HCl or Sn/HCl}}{\text{\longrightarrow}} \text{C}_6\text{H}_5\text{-NH}_2 + 2\text{H}_2\text{O} \\
\text{Nitrobenzene} & \text{Aniline}
\end{align*}
\]

A mixture of SnCl₂ and conc. HCl has also been used for the reduction of aromatic nitro compounds.

The reduction of nitro compounds to primary amines is one of the most convenient methods for the preparation of aromatic primary amines since they cannot be prepared from the corresponding aryl halides on treatment with ammonia. The required nitro compounds can be easily prepared by the nitration of arenes.

(iii) With lithium aluminium hydride (LiAlH₄)

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{-NO}_2 & \overset{\text{LiAlH}_4/\text{Ether}}{\text{\longrightarrow}} \text{CH}_2\text{CH}_2\text{-NH}_2 \\
\text{Nitroethane} & \text{Lithylamine}
\end{align*}
\]

3. **By the reduction of nitriles (or cyanides) and isonitriles (isocyanides):** Aliphatic and aralkyl primary amines can be easily prepared by the reduction of the corresponding nitriles either catalytically with H₂ and Raney nickel or chemically with lithium aluminium hydride or sodium and alcohol (reduction with sodium and alcohol is called Mendius reduction).

For example,

\[
\begin{align*}
\text{CH}_3\text{C}≡\text{N} & \overset{\text{H}_2/\text{Raney Ni or LiAlH}_4}{\text{\longrightarrow}} \text{CH}_3\text{CH}_2\text{-NH}_2 \\
\text{Acetonitrile} & \text{Ethylamine}
\end{align*}
\]

\[
\begin{align*}
\text{C}≡\text{N} & \overset{\text{H}_2/\text{Raney Ni or LiAlH}_4}{\text{\longrightarrow}} \text{CH}_2\text{NH}_2 \\
\text{Benzonitrile} & \text{Benzyamine}
\end{align*}
\]
Reduction of isocyanides gives secondary amines i.e., N-methylamines.

\[
\text{R} - \text{N} \equiv \text{C} + \text{2H}_2 \text{or 4[H]} \xrightarrow{\text{Raney Ni or LiAlH}_4} \text{R} - \text{NH} - \text{CH}_3 \quad \text{N-Methylalkylamine (2°)}
\]

\[
\text{CH}_2\text{CH}_2 - \text{N} \equiv \text{C} + \text{2H}_2 \text{or 4[H]} \xrightarrow{\text{Raney Ni or LiAlH}_4} \text{CH}_2\text{CH}_2 - \text{NH} - \text{CH}_3 \quad \text{Ethylmethylamine}
\]

\[
\text{C}_6\text{H}_5 - \text{N} \equiv \text{C} + \text{2H}_2 \text{or 4[H]} \xrightarrow{\text{Raney Ni or LiAlH}_4} \text{C}_6\text{H}_5 - \text{NH} - \text{CH}_3 \quad \text{Methylphenylamine or N-Methylaniline}
\]

**Limitation**: This method can be used only for the preparation of 2° amines in which one of the groups is always methyl.

**Synthetic importance**: Since alkyl cyanides can be easily prepared by the action of alcoholic NaCN or KCN on alkyl halides, this gives us an excellent method for converting alkyl halides into primary amines having one carbon atom more than the parent alkyl halides. Thus,

\[
\text{R} - \text{X} \quad \text{Alkylhalide} \xrightarrow{\text{KCN (aq)}} \xrightarrow{\text{KX}} \text{R} - \text{CN} \quad \text{Alkylcyanide} \xrightarrow{\text{LiAlH}_4 \text{/ Ether}} \text{RCH}_2 - \text{NH}_2 \quad \text{1° Amine}
\]

**4. Reduction of amides**: Primary, secondary and tertiary amines can be prepared by the reduction of the corresponding amides with lithium aluminium hydride (LiAlH₄).

\[
\text{CH}_3\text{CONH}_2 \quad \text{Acetamide} \xrightarrow{\text{LiAlH}_4 \text{/ Ether}} \text{CH}_3\text{CH}_2\text{NH}_2 \quad \text{Ethylamine}
\]

\[
\text{C}_6\text{H}_5\text{CONH}_2 \quad \text{Benzamide} \xrightarrow{\text{LiAlH}_4 \text{/ Ether}} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \quad \text{Benzylamine}
\]

Secondary and tertiary amines can be prepared by the reduction of secondary and tertiary amides respectively.

\[
\text{CH}_3\text{CONHCH}_3 \quad \text{N-Methylacetamide(2°)} \xrightarrow{\text{LiAlH}_4 \text{/ Ether}} \text{CH}_3\text{CH}_2\text{NHCH}_3 \quad \text{Ethylmethylamine(2°)}
\]

\[
\text{CH}_3\text{CON} \quad \text{N,N-Dimethylacetamide (3°)}
\]

**5. Reduction of oximes**: Primary amines can be prepared by the reduction of oximes of aldehydes and ketones with either lithium aluminium hydride or with sodium and alcohol.

\[
\text{RCH} = \text{NOH} + 4\text{[H]} \xrightarrow{\text{LiAlH}_4 \text{ or Na/C}_2\text{H}_5\text{OH \text{/ Ether}}} \text{RCH}_2 - \text{NH}_2 + \text{H}_2\text{O} \quad \text{1° Amine}
\]

\[
\text{R} - \text{C} = \text{NOH} + 4\text{[H]} \xrightarrow{\text{LiAlH}_4 \text{ or Na/C}_2\text{H}_5\text{OH \text{/ Ether}}} \text{R} - \text{CH} - \text{NH}_2 - \text{H}_2\text{O} \quad \text{1° Amine}
\]
For example,

\[
\text{CH}_3\text{CH} = \text{NOH} \quad \xrightarrow{\text{LiAlH}_4 \text{ or Na/C}_2\text{H}_5\text{OH}} \quad \text{CH}_3\text{CH}_2 - \text{NH}_2 \quad \text{Ethylamine}
\]

\[
\text{CH}_3\text{Cl} \quad \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \quad \text{LiAlH}_4 \quad \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \quad \text{CH}_3 \quad \xrightarrow{\text{LiAlH}_4} \quad \text{CH}_3 - \text{NH}_2 \quad \text{Isopropylamine}
\]

6. **By Hofmann degradation of primary amides**: (*Hofmann bromamide reaction*). When a primary amide is treated with an aqueous solution of potassium hydroxide and bromine (or potassium hypobromite, KOBr), it gives a primary amine which has one carbon atom less than the original amide:

\[
\text{R} - \text{CONH}_2 + \text{Br}_2 + 4\text{KOH} \underset{\text{1}^\circ \text{Amine}}{\longrightarrow} \text{R} - \text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}
\]

For example,

\[
\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{Br}_2 + 4\text{KOH} \quad \xrightarrow{\text{1}^\circ \text{Amine}} \quad \text{CH}_3\text{CH}_2 - \text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}
\]

This reaction is widely used for stepping down or descent of homologous series.

7. **Gabriel phthalimide reaction**: This is a very convenient method for the preparation of pure aliphatic and aralkyl primary amines. Potassium phthalimide (obtained by the action of ethanolic solution of KOH on phthalimide) on treatment with a suitable alkyl or aralkyl halide gives N-substituted phthalimides. These upon subsequent hydrolysis with dil. HCl under pressure or with alkali give primary amines.

Phthalaldehyde can again be converted into phthalimide and used over and over again.

Similarly benzylamine can be prepared by using benzyl chloride and glycine (NH\textsubscript{2}CH\textsubscript{2}COOH) by using chloroacetic acid in place of ethyl iodide in the above reaction.

**Hydrazinolysis** (*Cleavage by hydrazine*) of N-alkylphthalimides is a more convenient and efficient method as compared to acidic/basic hydrolysis for obtaining 1\textsuperscript{°} amines using *Gabriel synthesis*. For example,
8. **By reductive amination of aldehydes and ketones:** Aldehydes and ketones react with ammonia in presence of a reducing agent such as H₂/Ni or NaBH₃CN (sodium cyanoborohydride) to form primary amines. The reaction, in fact, occurs through the intermediate formation of an *imine*. For example,

\[
\text{R} - \text{CH} = \text{O} + \text{NH}_3 \xrightarrow{\Delta - \text{H}_2\text{O}} \left[ \begin{array}{c} \text{R} - \text{CH} = \text{NH} \\ \text{R} - \text{C} = \text{NH} \end{array} \right] \xrightarrow{\text{H}_2/\text{Ni or NaBH}_3\text{CN}} \text{R} - \text{CH}_2 - \text{NH}_2 \]

For example,

\[
\begin{align*}
\text{CH}_3 - \text{CH} = \text{O} + \text{NH}_3 & \xrightarrow{\Delta - \text{H}_2\text{O}} \left[ \begin{array}{c} \text{CH}_3 - \text{CH} = \text{NH} \\ \text{CH}_3 - \text{C} = \text{NH} \end{array} \right] \\
\xrightarrow{\text{H}_2/\text{Ni or NaBH}_3\text{CN}} & \text{CH}_3 - \text{CH}_2 - \text{NH}_2
\end{align*}
\]

*This reaction leading to the conversion of an aldehyde or a ketone to the corresponding amine on treatment with ammonia in presence of a reducing agent, i.e. H₂/Ni or NaBH₃CN is called reductive amination.*

If instead of NH₃, a primary amine is used in the above reaction, secondary amine is obtained. For example,

\[
\begin{align*}
\text{CH}_3 - \text{C} = \text{O} + \text{H}_2\text{NC}_6\text{H}_5 & \xrightarrow{\Delta - \text{H}_2\text{O}} \left[ \begin{array}{c} \text{CH}_3 - \text{C} = \text{NH} \\ \text{CH}_3 - \text{C} = \text{N}\text{C}_6\text{H}_5 \end{array} \right] \\
\xrightarrow{\text{H}_2/\text{Ni or NaBH}_3\text{CN}} & \text{CH}_3 - \text{CH} = \text{NH}_2
\end{align*}
\]

**CONCEPTUAL QUESTIONS**

Q.1. *tert*-Butylamine cannot be prepared by the action of NH₃ on *tert*-butyl bromide. Explain why?

Ans. *tert*-Butyl bromide being a 3° alkyl halide on treatment with a base (*i.e.* NH₃) prefers to undergo elimination rather than substitution. Therefore, the product is isobutylene rather than *tert*-butylamine.

Q.2. Can we prepare aniline by Gabriel-phthalimide reaction?

Ans. No. The preparation of aniline by Gabriel-phthalimide reaction requires the treatment of pot. phthalimde with C₆H₅Cl or C₆H₅Br. Since aryl halides do not undergo nucleophilic substitution under ordinary laboratory conditions, therefore, C₆H₅Cl or C₆H₅Br does not react with pot. phthalimde to give N-phenylphthalimide and hence aniline cannot be prepared by this method.
Q.3. Suggest chemical reactions for the following conversions:

(i) Cyclohexanol $\rightarrow$ Cyclohexylamine

(ii) \( n \)-Hexanenitrite $\rightarrow$ 1-Aminopentane

Ans. (i) \[ \begin{array}{c}
\text{Cyclohexanol} \\
\text{Oxidation} \quad \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \quad \text{Cyclohexanone} \\
\end{array} \]

(ii) \[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{N} \\
\text{O} \\
\Delta \quad \rightarrow \\
\text{CH}_3(\text{CH}_2)_4\text{CONH}_2 \\
\text{Hexanamide} \\
\end{array} \]

\[ \text{NaOH/Br}_3 \quad \xrightarrow{\text{(Hofmann bromamide reaction)}} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\
\rightarrow \quad \text{1-Aminopentane} \]

6 Physical Properties:

Some important physical properties of amines are discussed below:

1. **Solubility**: All the three classes of aliphatic amines (1°, 2° and 3°) form H-bonds with water. As a result, lower aliphatic amines are soluble in water. Methylamine and ethylamine are gases but they are highly soluble in water. That is why they are sold in the market as their 34% aqueous solutions. However, as the size of the alkyl group increases (with increase in molecular mass), the solubility decreases due to a corresponding increase in the hydrocarbon part of the molecule. The borderline solubility is reached with amines of about six carbon atoms in the molecule. However, amines are quite soluble in organic solvents such as benzene, ether, alcohol etc. Aromatic amines, on the other hand, are insoluble in water. This is due to the larger hydrocarbon part which tends to retard the formation of H-bonds. Thus, aniline is almost insoluble in water. However, it is quite soluble in benzene, ether, alcohol etc.

2. **Boiling points**: Amines have higher boiling points than hydrocarbons of comparable molecular masses. This is due to the reason that amines being polar, form intermolecular H-bonds (except tertiary amines which do not have hydrogen atoms linked to the nitrogen atom) as shown below and thus exist as associated molecules.

\[ \begin{array}{c}
\text{R} \\
\text{H} \\
\text{O} \\
\text{R} \\
\end{array} \quad \begin{array}{c}
\text{R} \\
\text{H} \\
\text{N} \\
\text{R} \\
\end{array} \quad \begin{array}{c}
\text{R} \\
\text{H} \\
\text{N} \\
\text{R} \\
\end{array} \]

(where R is any alkyl or aryl group)
Further, since the electronegativity of nitrogen is lower than that of oxygen, therefore, amines form weaker H-bonds as compared to alcohols and carboxylic acids. As a result, amines are not associated to the extent of alcohols and carboxylic acids and hence the boiling points of amines are lower than those of alcohols and carboxylic acids of comparable molecular masses. For example, ethylamine (mol. mass 45) boils at 292 K while ethyl alcohol (mol. mass 46) and formic acid (mol. mass 46) boil at 351 K and 374 K respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. mass</th>
<th>b.p. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅NH₂</td>
<td>45</td>
<td>292</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>44</td>
<td>231</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>46</td>
<td>351</td>
</tr>
<tr>
<td>HCOOH</td>
<td>46</td>
<td>374</td>
</tr>
</tbody>
</table>

3. **Colour and odour:** Pure amines are almost colourless but develop colour on keeping in air for long time. This is due to the reason that amines, especially aromatic amines, are readily oxidised in air to form coloured oxidation products.

Lower aliphatic amines are gases and smell very much like ammonia but the higher amines are liquids with fishy odours. Lower aromatic amines are liquids having characteristic unpleasant odours but the higher ones are low melting solids which are almost odourless.

### CONCEPTUAL QUESTIONS

**Q.1.** Although trimethylamine and n-propylamine have the same molecular weight, the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

**Ans.** n-Propylamine has two H-atoms on the N-atom and hence undergoes *intermolecular H-bonding* thereby raising the boiling point.

Trimethylamine, (CH₃)₃N being a 3° amine does not have a H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low.

4. **Basic Character of Amines:** All the three classes of amines (1°, 2° and 3°) because of the presence of a lone pair of electrons on the nitrogen atom behave as bases. Their basic character is shown by the following reactions.

(i) **Reaction with water:** Due to the presence of a lone pair of electrons on the N-atom, amines like NH₃ are stronger bases than H₂O. Therefore, they react with water to form alkyl or arylammonium hydroxides which ionize to furnish hydroxyl ions:

\[
\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ \text{OH}^- \rightleftharpoons \text{RNH}_3 + \text{OH}^{-}
\]

*(cf. NH₃ + H₂O \rightleftharpoons \text{NH}_4^+ \text{OH}^-)*

*Due to the formation of hydroxide ions, the aqueous solutions of amines are basic in nature.*

The presence of the hydroxide ions in the aqueous solutions of amines is detected by the precipitation of metal hydroxides such as aluminium hydroxide (*gelatinous white ppt.*) or ferric hydroxide (*brown ppt.*) when AlCl₃ or FeCl₃ is added to their aqueous solutions.

\[
\text{AlCl}_3 + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 + 3\text{Cl}^- \quad \text{(Gelatinous white ppt.)}
\]

\[
\text{FeCl}_3 + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 + 3\text{Cl}^- \quad \text{(Brown ppt.)}
\]
(ii) **Reaction with acids:** Being basic, all types of amines react with mineral acids such as HCl, HNO₃, H₂SO₄ etc. to form soluble salts.

\[
\begin{align*}
\text{RNH}_2 + \text{HCl} & \rightarrow \text{RNH}_2\text{Cl}^- \\
1^\circ \text{Amine} & \quad \text{Alkylammoniumchloride} \\
2\text{RNH}_2 + \text{H}_2\text{SO}_4 & \rightarrow [\text{RNH}_2\text{HSO}_4^-] \\
2^\circ \text{Amine} & \quad \text{Dialkylammoniumsulphate} \\
\text{R}_3\text{N} + \text{HNO}_3 & \rightarrow \text{R}_3\text{NH}^+\text{NO}_3^- \\
3^\circ \text{Amine} & \quad \text{Trialkylammoniumnitrate}
\end{align*}
\]

For example

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HCl} & \rightarrow [\text{CH}_3\text{CH}_2\text{NH}_3]^+\text{Cl}^- \\
\text{Ethylamine} & \quad \text{Ethylammoniumchloride} \\
(\text{CH}_3)_2\text{NH} + \text{HCl} & \rightarrow [(\text{CH}_3)_2\text{CH}_2\text{NH}_3]^+\text{Cl}^- \\
\text{Dimethylamine} & \quad \text{Dimethylammoniumchloride} \\
\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} & \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^- \\
\text{Aniline} & \quad \text{Aniliniumchloride} \\
\text{cf. } \text{NH}_3 + \text{HCl} & \rightarrow \text{NH}_4^+\text{Cl}^-
\end{align*}
\]

*These amine salts are ionic compounds. They are non-volatile solids and generally decompose before their melting points are reached. They are soluble in water but are insoluble in non-polar solvents such as benzene, chloroform, ether etc. In contrast, higher amines are generally insoluble in water but are soluble in organic solvents. This difference in solubility behaviour of amines and their salts is often used to detect amines and separate (or purify) them from non-basic compounds.*

Further, amines react with chloroplatinic acid (H₂PtCl₆) to form insoluble salts called *chloroplatinates*.

\[
\begin{align*}
2\text{RNH}_2 + \text{H}_2\text{PtCl}_6 & \rightarrow (\text{RNH}_3)^+\text{PtCl}_6^2- \\
\text{Chloroplatininate}
\end{align*}
\]

Chloroplatinates of amines are used for the determination of equivalent and molecular masses of amines.

**Explanation of the basic character of amines**

(a) **Aliphatic amines.** All the three classes of aliphatic amines contain a lone pair of electrons on the nitrogen atom. Therefore, they have a strong tendency to donate this lone pair of electrons to electron acceptors. As a result, all the amines behave as bases.

**Aliphatic amines are stronger bases than ammonia.** All the three classes of aliphatic amines are stronger bases than ammonia. This is due to the reason that alkyl groups are electron-donating groups. As a result, the electron density on the nitrogen atom increases and thus they can donate the lone pair of electrons more easily than ammonia.

![Diagram of aliphatic amines and their basic character](image-url)
On the basis of the electron-donating inductive effect of the alkyl groups alone, the expected order of basicity in aqueous solution should be

3° Amine > 2° Amine > 1° Amine > NH₃

However, the actual order of basicity in aqueous solution is

2° Amine > 1° Amine > 3° Amine > NH₃.

The reason why the actual order is different from the expected order can be explained as follows:

The basicity of an amine in aqueous solution does not entirely depend upon the electron density on the N-atom but also depends upon the stability of the conjugate acid formed by accepting a proton from the solution. The stability of the conjugate acid, in turn, depends upon the extent of H-bonding. Obviously, greater the number of H-atoms on N-atom, more stable is the conjugate acid. Thus, the conjugate acid of a 1° amine is the most stable since it has three H-atoms which can form H-bonds with H₂O; the conjugate acid of the 2° amine is less stable since it has two H-atoms while that of the 3° amines is the least stable since it has only one H-atom which can form H-bonds with H₂O as shown below:

\[
\text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+ \\
\text{(Most stable)}
\]

\[
\text{R}_2\text{NH} - \text{H}^+ \rightleftharpoons \text{R}_2\text{NH}_2^+ \\
\text{(Less stable)}
\]

Thus, on the basis of the stability of the conjugate acids alone, the basic strength of amines in aqueous solution should follow the order:

1° Amine > 2° Amine > 3° Amine, i.e.,

\[
\text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}
\]

In actual practice, these two opposing factors balance each other in case of 2° amines. This makes 2° amines to be the strongest. 3° Amines are weaker bases than 2° amines since their conjugate acids are less stable than 2° amines since their conjugate acids are less stable than those of 2° amines while 1° amines are less basic than 2° amines since the electron density on the N-atom is less and hence the lone pair of electrons is less easily available for protonation.

**ADITIONAL INFORMATION**

In gas phase or in non-aqueous solvents such as chlorobenzence etc., the solvation effects, i.e., the stabilization of the conjugate acid due to H-bonding are absent and hence in these media the basicity of amines depends only on the +I-effect of the alkyl groups. Thus, the basicity of 1°, 2° and 3° amines in the gas phase or in non-aqueous solvents follows the order: 3° Amine > 2° Amine > 1° Amine > NH₃

The basic strength of an amine is determined by its basicity constant, \(K_b\).

\[
\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNAH}_3^+ + \text{OH}^-
\]
According to the law of mass action, the equilibrium constant $K$ may be expressed as

$$K = \frac{[\text{RNH}_2^+] [\text{OH}^-]}{[\text{RNH}_2] [\text{H}_2\text{O}]}$$

Since water is taken in large excess, its concentration, $[\text{H}_2\text{O}]$ remains constant, therefore, the above equation may be rewritten as

$$\frac{[\text{RNH}_2^+] [\text{OH}^-]}{[\text{RNH}_2]} = K [\text{H}_2\text{O}] = K_b$$

Evidently, greater the value of $K_b$, stronger is the base.

**$pK_b$ values.** Alternatively, the basicity of an amine can also be expressed in terms of its $pK_b$ value which is the negative logarithm of the basicity constant, $K_b$ i.e., $pK_b = -\log K_b$

Evidently, smaller the value of $pK_b$, stronger is the base.

The $K_b$ and $pK_b$ values of some amines are given below:

<table>
<thead>
<tr>
<th>AMINE</th>
<th>$K_b$</th>
<th>$pK_b$</th>
<th>AMINE</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.75</td>
<td>(CH$_3$CH$_2$)$_3$N</td>
<td>$5.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{NH}_2$</td>
<td>$4.5 \times 10^{-4}$</td>
<td>3.38</td>
<td>$\text{C}_6\text{H}_5\text{NH}_2$</td>
<td>$4.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>(CH$_3$)$_2$NH</td>
<td>$5.4 \times 10^{-4}$</td>
<td>3.27</td>
<td>$\text{C}_6\text{H}_5\text{NHCH}_3$</td>
<td>$5.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$N</td>
<td>$0.6 \times 10^{-4}$</td>
<td>4.22</td>
<td>$\text{C}_6\text{H}_5$</td>
<td>$11.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CH}_2\text{NH}_2$</td>
<td>$5.1 \times 10^{-4}$</td>
<td>3.29</td>
<td>$\text{C}_6\text{H}_5 - \text{CH}_2\text{NH}_2$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>(CH$_3$CH$_2$)$_2$NH</td>
<td>$10.0 \times 10^{-4}$</td>
<td>3.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) Aromatic amines are weaker bases than ammonia and aliphatic amines. Aromatic amines are far less basic than ammonia and aliphatic amines.

For example, aniline ($K_b = 4.2 \times 10^{-10}$) is a weaker base, than ammonia ($K_b = 1.8 \times 10^{-5}$) as well as ethylamine ($K_b = 5.1 \times 10^{-4}$). The weaker basic character of aniline may be explained as follows:

(i) **Due to resonance in aniline.** Aniline may be regarded as a resonance hybrid of the following structures:

As a result of resonance, the lone pair of electrons on the nitrogen atom gets delocalized over the benzene ring and thus is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia.

(ii) **Lower stability of anilinium ion than aniline.** If we compare the relative stabilities of aniline and the anilinium ion, which aniline forms by accepting a proton, we find that whereas aniline is a resonance hybrid of five structure, i.e. I–V, anilinium ion is a resonance hybrid of only two structures, i.e. VI and VII. Structures analogous to III, IV and V are not possible in this case due to localization of the lone pair of electrons on nitrogen because of the formation of an additional nitrogen-hydrogen bond.
In other words, aniline is more stable than anilinium ion. Hence, aniline has very little tendency to combine with a proton to form anilinium ion. On the other hand, in case of ammonia and aliphatic amines, delocalization of the lone pair of electrons on the nitrogen atom by resonance is not possible. Furthermore, the electron density on the nitrogen atom is increased by electron-donating inductive effect of the alkyl groups. As result, ammonia and aliphatic amines are much stronger bases than aniline and other aromatic amines.

**Effect of substituents on the basicity of aromatic amines.** The basic character of an aromatic amine depends upon the nature of the substituents present in the benzene ring.

(i) In general, electron-donating groups such as – CH$_3$, – OCH$_3$, – NH$_2$ etc. increase the basicity while electron-withdrawing substituents such as NO$_2$, – CN, – X (halogen) etc. decrease the basicity of amines.

Electron-donating group (EDG) releases electrons, stabilizes the conjugate acid (cation) and thus increases the basic strength.

\[
\text{NH}_2 + \text{H}^+ \rightarrow \text{NH}_3^+ \\
\text{EDG}
\]

(where EDG = CH$_3$, – OCH$_3$, – NH$_2$ etc.)

Electron-withdrawing group (EWG) withdraws electrons, destabilizes the conjugate acid (cation) and thus decreases the basic strength.

\[
\text{NH}_2 + \text{H}^+ \rightarrow \text{NH}_3^+ \\
\text{EWG}
\]

(where EWG = – NO$_2$, – CN, – X (halogen) etc.)

(ii) The base-strengthening effect of the electron-donating groups and base-weakening effect of the electron-withdrawing groups is more marked at p-positions than at m-positions. Thus,

\[
\begin{align*}
\text{p-Toluidine} & \quad (K_b = 12 \times 10^{-10}) \\
\text{m-Toluidine} & \quad (K_b = 5.0 \times 10^{-10}) \\
\text{p-Nitroaniline} & \quad (K_b = 1.0 \times 10^{-13}) \\
\text{m-Nitroaniline} & \quad (K_b = 2.9 \times 10^{-13})
\end{align*}
\]
(iii) o-Substituted anilines are usually weaker bases than anilines regardless of the nature of the substituent whether electron-donating or electron-withdrawing. This is called ortho-effect and is probably due to a combination of steric and electronic factors. Thus, the basicity of o-, m- and p-toluidines relative to aniline follows the sequence.

\[
\begin{align*}
\text{p-Toluidine} & \quad (K_b = 12.0 \times 10^{-10}) \\
\text{m-Toluidine} & \quad (K_b = 5 \times 10^{-10}) \\
\text{Aniline} & \quad (K_b = 4.2 \times 10^{-10}) \\
\text{o-Toluidine} & \quad (K_b = 2.6 \times 10^{-10})
\end{align*}
\]

Similarly, the basicity of o-, m- and p-nitroanilines relative to aniline follow the sequence:

\[
\begin{align*}
\text{Aniline} & \quad (K_b = 4.2 \times 10^{-10}) \\
\text{m-Nitroaniline} & \quad (K_b = 2.9 \times 10^{-13}) \\
\text{p-Nitroaniline} & \quad (K_b = 1.0 \times 10^{-13}) \\
\text{o-Nitroaniline} & \quad (K_b = 6.0 \times 10^{-14})
\end{align*}
\]

**Effect of substituents on the nitrogen atom.** When the hydrogen atoms of the amino group in primary arylamines are replaced by electron-donating alkyl groups, the basicity of the resultant arylamine increases. For example, **N-methylaniline is a stronger base than aniline and N, N-dimethylaniline is even stronger than N-methylaniline.** Thus,

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{N, N – Dimethylaniline} \\
& \quad (pK_b = 8.92)
\end{align*}
\]

On the other hand, replacement of hydrogen atoms(s) of the amino group by electron-withdrawing groups (such as phenyl groups) decreases the basic character. For example, **aniline is a stronger base than diphenylamine which, in turn, is a much stronger base than triphenylamine.** Thus,

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} & \quad \text{Aniline} \\
& \quad (pK_b = 9.38) \\
\text{C}_6\text{H}_5\text{–} & \quad \text{N} \quad \text{–} \quad \text{CH}_3 \\
\text{N} & \quad \text{Methylaniline} \\
& \quad (pK_b = 13.2) \\
\text{C}_6\text{H}_5 \text{–} & \quad \text{NH}_2 \\
\text{Aniline} & \quad (pK_b = 9.38)
\end{align*}
\]

**Basic character of aralkylamines.** The lone pair of electrons on the N-atom of aniline is delocalized over the benzene ring. However, in aralkylamines, the lone pair of electrons on the N-atom is not conjugated with the benzene ring and hence is not delocalized. In other words, the lone pair of electrons on the N-atom in aralkylamines is more easily available for protonation than that on the N-atom of aniline. Thus, **aralkylamines are stronger bases than arylamines.** For example, benzylamine is a stronger base than aniline.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 & \quad \text{Benzylamine} \\
& \quad (pK_b = 4.70) \\
\text{C}_6\text{H}_5\text{NH}_2 & \quad \text{Aniline} \\
& \quad (pK_b = 9.38)
\end{align*}
\]
Further due to electron-withdrawing inductive effect (or –I-effect) of the aryl group, the one pair of electrons on the N-atom of aralkylamines is less easily available for protonation than that on the N-atom of alkylamines and ammonia. Therefore, \textit{aralkylamines are weaker bases than alkylamines and ammonia}. For example,

\[
\begin{align*}
\text{CH}_3\text{NH}_2 \quad & \quad > \quad \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \quad > \quad \text{NH}_3 \\
\text{(}pK_b=3.28\text{)} \quad & \quad \text{(}pK_b=4.70\text{)} \quad \text{Ammonia} \quad \text{(}pK_b=4.75\text{)}
\end{align*}
\]

7 Chemical Reactions

Some important chemical reactions of amines are discussed below:

1. Reactions with electrophilic\[2\]

Due to the presence of a lone pair of electrons on the nitrogen atom, amines like ammonia are good nucleophiles and hence react with a variety of \textit{electrophiles} (electron-deficient compounds) such as metal ions, alkyl halides, acid chlorides, acid anhydrides, chloroform etc. as discussed below:

1. \textbf{Reaction with metal ions}: Like ammonia, amines also form soluble co-ordination compounds with transition metal ions such as Ag$^{2+}$ ions etc. Thus, silver chloride dissolves in methylamine solution due to the formation of a soluble complex salt as shown below:

\[
\text{AgCl (Insoluble) + 2CH}_3\text{NH}_2 \longrightarrow [\text{CH}_3\text{NH}_2]^{\text{+}}\text{Cl}^{-} \quad \text{Ag} \leftarrow \text{NH}_2\text{CH}_3^{\text{+}}\text{Cl}^{-} \quad \text{or} \quad [\text{Ag(CH}_3\text{NH}_2)_2]^{\text{+}}\text{Cl}^{-}
\]

Similarly like ammonia, amines such as methylamine, ethylamine etc. react with Cu$^{2+}$ ions to form a deep blue solution due to the formation of the following soluble co-ordination compound.

\[
\text{CuCl}_2 + 4\text{CH}_3\text{NH}_2 \rightarrow \text{Methylamine} \quad \text{Bis (methylamine) silver (I) chloride (Soluble)}
\]

\[
\text{(cf.} \text{AgCl} + 2\text{NH}_3 \longrightarrow [\text{Ag(NH}_3)_2]^{\text{+}}\text{Cl}^{-}
\]

\[
\text{CuSO}_4 + 4\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{Ethylamine} \quad \text{[Cu(CH}_3\text{CH}_2\text{NH}_2)_4]^{2+}\text{SO}_4^{2-} \quad \text{Tetrakis(ethylamine)copper(II)sulphate} \quad \text{(Soluble)}
\]

\[
\text{(cf.} \text{CuCl}_2 + 4\text{NH}_3 \longrightarrow [\text{Cu(NH}_3)_4]^{2+}(\text{Cl}^{-})_2
\]

\[
\text{NH}_2\text{CH}_3
\]

\[
\text{H}_3\text{CH}_2\text{N} \rightarrow \text{Cu} \leftarrow \text{NH}_2\text{CH}_3
\]

\[
\text{Tetrakis(methylamine)copper(II)chloride (Soluble)}
\]\n
\[
\text{NH}_2\text{CH}_3
\]

\[
\text{H}_3\text{CH}_2\text{N} \rightarrow \text{Cu} \leftarrow \text{NH}_2\text{CH}_3
\]

\[
\text{Tetrakis(ethylamine)copper(II)sulphate (Soluble)}
\]

\[
\text{(cf.} \text{CuCl}_2 + 4\text{NH}_3 \longrightarrow [\text{Cu(NH}_3)_4]^{2+}(\text{Cl}^{-})_2
\]

\[
\text{NH}_2\text{CH}_3
\]

\[
\text{H}_3\text{CH}_2\text{N} \rightarrow \text{Cu} \leftarrow \text{NH}_2\text{CH}_3
\]

\[
\text{Tetrakis(ethylamine)copper(II)sulphate (Soluble)}
\]

\[
\text{(cf.} \text{CuCl}_2 + 4\text{NH}_3 \longrightarrow [\text{Cu(NH}_3)_4]^{2+}(\text{Cl}^{-})_2
\]
2. **Alkylation – Reaction with alkyl halides.** *The process of introducing an alkyl group into any molecule is called alkylation.*

(a) With aliphatic amines. All the three classes of amines undergo alkylation when treated with alkyl halides. Thus a primary amine can be converted into secondary and tertiary amines and finally into quaternary ammonium salts. For example, when treated with excess of ethyl bromide, ethylamine undergoes alkylation to produce a mixture of diethylamine, triethylamine and tetaethyl-ammonium bromide.

\[
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3\text{CH}_2)_2\text{NH} + \text{HBr}
\]

Diethylamine

\[
(\text{CH}_3\text{CH}_2)_2\text{NH} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3\text{CH}_2)_3\text{N} + \text{HBr}
\]

Triethylamine

\[
(\text{CH}_3\text{CH}_2)_3\text{N} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3\text{CH}_2)_4\text{N}^+ \text{Br}^-
\]

Tetraethylammonium bromide

Quaternary ammonium halides on treatment with moist silver oxide or methanolic KOH are converted into their corresponding hydroxides

\[
[R_4\text{N}]^+\text{X}^- + \text{AgOH} \rightarrow [R_4\text{N}]\text{OH}^- + \text{AgX}\text{↓}
\]

These quaternary ammonium hydroxides are white deliquescent crystalline solids which are as strongly basic as NaOH or KOH.

(b) With aromatic amines. Aniline when heated with excess of methyl iodide under pressure gives first N-methylaniline, then N, N-dimethylaniline and finally trimethylanilinium iodide.

This process of converting an amine (1°, 2° or 3°) into its quaternary ammonium salt on treatment with excess of an alkyl halide is called exhaustive alkylation. However, if the alkyl halide used is methyl iodide, the process is commonly known as exhaustive methylation.

When the quarternary ammonium halide obtained through exhaustive methylation of any amine is treated with moist silver oxide, silver halide gets precipitated and the corresponding quarternary ammonium hydroxide is produced. This when heated to 400 K or above undergoes an elimination reaction to produce an alkene, trimethylamine and water. For example,
This pyrolysis of quarternary ammonium hydroxides to produce alkenes is called **Hofmann elimination reaction** and is used for determination of the structure of amines.

If all the alkyl groups in quaternary ammonium hydroxide are methyl groups *i.e.*, tetramethylammonium hydroxide, then pyrolysis does not produce an alkene but instead gives trimethylamine and methanol.

\[
(\text{CH}_3)_4\text{N}^+\text{OH}^- \xrightarrow{400\text{K}} (\text{CH}_3)_3\text{N} + \text{CH}_3\text{OH}
\]

---

**ADITIONAL INFORMATION**

In **Hofmann elimination reaction**, it is the less sterically hindered \(\beta\)-hydrogen that is removed and hence in this reaction, less substituted alkenes are the major products. For example,

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 & \quad \xrightarrow{\Delta} \quad \text{CH}_2 = \text{CHCH}_2\text{CH}_3 + \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \\
\text{2 – Chlorobutane} & \quad \xrightarrow{\Delta} \quad \text{2 – Butene (80%)} \\
\text{2 – Butanol} & \quad \xrightarrow{\Delta} \quad \text{1 – Butene (20%)}
\end{align*}
\]

In contrast during saytzeff elimination reaction, i.e., base-catalysed dehydrohalogenation of alkyl halides and acid-catalysed dehydration of alcohols, it is always the more highly substituted alkene that predominates. For example,

\[
\begin{align*}
\text{Cl} & \quad \xrightarrow{\text{KOH (aq), } \Delta} \quad \text{O} \\
\text{2 – Chlorobutane} & \quad \xrightarrow{\text{KOH (aq), } \Delta} \quad \text{2 – Butene (80%)} \\
\text{OH} & \quad \xrightarrow{\text{KOH (aq), } \Delta} \quad \text{1 – Butene (20%)}
\end{align*}
\]

3. **Acylation**– Reaction with acid chlorides and acid anhydrides. The process of introducing an acyl group \(\text{O} (R – \text{C}–)\) into any molecule is called **acylation**.

(a) **With aliphatic amines.** Primary and secondary amines (but not tertiary amines because they do not contain a \(\text{H}\)-atom on the \(\text{N}\)-atom) undergo acylation when treated with acid chlorides or acid anhydrides to form \(\text{N}\)-substituted amides. Thus,

\[
\begin{align*}
\text{Acidchloride} & \quad \xrightarrow{1^\circ\text{Amine}} \quad \text{N-Substitutedamide} \\
\text{R} & \quad \xrightarrow{1^\circ\text{Amine}} \quad \text{R’CNHR} + \text{HCl}
\end{align*}
\]
If acetyl chloride or acetic anhydride is used as an acylating agent, an acetyl (CH₃–CO–) group is introduced into the molecule and the process is called **acetylation**. For example, acetylation of ethyamine gives N-ethylacetamide and that of diethylamine gives N,N-diethylacetamide.

\[
\text{RCOCl + R}_2\text{NH} \rightarrow \text{RNHR} + \text{HCl}
\]

**Acetylation**

If acetyl chloride or acetic anhydride is used as an acylating agent, an acetyl (CH₃–CO–) group is introduced into the molecule and the process is called **acetylation**. For example, acetylation of ethyamine gives N-ethylacetamide and that of diethylamine gives N,N-diethylacetamide.

\[
\text{Acetyl chloride} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{CH}_3\text{C}–\text{NH}_2 + \text{HCl}
\]

Acetyl chloride

\[
\text{C}_2\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}
\]

Acetic anhydride

(b) **With aromatic amines:** Acylation of aromatic amines is usually carried out in presence of a catalyst. For example, acetylation with acetyl chloride is carried out in presence of pyridine as catalyst while with acetic anhydride it is carried out in presence of acetic acid or a few drops of conc. H₂SO₄ as catalyst. Benzoylation of aromatic amines is, however, carried out in presence of aqueous NaOH solution as shown below:

\[
\text{Aniline} + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{CONH}2 + \text{HCl}
\]

Acetanilide or N-Phenylenethanamide

**Benzoylation** of compounds containing an active hydrogen atom such as alcohols, phenols and amines with benzoyl chloride in presence of dilute aqueous NaOH solution is called **Schotten Beumann reaction**.

4. **Reaction with aldehydes and ketones:** Primary amines react with aldehydes and ketones in presence of a trace of an acid as catalyst to produce azomethines called **Schiff’s bases or anils**.

\[
\text{RNH}_2 + \text{CHR} \rightarrow \text{RN} = \text{CHR} + \text{H}_2\text{O}
\]

**Schiff’s base or anil**
Schiff’s bases can be easily reduced to the corresponding secondary amines. Therefore, this method offers a convenient route for their preparation. For example,

\[
\text{CH}_3\text{CH}_2\text{N} = \text{CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{NH} - \text{CH}_2\text{CH}_3
\]

Secondary amines also react with aldehydes and ketones containing α-hydrogen atoms/s to form first carbinolamines which being unstable readily lose a molecule of H\(_2\)O to form stable enamines. For example,

\[
\text{R} - \text{C} - \text{R}' + \text{R}_2\text{NH} \xrightarrow{\text{C}_6\text{H}_5\text{PTS}} \text{Carbinolamine (unstable)} \xrightarrow{-\text{H}_2\text{O}} \text{R} - \text{C} - \text{R}' = \text{Enamine}
\]

The equilibrium is shifted in the forward direction by removing H\(_2\)O as an azeotrope with benzene. Thus, enamine formation is usually carried out by refluxing the benzene solution of an aldehyde or a ketone with a secondary amine in presence of a trace amount of an acid such as p-toluenesulphonic acid (PTS).

5. Reaction with chloroform–Carbylamine reaction or Isocyanide test. Both aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH produce isocyanides or carbylamines which have very unpleasant odours.

\[
\text{R} - \text{NH}_2 + \text{CHCl}_3 + 3\text{KOH(alc.)} \xrightarrow{\Delta} \text{R} - \text{N} = \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}
\]

For example,

\[
\text{CH}_3\text{CH}_2 - \text{NH}_2 + \text{CHCl}_3 + 3\text{KOH(alc.)} \xrightarrow{\Delta} \text{CH}_3\text{CH}_2 - \text{N} = \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}
\]

In contrast, secondary and tertiary amines (both aliphatic and aromatic) do not give this test. Therefore, this test is used to distinguish primary amines from secondary and tertiary amines.
II. Miscellaneous reactions: In addition to the two classes of reactions already discussed, amines give certain other reactions as described below:

1. **Reaction with nitrous acid**: Primary, secondary and tertiary amines react differently with nitrous acid. Since nitrous acid is unstable, it is prepared in situ by the action of dilute hydrochloric acid on sodium nitrite.

(a) **Primary amines**

(i) **Aromatic primary amines** react with nitrous acid at 273 – 278 K (0 – 5° C) to form arenediazonium salts. Thus,

\[
\text{NaNO}_2 + \text{HCl} \xrightarrow{\text{273–278K}} \text{HNO}_2 + \text{NaCl}
\]

\[
\begin{array}{c}
\text{NH}_2 \\
\text{Aniline}
\end{array}
\quad \xrightarrow{273–278K} \quad \begin{array}{c}
\text{N} \equiv \text{NCl}^- \\
\text{Benzenediazonium chloride}
\end{array}
\]

This reaction of converting aromatic primary amines into diazonium salts by treatment with a cold (273–278 K) solution of nitrous acid is called **diazotisation**: If, however, the temperature rises above 278 K, the initially formed diazonium salts decompose to form phenols.

\[
\text{C}_6\text{H}_5\text{N} + \text{HNO}_2 + \text{HCl} \xrightarrow{\text{H}^+; >278K} \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}
\]

(ii) **Aliphatic primary amines**, on the other hand, react with cold nitrous acid to give alcohols with the quantitative evolution of \( \text{N}_2 \) gas:

\[
\text{R – NH}_2 + \text{HONO} \xrightarrow{273–278K} \text{R – OH} + \text{N}_2 + \text{H}_2\text{O}
\]

eg.,

\[
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HONO} \xrightarrow{273–278K} \text{CH}_3\text{CH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}
\]

Since no other class of amines liberates \( \text{N}_2 \) gas on treatment with \( \text{HNO}_2 \), this reaction is used as a test for aliphatic primary amines.

Aliphatic primary amines like aromatic primary amines also react with nitrous acid in the cold (273–278 K) to form alkanediazonium salts. These, however, being unstable even in the cold (273–278 K) decompose to form a mixture of alcohols, alkenes, alkyl halides along with the evolution of \( \text{N}_2 \) gas:

\[
\text{HONO}/\text{HCl} \xrightarrow{273–278K} \text{Decompose (273–278K)} \quad \text{CH}_3\text{CH}_2\text{N} \equiv \text{NCl}^- \quad \text{Ethanediazonium chloride (Unstable)}
\]

\[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2 = \text{CH}_2 + \text{CH}_3\text{CH}_2\text{Cl} + \text{N}_2
\end{array}
\]

(b) **Secondary amines**: Both aliphatic and aromatic secondary amines react with nitrous acid to give \( \text{N} \)-nitrosoamines which being insoluble in dilute mineral acids separate out as yellow oily compounds:

\[
(\text{CH}_3\text{CH}_2)_2\text{NH} + \text{HONO} \xrightarrow{\text{Decompose (273–278K)}} (\text{CH}_3\text{CH}_2)_2\text{N} \equiv \text{NCl}^- + \text{H}_2\text{O}
\]

(\( \text{N-Nitrosodimethylamine (Yellow oil)} \))

\[
\begin{array}{c}
\text{CH}_3 \\
\text{N-Methylaniline}
\end{array}
\quad \text{NH} + \text{HONO} \xrightarrow{\text{Decompose (273–278K)}} \begin{array}{c}
\text{N} \equiv \text{N} \equiv \text{O} + \text{H}_2\text{O}
\end{array}
\]

(\( \text{N-Nitroso-N-methylaniline (Yellow oil)} \))
These N-nitrosoamines on warming with a crystal of phenol and a few drops of conc. H$_2$SO$_4$, form a green solution which when made alkaline with aqueous NaOH, turns deep blue and then red on dilution. This reaction is called **Libermann's nitroso reaction** and is used as a test for secondary amines.

**Chemistry of the test:** When a N-nitrosoamine is heated with an acid (H$_2$SO$_4$), the parent secondary amine is regenerated and nitrous acid is produced.

$$\text{C}_6\text{H}_4 - \text{N} = \text{N} = \text{O} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5 - \text{NH} - \text{CH}_3 + \text{HNO}_2$$

Nitrous acid thus reacts with phenol to form $p$-nitrosophenol (*benzenoid form*) which then changes to the *quinoid form*. This then condenses with another molecule of phenol to give indophenol hydrogen sulphate which is blue. On dilution, it changes to free indophenol which is red. With excess of NaOH, sodium salt of indophenol is produced which is blue.

(c) **Tertiary amines**: Aliphatic tertiary amines on reaction with nitrous acid form soluble nitrite salts while aromatic tertiary amines undergo electrophilic substitution reaction in the ring to form green-coloured $p$-nitrosoamines. For example,

$$\text{CH}_3\text{N,N-Dimethylaniline} + \text{HONO} \rightarrow \text{N}_{\text{green}}\text{Nitroso-N,N-Dimethylaniline (green)}$$

Thus, it is evident from the above discussion that reaction with nitrous acid can be used for the distinction of 1°, 2° and 3° amines and in some cases, it is also possible to determine whether the amine is aliphatic or aromatic.
2. **Reaction with Grignard reagents:** Primary and secondary amines (but not tertiary amines since they do not contain a N – H proton) react with Grignard reagents to form alkanes corresponding to the alkyl group of the Grignard reagent. Thus,

\[
\text{RNH}^–\text{H} + \text{R' – MgX} \rightarrow \text{R' – H} + \text{Mg} \left\langle \text{X} \right\rangle
\]

\[
\text{R}^\circ \text{N}^–\text{H} + \text{R' – MgX} \rightarrow \text{R' – H} + \text{Mg} \left\langle \text{X} \right\rangle
\]

**e.g.,**

\[
\text{CH}_3\text{CH}_2\text{NH} \quad \text{H} + \text{CH}_3\text{MgBr} \quad \text{CH}_3 + \text{Mg} \left\langle \text{Br} \right\rangle
\]

\[
(\text{CH}_2)_2\text{N}^–\text{H} + \text{CH}_3\text{MgI} \rightarrow \text{CH}_3\text{CH}_3 + \text{Mg} \left\langle \frac{\text{N}((\text{CH}_3)_2)}{\text{I}} \right\rangle
\]

3. **Reaction with carbon disulphide** (a) **With aliphatic amines.** When warmed with carbon disulphide, aliphatic primary amines form *dithioalkyl-carbamic acids* which decompose on heating with mercuric chloride to give *alkyl isothiocyanates* having a characteristic smell like that of mustard oil. For example,

\[
\text{RNH}_2 + \text{S} = \text{C} = \text{S} \quad \text{Warm} \quad \rightarrow \quad \text{RNH} – \text{C} = \text{SH} \quad \text{HgCl}_2 \quad \rightarrow \quad \text{R} – \text{N} = \text{C} = \text{S} + \text{HgS} + 2\text{HCl}
\]

**e.g.**

\[
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{S} = \text{C} = \text{S} \quad \text{Warm} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{NH} – \text{C} = \text{SH} \quad \text{HgCl}_2 \quad \rightarrow \quad \text{CH}_3\text{CH}_2 – \text{N} = \text{C} = \text{S} + \text{HgS} + 2\text{HCl}
\]

*This reaction is called Hofmann mustard oil reaction and is used as a test for primary amines.*

(b) **With aromatic amines:** Aromatic primary amines, however, react in a slightly different manner. For example, when aniline is heated with ethanolic CS\(_2\) and solid KOH, it gives N, N'-diphenylthiourea which upon treatment with conc. HCl gives phenyl isothiocyanate.

\[
\text{C}_6\text{H}_5 – \text{NH} – \text{H} + \text{S} = \text{C} = \text{S} + 2\text{KOH} \quad \Delta \quad \rightarrow \quad \text{C}_6\text{H}_5 – \text{NH} – \text{C} – \text{NH} – \text{C}_6\text{H}_5 + \text{K}_2\text{S} + 2\text{H}_2\text{O}
\]

\[
\text{S} + \quad \text{C}_6\text{H}_5 – \text{NH} – \text{C} – \text{NH} – \text{C}_6\text{H}_5 \quad \text{Cons. HCl}
\]

\[
\text{C}_6\text{H}_5 – \text{N} = \text{C} = \text{S} + \text{C}_6\text{H}_5 \text{NH}^+ \text{Cl}^–
\]

N, N' -Diphenylthiourea (or thiocarbanilide or *sym*-diphenylthiourea) is used as an accelerator during vulcanization of rubber.
4. **Reaction with phosgene or carbonyl chloride:** Primary and secondary aliphatic amines react with carbonyl chloride to form substituted ureas.

\[
\begin{align*}
2 \text{R} - \text{NH}_2 + \text{Cl} - \text{C} - \text{Cl} & \quad \text{1° Amine} \quad \text{Carbonylchloride} \quad \text{Sym-Disubstitutedurea} \\
2\text{RNHClCCl}^{-} & \quad \rightarrow \quad \text{R} - \text{NH} - \text{C} - \text{NH} - \text{R} + 2\text{HCl} \\
\text{2R}_2\text{NH} + \text{COCl}_2 & \quad \text{2° Amine} \quad \text{Sym-Tetrasubstitutedurea} \\
\rightarrow \quad \text{R}_2\text{N} - \text{CO} - \text{NR}_2 + 2\text{HCl}
\end{align*}
\]

Tertiary aliphatic amines, however, form salts.

Aromatic 1° amines, *i.e.* aniline reacts with COCl₂ to form aryl isocyanate. For example,

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH}_2 + \text{COCl}_2 & \quad \text{Aniline} \quad \text{HCl} \quad \text{Δ} \quad \rightarrow \quad \text{C}_6\text{H}_5\text{NH} - \text{COCl} \\
\Delta & \quad \rightarrow \quad \text{C}_6\text{H}_5 - \text{N} = \text{C} = \text{O} \quad \text{Phenylisocyanate}
\end{align*}
\]

5. **Oxidation:** Oxidation of amines gives different products depending upon the nature of amine and the oxidising agent. For example,

\(i\)  Primary aliphatic amines on oxidation with KMnO₄ followed by hydrolysis give aldehydes or ketones.

\[
\begin{align*}
\text{R} - \text{CH}_2 - \text{NH}_2 & \quad \text{1° Amine} \quad \text{KMnO}_4 \quad \text{H}^+ / \text{H}_2\text{O} \quad \rightarrow \quad \text{R} - \text{CH} = \text{NH} \quad \text{Aldimine} \quad \text{H}^+ / \text{H}_2\text{O} \quad \rightarrow \quad \text{R} - \text{CH} = \text{O} + \text{NH}_3 \quad \text{Aldehyde} \\
\text{R}_2\text{CH} - \text{NH}_2 & \quad \text{1° Amine} \quad \text{KMnO}_4 \quad \text{H}^+ / \text{H}_2\text{O} \quad \rightarrow \quad \text{R}_2\text{C} = \text{NH} \quad \text{Ketimine} \quad \text{H}^+ / \text{H}_2\text{O} \quad \rightarrow \quad \text{R}_2\text{C} = \text{O} + \text{NH}_3 \quad \text{Ketone}
\end{align*}
\]

\(ii\)  Secondary aliphatic amines on oxidation with KMnO₄ give tetra-alkylhydrazines.

\[
\begin{align*}
\text{R}_2\text{NH} & \quad \text{2° Amine} \quad \text{KMnO}_4 \quad \text{H}_2\text{SO}_5 \quad \rightarrow \quad \text{R}_2\text{N} - \text{NR}_2 \quad + \text{H}_2\text{O} \quad \text{Tetra-alkylhydrazine} \\
\text{R}_2\text{NH} & \quad \text{2° Amine} \quad \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{R}_2\text{N} - \text{OH} \quad \text{N-Hydroxydialkylamine}
\end{align*}
\]

\(iii\)  Tertiary aliphatic amines are not oxidised by KMnO₄ but are oxidised to the corresponding amine N-oxides by Caro’s acid, ozone or H₂O₂.

\[
\begin{align*}
\text{R}_3\text{N} + [\text{O}] & \quad \text{3° Amine} \quad \text{H}_2\text{O}_2 \quad \text{or} \quad \text{H}_2\text{SO}_5 \quad \rightarrow \quad \text{R}_3\text{N} - \text{O} \quad \text{AmineN-oxide}
\end{align*}
\]

Aromatic amines, on the other hand, because of the presence of high electron-density on the benzene ring are easily oxidised on exposure to air or oxidising agents leading to the formation of complex coloured products. For example,

\[
\text{Aniline} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \quad \rightarrow \quad \text{A black dye called aniline black}
\]

Controlled oxidation of aniline with K₂Cr₂O₇ + H₂SO₄, however, gives *p*-benzoquinone.

\[
\begin{align*}
\text{Aniline} & \quad \text{NH}_2 \quad \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \quad \rightarrow \quad \text{O} = \text{C} \quad \text{O} \\
\text{*p*-Benzoquinone}
\end{align*}
\]
6. **Electrophilic substitution reactions:** In addition to the reactions of the amino group, aromatic amines also undergo typical electrophilic substitution reactions of the aromatic ring. In all these reactions, the NH\(_2\) group strongly activates the aromatic ring through delocalization of the lone pair of electrons of the N-atom over the aromatic ring (refer to structures I-V on page 9/41).

As a result, electron density increases more at \(o\)- and \(p\)-positions as compared to \(m\)-positions. Therefore, the \(-\text{NH}_2\) group directs the incoming group to \(o\)- and \(p\)-positions, i.e., \(\text{NH}_2\) is an \(o\)-, \(p\)-directing group.

Due to the strong activating effect of the \(\text{NH}_2\) group, aromatic amines undergo electrophilic substitution reactions readily and it is difficult to stop the reaction at the monosubstitution stage. Usually the reaction proceeds to give 2, 4, 6-trisubstituted amines. However, sometimes a monosubstitution product is required. In order to do so, the activating effect of the amino group is reduced by acetylation. The acetyl group being electron-withdrawing attracts the lone pair of electrons of the N-atom towards itself. As a result, the activating effect of the amino group is reduced. This method is known as protection of the amino group by acetylation and can be used to control the rate of the substitution and to prevent the formation of di- and tri-substitution products.

![Diagram of acetylation and bromination processes](image)

Some typical electrophilic substitution reactions of aromatic amines are discussed below:

(i) **Halogenation:** Due to the strong activating effect of the amino group, halogenation of amines occurs very fast and the halogen enters the \(p\)-and both the \(o\)-positions even in the absence of a catalyst. For example, aniline on treatment with bromine-water gives 2, 4, 6-tribromoaniline.

\[
\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + 3\text{HBr} \rightarrow 2\text{H}_2\text{O} 
\]

2, 4, 6 – Tribromoaniline

If, however, a monohalogenated derivative is required, the amino group is first acetylated and then halogenation of the ring is carried out. After halogenation, the monohalogenated amine is obtained.
(ii) **Nitration:** Nitric acid is not only a nitrating agent but also acts as a strong oxidizing agent. As a result, direct nitration of aromatic amines is not a useful reaction since it often gives tarry oxidation products along with some nitration products. However, under controlled conditions, nitration of aniline gives a mixture of \( p \)-nitroaniline and \( m \)-nitroaniline in the ratio, 1 : 2.

\[
\begin{align*}
\text{Aniline} & \xrightarrow{\text{conc. HNO}_3 \text{, conc. H}_2\text{SO}_4, 293K} \text{m-Nitroaniline (60\%)} + \text{p-Nitroaniline (30\%)} + \text{Some} \; o\text{-isomer} \\
\end{align*}
\]

The reason for formation of larger amount of \( m \)-nitroaniline over \( p \)-nitroaniline is that under strongly acidic conditions of nitration, most of the aniline is converted into anilinium ion and since \( ^+\text{NH}_3 \) is a \( m \)-directing group, therefore, the major product is \( m \)-nitroaniline.

Therefore, to avoid these problems, the most convenient method to carry out the nitration of aniline is to first protect the amino group by acetylation. The acetyl group is finally removed by hydrolysis to give a mixture of \( o \)- and \( p \)-nitroanilines. Thus,

\[
\begin{align*}
\text{Aniline} & \xrightarrow{(\text{CH}_3\text{CO})_2\text{O, -CH}_3\text{COOH}} \text{Acetanilide} \\
\text{Acetanilide} & \xrightarrow{\text{Conc. HNO}_3 \text{, Conc. H}_2\text{SO}_4 \text{, 288K}} \text{p-Nitroacetanilide (major product)} + \text{o-Nitroacetanilide (minor product)} \\
\text{p-Nitroacetanilide} & \xrightarrow{\text{H}^+ / \text{H}_2\text{O, -CH}_3\text{COOH}} \text{o-Nitroacetanilide (minor product)} \\
\end{align*}
\]
Sulphonation: In spite of the presence of activating amino group, sulphonation of aromatic amines occurs only under drastic conditions. For example, when aniline is treated with conc. H$_2$SO$_4$ at 455 - 475 K, it gives $p$-aminobenzenesulphonic acid also called *sulphanilic acid*. This reaction is believed to occur through the amine salt as depicted below:

\[
\begin{align*}
\text{Aniline} & \quad \begin{array}{c}
\text{NH}_2 \\
+ \text{H}_2\text{SO}_4
\end{array} \quad \begin{array}{c}
\text{Aniline hydrogen} \\
\text{sulphate}
\end{array} \\
\text{455-475K} & \quad \text{-H}_2\text{O} \\
\text{NH}_3\text{SO}_4 & \quad \begin{array}{c}
\text{Sulphanilic} \\
\text{acid (Zwitterion)}
\end{array}
\end{align*}
\]

Sulphanilic acid contains both an acidic (SO$_3$H) as well as a basic (NH$_2$) group. It is, therefore, quite understandable that sulphanilic acid exists as an internal salt. During the formation of this salt, the NH$_2$ group has accepted the proton donated by the SO$_3$H group. Such types of internal salts are called *dipolar ions* or *zwitterions*. Due to zwitterion character, sulphanilic acid has high melting point and is practically insoluble in water and organic solvents.

Sulphanilic acid is an important intermediate in the manufacture of dyes and drugs. Sulphailic acid and its derivatives are also used in the manufacture of well-known sulpha drugs such as sulphathiazole, sulphadiazine, sulphapyridine etc. which are widely used against bacterial infections.

---

**Follow-up conceptual questions**

1. In the following compounds:

\[
\begin{align*}
\text{I} & \quad \begin{array}{c}
\text{O} \\
\text{II} \\
\text{III}
\end{array} \\
\text{IV}
\end{align*}
\]

the order of basicity is:

(a) IV > I > III > II  
(b) III > I > IV > II  
(c) II > I > III > IV  
(d) I > III > II > IV

Ans. (i) In compound II (pyridine), the lone pair of electrons on N is present in a $sp^2$-orbital while in compounds I (piperidine) and III (morpholine), the lone pair of electrons on N is present in a $sp^3$-orbital. Since a $sp^2$-orbital has more $s$-character (33.33%) than a $sp^3$-orbital (25%), therefore, the lone pair of electrons on N is more readily available for protonation in I and III than in II. In other words, *compound (II) is less basic than I and III*. Among I and III, III contains an oxygen atom which has —I-effect. As a result, it will attract the lone pair of electrons on N towards itself. Consequently, the lone pair of electrons on N in III is less readily available for protonation than in I. In other words, *compound I is more basic than III*.

(ii) Compound IV (pyrrole) is *aromatic in character*. Therefore, in accordance with *Huckel's rule* it has a cyclic cloud of six $\pi$-electrons. Out of these, four are contributed by two double bonds while the remaining two are the lone pair of electrons on the N-atom. In other words, the lone pair of electrons on N-atom is contributed towards the aromatic sextet formation and hence is not at all available for protonation. Therefore, compound IV is the least basic. *In fact, it is such a weak base that it is weakly acidic in character* and thus reacts with K metal when heated to form the corresponding potassium salt.

Thus, the basicity of the above four compounds decreases in the order: I > III > II > IV, i.e., option (d) is correct.
2. Sulphanilic acid is soluble in dil. NaOH but not in dil. HCl. Explain.

**Ans.** Sulphanilic acid exists as a zwitterion. In presence of dil. NaOH, the weakly acidic —\( \text{NH}_3^+ \) transfers its \( \text{H}^+ \) to \( \text{OH}^- \) to form a soluble \( p-\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-\text{Na}^+ \). On the other hand, — \( \text{SO}_3^- \) group is a very weak base and hence does not accept \( \text{H}^+ \) from dil. HCl to form \( p-\text{NH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \) and hence it does not dissolve in dil. HCl.

8. Separation of Primary, Secondary and Tertiary Amines.

Primary (1°), secondary (2°) and tertiary (3°) amines can be separated from one another by the following methods:

1. **Fractional distillation.** A mixture of 1°, 2° and 3° amines can be separated into individual components by fractional distillation since their boiling points are fairly apart. For example,

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{NH}_2 & \quad (\text{CH}_3\text{CH}_2)_2\text{NH} \\
1° \text{ Amine (290 K)} & \quad 2° \text{ Amine (329 K)} \\
\text{(CH}_3\text{CH}_2)_3\text{N} & \quad 3° \text{ Amine (371 K)}
   \end{align*}
   \]

2. **Hinsberg's method—Reaction with benzenesulphonyl chloride.** This is an excellent method for separating a mixture of 1°, 2° and 3° amines. In this method, a mixture of 1°, 2° and 3° amines is treated with benzenesulphonyl chloride (Hinsberg's reagent) and the resulting reaction mixture is basified with aq. KOH solution when the three amines react differently as discussed below:

   (i) A primary amine forms N-alkylbenzenesulphonamide which because of the presence of an acidic hydrogen on the N-atom dissolves in KOH.

   \[
   \begin{align*}
   & \text{N-alkylbenzenesulphonamide} \\
   & \text{Potassium salt} \quad (\text{soluble in KOH})
   \end{align*}
   \]

   (ii) A secondary amine forms N, N-dialkylbenzenesulphonamide which due to the absence of acidic hydrogen on N-atom does not dissolve in KOH.

   \[
   \begin{align*}
   & \text{N,N-dialkylbenzenesulphonamide} \quad (\text{Insoluble in KOH})
   \end{align*}
   \]

   (iii) The tertiary amine under these conditions does not react at all since it does not contain a replaceable hydrogen on the nitrogen atom.

   The reaction mixture obtained after treatment with benzenesulphonyl chloride in presence of alkali is distilled when tertiary amine distills over. The remaining mixture is filtered and the filtrate on acidification gives the sulphonamide of 1° amine while the solid residue left on the filter paper is the sulphonamide of 2° amine.
The two sulphonamides thus isolated are hydrolysed separately to regenerate the corresponding 1° and 2° amines.

\[
\text{HCl} \xrightarrow{\Delta} \text{R} - \text{R}', \quad \text{R}', \text{O} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{R} - \text{R}', \text{S} - \text{OH} + \text{NH}_2^+ + \text{RNH}_2
\]

Recently benzenesulphonyl chloride is replaced by \( p \) - toluenesulphonyl chloride (tosyl chloride) since the substituted sulphonamides thus formed are stable solids which can be easily purified by crystallization.

3. Hofmann's method — Reaction with diethyl oxalate: In this method, a mixture of 1°, 2° and 3° amines is treated with diethyl oxalate when the three amines react differently as discussed below:

(i) The primary amine forms the corresponding substituted oxamide which is usually a crystalline solid.

\[
\text{CO} - \text{OC}_2\text{H}_4 + \text{H} - \text{NHR} \quad \xrightarrow{} \quad \text{CONHR} - \text{OC}_2\text{H}_4
\]

(ii) The secondary amine forms a diethyl oxamic ester which is generally a liquid.

\[
\text{CO} - \text{OC}_2\text{H}_4 + \text{H} - \text{NR}_2 \quad \xrightarrow{} \quad \text{CO} - \text{NR}_2 + \text{C}_2\text{H}_5\text{OH}
\]

(iii) The tertiary amine under these conditions does not react at all since it does not contain a replaceable hydrogen atom. The reaction mixture containing the substituted oxamide, oxamic ester and unreacted tertiary amine is distilled when the tertiary amine distils over. The residual mixture containing the substituted oxamide (solid) and the oxamic ester (liquid) is separated by simple filtration. Both the oxamide and the oxamic ester when boiled separately with a strong base, regenerate the corresponding amines. Thus.

\[
\text{CONHR}_2 + 2\text{KOH} \xrightarrow{\Delta} \text{COOK} + \text{RNH}_2 + \text{C}_2\text{H}_5\text{OH}
\]

\[
\text{COO}_2\text{C}_2\text{H}_4 + 2\text{KOH} \xrightarrow{\Delta} \text{COOK} + \text{H}_2\text{O}
\]
9 Tests for Amines

1. **Solubility Test.** All the three classes of amines (1°, 2° and 3°) being basic dissolve in mineral acids like HCl, H\(_2\)SO\(_4\) to form the corresponding salts.

2. **Hinsberg's Test:** This is an excellent test for distinguishing primary, secondary and tertiary amines. In this test, the amine is shaken with benzenesulphonyl chloride (Hinsberg's reagent) in the presence of excess of aqueous KOH solution when

   (i) A primary amine gives a clear solution which on acidification gives an insoluble N-alkylbenzene sulphonamide.

   ![Solubility Test](image)

   (ii) A secondary amine gives an insoluble N, N-dialkylbenzenesulphonamide which remains unaffected on addition of acid.

   ![Hinsberg's Test](image)

   (iii) A tertiary amine does not react at all; Therefore, it remains insoluble in the alkaline solution but dissolves on acidification to give a clear solution.

   ![Hinsberg's Test](image)

3. **Carbylamine Test or Isocyanide Test:** Both aliphatic and aromatic primary amines can be detected by heating with chloroform in presence of alcoholic KOH when isocyanides having extremely unpleasant smell are obtained. This test is called carbylamine test or isocyanide test.

   \[
   \text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH (alc)} \xrightarrow{\Delta} R-N = \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}
   \]

   1° Amine  Isocyanide
4. **Azo dye test** (only for 1° aromatic amines): Aromatic primary amines can be distinguished from aliphatic 1° amines by azo dye test. To carry out this test, dissolve the 1° amine in dil. HCl and cool it to 273-278 K and then treat it with an ice-cold solution of HNO\(_2\) (NaNO\(_2\) + dil. HCl) at 273-278 K. The resulting solution is then added to cold alkaline solution of 2-naphthol (or 3-naphthol). Appearance of an orange or red dye confirms the presence of an aromatic 1° amine.

\[
\text{Aniline} \quad \text{NH}_2 + \text{HONO} + \text{HCl} \xrightarrow{273-278\,\text{K}} \text{Benzenediazonium chloride} \equiv \text{NCl}^- + 2\text{H}_2\text{O}
\]

\[
\begin{align*}
\text{N} & \equiv \text{NCl}^- + \text{OH}^- \\
\text{2-Naphthol} & \xrightarrow{\text{DilNaOH}\quad \text{pH}9-10} \text{1-Phenylazo -2-naphthol} \\
& \quad \text{(Orange dye)} + \text{HCl}
\end{align*}
\]

10 **Uses**

1. Low molecular mass aliphatic amines such as diethylamine, triethylamine etc. are used:
   (i) as reagents in organic synthesis.
   (ii) as solvents in the laboratory and industry
   (iii) as intermediates in the manufacture of drugs.

2. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are used as detergents. For example, \( \text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Cl}^- \).

   \( n \)-Hexadecyltrimethylammonium chloride

3. Aromatic amines such as aniline are widely used
   (i) in the manufacture of dyes and drugs.
   (ii) as additives (antioxidants) and vulcanization accelerators in rubber industry.
   (iii) for the preparation of phenyl isocyanide needed for the manufacture of polyurethane plastics;
   (iv) for the preparation of arenediazonium salts which, in turn, are widely used for preparation of a variety of aromatic compounds via substitution and coupling reactions.

11 **Some Commercially Important Compounds**

1. **Hexamethylenediamine**: It is manufactured by catalytic hydrogenation of adiponitrile prepared from adipic acid.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{COOH} & \xrightarrow{\text{NH}_3\quad \text{Catalyst}} \text{CH}_2\text{CH}_2\text{CN} \\
\text{CH}_2\text{CH}_2\text{COOH} & \xrightarrow{\text{Catalyst}} \text{CH}_2\text{CH}_2\text{CN} \\
\text{Adipic acid} & \xrightarrow{\text{Catalyst}} \text{Adiponitrile} \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 & \xrightarrow{\text{Catalyst}} \text{Hexamethylenediamine}
\end{align*}
\]

Hexamethylenediamine is extensively used in the manufacture of nylon (For details refer to unit 16).
2. **Aniline**: It is manufactured by either of the following two methods.

(i) **From nitrobenzene**: Aniline can be prepared commercially by vapour-phase reduction of nitrobenzene with hydrogen using cupric oxide or vanadium-platinum as catalyst at 680 K.

\[
\text{NO}_2 + 3\text{H}_2 \xrightarrow{\text{CuO or V-Pt, 680K}} \text{NH}_2 + 2\text{H}_2\text{O}
\]

(ii) **From chlorobenzene**: Aniline can be prepared commercially from chlorobenzene by the action of NH\(_3\) at 475 K under high pressure (60 atm.) and in the presence of cuprous oxide (Cu\(_2\)O), as catalyst.

\[
2\text{Cl} + 2\text{NH}_3 + \text{Cu}_2\text{O} \xrightarrow{\text{475K, 60atm.}} 2\text{NH}_2 + \text{CuCl} + \text{H}_2\text{O}
\]

**Aniline is extensively used:**

(i) in medicine, drugs and dyes

(ii) for making isocyanates required for polyurethane plastics

(iii) in the manufacture of antioxidants and vulcanization accelerators for rubber.