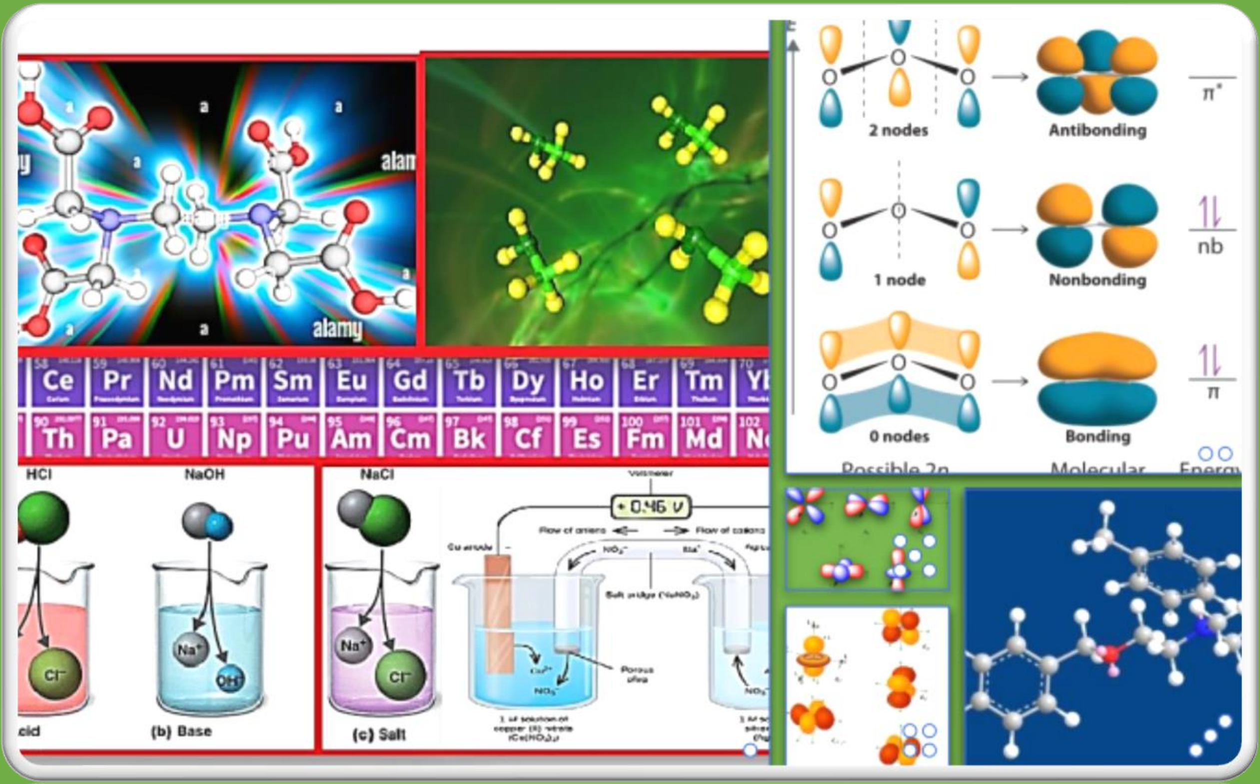
CHE (N)-202

B.Sc. IVth Semester

GENERAL CHEMISTRY-II



UTTARAKHAND OPEN UNIVERSITY
HALDWANI, NAINITAL
SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY

CHE (N)-202

GENERAL CHEMISTRY-II AND LABORATORY WORK

BSc. FOURTH SEMESTER

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BLOCK 1

UNIT-1: CHEMISTRY OF THE LANTHANIDE ELEMENTS

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1.1 INTRODUCTION

Lanthanides, also sometimes called lanthanons, are the elements that constitute a distinct series of fourteen elements from cerium (Ce, Z = 58) to lutetium (Lu, Z = 71). They are so called because these elements succeed lanthanum (La, Z =57), the element of Group 3 and lie between it and hafnium (Hf, Z = 72), the element of Group 4, both belonging to the third transition series (or 5d-transition series). That is why they are also known as inner transition elements. These fourteen elements belong to the f-block and are the members of the 4f-series because the last or differentiating electron in the atoms of these elements enters the 4f-subshell, i.e., the f-subshell of ante-penultimate shell (here n=6). Thus, f-block elements have partly filled f-subshells of $(n-2)^{th}$ shell in the elementary or ionic state.

The first and the last elements of the 4f-series have been mentioned above (i.e., Ce and Lu). The rest twelve elements along with their symbols and atomic numbers are given below:

praseodymium (Pr, Z = 59), neodymium (Nd, Z = 60), promethium (Pm, Z = 61), samarium (Sm, Z = 62), europium (Eu, Z = 63), gadolinium (Gd, Z = 64), terbium (Tb, Z = 65), dysprosium (Dy, Z = 66), holmium (Ho, Z = 67), erbium (Er, Z = 68), thulium (Tm, Z =69) and ytterbium (Yb, Z = 70). In analogy with various series of d-block elements, these elements are called first inner transition series elements. All the fourteen elements of the series resemble closely in their electronic configuration and chemical properties with one as well as lanthanum which may be called a prototype of lanthanide elements. All these elements are said to be the members of Group 3 i.e., Sc group, and have been allotted one position in the periodic table.

These elements were originally called rare earth elements because the elements then known occurred as oxides (earths) and were available scarcely. All the elements have similar physical and chemical properties and are considered together for their study.

Interestingly, the elements with even atomic numbers are relatively more abundant and have a larger number of isotopes. Still, those with odd atomic numbers are less abundant and do not have more than two. Promethium (Z = 61) has been made artificially only and does not occur in nature.

1.2 OBJECTIVES

The objectives of this unit are to make the learners understand various aspects regarding:

- Lanthanides or 4f-block elements such as their electronic structure or configuration, oxidation states, ionic radii and corresponding lanthanide contraction, complex formation by these elements, etc.
- It is also aimed at giving the readers an idea of the occurrence and isolation of these elements along with the discussion of the lanthanide compounds.

1.3 ELECTRONIC STRUCTURE OF LANTHANIDES

The electronic configurations of the lanthanides have been derived from the electronic spectra of the atoms of these elements. These spectra have great complexity thereby inferring to some doubt about the configurations. In the following table, the expected and alternative probable configurations of the elements have been listed. The expected configurations have been derived by taking into account the electronic configuration of lanthanum and supposing that in all the lanthanide elements succeeding lanthanum, additional electrons are filled in 4f-subshell successively from cerium to lutetium. Thus, the 4f-electrons are embedded in the interior while 5d and 6s electrons are exposed to the surroundings. The electronic configurations of lanthanide elements are given in Table 1.1.

Table 1.1 Electronic structures of lanthanum and lanthanides

Element	At. number (Z)	Expected electronic configuration	Alternative probable configuration
Lanthanum (La)	57	$[Xe]5d^1 6s^2$	-
Cerium (Ce)	58	$[Xe]4f^1 5d^1 6s^2$	$[Xe]4f^2 6s^2$
Praseodymium (Pr)	59	$[Xe]4f^2 5d^1 6s^2$	$[Xe]4f^3 6s^2$
Neodymium (Nd)	60	$[Xe]4f^3 5d^1 6s^2$	$[Xe]4f^4 6s^2$
Promethium (Pm)	61	$[Xe]4f^4 5d^1 6s^2$	$[Xe]4f^5 6s^2$
Samarium (Sm)	62	$[Xe]4f^5 5d^1 6s^2$	$[Xe]4f^6 6s^2$
Europium (Eu)	63	$[Xe]4f^6 5d^1 6s^2$	$[Xe]4f^7 6s^2$
Gadolinium (Gd)	64	$[Xe]4f^7 5d^1 6s^2$	$[Xe]4f^7 5d^1 6s^2$
Terbium (Tb)	65	$[Xe]4f^8 5d^1 6s^2$	$[Xe]4f^9 6s^2$
Dysprosium (Dy)	66	$[Xe]4f^9 5d^1 6s^2$	$[Xe]4f^{10} 6s^2$
Holmium (Ho)	67	$[Xe]4f^{10} 5d^1 6s^2$	$[Xe]4f^{11} 6s^2$
Erbium (Er)	68	$[Xe]4f^{11} 5d^1 6s^2$	$[Xe]4f^{12} 6s^2$

Thulium (Tm)	69	$[Xe]4f^{12}5d^16s^2$	$[Xe]4f^{13}6s^2$
Ytterbium (Yb)	70	$[Xe]4f^{13}5d^16s^2$	$[Xe]4f^{14}6s^2$
Lutetium (Lu)	71	$[Xe]4f^{14}5d^16s^2$	$[Xe]4f^{14}5d^16s^2$

According to the latter view, as is evident from the table, the solitary 5d-electron shifts into the 4f-subshell in all the cases except in Gd (64) and Lu (71) because it is favorable energetically to move the single 5d-electron into 4f-orbital in most of the elements and give more appropriate electronic configuration which in widely accepted. In Gd such a shift would have destroyed the symmetry of a half-filled f-subshell and the resulting configuration would have been less stable than the probable configuration i.e., $4f^7$ is more stable than $4f^8$ configuration. In lutetium, the f-subshell is already filled and cannot accommodate any additional electrons.

From the above, it may be concluded that the general electronic configuration of lanthanide elements could be written as $[Xe](n-2)f^{1-14}(n-1)d^{0,1}ns^2$ where n is the principal quantum number, i.e., 6. The three subshells, *viz.*, (n-2)f, (n-1)d and ns together form the valence shell of these elements, i.e., 4f.5d.6s = valence shell.

1.4 OXIDATION STATES

It has been shown that the lanthanide elements are highly electropositive and form essentially ionic compounds. It is observed for these elements that +3 (i.e. formation of tripositive ions, Ln^{3+}) is the principal or common oxidation state exhibited by all of them. This is said to be the most stable oxidation state of the lanthanides. Some of these elements also show + 2 and +4 oxidation states but except a few such ions, they tend to get converted to +3 state. For example, Sm and Ce form Sm^{2+} and Ce^{4+} ions but are easily converted to +3 states. That is why Sm^{2+} is a good reducing agent while Ce^{4+} is a good oxidizing agent, i.e.,

$$Sm^{2+} \rightarrow Sm^{3+} + e \text{ (electron provider, a reductant)}$$

$$Ce^{4+} + e \rightarrow Ce^{3+} \text{ (electron acceptor, an oxidant)}$$

It means Ln^{2+} and Ln^{4+} ions are less frequent than Ln^{3+} ions among the lanthanides. +2 and +4 oxidation states are shown by the elements particularly when they lead to:

(a) Noble gas electronic configuration, e.g., Ce^{4+} ($4f^0$),

(b) Half-filled f-orbital, e.g., Eu^{2+} and Tb^{4+} ($4f^7$), and

(c) filled f-orbital, e.g., Yb^{2+} ($4f^{14}$) in the valence shell.

Among the above, +2 and +4 oxidation states, which exist only in aqueous solutions, are exemplified by Sm^{2+}, Eu^{2+}, Yb^{2+} and Ce^{4+}.

There are some exceptions also, i.e., sometimes +2 and +4 oxidation states are also shown by the elements which are close to f^0, f^7 and f^{14} states, e.g., the valence shell configurations of the ions given below are $4f^1$, $4f^2$, $4f^3$, $4f^6$ and $4f^8$, etc.:

Ce^{3+}: $4f^1$; Ce^{2+}: $4f^2$; Sm^{2+}: $4f^6$; Pr^{4+}: $4f^1$; Pr^{3+} : $4f^2$; Dy^2: $4f^8$; Nd^{4+}: $4f^2$; Tm^{2+}: $4f^{13}$.

No satisfactory explanation for these exceptions has yet been given. These oxidation states have only been explained based on thermodynamic and kinetic factors, too arbitrarily. Due to the only one stable oxidation state (i.e., +3), lanthanide elements resemble each other much more than do the transition (or d-block) elements. It has also been observed that the higher oxidation states of the lanthanides are stabilized by fluoride or oxide ions, while the lower oxidation states are favored by bromide or iodide ions. Among the lanthanides, in addition to +3 states, +2 states are shown by Nd, Sm, Eu, Tm, and Yb only whereas the +4 state is exhibited by Ce, Pr, Nd, Tb and Dy elements. The rest five elements show only +3 states.

1.5 LANTHANIDE CONTRACTION

Here, ionic radii of tripositive ions (i.e., Ln^{3+}) have only been considered because +3 is the most stable and common oxidation state of all the lanthanides, in general. It has been observed that the atomic as well as the ionic radii of lanthanides decrease steadily as we move from Ce to Lu. The ionic radii have been listed below (for Ln^{3+} ions):

Ln^{3+} ions	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
Ionic radii (pm)	103	101	100	98	96	95	94	92	91	90	89	88	86	85

From the above list, it is clear that the ionic radii decrease steadily all along the series amounting in all to 18 pm. This shrinking in the ionic size of the Ln^{3+} ions with increasing atomic number is called **lanthanide contraction**. The term steadily decrease means the values decrease regularly and with a very small difference though the nuclear charge increases by +14 units from the first to the last element.

The atomic radii of these elements also decrease from Ce to Lu (Ce: 165 pm, Lu: 156 pm) but the overall shift is only 165-156 = 9 pm. These values do not decrease regularly like ionic radii rather there are some irregularities at Eu and Yb which have abnormally high atomic radii. (Eu: 185 pm, Yb: 170 pm).

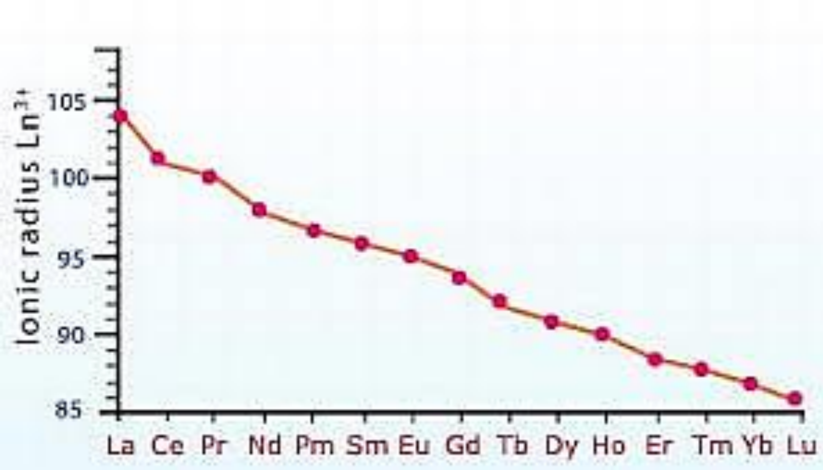
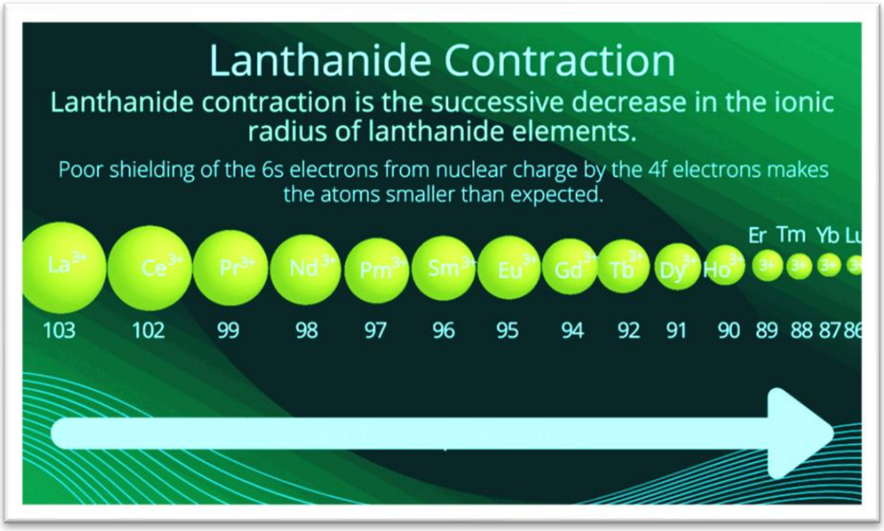


Fig. 1.1 Lanthanide contraction


Lanthanide Contraction

Lanthanide contraction is the successive decrease in the ionic radius of lanthanide elements.

Poor shielding of the 6s electrons from nuclear charge by the 4f electrons makes the atoms smaller than expected.

Fig. 1.2 Decreasing order of ionic radii of the Lanthanide ions1

The atomic radii for the metals are the metallic radii which are recorded for the metal atoms surrounded by 8 or 12 nearest neighbors (in bulk). Various metal atoms in metal crystals are bonded together by metallic bonding. In Eu and Yb, only two 6s-electrons participate in metallic bonding, 4f-subshells being stable. For other lanthanides, three electrons are generally available for this purpose. This results in larger atomic volumes for Eu and Yb because of weaker bonding among atoms. The larger values ultimately give rise to the larger size of the atoms of the elements.

1.5.1 Cause of Lanthanide Contraction

As we move along the lanthanide series from Ce to Lu, the addition of electrons takes place to the 4f-orbitals, one at each step. The mutual shielding effect of f-electrons is very little, being even smaller than that of d-electrons, due to the scattered or diffused shape of these orbitals. However, the nuclear charge (i.e. atomic number) goes on increasing by one unit at each step (i.e., each next element). Thus, the attraction between the nucleus and the outermost shell electrons also goes on increasing gradually at each step. The 4f-electrons are not able to shield effectively the attraction of the nucleus (i.e. inward pull) for the electrons in the outer most shell as the atomic number of lanthanide elements increases. This results in the increased inward pull of the outer most electrons by the nucleus, finally causing the reduction in the atomic or ionic size of these elements. The sum of the successive reductions gives the total lanthanide contraction.

It may be concluded that the lanthanide contraction among the 4f-series elements and their ions takes place due to the poor shielding effect of 4f-electrons and the gradual increasee in the nuclear charge.

1.5.2 Consequences of Lanthanide Contraction

Lanthanide contraction plays an important role in determining the chemistry of lanthanides and heavier transition series elements. Some important consequences of lanthanide contraction are discussed below:

1.5.2.1 Basic character of lanthanide hydroxides, $Ln(OH)_3$

Because the size of tripositive lanthanide ions (Ln^{3+}) decreases regularly with increasing atomic number (or nuclear charge), the process is called lanthanide contraction, therefore, the covalent character between Ln^{3+} ion and OH^- ions increases from $La(OH)_3$ to $Lu(OH)_3$ (Fajans' rules). As a result, the basic character of the hydroxides decreases with increasing atomic number. Consequently, $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic.

1.6 COMPARISON WITH TRANSITION ELEMENTS

1.6.1 Resemblance between the atomic radii of the second and third transition series elements

The lanthanide contraction is an important factor in allowing the separation of lanthanides from one another. Also, it has a significant effect on the relative properties of the elements that precede and succeed the lanthanides. Normally in the same group, the atomic (or covalent) radii increase as the value of n (principal quantum number) increases due to the increased distance between the nucleus and the outermost shell of the electrons which counterbalances the increased nuclear charge. This fact is evident when the values of atomic radii are compared for the elements of the first and second transition series. On the same analogy, the atomic radii of the elements of the third transition series should be greater than those of the second transition series elements. This statement is valid only for the elements of Group 3, i.e. Sc, Y and La in terms of their atomic radii (see the table given below). But, when these values are compared for the elements of 4d and 5d series in the next group, *viz*. Group 4, 5 ……………..12, it is observed that the values are unexpectedly almost equal. The similarity in the values of atomic radii for the elements of the second and third transition series is attributed to the inclusion of 14 lanthanides between La (Z = 57, Group 3) and Hf (Z = 72, Group 4) of the third transition series which due to "lanthanide contraction" cancel the increase in the values of atomic radii. Due to the similarity in the size of the elements of the two series (i.e., second and third), the elements of a particular Group resemble each other more closely in their properties than do the elements of the first and second transition series. The examples of the pairs of elements which show similar properties and hence are difficult to separate are Zr-Hf, Nb-Ta, Mo-W, Ru-Os, Rh-Ir, Pd-Pt, and Ag-Au. The atomic radii of the elements of the three-transition series are given below to justify the above statement.

Groups	3	4	5	6	7	8	9	10	11	12
Elements of 3d-sereis	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii (pm)	144	132	122	117	117	117	116	115	117	125
Elements of 4d-sereis	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

Atomic radii (pm)	162	145	134	130	127	125	125	128	134	148
Elements of 5d-sereis	La-Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic radii (pm)	169	144	134	130	128	126	127	130	136	150

From this table, it is evident that due to lanthanide contraction, the atomic and ionic radii of second and third transition series elements do not differ much though they are appreciably higher than those of first transition series elements. It is also observed that the atomic radii of the elements falling immediately after the lanthanide series are closer to those of their 4d-congeners and the effect slowly decreases along the series of 5d-elements as we move away from it.

1.6.2 Densities of the elements of the three-transition series

The density and atomic volume are inversely proportional to each other. All the transition metals have low values for their atomic volumes and hence their densities are high. In a given transition series, the atomic volumes of the elements first decrease on proceeding from left to right and generally attain a minimum value for the elements of group VIII (i.e., Groups 8,9,10). They then start increasing further up to Group 12 elements. Accordingly, the density of the elements increases from left to right up to the elements of Group VIII (Groups 8,9,10) and then decreases up to Group 12.

Down the group, the densities of the elements increase regularly. But the striking feature that has been observed on moving from the first element to the last element in every group is that the densities of the elements belonging to the second transition series are only slightly higher than those of the corresponding elements of the 3d-series while the values for the elements from Hf (Z =72) to Hg (Z =80) (i.e., 5d-series) are almost double of those for the elements from Zr (Z=40) to Cd (Z=48), respectively (4d-series). This analogy does not apply to Y(Z=39) and La (Z=57). This can be explained as follows:

Because of lanthanide contraction, the atomic sizes of the elements of the third transition series after La (Z=57) i.e. from Hf onwards become very small and as a result, the packing of atoms in their metallic crystals becomes much compact which results in high densities. Also, there is only a small difference in the atomic sizes of the elements of the two series, *viz*., 4d-and 5d-series but the atomic masses of the elements of the 5d-series are almost double to the corresponding elements of 4d-series. This makes the densities of 5d-series elements almost double those of the elements of 4d-series.

1.6.3 Similarities among lanthanides

There is very small change in the radii of lanthanides and hence their chemical properties are quite similar. This makes the separation of these elements using the usual physical and chemical methods difficult. Consequently, new methods like ion exchange technique, solvent extraction, etc. have now been used for their separation which are based on slight differences in properties like hydration, complex ion formation, etc.

1.7 COMPLEX FORMATION BY LANTHANIDES

The lanthanides have low charge density due to their larger size despite having high charge (+3). Hence, they do not cause much polarization of the ligands and have a weak tendency for complex formation. This reluctance for complex formation may be attributed mainly to:

(i) The unfavourable electronic configuration on the lanthanide ions.

(ii) The larger size which leads to little attraction for electron rich species.

Because of the above reasons, only the high energy 5d, 6s and 6p-orbitals are available for coordination, the 4f-orbitals being screened, so that only strong (usually chelating) coordinating groups can interact. Thus, only a few complexes with unidentate ligands are formed but stable complexes are formed by Ln^{3+} ions with chelating ligands such as (i) oxygen containing, *viz.,* EDTA, β-diketones, citric acid, oxalic acid, acetyl acetone, oximes, (ii) nitrogen containing, *viz*., ethylene diamine, NCS, etc. The Ln^{3+} ions do not form complexes with π-bonding ligands such as CO, NO, CNR, etc., at all. The complex forming tendency and the stability of the complexes increases with increasing atomic number. This fact is taken as a basis to take advantage in their separation from one another. Ce(IV) complexes are relatively common, an example of high oxidation state ion seeking stabilization through complexation.

The most important class of lanthanide complexes are the anionic type. Complexation with hydroxycarboxylic acids such as citric and tartaric acid is used in the separation procedure of lanthanides. The EDTA complexes have achieved importance in the recent years. The coordination number of lanthanide complexes is usually six.

1.8 OCCURRENCE AND ISOLATION OF LANTHANIDE ELEMENTS

Except promethium which is unstable and occurs only in traces, all the lanthanides occur in nature to a considerable extent, cerium being the most abundant of all the elements. There are more than a hundred minerals known to contain lanthanides but very few are of commercial importance. Monazite sand is the best known and most important mineral of lanthanide elements which is essentially a mixture of orthophosphates, $LnPO_4$ containing upto 12% thorium, the element of 5f-series, small amounts of Zr, Fe and Ti as silicates, lanthanum and about 3% yttrium. Among lanthanides contained in monazite, the bulk is of Ce, Nd, Pr and others occur in minute quantities.

1.8.1 Extraction of lanthanide metals

After conventional mineral dressing which gives minerals of more than 90 percent purity, the mineral is broken down by either acidic or alkaline attack. By making use of different solubilities of double salts: $Ln_2(SO_4)_3.Na_2SO_4.xH_2O$ for light and heavy lanthanides and low solubility of hydrated oxide of thorium, the lanthanide fractions and thorium-containing portions are separated in an acidic medium.

Monazite is treated with hot conc. H_2SO_4 when thorium, lanthanum and lanthanoids dissolve as sulfates and are separated from insoluble material (impurities). On partial neutralisation by NH_4OH, thorium is precipitated as ThO_2. Then Na_2SO_4 is added to the solution. Lanthanum and light lanthanides are precipitated as sulphates leaving behind the heavy lanthanides in solution. To the precipitate obtained as above, is added hot conc. NaOH. The resulting hydroxides of light lanthanides are dried in air at 100^0C to convert the hydroxides to oxides. The oxide mixture is treated with dil. HNO_3. This brings CeO_2 as precipitate and other lanthanides in the solution. From the solutions obtained above for heavy and light lanthanides, individual members of the lanthanide series are isolated by the following methods:

1.8.2 Isolation of Individual Lanthanide Elements

All the lanthanides have the same size and charge (of +3 unit). The chemical properties of these elements which depend on the size and charge are, therefore, almost identical. Hence, their isolation from one another is quite difficult. However, the following methods have been used to separate them from one another.

1.8.3 Fractional Crystallization Method

This method is based on the difference in solubility of the salts such as nitrates, sulphates, oxalates, bromates, perchlorates, carbonates and double salts of lanthanide nitrates with magnesium nitrate which crystallize well and form crystals. Since, the solubility of these simple and double salts decreases from La to Lu, the salts of Lu will crystallize first followed by those of lighter members. The separation can be achieved by repeating the crystallization process several times. A non-aqueous solvent, *viz*., diethyl ether has been used to separate $Nd(NO_3)_3$ and $Pr(NO_3)_3$.

1.8.4 Fractional Precipitation Method

This method is also based on the difference is the solubility of the precipitate formed, which is formed on the addition of the precipitant, i.e. Precipitating agent. If a small amount of precipitant is added, the salt with the lowest solubility is precipitated most readily and rapidly. For example, when NaOH is added to a solution of $Ln(NO_3)_3$, Lu-hydroxide being the weakest base and having the lowest solubility product is precipitated first while La-hydroxide which is the strongest base and has the highest solubility product is precipitated last. By dissolving the precipitate in HNO_3 and reprecipitating the hydroxides several times, it is possible to get the complete separation of lanthanide elements.

1.8.5 Valency Change Method

This method is based on the change of chemical properties by changing the oxidation state of the lanthanide elements. The most important application of this method is made in the separation of cerium and europium elements from a mixture of lanthanides.

(i) The mixture containing Ln^{3+} ions if treated with a strong oxidising agent such as alkaline $KMnO_4$, only Ce^{3+} ion is oxidized to Ce^{4+} while other Ln^{3+} ions remain unaffected. To this solution, alkali is added to precipitate $Ce(OH)_4$ only, which can be filtered off from the solution.

(ii) Eu^{2+} can be separated almost completely from Ln^{3+} ions from a solution by reducing it with zinc-amalgam and then precipitating as $EuSO_4$ on adding H_2SO_4 which is insoluble in water and hence can be separated. The sulfates of other Ln^{3+} ions are soluble and remain in solution.

1.8.6 Complex Formation Method

This method is generally employed to separate heavier lanthanide elements from the lighter ones by taking advantage of the stronger complexing tendency of smaller cations with complexing agents. When EDTA is added to the Ln^{3+} ion solution, lanthanides form strong complexes. If oxalate ions are added to the solution containing EDTA and Ln^{3+} ions, no precipitate of oxalates is obtained. However, on adding a small amount of acid, the least stable complexes of lighter lanthanides are dissociated and precipitated as oxalates, but the heavier lanthanides remain in solution as EDTA complexes.

1.8.7 Solvent Extraction Method

This method is based on the difference in the values of the partition coefficient of lighter and heavier lanthanides between two solvents, e.g., water and tri-butyl phosphate (TBP). Heavier lanthanides are more soluble in TBP than lighter ones whereas the reverse trend of solubility is found in water and other ionic solvents. $La(NO_3)_3$ and $Gd(NO_3)_3$ have been separated by this method because the partition coefficient of Gd-nitrate in water and TBP is different from that of La-nitrate. Thus, Gd-nitrate can be separated from La-nitrate by continuous extraction with water from a solution of these salts in TBP in kerosene oil or by using a continuous counter-current apparatus that gives a large number of partitions automatically.

1.8.8 Modern Ion-Exchange Method

This is the most rapid and most effective method for the isolation of individual lanthanide elements from the mixture. An aqueous solution of the mixture of lanthanide ions (Ln^{3+}aq) is introduced into a column containing a synthetic cation exchange resin such as DOWAX-50 [abbreviated as HR (solid)]. The resin is the sulfonated polystyrene containing SO_3H as the functional group. As the solution of the mixture moves through the column, Ln^{3+}aq ions replace H^+ ions of the resin and get themselves fixed on it:

$$Ln^{3+}aq + 3H(resin) \rightarrow Ln(resin)_3 + 3H^+aq$$

The H^+aq ions are washed through the column. The Ln^{3+}aq. ions are fixed at different positions on the column. Since Lu^{3+}aq. is the largest (Lu^{3+} anhyd. is smallest and is hydrated to the maximum extent) and Ce^{3+}aq. is the smallest, Lu^{3+}aq. ion is attached to the column with minimum firmness remaining at the bottom and Ce^{3+}aq. ion with maximum firmness remaining at the top of the resin column. To move these Ln^{3+}aq. ions down the column and recover them, a solution of anionic ligand such as citrate or 2-hydroxy butyrate is passed slowly through the column (called elution). The anionic ligands form complexes with the lanthanides which possess lower positive charge than the initial Ln^{3+}aq ions. These ions are thus displaced from the resin and moved to the surrounding solutions as eluant- Ln complexes.

For example, if the citrate solution (a mixture of citric acid and ammonium citrate) is used as the eluant, during elution process, NH_4^+ ions are attached to the resins replacing Ln^{3+}aq. ions which form Ln-citrate complexes:

$$\text{Ln (resin)}_3 + 3NH_4^+ \rightarrow 3NH_4\text{- resin} + Ln^{3+}\text{aq}$$

$$Ln^{3+}\text{aq} + \text{citrate ions} \rightarrow \text{Ln-citrate complex}$$

As the citrate solution (buffer) runs down the column, the metal ions get attached alternately with the resin and citrate ions (in solution) many times and travel gradually down the column and finally pass out of the bottom of the column as the citrate complex. The Ln^{3+}aq cations with the largest size are, eluted first (heavier Ln^{3+}aq ions) because they are held with minimum firmness and lie at the bottom of the column. The lighter Ln^{3+}aq ions with smaller size are held at the top of the column (with maximum firmness) and are eluted at last. The process is repeated several times by careful control of the concentration of citrate buffer in actual practice.

1.9 LANTHANIDE COMPOUNDS

The lanthanides are very electropositive and reactive metals, the reactivity depends on the size. Europium with the largest size is most reactive. All the lanthanides generally give normal and complex compounds.

Oxides

If lanthanide elements are ignited in air or O_2, they readily form the oxides of Ln_2O_3 type except Ce which gives a dioxide, CeO_2. The oxides are ionic and basic. The basic nature of oxides decreases along the series with decreasing ionic size.

$$2\,Ln + 3O_2 \xrightarrow{\Delta} Ln_2O_3$$

$$Ce + O_2 \xrightarrow{\Delta} CeO_2$$

Ytterbium resists the action of air even at 1000^0C due to the formation of a protective layer of oxide on its surface.

Hydroxides

The lanthanides react slowly with cold water but readily with hot water:

$$2\ Ln + 6\ H_2O \rightarrow 2\ Ln(OH)_3 + 3H_2$$

On adding aqueous ammonia to this aqueous solution, hydroxides are precipitated as gelatinous precipitate. These hydroxides are also ionic and basic, the basic nature decreasing with increasing atomic number. $La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. Their basic character is more than that of $Al(OH)_3$ but less than that of $Ca(OH)_2$.

Oxo-salts

Lanthanides form oxo-salts such as nitrates, sulpates, perchlorates and salts of oxo-acids which are soluble in water but carbonates and oxalates are insoluble. The difference in basicity is responsible for the difference in thermal stability of the oxo- salts which decreases along the series. Thus, $La(NO_3)_3$ is more stable than $Lu(NO_3)_3$.

Halides and Hydrides

The lanthanides also burn in halogens to produce LnX_3 type halides and combine with H_2 at high temperature to give stable MH_2 or MH_3 type hydrides. Among halides, fluorides are insoluble but other halides are soluble in water.

Ln also form complexes with chelating ligands, the detailed account has been given earlier.

1.10 SUMMARY

The summery of the present unit is the:

- The present unit covers all the important and interesting aspects of lanthanides such as their electronic structure, oxidation states, ionic radii and corresponding lanthanide contraction, consequences of lanthanide contraction, complex formation by lanthanides, their occurrence, extraction and various methods employed for the isolation of the elements and a brief account of the lanthanide compounds.

- The readers can understand well all these aspects after going through the unit text.

1.10TERMINAL QUESTIONS

1. Why are the lanthanides grouped together?
2. Why the f-block elements are also called the inner transition elements?
3. Give a brief account of lanthanide contraction.
4. The number of f-electrons in Eu^{2+} and Yb^{2+} ions is

   (a) 7 and 14 (b) 7 and 13 (c) 6 and 14 (d) 6 and 13
5. Tb^{4+} ions are stable, explain.
6. Discuss the ion exchange method of isolation of lanthanides.

Which one is more basic $La(OH)_3$ or $Lu(OH)_3$ and why?

1.11 ANSWERS

4. (a)

5. Due to $4f^7$ valence shell electronic configuration.

6. $La(OH)_3$ due to larger cationic size

For answers to other questions, please refer to the text.

UNIT-2: CHEMISTRY OF THE ACTINIDE ELEMENTS

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2.1 INTRODUCTION

The group of fourteen elements from thorium (Th, Z = 90) to lawrencium (Lr, Z=103) are called actinides, actinoids or actinons. These are named so because these elements succeed the element actinium (Ac, Z = 89). These elements are also known as inner-transition elements as they lie between actinium and rutherfordium (Rf, Z =104), i.e., the elements of the fourth transition series. Thus, they constitute the second inner-transiton series of which actinium is the prototype.

In these elements 5f-subshell of the antepenultimate shell (n=7) is successively filled by the additional or differentiating electrons, one at a time in each step, which are embedded in the interior while 6d- and 7s-electons are exposed to the surroundings. In the outermost and penultimate shell of these elements, the number of electrons remains almost the same. That is why the actinide elements resemble one another very closely. The actinides lying beyond uranium, i.e., the elements with Z = 93 to 103 are called transuranium elements. The first and the last elements of 5f-series have been mentioned above with their names and symbols, i.e., Th and Lr. The remaining twelve elements are listed below:

protactinium (Pa, Z = 91), uranium (U, Z = 92), neptunium (Np, Z = 93), plutonium (Pu, Z = 94), americium (Am, Z = 95), curium (Cm, Z = 96), berkelium (Bk, Z = 97), californium (Cf, Z= 98), einsteinium (Es, Z = 99), fermium (Fm, Z= 100), mendelevium (Md, Z = 101) and nobelium (No, Z= 102).

These elements of 5f-series are also said to belong to Group 3 and Period 7 and have been allotted a position below those of 4f-series in the periodic table and thus the elements of both f-series have been placed separately below the main body of the table to avoid unnecessary expansion of the periodic table.

2.2 OBJECTIVES

After completion of this unit, learners will be able to do the:

- The actinide or 5f-block elements such as the general features of these elements, e.g., their occurrence and nature, their electronic structure, oxidation states, complex formation tendency, magnetic and spectral properties, atomic and ionic sizes, etc. as well as to throw light on the chemistry of the actinides and the chemistry of separation of Np, Pu and Am from U. It is also aimed at to discuss the similarities between lanthanides and actinides.

2.3 GENERAL FEATURES OF THE ACTINIDES

2.3.1 Occurrence and Nature

Only the first four elements, *viz*., Ac, Th, Pa and U occur in nature in uranium minerals that too only Th and U occur to any useful extent. All the remaining actinides, i.e. trans-uranium elements are unstable and are made artificially. The elements above Fm (Z =100) exist as short-lived species, some of them existing only for a few seconds. All the actinides are radioactive.

2.3.2 Electronic Structure (or Configuration)

The electronic configuration of actinium (Z = 89) which is followed by fourteen actinides is $[Rn]5f^{0}6d^{1}7s^{2}$, the last electron entering the 6d-subshell. In the next element, Th, the first member of the actinide series, the additional electron must enter the 5f-subshell and the filling of the 5f-subshell must continue progressively till the last element, Lr. Thus, 6d-subshell in all the elements must remain singly filled thereby giving the expected valence shell configuration of $5f^{1-14}6d^{1}7s^{2}$ for these elements. Since, the energies of 6d- and 5f- subshells are almost the same and the atomic spectra of the elements are very complex, it is difficult to identify the orbital in terms of quantum numbers as well as to write down the configuration. For chemical behaviour, the valence shell electronic configuration of the elements is of great importance and the competition between $5f^{n}6d^{0}7s^{2}$ and $5f^{n-1}6d^{1}7s^{2}$ is of interest. It has been observed that the electronic configuration of actinides does not follow the simple pattern as is observed for the lanthanides. For the first four actinide elements, *viz*., Th, Pa U and Np, due to almost equal energies of 5f and 6d, the electrons may occupy the 5f or 6d subshells or sometimes both. From Pu (Z=94) onwards, $6d^{1}$ electron gets shifted to 5f-subshell except for Cm (Z=96) and Lr (Z=103) in which $6d^{1}$ electron does not shift to 5f due to stable $5f^{7}$ and $5f^{14}$ configurations. In view of the above considerations, the general valence shell electronic configuration of the actinide elements may be written as: $5f^{0-14}6d^{0-2}7s^{2}$. For individual elements the observed or actual valence shell configurations are listed below:

Element (Z)	Valence shell configuration	Element (Z)	Valence shell configuration
Thorium (90)	$5f^06d^27s^2$	Berkelium (97)	$5f^96d^07s^2$
Protactinium (91)	$5f^26d^17s^2$	Californium (98)	$5f^{10}6d^07s^2$
Uranium (92)	$5f^36d^17s^2$	Einsteinium (99)	$5f^{11}6d^07s^2$
Neptunium (93)	$5f^46d^17s^2$	Fermium (100)	$5f^{12}6d^07s^2$
Plutonium (94)	$5f^66d^07s^2$	Mendelevium (101)	$5f^{13}6d^07s^2$
Americium (95)	$5f^76d^07s^2$	Nobelium (102)	$5f^{14}6d^07s^2$
Curium (96)	$5f^76d^17s^2$	Lawrencium (103)	$5f^{14}6d^17s^2$

From the above valence shell configurations of the actinide elements, it is clear that Th does not have any f-electron though this element belongs to 5f-series (i.e., actinides). For Pa, U, Np, Cm and Lr, both the expected and observed (actual) configurations are the same. For the rest of the actinides, the 6d-subshell does not contain any d-electron.

2.3.3 Oxidation States

The important oxidation states exhibited by actinides are compiled below in tabular form. Some of them are stable but most of these oxidation states are unstable. It may be seen from these oxidation states that the +2 state is shown by Th and Am only in a few compounds like $ThBr_2$, ThI_2, ThS, etc. The +3-oxidation state is exhibited by all the elements and it becomes more and more stable as the atomic number increases. The +4-oxidation state is shown by the elements from Th to Bk, the +5-oxidation state by Th to Am, the +6 state by the elements from U to Am and the +7 state is exhibited by only two elements, *viz*., Np and Pu. Np in the +7 state acts as an oxidising agent.

The principal cations given by actinide elements are M^{3+}, M^{4+} and oxo-cations such as MO_2^+ (oxidation state of M = + 5) and MO_2^{2+} (oxidation state of M = +6). Examples of oxo-cations are UO_2^+, PuO_2^+, UO_2^{2+} and PuO_2^{2+} which are stable in acid and aqueous solutions. Most of the M^{3+} ions are more or less stable in aqueous solution. Np^{3+} and Pu^{3+} ions in solution are oxidised to Np^{4+} and Pu^{4+} by air. The latter ions are further oxidised slowly to UO_2^{2+} and PuO_2^{2+} by air. Various oxidation states of the actinides are listed below:

Element	Oxidation states	Element	Oxidation states
Th	+2, +3, +4	Bk	+3, +4
Pa	+3, +4, +5	Cf	+3

U	+3, +4, +5, + 6	Es	+3
Np	+3, +4, +5, +6, +7	Fm	+3
Pu	+3, +4, +5, +6, +7	Md	+3
Am	+2, +3, +4, +5, +6,	No	+3
Cm	+3, +4	Lr	+3

The lighter elements up to Am show variable oxidation states, the maximum being for Np, Pu and Am, but the heavier elements show a constant oxidation state of +3.

2.3.4 Atomic and Ionic Radii

The atomic (metallic) and ionic radii of cations in common oxidation states (i.e. M^{3+} and M^{4+} cations) of some of the actinide elements have been evaluated. A look into the values of the atomic radii reveals that the metallic radii first decrease from Th to Np and then increase gradually up to Bk. For the higher actinides, the values are not known. The values of ionic radii for both types of ions go on decreasing. This steady fall in the ionic radii along the actinide series is called actinide contraction which is analogous to lanthanide contraction found in lanthanides. The cause of actinide contraction is the same as has been discussed for the lanthanides. Here also, increasing nuclear change and the poor shielding effect of 5f-electrons play an important role. The atomic and ionic radii are listed below:

Element	Atomic radius (pm)	The ionic radius of M^{3+} ion (pm)	The ionic radius of M^{4+} ion (pm)
Th	180	108	96
Pa	164	105	93
U	157	103	92
Np	156	101	91
Pu	160	100	90
Am	174	99	89
Cm	175	99	88
Bk	176	98	87
Cf	-	97	-

It is clear from the above table that there is only a small variation in the atomic and ionic radii of the actinide elements; hence they show similar chemical properties.

2.3.5 Magnetic and Spectral Properties

It has already been mentioned that the paramagnetic nature of the substances is due to the presence of unpaired electrons. The actinide elements like lanthanides show paramagnetism in the elemental and ionic states. Tetravalent thorium (Th^{4+}) and hexavalent uranium (U^{6+}) ions are diamagnetic due to the absence of unpaired electrons. $Th^{4+} = U^{6+}$ = Rn (Z= 86) structure (diamagnetic, paired electrons). Since actinides constitute the second f-series, it is natural to expect similarities with lanthanides (the first f-series) in their magnetic and spectroscopic properties. But there are some differences between the lanthanides and actinides. Spin-orbit coupling is strong (2000-4000cm^{-1}) in the actinides as happens in the lanthanides but because of the greater exposure of the 5f-electrons, crystal field splitting is now of comparable magnitude and J is no longer such a good quantum number. It is also noted that 5f-and 6d-subshells are sufficiently close in energy for the lighter actinides to make 6d-levels accessible. As a result, each actinide compound has to be considered individually. This must allow the mixing of J levels obtained from Russel-Saunders coupling and a population of thermally available excited levels.

Accordingly, the expression $\mu = g\sqrt{J(J+1)}$ is less applicable than for the lanthanides and magnetic moment values obtained at room temperature are usually lower and are much more temperature dependent than those obtained for compounds of corresponding lanthanides.

The electronic spectra of actinide compounds arise from the following three types of electronic transitions:

(a) **f-f transitions:** These are Laporte (orbitally) forbidden but the selection rule is relaxed partially by the action of the crystal field in distorting the symmetry of the metal ion. Because the actinides show a greater field, hence the bands are more intense. These bands are narrow and more complex, are observed in the visible and UV regions and produce the colours in aqueous solutions of simple actinide salts.

(b) **5f-6d transitions:** These are Laporte and spin-allowed transitions and give rise to much more intense bands which are broader. They occur at lower energies and are normally confined to the UV region hence do not affect the colours of the ions.

(c) **Metal to ligand charge transfer:** These transitions are also fully allowed and produce broad, intense absorptions usually found in UV region, sometimes trailing in the visible region. They produce the intense colours which are characteristic of the actinide complexes.

The spectra of actinide ions are sensitive to the crystal field effects and may change from one compound to another. It is not possible to deduce the stereochemistry of actinide compounds due to the complexity of the spectra. Most of the actinide cations and salts are coloured due mainly to f-f transitions. Those with f^0, f^7 and f^{14} configurations are colourless. The colours of some of the compounds in different oxidation states are given below:

$NpBr_3$: green; NpI_3 : brown; $NpCl_4$: red-brown; NpF_6 : brown
PuF_3 : purple; $PuBr_3$: green; PuF_4 : brown; PuF_6 : red brown
AmF_3 : pink; AmI_3 : yellow; AmF_4 : dark tan.

The coordination chemistry of actinides is more concerned with aqueous solutions. Because of the wider range of oxidation states available in actinides, their coordination chemistry is more varied. Most of the actinide halides form complex compounds with alkali metal halides. For example, $ThCl_4$ with KCl forms complexes such as $K[ThCl_5]$ and $K_2[ThCl_6]$, etc. $ThCl_4$ and $ThBr_4$ also form complexes with pyridine, e.g. $ThCl_4$.py Chelates are formed by the actinides with multidentate organic reagents such as oxine, EDTA, acetylacetone, etc.

The actinides with small size and high charge have the greatest tendency to form complexes. The degree of complex formation for the various ions decreases in the order: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$. The complexing power of different anions with the above cations is in the order:

Monovalent anions : $F^- > NO_2^- > Cl^-$
Bivalent anions : $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

2.4 CHEMISTRY OF ACTINIDES

The actinide elements are highly electropositive and reactive. They show similar properties to those of lanthanides. However, these elements have a much higher tendency to form complexes. They react with water and tarnish in the air forming an oxide coating. They react readily with HCl but slowly with other acids. The metals show basic nature and do not react with NaOH but they react with halogens, oxygen and hydrogen to form halides, oxides and hydrides. Some of the compounds of the actinides are discussed below:

(i) **Oxides:** The metals on reacting with air or oxygen give various oxides under different experimental conditions. Uranium is one of the reactive elements and gives the oxides: UO, UO_2, U_3O_8 and UO_3:

$$U + O_2 \xrightarrow{\Delta} U_3O_8$$

$$UO_3 \xrightarrow{\Delta} UO_2$$

Similarly, the oxides of Np, Pu and Am are: NpO, NpO_2, Np_3O_8, PuO, Pu_2O_3, Pu_2O_7, PuO_2, AmO and AmO_2.

(ii) **Hydrides, nitrides and carbides:** U and Pu form hydrides UH_3 and PuH_3, by the direct union of the elements. U reacts with H_2 even at room temperature but the reaction is faster at 250 ^{0}C as compared to room temperature:

$$2U + 3H_2 \rightarrow 2UH_3$$

This compound is reactive and is hydrolysed by water:

$$2UH_3 + 4H_2O \rightarrow 2UO_2 + 7H_2$$

This also reacts with Cl_2, HF and HCl as follows:

$$2UH_3 + 4Cl_2 \rightarrow 2UCl_4 + 3H_2$$

$$2UH_3 + 8HF \rightarrow 2UF_4 + 7H_2$$

$$UH_3 + 3HCl \rightarrow UCl_3 + 3H_2$$

When treated with ammonia, the metals give nitrides of the type: UN, U_2N_3, UN_2 and PuN.

These metals also give carbides: UC and PuC.

All the MX type compounds where M = U, Np, Pu or Am and X = O, C or N have the rock-salt (or NaCl) structure.

(iii) **Halides:** Actinide elements on reacting with halogens or hydrogen halides form halides, the most common being those of U and Np. Trihalides of MX_3 type are formed by the actinides which are isomorphous with one another. Some of the actinides also form the tetra, penta and hexa halides as well. For example, U fluorides are obtained as is shown by the following reactions:

(iv)

$$UO_2 \xrightarrow{HF} UF_4 \xrightarrow{F2,\ 240^0c} UF_5 \xrightarrow{HF} UF_6 \text{ and } UF_8^{2-}$$

$$UF_4 \xrightarrow{900^0c} UF_3$$

$$UF_4 \xrightarrow{F_{2,400}{}^0c} UF_6$$

Np, Pu and Am are also reactive similar to U and give the analogous reactions and products. Some examples of halides are: UF_6, UF_5, UF_4, UF_3, UCl_4, UCl_3, UBr_4, UBr_3, NpF_6, NpF_4, NpF_3, $NpCl_3$, NpI_3, etc.

2.5 CHEMISTRY OF SEPARATION OF NP, PU AND AM FROM U

Although several isotopes of Np, Pu and Am elements are known yet only a few are obtained. But Np^{237} and Pu^{239} are found in the uranium fuel elements of nuclear reactors from which Pu is isolated on a kilogram scale. Np^{237} is also found in substantial amounts and is recovered primarily for conversion by neutron irradiation of NpO_2 into Pu^{238} which is used as a power source for satellites. Am produced from intense neutron irradiation of pure plutonium. The main problem involved in the extraction of these elements includes the recovery of the expensive signatory material and the removal of hazardous fission products that are formed simultaneously in amounts comparable to the amount of the synthetic elements themselves. There are various methods available for the separation of Np, Pu and Am which are based on precipitation, solvent extraction, differential volatility of compounds and ion exchange. The chemistry of the most important methods of separation is given below:

2.5.1 Method based on stabilities of oxidation states

The stabilities of major ions of these elements involved are $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+}$ and $Am^{3+} > Pu^{3+} >> Np^{3+} > U^{4+}$. By choosing a suitable oxidising or reducing agent, it is possible to obtain a solution containing the elements in different oxidation states. The elements can then be separated by precipitation or solvent extraction method. For example, Pu can be oxidized to PuO_2^{2+} whereas Am remains as Am^{3+}. Thus PO_2^{2+} can be easily removed by solvent extraction or Am^{3+} by precipitation as AmF_3.

2.5.2 Method based on extraction by using organic reagents

It is a well-known fact that MO_2^{2+} ions can be extracted from nitrate solutions into organic solvents. The M^{4+} ions can be extracted into tributyl phosphate in kerosene from a 6M-HNO_3 solution. Similarly, M^{3+} ions can be separated from 10-16M HNO_3. Thus, the actinides close to each other can be separated by changing the conditions.

2.5.3 Method based on precipitation

The actinide ions in M^{3+} or M^{4+} state only give insoluble fluorides or phosphates in an acid solution. In the higher oxidation states these elements are either soluble or can be prevented from getting precipitated by complex formation with sulphate or other ions.

2.5.4 Method based on ion-exchange

This method has been found suitable for small amounts of material. In this method, both cationic and anionic ion exchangers can be used to separate the actinide ions. The separation of the actinides by ion-exchange methods is given below:

1. **Isobutyl methyl ketone method:** In this method, the following scheme is used:

$$UO_2^{2+} + Ac^{4+} \xrightarrow{Cr_2O_7^{2-}} UO_2^{2+} + AcO_2^{2+} \xrightarrow[\text{Extract}]{Al(NO_3)_3} \text{Aqueous portion} + \text{solvent}$$

$$\text{portion } (UO_2^{2+} + AcO_2^{2+}) \xrightarrow[+H_2O]{SO_2} \text{solvent } (UO_2^{2+}) + \text{Aqueous } (Ac^{4+})$$

The two layers are separated and collected. Here Ac^{4+} represents the actinide ions

such as Np^{4+}, Pu^{4+} and Am^{4+}.

2. **Tributyl phosphate method:** This method is dependent on the difference in extraction coefficients from 6N-HNO_3 into 30% tributyl phosphate in kerosene. The order of extraction is:

$$Pu^{4+} > PuO_2^{2+}, Np^{4+} > Np^+O_2 >> Pu^{3+} \text{ and } UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}.$$

The Ac^{3+} ions have very low extraction coefficients in 6M-HNO_3 but in 12M HCl or 16M HNO_3 the extraction increases. The order of extraction is: Np < Pu < Am < Cm, etc. In this method, the scheme used is as follows:

$$UO_2^{2+} + Ac^{4+} \xrightarrow[\text{TBP}]{\text{Exces}} \text{Aqueous portion} + \text{Solvent portion } (UO_2^{2+} + Ac^{4+}) \xrightarrow[\text{HNO3}]{\text{H2O}}$$

solvent portion (UO_2^{2+} or U^{4+}) + aqueous portion (Ac^{4+}) → Ac^{4+}. Repeat extraction to get Ac^{4+}. Here also, Ac = Actinide particularly Np and Pu.

3. **Method Based on Lanthanum fluoride cycle:** This method was developed for the isolation of Np but is of great utility in the separation of Pu from U. The scheme used for the separation is given below:

$$UO_2^{2+} + Ac^{4+} \xrightarrow[\text{with hexane}]{\text{Extract}} \text{Solvent } (UO_2^{2+}) + \text{Aqueous soln } (Ac^{4+} + \text{some } UO_2^{\ 2+}) \xrightarrow[La^{3+}]{\text{Ag.HF}}$$

$$\text{Filtrate } (UO_2^{2+}) + \text{ppt } (LaF_3 + AcF_3) \xrightarrow[SO_2]{\text{Boil with}} Ac^{3+} + Ac^{4+} \xrightarrow[\text{NaoH,}]{BrO_3^-} La^{3+} + AcO_2^{2+} \xrightarrow[\text{dissolve in HNO3}]{\text{HF}}$$

Ppt (LaF_3) + Filtrate (AcO_2^{2+}) → Ac^{4+} → Repeat the cycle to get more and pure Ac^{4+}, where Ac carries the usual meaning.

2.6 SIMILARITIES BETWEEN LANTHANIDES AND ACTINIDES

1. In the atoms of the elements of both the series, three outermost shells are partially filled and the remaining inner shells are completely filled but the additional or differentiating electron enters (n-2) f-subshell.
2. The elements of both series exhibit +3 oxidation state which is the prominent and predominant state.
3. Like Lanthanide contraction found in the lanthanide elements, there occurs a contraction in size in the actinide elements called actinide contraction. Both the contractions are due to poor shielding effect produced by f-electron with increasing nuclear charge.
4. The elements of both the series are quite reactive and are electropositive.
5. The electronic absorption bands of the elements of both the series are sharp and appear like lines. These bands are produced due to f-f transitions within (n-2)f-subshell though such transitions are orbital forbidden.
6. Most of the lanthanide and actinide cations are paramagnetic.
7. The nitrates, perchlorates and sulphates of trivalent lanthanide and actinide elements are soluble while the hydroxides, fluorides and carbonates of these elements are insoluble.
8. The lanthanide and actinide elements show similarity in properties among their series though the lanthanides are closer among them sieves in properties as compared to actinides.

2.7 SUMMARY

The text material of this unit contains the:

- The introductory part which is quite interesting and important from the view point of the readers and a detailed account of the general features of the actinides such as their occurrence, electronic structure, oxidation states which have greater variability than those of lanthanides, atomic and ionic radii-the actinide contraction, their magnetic and spectral properties along with exhibition of colour, formation of complexes, etc has been given.
- The chemistry of actinides including the formation of various compounds, e.g., oxides, hydrides, nitrides, carbides and halides in various oxidation states has also been discussed. The unit also contains a detailed account of the chemistry of separation of Np, Pu and Am from U including the method used for separation. At last, the points of similarities between the lanthanides and actinides have been mentioned.

2.8 TERMINAL QUESTIONS

1. Why do actinides show higher oxidation states than lanthanides?
2. Oxocations MO_2^{2+} are formed by U, Np, Pu and Am only whereas heavier actinides do not form such ions, why?
3. The elements beyond atomic number 102 are unstable, Explain.
4. Write the electronic configuration of Th, Cm and No.
5. Name the actinides along with their symbols and atomic numbers.
6. Which actinide ion in +3 oxidation state has just half-filled 5f-subshell?
   (a) Pu^{3+} (b) Am^{3+} (c) Cm^{3+} (d) Bk^{3+}
7. The first member of the post actinide transition series is:
   (a) Rutherfordium (b) Seaborgium (c) Meitnerium (d) Hahnium

2.9 ANSWERS

1. Due to high charge density actinides are capable of forming oxo cations in which these elements show higher oxidation states.
2. Because the tendency of disproportionation of these oxocations increases with increasing atomic number. Hence the oxocations of heavier actinides do not exist.
3. Beyond atomic number 102, the size of the nucleus increases thereby decreasing the nuclear stability. This causes a lower probability of the existence of stable elements beyond this atomic number.

4. & 5. Pl. refers to the text. 6. C, 7. a

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UNIT 3- ACIDS AND BASES

CONTENTS:

3.1 Introduction
3.2 Objectives
3.3 General concept of acids and bases
3.4 Theory of acids and bases
  3.4.1 Arrhenius theory
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3.1 INTRODUCTION

We all know that acids and bases play an essential and important role in our everyday life. The knowledge of acid/base chemistry helps in classifying daily household substances and items. A substance can be classified as an acid or a base depending on certain properties. There are several theories to define and classify acids and bases that including Arrhenius theory, Bronsted-Lowry acid/base concept, Lux-flood acid/base theory and Lewis acid-base concept. The strength of acids and bases can be determined by measuring pH values of solutions. Every theory of acid and base shows some advantages and some limitations to overcome; the drawback of each theory. A new theory was proposed which was observed to be more advanced as compared to the previous one. This unit will throw light on different theories of acids/bases, their drawbacks and relative strengths of acids and bases.

3.2 OBJECTIVES

The main goal of this Unit is to broaden your understanding about the following issues:

- Definitions of acids and bases,
- Different theories of acids and bases,
- Acid and base strength,
- Periodic variations of acidic and basic properties,

3.3 GENERAL CONCEPT OF ACIDS AND BASES

In general, acids and bases can be classified on the basis of their properties. The basic concept of acids and bases can be summarized as follows:

Acids:

- They are sour in taste.
- They react with some metals and produce hydrogen:

$$2HCl_{(aq)} + Zn_{(s)} \rightarrow ZnCl_2 + H_2$$

- They react with carbonate (Na_2CO_3) and bicarbonate ($NaHCO_3$) and produce CO_2:

$$NaHCO_3 + HCl_{(aq)} \rightarrow NaCl + H_2O + CO_2$$

- Solution of acids in water conducts electricity.
- They change the colour of litmus from blue to red.

Base:

- They have bitter taste.
- They change colour of litmus from red to blue.
- They are slippery in nature.
- Aqueous base solution conducts electricity.

3.4 THEORY OF ACID AND BASES

The different theories to define acids and bases are discussed along with their advantages and drawbacks in this section.

3.4.1. Arrhenius theory (Water system concept, 1884)

In 1884, the Swedish chemist Arrhenius defined acid as the species which ionize in water to produce H^+ ion or (H_3O^+ ions) and bases as the substances that ionize in water to produce OH^- ions. For example,

$$\text{Acid} \rightarrow HCl_{(g)} \underset{}{\overset{420}{\rightleftharpoons}} H^+_{(aq)} + Cl^-_{(aq)}$$

$$\text{Base} \rightarrow NaOH \overset{420}{\rightleftharpoons} Na^+_{(aq)} + OH^-_{(aq)}$$

The H^+ ion produced is always associated with a water molecule to form $H_3O^+(aq)$ (hydronium) ion. Hence, Arrhenius acids are called as proton donors / hydrogen ion donors / hydronium ion donors. The complete reaction will be –

$$HCl_{(s)} + H_2O_{(e)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(a)}$$

3.4.2. Bronsted–Lowry acids and bases (Protonic concept, 1923)

Arrhenius's definitions of acids and bases are limited to aqueous solutions. Hence, Bronsted in 1923 proposed that a substance capable of donating a proton to any substance is acid and a base can be defined as a species capable of accepting a proton from any other substance.

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Bronsted acid

$NH_3 + H^+ \rightarrow NH_4^+$

Bronsted base

There are three types of acids and bases according to Bronsted-Lowry (Table 9.1).

Acids:

(i) Molecular acids, HCl, H_2SO_4, CH_3 COOH

$$HCl \rightleftharpoons Cl^- + H^+$$

$$H_2SO_4 \rightleftharpoons HSO^- + H^+$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

(ii) Anion acids

$$\underset{\text{(Bisulphate)}}{HSO_4^-} \rightleftharpoons SO_4^{2-} + H^+$$

$$\underset{\text{(bio-oxalate)}}{HC_2O_4^-} \rightleftharpoons C_2O_4^{2-} + H^+$$

(iii) Cation acids

$$\underset{\text{Hydroxonium}}{H_3O^+} \rightleftharpoons H_2O + H^+$$

$$\underset{\text{Ammonium}}{NH_4^+} \rightleftharpoons NH_3 + H^+$$

Bases:

(i) Molecular bases

$$CH_3NH_2 + H^+ \rightleftharpoons CH_3NH_3^+ \text{(Cations)}$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

(ii) Anion bases (OH^-, S^{2-}, CO_3^{2-}, Cl^-, Br^-, NO_3^-)

$$OH^- + H^+ \rightleftharpoons H_2O \text{ (Neutral molecule)}$$

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$$

(iii) Cationic bases

$$[Fe(H_2O)_5OH] \overset{2^+H^+}{\rightleftharpoons} (Fe(H_2O)_6)^{3+}$$

3.4.2.1 Acid-Base Neutralization reaction:

According to Arrhenius concept, acid-base neutralization reaction takes place in water, where a compound containing or making available H_3O^+ (or H^+) ions (acid) combines with a compound containing or making available OH^- ions (base) to form the salt and water:

$$\begin{array}{ccccccc} \textbf{Acid} & & \textbf{Base} & & \textbf{Salt} & & \textbf{Water} \\ HCl & + & NaOH & \xrightarrow{420} & NaCl & + & H_2O \end{array}$$

Mechanism:

$$HCl \overset{420}{\rightleftharpoons} H^+ + Cl^-$$
$$NaOH \overset{420}{\rightleftharpoons} Na^+ + OH^-$$
$$HCl + NaOH \rightleftharpoons Na^+Cl^- + H^+[OH]^-$$
$$\text{Or } HCl + NaOH \overset{420}{\rightleftharpoons} NaCl + H_2O$$

This reaction is also known as salt formation reaction because salt formation takes place in this reaction.

3.4.2.2 Application (advantages) of Arrhenius concept

(i) Aqueous solutions of non-metallic oxides (e.g. CO_2, SO_2, SO_3, N_2O_3, N_2O_5, P_4O_6, P_4O_{10} etc.) are acidic in nature, since they give H^+ ions in water:

$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3 \rightleftharpoons 2H^+ + NO_3^-$$

(ii) Aqueous solutions of metallic oxides (e.g. CaO, Na_2O etc.) and the compounds like NH_3, N_2H_4, NH_4OH etc. are basic, since these substances give OH^- ions in aqueous solution:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$
$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(iii) The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the ionization (or dissociation) constant of the acid and base in aqueous solution.

$$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + A^-, \quad ka = \frac{CH^+ \text{ x } CA^-}{C_{HA}}$$
$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-, \quad kb = \frac{CB^+ \text{ x } COH^-}{C_{BOH}}$$

(iv) The catalytic property of acids in many reactions can be explained because of H^+ ions that become available from the acid in aqueous medium.

3.4.2.3 Limitations of Arrhenius concept

(i) According to this concept, the acid or base property of a substance is not supposed to inherit in the substance itself, but depends on its aqueous solution. For example, HCl is an acid, only when it is dissolved in water, but it is not considered as an acid in its gaseous state.

(ii) According to this concept, acid base neutralization reactions take place only in water and hence can't explain the reactions that occur in other solvents or in the gas phase. For example, the formation of $NH_4Cl_{(s)}$ by the combination of $NH_{3(g)}$ and $HCl_{(g)}$ cannot be explained by Arrhenius concept.

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

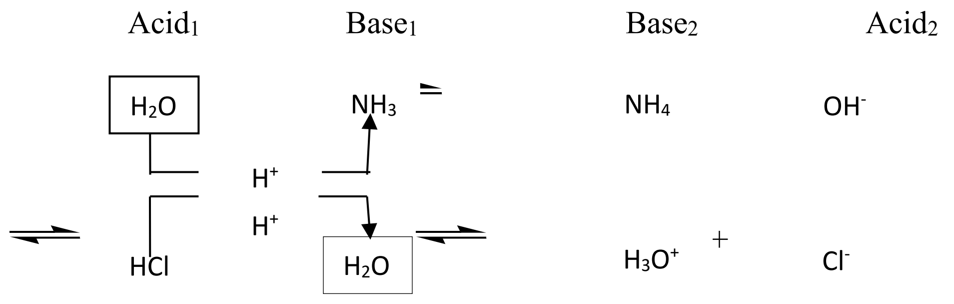
(iii) According to this concept, acids and bases undergo dissociation only in water (aqueous solvent). Thus, it is unable to explain the dissociation of acids and bases in non-aqueous solvents like liq. NH_3, liq. SO_2 etc.

Table 3.1 Bronsted–Lowry acids and bases

Type	**Acid**	**Base**
Molecular	HCl, HBr, $HClO_4$, H_2SO_4, H_3PO_4, H_2O	NH_3, N_2H_4, amines, H_2O
Cationic	NH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$	$[Fe(H_2O)_5(OH)]^{2+}$ $[Al(H_2O)_5(OH)]^{2+}$
Anionic	HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$	Cl^-, Br^-, OH^-, HSO_4^-, CO_3^{2-}, SO_4^{2-}

3.4.2.4 Amphoteric substances / Amphiprotonic substances

A substance which acts both as an acid as well as a base in different reactions is called amphoteric. Molecules or ions that can lose as well as accept proton are called amphoteric substances i.e. the molecules or ions that can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphoteric substances. For example, H_2O:



i) Acid$_1$ Base$_1$ Base$_2$ Acid$_2$

$$\boxed{CH_3COOH} \quad H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

HF $\boxed{CH_3COOH}$ $CH_3COOH_2^+$

3.4.2.5 Conjugate acids and bases

Bronsted-Lowry also gave the concept of conjugate acid base pair. Conjugate base is a species that remains when one proton has been removed from the acid.

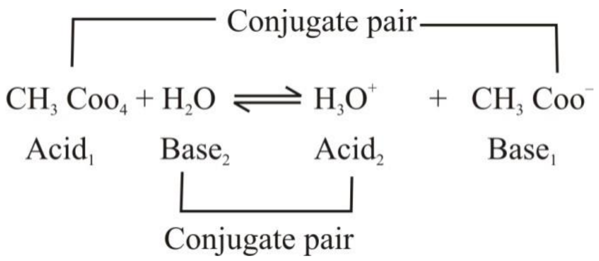
$$\text{Acid}_1 \rightleftharpoons H^+ + \underset{\text{Conjugate base}}{\text{base}}$$

Conjugate acid results from the addition of proton to a base

$$\text{Base}_2 \rightleftharpoons H^+ \rightleftharpoons \underset{\text{Conjugate acid}}{\text{acid}_2}$$

An acid base pair which is different by a proton is called conjugate acid base pair.

$$\text{Conjugate acid} \rightleftharpoons \text{Conjugate base} + H^+$$



$$\underset{\text{Acid}_1}{CH_3\,Coo_4} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{CH_3\,Coo^-}$$

Conjugate pair

Conjugate pair

The sum of these two reactions is

$$\text{Acid}_1 + \text{base}_2 \rightleftharpoons \text{Acid}_2 + \text{base}_1$$

Therefore, any acid-base reaction involves two acids and two bases. These acids and bases are called conjugate pairs.

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O} + \underset{\text{Base}_1}{Cl^-}$$

Relative strength of conjugate acid – base pairs

	Acid	Conjugate base	
Strong acids	$HClO_4$	ClO_4^-	↓ Increasing base Strength
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	

	HSO_4^-	SO_4^{2-}
Weak acids	HF	F^-
	HNO_2	NO_2^-
	HCOOH	$HCOO^-$
	CH_3COOH	HCOO
	NH_4^+	NH_3
	HCN	CN^-
	H_2O	OH^-
	NH_3	NH_2^-

- Acids stronger than H_3O^+, react with water to produce H_3O^+ and their conjugate bases.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-_{(aq)}$$

- Acids weaker than H_3O^+, react with water to a much smaller extent. Bases like O^{2-} (oxide) stronger than OH^-, react with water to produce OH^-.

$$O^{2-}\ (aq) + H_2O \rightarrow 2OH^-\ (aq)$$

Therefore, oxide ion does not exist in solution.

$$NH_2^- + H_2O \longrightarrow NH_3 + OH^-$$

3.4.2.6 Advantages of Bronsted–Lowry Concept:

1. This concept can explain the acidic/basic nature of a substance in aqueous (H_2O) as well as in other protonic solvents like liq. NH_3, liq. HF.
2. This concept also explains acid base reaction taking place in gaseous phase.

$$\begin{array}{ccccccc} \text{Acid} & & \text{Base} & & \text{Acid} & & \text{Base} \\ HCl\ (g) & + & NH_3\ (g) & \rightleftharpoons & NH_4^+ & + & Cl^- \quad \text{or}\ NH_4^+\ Cl^- \end{array}$$

3.4.2.7 Limitations of Bronsted–Lowry concept:

This concept cannot explain the acid-base reactions taking place in non-protonic solvents, like liq. SO_2, liq. BF_3, BrF_3, $AlCl_3$, $POCl_3$ etc. in which no proton transfer takes place.

$$\begin{array}{ccccccc} \text{Acid} & & \text{Base} & & \text{Acid} & & \text{Base} \\ SO_2 & + & SO_2 & \rightleftharpoons & SO^{2+} & + & SO_4^{2-} \\ BrF_3 & + & BrF_3 & \rightleftharpoons & BrF_4^+ & + & BrF_2^- \end{array}$$

3.4.3 Lux-Flood concept

According to Lux-Flood concept, the base is an oxide donor and the acid is an oxide acceptor. Lux-Flood definition is useful for limited systems such as molten oxides.

$$\underset{\text{Acid}}{CO_2} + \underset{\text{Base}}{BaO} \rightleftharpoons BaCO_3 \qquad \underset{\text{Base}}{B} \rightleftharpoons \underset{\text{Oxide ion}}{O^{2-}} + \underset{\text{acid}}{A^{2+}}$$

$$\underset{\text{Acid}}{SiO_2} + \underset{\text{Base}}{CaO} \rightleftharpoons CaSiO_3$$

$$\underset{\text{Base}}{3Na_2O} + P_2O_5 \longrightarrow 2Na_3PO_4$$

$$\underset{\text{Base}}{ZnO} + S_2O_7^{2-} \longrightarrow Zn^{2+} + 2SO_4^{2-}$$

The Lux-Flood oxide transfer concept of acid-base reactions can be extended to any negative and positive ion species. Base is the species that can form negatively charged species and acid is the species that can produce positively charged species.

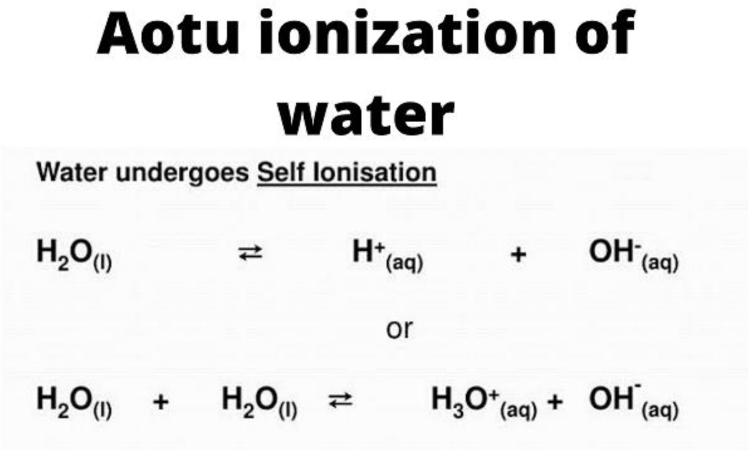
$$3NaF + AlF_3 \longrightarrow 3Na^+ + (AlF_6)^{3-}$$

$$\underset{\text{Base}}{EtNa} + \underset{\text{acid}}{Et_2Zn} \longrightarrow Na^+ + ZnEt_3^-$$

3.4.4 Solvent system (auto-ionization) concept (1928)

The concept was introduced by Franklin in 1905 and was extended by Cady-Esley in 1928. The definition of acids and bases given by this concept can be applied for protonic as well as for non-protonic solvents. According to this concept, the solvents usually undergo self-ionization (auto-ionization) and give rise to cations and anions called solvent cations and solvent anions, respectively. The substances which form solvent cations when dissolved in that solvent are called acids while the substances which give solvent anions when dissolved in that solvent are called bases. We can now also conclude that solvent cations can also be called acid cations and solvent anions can also be called base anions.

Auto-ionization of water –Water (H_2O) undergoes self-ionization in the following three ways:



Aotu ionization of water

Water undergoes Self Ionisation

$$H_2O_{(l)} \rightleftarrows H^+_{(aq)} + OH^-_{(aq)}$$

or

$$H_2O_{(l)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + OH^-_{(aq)}$$

These three different modes of ionization suggest that, according to the solvent system concept, the substance that gives H^+ or H_3O^+ ions in water, act as acid in aqueous solution, while the substances which furnish OH^- or O^{2-} ions in water, behave as bases.

HCl gives H^+ or H_3O^+ ions in water, hence; it behaves as an acid in aqueous solution.

$$HCl \overset{Water}{\rightleftharpoons} H^+ + Cl^-$$

$$\text{Or } Hcl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Similarly, NaOH, which furnish OH^- ions in its aqueous solution, acts as a base.

$$NaOH \overset{Water}{\rightleftharpoons} Na^+ + OH^-$$

Likewise, for a solvent system of BrF_3, the autoionization reaction is-

$$2BrF_3 \rightleftharpoons \underset{\text{acidic}}{BrF_2^+} + \underset{\text{base}}{BrF_4^-}$$

Hence, according to solvent system concept, the substance which can give BrF_2^+ in BrF_3 is acid and the substance which can form BrF_4^- is base.

$SbF_5 + BrF_3 \rightarrow BrF_2^+ + SbF_6^-$
Acid
$KF + BrF_3 \rightarrow BrF_4^- + K^+$
Base

3.4.4.1 Advantages of solvent system concept

1. The definition of acids and bases given by solvent system concept can be used for both protonic (e.g. H_2O, NH_3 etc.) as well as non-protonic (e.g. SO_2, $SOCl_2$ etc.) solvents.
2. The definition is applicable for aqueous (H_2O) as well as non-aqueous solvents (NH_3, HF, H_2SO_4 etc).

3.4.4.2 Disadvantages

1. The definition of acids and bases is based on the nature of the solvent cation and solvent anion obtained by auto-ionization of the solvent.
2. Acid base reaction taking place in the absence of a solvent can’t be explained, i.e., acid-base reaction takes place only in presence of solvent.
3. The concept can’t account for the acid-base reaction occurring in non-ionizing solvents like C_6H_6, $CHCl_3$ etc.

3.4.5 Lewis concept: Electron pair acceptor-donor concept (1923)

According to G.N. Lewis, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

Lewis acid	Lewis base
Electrophile	Nucleophile
Contain vacant orbitals	Contain a lone pair of electrons
Example – BeF_2, BH_3, BF_3 etc.	Example–NH_3, H_2O, H^- etc.

3.4.5.1 Neutralization reaction according to Lewis's concept

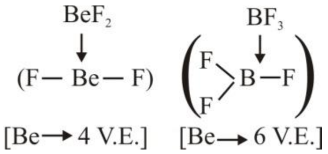
- Lewis's acid reacts with Lewis's base and forms a compound which is called adduct or complex compound.
- The compound contains (Lewis base – Lewis acid) co-ordinate bond.
- Lewis acid + Lewis base → Adduct

$$BF_3 \quad + \quad :NH_3 \quad \rightarrow \quad [NH_3 \rightarrow BF_3]$$

3.4.5.2 Examples of Lewis acids

1. Molecules whose central atoms have vacant p-orbital or incomplete octet of electrons in its valence shell.

Examples –



The Arrhenius, Bronsted-Lowry and solvent system neutralization reactions can be compared as follows:-

Arrhenius : acid + base → salt + water

Bronsted-Lowry : $acid_1 + base_2 \rightarrow base_1 + acid_2$

Solvent system : acid + base → solvent

Lewis system : acid + base → adduct/coordination compound.

2. Molecules whose central atoms have vacant d-orbitals in their valence shell.

e.g. AlF_3, $AlCl_3$, GeX_4, $TeCl_4$, SF_4, SbF_3 etc.

3. Molecules whose central atom is linked with more electronegative atom by double bonds.

e.g.

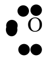
$$CO_2\ [\overset{-\delta}{O} = \overset{+2\delta}{C} = \overset{-\delta}{O}], \quad SO_2\ [\overset{-\delta}{O} = \overset{+2\delta}{S} = \overset{-\delta}{O}]$$

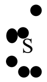
4. Simple cations, with low lying empty orbitals.

e.g. Ag^{+}, Cu^{2+}, Cd^{2+} etc.

5. Elements which have a sextant of electrons in their valence shell.

e.g.

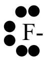


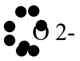


Examples of Lewis base:

1. Molecules whose central atom has one or more unshared electron pairs (lone pair of electrons), e.g.

e.g.





2. Molecules containing C = C double bond

3. Halides, e.g. – XeF_2, XeF_4, CsF, $CoCl_2$ etc.

3.4.5.3 Pearson's classification of Lewis acids and Lewis bases into hard and soft acids and bases.

R. G. Pearson (1963) has classified the Lewis acids and Lewis bases as hard and soft acids and bases. Third categories whose characteristics are intermediate between those of hard and soft acids/bases are called borderline acids/bases.

Hard acids	Soft acids
d-orbitals are either vacant or non-existent	Nearly full d-orbitals
Smaller in size	Larger in size
Not so easily polarizable	Easily polarizable
These are mostly light metal ions generally associated with high positive oxidation state.	These are mostly heavy metal ions generally associated with low (or even zero) positive oxidation state.

Hard Acids	Borderline Acids	Soft Acids

H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Si^{4+}, Ti^{4+}, U^{4+}, Ce^{3+}, Sn^{4+}, VO^{2+}, UO_2^{2+}, MoO_3^{3+}, BF_3	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, SO_2, NO^+, GaH_3	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pb^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}, TI^{3+}, BH_3, $GaCl_3$, $InCl_3$, carbenes, π - acceptor ligands I^+, Br^+, O, Cl, Br, I, N Zero valent metal atoms.

Hard bases	**Soft bases**
Donor atoms having low polarisabilities and high electronegativity	Donor atoms that can be easily polarized and have low electronegativity.

Hard Bases	**Borderline Bases**	**Soft Bases**
H_2O, OH^-, F^-, CH_3COO^-, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-, ROH, RO^-, R_2O, NH_3, NH_2, N_2H_4	$C_6H_5NH_2$, C_6H_5N, N_3^-, NO_2, SO_3^{2-}, N_2, Br^-	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, CN^-, RCN, CO, C_2H_4, C_6H_6, H^-

According to HSAB principle, hard acids form stable complexes with hard bases and soft acids with soft bases.

3.4.5.4 Utility of Lewis Concept

1. This concept includes those reactions also in which no protons are involved.
2. It is more significant than Bronsted – Lowry concept because according to this concept, acid-base behavior is independent of solvent's presence or absence.
3. It explains basic properties of metallic oxides and acidic properties of non-metallic oxides.
4. This concept also explains gas phase, high temperature and non-solvent reactions.

3.4.5.5 Limitations

1. It is not possible to arrange Lewis's acids and Lewis bases in order of their acid or base strength.

2. Protonic acids like H_2SO_4 and HCl are not covered under Lewis's concept, as they do not establish a covalent bond by accepting a pair of electrons (which a Lewis acid ought to).

3. According to this concept, acid-base reaction should be fast but it is not so in actual practice for many reactions due to kinetic factors.

4. The reactions catalyzed by Lewis's acids are generally not catalyzed by the protonic acids.

3.4.6 Stanovich concept (1939)

Acid

- An acid is any chemical species which reacts with a base.
- It gives up cation or accepts anions or electrons.

Base

- A base is a species which reacts with acids.
- It gives up anion or electrons or combines with cations.

All the oxidizing agents are acids and the reducing agents as bases.

Example –

$$\underset{\text{(Base)}}{Fe^{2+}} \rightleftharpoons \underset{\text{(Acid)}}{Fe^{3+}} + e^{-}$$

3.4.6.1 Limitations

This concept is very general and all chemical reactions are to be considered.

3.5. RELATIVE STRENGTHS OF ACIDS AND BASES

3.5.1. Acidity and basicity of binary hydrogen compounds

- Higher the values of Ka and K_b, stronger the acid or base

- Higher the pK_a or pK_b values, weaker the acid or base.

- The greater bond strength, less acidic is the hydride. On descending a group, the change in bond strength is greater than the change in the decreasing electronegativity.

- In a period from left to right, the change in electronegativity is greater than the changes in bond strength and the trend of electronegativity determines the trend in acidity.

Increasing order of acid strength as a result of increase in electronegativity

Increasing order of acid strength as a result of decrease in bond energy

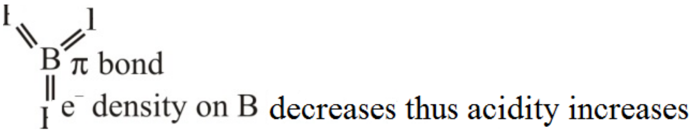
	CH_4	<	NH_3	<	H_2O	<	HF
pK_a	38		35		16		3
Bond energy (kJ/ mole	414		389		464		565

	PH_3	<	H_2S	<	HCl
pK_a	27		7		-7
Bond energy	320		368		431

3.5.2. Inductive effect (I-effect)

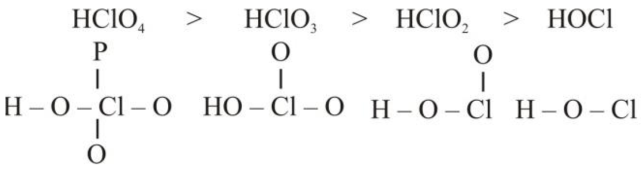
The strength of acids and bases can be explained by inductive effect. In case of electronegative groups, due to –I effect, availability of electrons on the central metal atom decreased and thus, basicity of a base decreased. Electron donor groups (+I effect) like methyl ($-CH_3$) group, increase electron density on central atom, thus, increase its basicity. In case of aliphatic amines, steric factors are responsible for weak basicity of tertiary amine.

- PF_3 is weaker base than PH_3.
- Base strength order $NHMe_2 > NH_2Me > NMe_3 > NH_3$.
- Boron halides do not follow this argument, acid strength $BF_3 < BCl_3 < BBr_3$. In such cases, the atom with empty orbitals (like Cl and Br), receive electrons from filled valence orbitals (in boron, all the four orbitals are filled), thus, create a double bond between boron and halogen atom and boron atom become more electron deficient. Bromine can more easily receive electrons from boron as compared to chlorine. Thus, BBr_3 is more acidic as compared to BCl_3.



3.5.3. Strength of oxoacids (Effect of electronegativity)

A) Presence of electronegative atoms tends to attract the shared pair of e^- towards themselves and thus, dissociation of O – H bond becomes easier and the acid will be stronger.



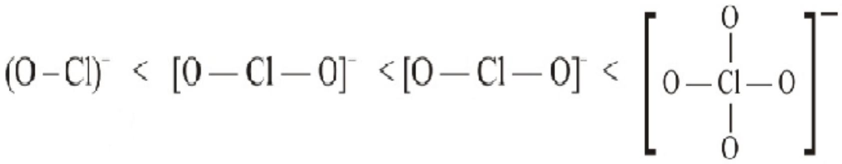
Order of acid strength

In $HClO_4$, the presence of maximum number of electronegative oxygen atoms increases its acidity.

$$\longrightarrow$$

$$Cl - OH - < OCl - OH < O_2Cl - OH < O_3Cl - OH$$

The other reason for the highest acidity of $HClO_4$ is that the negative charge after removing hydrogen can distribute over four oxygen atoms.



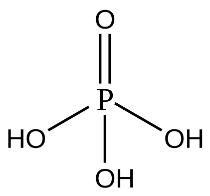
Maximum stability of ClO_4^- due to –ve charge distribution in four oxygen atoms, so minimum attraction of H^+ for distributed –ve charge and H^+ can be removed easily. While, in case of OCl^-, -ve charge delocalized on only one oxygen atom. Hence, shows minimum stability.

B) Among HClO, HBrO and HIO, HClO is the most acidic in nature.

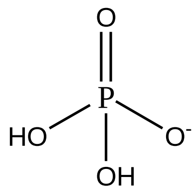
$$HClO > HBrO > HIO$$

Electronegativity of I is lowest. Hence, the acidity of HIO will be the least.

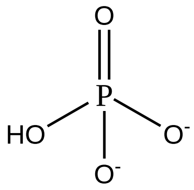
C) For oxoacids of phosphorus, having more than one ionizable hydrogen, the pKa value increases with decrease in the number of ionizable hydrogens.



H_3PO_4



$H_2PO_4^-$



HPO_4^{2-}

pK 2 7 12

The negative charge of the conjugate base is spread over all the nonhydrogenated oxygens. The larger the number of these oxygen atoms, the more stable and weaker the conjugate base and stronger the hydrogened acid.

D) Acidity of cations in aqueous solution

Metal ions with higher charges and smaller radii are stronger acids. The order of acidic strength is (Hydrated ions) alkali metals < alkaline earth metals < + 3 < +4 (transition metals). A high positive charge promotes more hydrogen ion dissociation:

$$\underset{\text{more acidic}}{[Fe(H_2O)_6]^{3+}} + H_2O \rightleftharpoons \underset{\text{less acidic}}{[Fe(H_2O)_5(OH)]^{2+}} + H_3O^+$$

Solubility of metal hydroxide is also a measure of cation acidity. The stronger cationic acid, the less soluble the hydroxide. Transition metal +3 ions are acidic enough to form hydroxides.

- Higher charged ions are so strong acids in aqueous solutions that they exist only as oxygenated ions

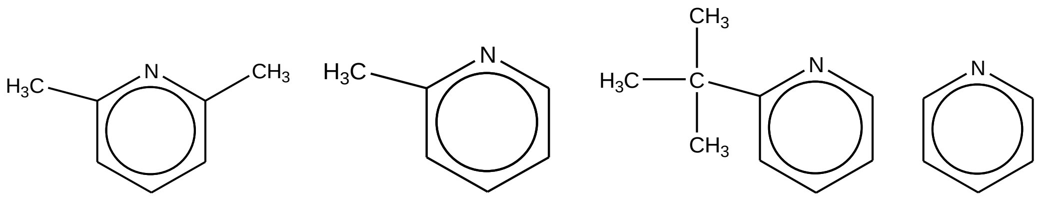
$$CrO_4^{2-},\ MnO_4^-,\ Cr_2O_7^{2-},\ UO_2^+$$

- $[Ni(OH)_4]^{2-}$ is a stronger base than $[Ni(OH)_4]^-$ ion

Acidity increases with increase of positive charge and basicity increases with increase in negative charge.

E) Steric effects

Steric effects also influence acid-base behavior. Reactions of series of substituted pyridines with hydrogen ions show the following order of base strength:



2,6-dimethylpyridine > 2-methylpyridine > 2-t- butylpyridine > pyridine

3.6 SUMMARY

A compound may be acid or base on the basis of certain properties. There are different theories which classify and define the compounds into acids and bases. Some of the important theories are summaries below.

- According to the **Arrhenius concept**, acids are the compounds that give off H^+ ions in aqueous medium and **bases** are the compounds that release OH^- ions in aqueous medium.
- The **Bronsted-Lowry acids** are the compounds that give off H^+ ions to the other substances and **bases** are the compounds that accept H^+ from other substances. They also bring the concept of conjugate acids and bases.
- **Lewis acids** are the compounds that are electron deficient and can easily accept an electron pair while **bases** are the electron efficient compounds and can donate lone pair of electrons to other substances (Lewis acids).
- According to the **solvent concept, acids** are the positive species donor while **bases** are negative species donor in a solvent system.
- **Lux-Flood acids** are those compounds which can accept oxide ion and bases are oxide ion donor.
- In general acids have pH values in between 0 – 6.9 (<7), bases between 7.1 – 14 (>7) and neutral substances have a value of 7.
- The strength of acids and bases can be defined on the basis of pK_a and pK_b values. Higher the pK_a value, lower its acidity and similarly higher the pK_b values, weaker will be the base and *vice-versa.*
- The different factors that affect acidity or basicity are inductive effect, resonance, steric effect, electronegativity and charge on the species.
- The hydrides of 2nd period viz. CH_4, NH_3, H_2O and HF become more acidic as we move from CH_4 to HF. As the basicity of their conjugate base decreases from CH_3^- to F^-, the acidity of their conjugate acid increases from CH_4 to HF.

3.7 REFERENCES

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b) G. S. Sodhi, *Textbook of Inorganic Chemistry*, Viva Books Private Limited, New Delhi, 2013.

c) M. S. Yadav. *Quick Review in Inorganic Chemistry*, Anmol Publications Pvt. Ltd., New Delhi, 2004.

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3.8 TERMINAL QUESTIONS

A. Fill in the blanks

i. In 1884, the Swedish chemist Arrhenius defined acid as the species which ionize in water to produce …….. or …….. ions.

ii. Arrhenius's definitions of acids and bases are limited to……………………...

iii. Hence, Bronsted in 1923 proposed that a substance capable of donating a proton to any substance is …………. and a ……….. can be defined as a species capable of accepting proton from any other substance.

iv. Aqueous solution of ………………………….. oxides is acidic.

v. Aqueous solution of …………….. oxides and is basic.

vi. The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the …………………………………………………. constant.

vii. A substance which acts both as an acid as well base in different reactions is called ……………………………..

viii. ……………………………. also gave the concept of conjugate acid base pair.

ix. Conjugate base is a species that remains when one …………… has been removed from the acid.

x. An acid base pair which is different by a proton is called ……………. acid base pair.

xi. Acid stronger than H_3O^+, react with water to produce H_3O^+ and their …………………………….. bases.

xii. According to ……………… concept, the base is an oxide donor and the acid is an oxide acceptor.

xiii. Base is the species that can form …………… charged species and acid is the species that can produce …………………… charged species.

xiv. Solvent system concept was introduced by ……………….. in 1905 and was extended by ………………….. in 1928.

xv. According to solvent system concept, the substance which can give BrF_2^+ in BrF_3 is ……………..

xvi. According to G. N. Lewis, a ………………... is an electron pair acceptor and a Lewis base is an electron pair donor.

xvii. According to HSAB principle, hard acids form stable complexes with …………………… and soft acids with……………………….

xviii. In Hard acids, d-orbitals are either ………….. or ....

xix. Higher the pK_a or pK_b values, ……………… the acid or base.

xx. PF_3 is ………………. base than PH_3.

xxi. Among HClO, HBrO and HIO, ……………… is the most acidic in nature.

xxii. Metal ions with higher charges and smaller radii are ………………….. acids.

xxiii. Higher charged ions are so strong acids in aqueous solutions that they exist only as ……………………… ions.

B. State True (T) or False (F)

i. Solution of acids in water conducts electricity.

ii. Arrhenius acids are called as proton donors / hydrogen ion donors / hydronium ion donors.

iii. H_3O^+ is a Bronsted acid.

iv. In the gas phase the formation of $NH_4Cl_{(s)}$ by the combination of $NH_{3(g)}$ and $HCl_{(g)}$ can be explained by Arrhenius concept.

v. The molecules or ions that can act as Bronsted acids as well as Bronsted bases are called amphoteric substances.

vi. Any acid-base reaction involves one acid and one base.

vii. The substances which form solvent cations when dissolved in that solvent are called bases while the substances which give solvent anions when dissolved in that solvent are called acids.

viii. Lewis acid reacts with Lewis base and forms a compound which is called adduct or complex compound.

ix. Molecules whose central atom is linked with more electronegative atom by double bonds are Lewis acids.

x. Pearson gave the classification of Lewis acids and Lewis bases into hard and soft acids and bases.

xi. Base strength order of amine and substituted amines is $NHMe_2 < NH_2Me < NMe_3 < NH_3$.

xii. $[Fe(H_2O)_6]^{3+}$ is more acidic as compared to $[Fe(H_2O)_5(OH)]^{2+}$.

xiii. $[Ni(OH)_4]^-$ is more basic as compared to $[Ni(OH)_4]^{2-}$.

xiv. Order of basic strength of substituted pyridine is 2,6-dimethylpyridine > 2-methylpyridine > 2-t- butylpyridine

C. Long answer questions

i. What are the general characteristics of acids and bases?

ii. Discuss Arrhenius theory of acids and bases.

iii. Write short notes on the following:

  a. Conjugate acid and base
  b. Neutralization reaction
  c. Lux-Flood concept
  d. Solvent system concept

iv. Discuss Lewis acid and base concept

v. Differentiate between hard and soft acids and bases.

vi. How electronegativity affects acid and base strength?

ANSWERS

A. Fill in the blanks

i. H^+ or $H_3O^{+,}$ ii. Aqueous solutions, iii. acid, iv. base-metallic, v. metallic
iv. ionization (or dissociation), vii. Amproteric, viii. Bronsted-Lowry, ix. proton
x. conjugate, xi, conjugate, xii. Lux-Flood, xiii. negatively, xiv. positivelyFranklin, Cady-Esley. xv. Acid, xvi. a Lewis acid, xvii. hard bases, soft bases, xviii. Xix. vacant, non-Existent, xx. Stronger, xxi. Weaker, xxii. HClO, xxiii. Stronger, xiv. Oxygenated

B. True (T) or False (F)

i. T, ii. T iii. T iv. F v. T vi. F vii. F viii. T ix. T x. T xi. F xii. T xiii. F xiv. T

BLOCK-II: CARBOXYLIC FUNCTIONAL GROUP CONTAINING COMPOUNDS

UNIT -4 CARBOXYLIC ACIDS

CONTENTS:

4.1 Introduction
4.2 Objectives
4.3 Nomenclature of carboxylic acids
4.4 Structure and Bonding
4.5 Physical properties
4.6 Acidity of carboxylic acids and effect of substituents on acid strength
4.7 Preparation of carboxylic acids
4.8 Reactions of carboxylic acids
4.9 Synthesis of acid chlorides, esters and amides.
4.10 Mechanism of decarboxylation
4.11 Methods of formation and chemical reactions of halo-acids
    4.11.1 Preparation of halo acids
    4.11.2 Chemical reactions of halo-acids
4.12 Hydroxy acids: malic, tartaric and citric acids
    4.12.1 Physical properties of hydroxyl acids
    4.12.2 Preparation and chemical properties of hydroxy acids
4.13 Summary
4.14 Terminal Question
4.15 Answers (MCQ)
4.16 References

4.1 INTRODUCTION

Carboxylic acids are aliphatic or aromatic compounds that contain at least one carboxyl group (-COOH) in the molecule. The word "carboxyl" is derived from the names of two functional groups *i.e.* carbonyl and hydroxyl. Carboxylic acids are classified as mono, di, tri, or polycarboxylic acids according to the number of carboxyl groups in the molecule. For example, the one–COOH group containing hydrocarbons such as formic acid, acetic acid, propionic acid, lactic acid, malic acid, benzoic acid etc. are called monocarboxylic acids whereas the two –-COOH groups containing compounds such as oxalic acid, succinic acid, adipic acid, fumaric acid, malic acid, tartaric acid phthalic acid etc. are called dicarboxylic acids similarly like citric acid contains three -COOH group and termed as tri-carboxylic acid. Long-chain monocarboxylic acids are also known as fatty acids such as stearic, palmitic, oleic, etc. The general chemical formula of aliphatic carboxylic acids is $C_nH_{2n+1}COOH$.

4.2 OBJECTIVES

- This unit aims to make you aware of carboxylic acids their common names and IUPAC naming system.
- To explain the structure of carboxylic acids, describe the acid strength of carboxylic acids, describe boiling points and solubility of carboxylic acids in water, synthesize carboxylic acids describe the physical and chemical properties of carboxylic acids.
- To discuss the methods for the conversion of carboxylic acids into acid chlorides, esters, and amides. To study the reduction of carboxylic acid and understand the mechanism of decarboxylation.
- To study how halo acids are synthesized from carboxylic acids. To describe the preparation, properties and uses of hydroxyl acids: malic, tartaric, and citric acids.

4.3 NOMENCLATURE OF CARBOXYLIC ACIDS

In IUPAC system, carboxylic acids are named by replacing the suffix "***–e***" of the corresponding alkane with "***-oic acid"***. It is not necessary to indicate the position of the -COOH group because this group will be at the end of the parent chain and its carbon is assigned as C-1. The common names and IUPAC names for some straight chain saturated carboxylic acids are given in *Table-4.1*.

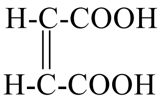
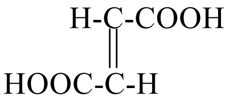
Table 4.1–Common names and IUPAC names of some straight chain saturated carboxylic acids

Carboxylic acids	**Common name**	**IUPAC name**
HCOOH	formic acid	methanoic acid
CH_3COOH	acetic acid	ethanoic acid
CH_3CH_2COOH	propionic acid	propanoic acid
$CH_3(CH_2)_2COOH$	butyric acid	butanoic acid
$CH_3(CH_2)_3COOH$	valeric acid	pentanoic acid
$CH_3(CH_2)_4COOH$	caproic acid	hexanoic acid
$CH_3(CH_2)_5COOH$	enanthic acid	heptanoic acid
$CH_3(CH_2)_6COOH$	caprylic acid	octanoic acid
$CH_3(CH_2)_7COOH$	pelargonic acid	nonanoic acid
$CH_3(CH_2)_8COOH$	capric acid	decanoic acid
$CH_3(CH_2)_9COOH$	-	undecanoic
$CH_3(CH_2)_{10}COOH$	lauric	dodecanoic

IUPAC nomenclature of di-carboxylic acids: If there are two -COOH groups are present in an acid; the acid is called dicarboxylic acid. To construct the IUPAC name of these compounds, add the suffix ***–dioic*** acid to the name of the parent alkane containing both carboxylic groups (*Table-4.2)*.

Table 4. 2-Common names and IUPAC names of some di-carboxylic acids

Carboxylic acids	**Common name**	**IUPAC name**
HOOC-COOH	oxalic acid	ethanedioic acid
$HOOC.CH_2COOH$	malonic acid	propanedioic acid
$HOOC.CH_2CH_2COOH$	succinic acid	butanedioic acid
$HOOC(CH_2)_4COOH$	adipic acid	hexanedioic acid

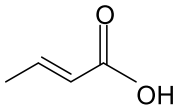
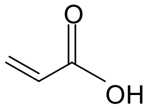
 $\begin{array}{c} H\text{-}C\text{-}COOH \\ \| \\ H\text{-}C\text{-}COOH \end{array}$	maleic acid	*cis*-2-butenedioic acid
 $\begin{array}{r} H\text{-}C\text{-}COOH \\ \| \\ HOOC\text{-}C\text{-}H \end{array}$	fumaric acid	*trans*-2-butenedioic acid

IUPAC nomenclature of hydroxyl derivatives of carboxylic acids: The hydroxyl derivatives of carboxylic acids are called hydroxyl carboxylic acids. In the common system, the position of the –OH group in a hydrocarbon chain is indicated by the *Greek alphabets* α, β, γ, δ *etc.* whereas in the IUPAC system the position of the –OH group in a hydrocarbon chain is indicated by the *numbering, 1, 2, 3, 4 etc. (Table-4.3)*

Table 4.3-Common names and IUPAC names of some hydroxyl derivatives of carboxylic acids.

Carboxylic acids	**Common name**	**IUPAC Name**
$HOCH_2COOH$	glycollic acid	hydroxyethanoic acid
$CH_3CHOHCOOH$	lactic acid	2-hydroxy propanoic acid
$HOOCCH_2CHOHCOOH$	malic acid	2-hydroxy butane dioic acid
$HOOC(CHOH)_2COOH$	tarteric acid	2,3-dihydroxy butanedioic acid
$HOC(COH)((CH_2)COOH)_2$	citric acid	2-hydroxypropane-1,2,3 tri carboxylic acid

Table 4.4–If a carboxylic compound contains double bond (alkene), then replace the infix from "*–an to –en*" and the placement of the infix is determined by the *numbering, 1, 2, 3, 4, etc.* ***(****Table-4.4).*

Carboxylic acids	**Common name**	**IUPAC name**
	crotonic acid	*trans*-2-Butenoic acid
	acrylic acid	propenoic acid

IUPAC nomenclature of aromatic carboxylic acids: Aromatic carboxylic acids are named by adding the suffix *"-carboxylic acid"* to the name of a parent hydride (*Table-4.5*).

Table 4.5–Common names and IUPAC names of some aromatic carboxylic acids:

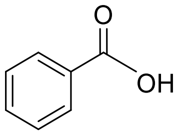
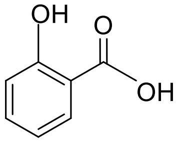
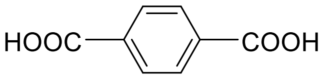
Carboxylic acids	**Common name**	**IUPAC name**
	benzoic acid	benzene carboxylic acid
	salicylic acid	2-hydroxybenzene carboxylic acid

Table 4.6–If the two carboxylic acid groups are in the benzene ring it is named as *"di-carboxylic acid".*

Carboxylic acids	**Common name**	**IUPAC name**
	phthalic acid	1,2-benzenedicarboxylic acid
	terephthalic acid	1,4-benzenedicarboxylic acid

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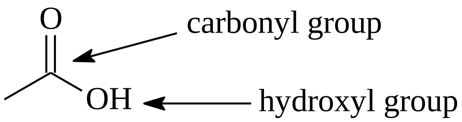
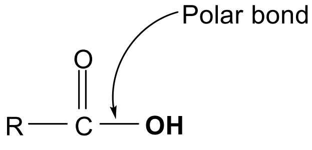
4.4 STRUCTURES AND BONDING

The carboxylic group (-COOH) in a carboxylic acid is constituted by a carbonyl group (C=O) and a hydroxyl group (-OH). The carboxyl carbon atom is double bonded with one oxygen atom and single bonded with another oxygen atom in a carboxylic group as shown in figure:

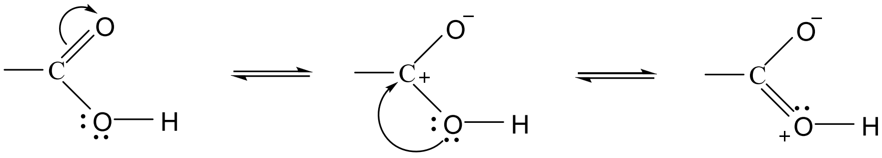


The carboxylic acids can be represented by R-COOH or R-CO_2H. The carboxylic carbon in a carboxylic acid is bonded with three functional groups, therefore the carboxylic carbon is sp^2 hybridized and hence the carboxylic group has a planer structure with bond angles of approximately 120°. In a carboxylic group, the C=O bond length is shorter than the bond length between C-O. One half-filled un-hybridized *p*-orbital of the carbon and the un-hybridized *p*-orbital of the oxygen atom undergo sideways overlap. This results in the formation of the delocalized p-electron cloud. This is confirmed by the C-O single bond length in formic acid being shorter than the C-O bond length in ethanol. The oxygen is more electronegative than either carbon or hydrogen therefore the C-O and O-H bonds are polar.



Carboxylic acid

The carboxyl group has the following resonating structures:



[I] [II] [III]

The third resonance structure (III) has all atoms with their full quota of electrons and thus is more stable and more important contribution to the resonance hybrid than the second structure (II) in which the positively charged carbon atom has only six electrons in its valence shell. Thus in two important resonance structures [I] and [III] the carboxyl carbon is electrically neutral. The carboxyl group is also polar due to resonance structures [II] and [III].

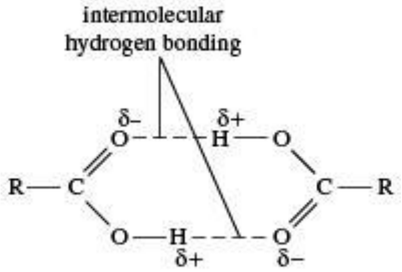
4.5 PHYSICAL PROPERTIES

1. Physical state

Lower members (C_1-C_3) are colorless liquids with having pungent smell. C_4-C_9 members are colorless oily liquids having an odor like goat butter. Higher members (C_{10} onwards) are colorless, odorless waxy solids.

2. Hydrogen bonding

The intermolecular hydrogen bonding occurs in carboxylic acids. The two molecules of carboxylic acids are associated by hydrogen bonding into dimers (pairs of molecules) in liquid state or gaseous state. The boiling points and solubility of carboxylic acids are associated with hydrogen bonding.



3. Boiling point

Carboxylic acids have higher boiling points than the organic compounds like, alcohols, ethers, aldehydes, or ketones of similar molecular weight. For example, acetic acid has a higher boiling point (118°C) than the 1-propanol (97°C) although the two have similar molecular weights (60.1). Similarly, the butanoic acid and 1-pentanol have similar molecular weights (MW 88.1), but the boiling point of butanoic acid (163 ºC) is more than that of 1-pentanol (137 ºC). Because the two molecules of a carboxylic acid form two hydrogen bonds with each other while two alcohol molecules can only form one hydrogen bond. The boiling points of carboxylic acids increase with the increase in molecular weight.

4. Solubility

The C_1-C_4 members are more soluble in water. This is due to the ability of the –COOH group to form hydrogen bonds with water molecules. Due to strong H……. bonding, carboxylic acids are more soluble in water than alcohols, ethers, aldehydes, or ketones of comparable molecular weight. The solubility of a carboxylic acid in water decreases as the molecular weight of carboxylic acids increases. This is due to, a carboxylic acid consists two different polarities: a polar hydrophilic carbonyl group and a non-polar hydrophobic hydrocarbon chain. The hydrophilic carbonyl group increases water solubility whereas the hydrophobic hydrocarbon chain decreases water solubility. Therefore, C_5 members are partly soluble and the higher carbon chain members are insoluble in water, but readily soluble in ethanol, ethers and benzene.

4.6 ACIDITY OF CARBOXYLIC ACIDS AND EFFECT OF SUBSTITUENTS ON ACID STRENGTH

A carboxylic acid can ionize in water into carboxylate ions and hydronium ions as:

$$R\text{-}COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

The equilibrium constant K for given equation can be expressed as:

$$K = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

Since water is in excess therefore, K H_2O]= Ka, hence the above equation can be written as:

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

K_a is known as acid dissociation constant which is a measure of acid strength of an acid. The pK_a of an acid is the negative logarithm of K_a, and commonly used parameter to measure the acid strength of an acid. The low value of pK_a corresponds to more acidity and high value relates to less acidity of acids.

$$pK_a = -logK_a$$

For example, the acetic acid is dissociated as:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The acid dissociation constant K_a for a given equation can be expressed as:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.74 \times 10^{-5}$$

$$pK_a = 4.76$$

The value of pK_a for aliphatic carboxylic acids is in the range of 4.0 -5.0. Therefore, carboxylic acids are weak acids and their acidic strength decreases with molecular weight increases.

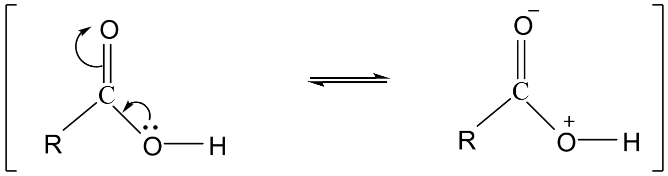
Table 6.7 – Values of pK_a for some simple carboxylic acids:

Compound	**IUPAC name**	***pK_a***
HCOOH	methanoic acid	3.75
CH_3COOH	ethanoic acid	4.74
CH_3CH_2COOH	propanoic acid	4.87
$CH_3(CH_2)_2COOH$	butanoic acid	4.82
$CH_3(CH_2)_3COOH$	pentanoic acid	4.81

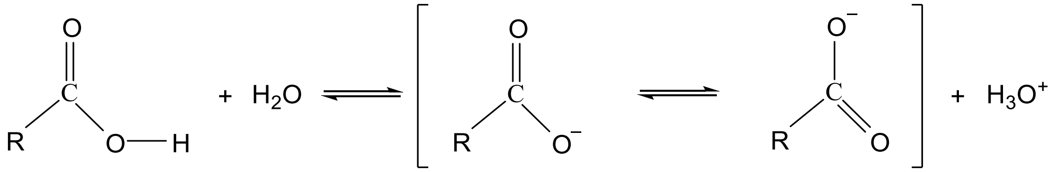
$CH_3(CH_2)_4COOH$	hexanoic acid	4.88
$CH_3(CH_2)_6COOH$	octanoic acid	4.89
$CH_3(CH_2)_8COOH$	decanoic acid	4.84
C_6H_5COOH	benzoic acid	4.19
p-$CH_3C_6H_4COOH$	*p*-toluic acid	4.36
p-ClC_6H_4COOH	*p*-chlorobenzoic acid	3.98
p-$NO_2C_6H_4COOH$	*p*-nitrobenzoic acid	3.41
FCH_2COOH	fluoroethanoic acid	2.59
$ClCH_2COOH$	chloroethanoic acid	2.86
$BrCH_2COOH$	bromoacetic acid	2.90
ICH_2COOH	iodoethanoic acid	3.18
$Cl_2CHCOOH$	di-chloroethanoic acid	1.26
Cl_3CCOOH	tri-chloroethanoic acid	0.64

There are two reasons of the acidic nature of carboxyl compounds:

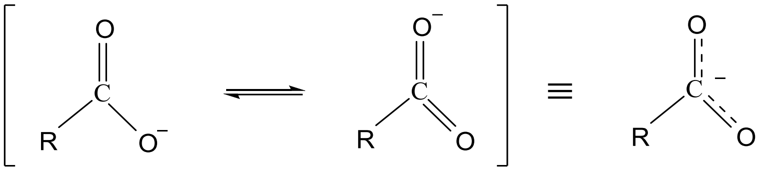
1. Resonance effect: -



The Carboxyl group shows resonance structures in which the oxygen atom of the –OH group contains a positive charge which is not stable and hence can lose a bonded hydrogen atom in the form of a proton and convert it into a carboxylate ion. That is the reason the equilibrium between the carboxyl group and carboxylate ion lies towards the right side.



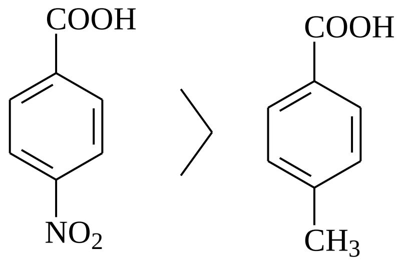
The carboxylate anion is also stabilized by resonance like carboxylic acid. The stabilization of the anion is much greater than that of the neutral carboxyl group. In the carboxylate anion, the C-O bonds are of equal length and the two contributing structures have equal weight in the hybrid.



2. Effect of substituents on acidity of carboxylic acids:-

Substituent affects carboxylic acids' acidity by affecting carboxylate anion's stability. A substituent that stabilizes the carboxylate anion promotes the dissociation and results in a stronger acid. Substituents on the α-carbon atom are most effective to increase in acid strength. *Electron withdrawing groups such as -NO_2, -CN, etc. enhance the acid strength of a carboxylic acid due to an increase in the stability of carboxylate anions through the delocalization of negative charge by inductive or resonance effects. However, the electron-releasing groups such as alkyl groups reduce the acidic strength of carboxylic acids***.**

For example, *p*-nitrobenzoic acid (*pK_a 3.41*) is a stronger acid than *p*-toluic acid (*pK_a 4.36*) because the *p*-nitrobenzoic acid has an electron-withdrawing –NO_2 substituent while the *p*-toluic acid has an electron releasing –CH_3 substituent. The –NO_2 group has a larger effect in *ortho* and *para* positions than in *meta* positions.



para nitrobenzoic acid   para toluic acid

Similarly, ethanoic acid (*pK_a 4.74*) is weaker than the methanoic acid (*pK_a 3.75)* because it has an electron releasing –CH_3 substituent.

$$CH_3COOH < HCOOH$$

The presence of an electron withdrawing group near the carbonyl group decreases its *pK_a* value. Means the magnitude of a substituent depends on its distance from the carbonyl group of a carboxylic acid. The higher electronegative substituent on the α-carbon atom further increases the acidity of carboxylic acids by the inductive effect. For example, the acidity of acetic acid and their halogen derivatives.

$CH_2FCOOH > CH_2ClCOOH > CH_2BrCOOH > CH_2ICOOH > CH_3COOH$

(*pKa 2.66*) (*pKa 2.86*) (*pKa 2.90*) (*pKa 3.18*) (*pKa 4.74*)

To study the effect of multiple halogen substitution, compare the value of pK_a for acetic acid with its chloro-, dichloro-, and trichloro derivatives. The chloro, dichloro, and trichloro derivatives are successively stronger because they have more electron withdrawing chlorine. You see that a single chlorine substituent increases acid strength by nearly 100.

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

(*pKa 0.64*) (*pKa 1.26*) (*pKa 2.86*) (*pKa 4.74*)

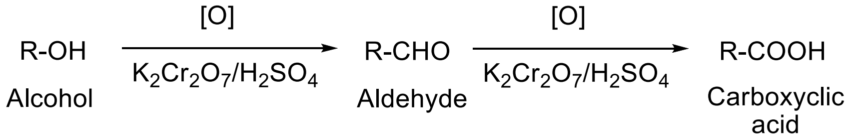
Carboxylic acids (pK_a 4-5) are stronger acids than alcohols (pK_a 16-18) because of delocalization of the negative charge of the carboxylate anion through resonance and the electron withdrawing inductive effect of the carbonyl group.

4.7 PREPARATION OF CARBOXYLIC ACIDS

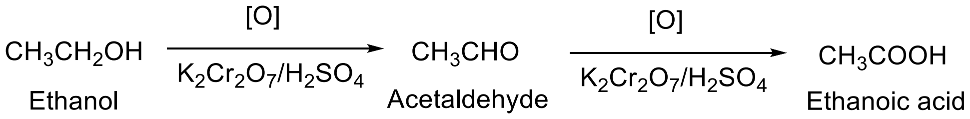
The carboxylic acids can be synthesized by various methods as follow: -

1. By the oxidation of primary alcohols and aldehydes

Carboxylic acids can be prepared by the oxidation of primary alcohols and aldehydes with acidic $KMnO_4$, or acidic $K_2Cr_2O_7$.



For example:

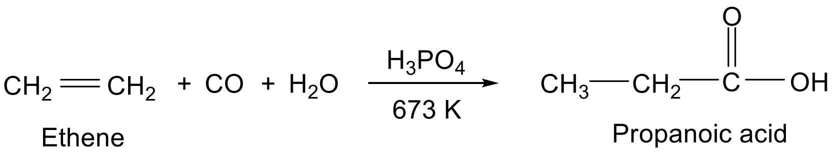


$$C_6H_5CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5COOH$$

Benzyl alcohol Benzaldehyde Benzoic acid

2. From Koch reaction

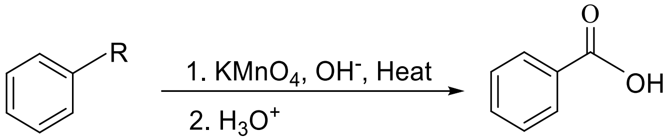
Koch reaction is an organic reaction used to convert olefins into tertiary carboxylic acids. In this reaction alkenes are treated with carbon monoxide and hydrogen in presence of strong mineral acids like phosphoric acid or hydrogen fluoride to form the tertiary carboxylic acids.



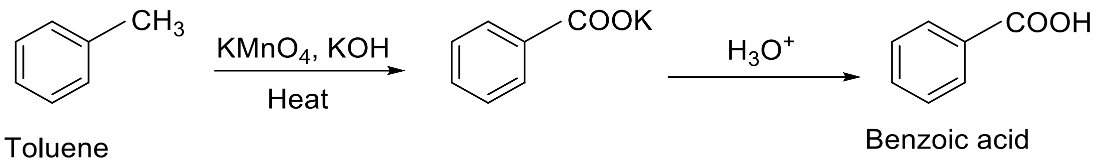
$$CH_2{=}CH_2 + CO + H_2O \xrightarrow[673\ K]{H_3PO_4} CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

3. By the oxidation of alkyl benzenes

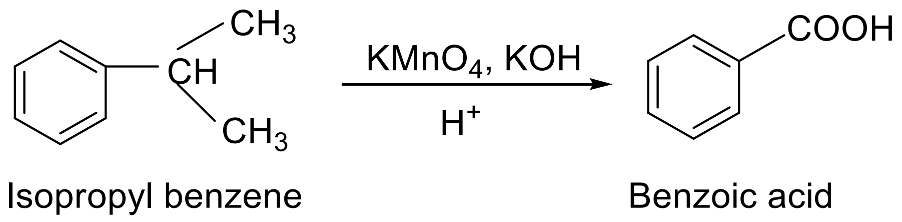
Aromatic carboxylic acids may be formed by the oxidation of alkyl benzene with $K_2Cr_2O_7$, or acidic or alkaline $KMnO_4$.

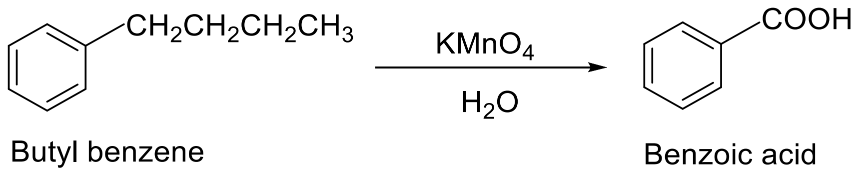


When toluene is heated with $KMnO_4$, it is oxidized to benzoic acid.

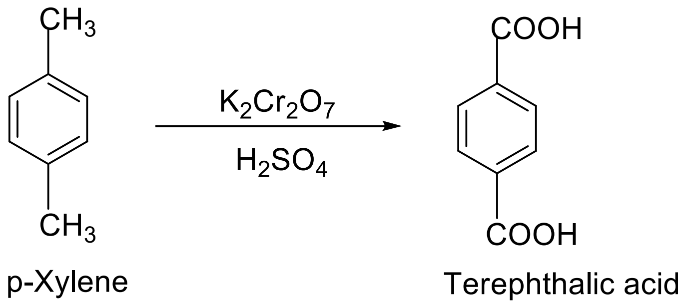


Similarly, the isopropyl benzene is oxidized into benzoic acid with alkaline $KMnO_4$.





Terephthalic acid can be obtained by the oxidation of *p*-xylene with acidic $K_2Cr_2O_7$.



4. By the hydrolysis of cyanides or nitriles

Alkyl halides react with sodium cyanide in S_N2 displacement to form a nitrile which on hydrolysis converted into carboxylic acid. The cyano group contains a hydrogen bond which under acid hydrolysis converted into carboxylic group.

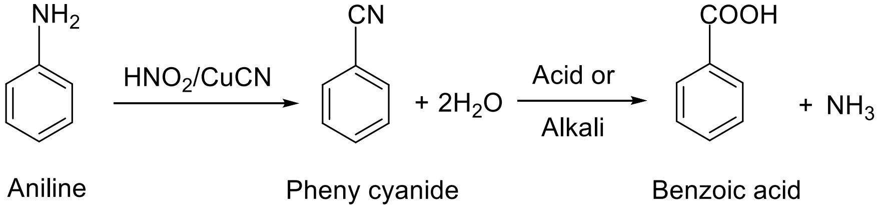
$$\underset{\text{Alkyl halide}}{R{-}X} \xrightarrow{\text{NaCN}} \underset{\text{Alkyl cynide}}{R{-}CN} \xrightarrow{\text{HCl}/H_2O} \underset{\text{Carboxylic acid}}{R{-}COOH}$$

(Where, R is an alkyl group and X is a halide)

$$\underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[\text{-NaCl}]{\text{NaCN}} \underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

Aromatic amine with nitrous acid produces aromatic nitrile which on acidic hydrolysis produces aromatic carboxylic acid.

$$\text{Ar-NH}_2 \xrightarrow{\text{HNO}_2/\text{CuCN}} \text{Ar-NO}_2 + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} \text{Ar-COOH} + NH_3$$



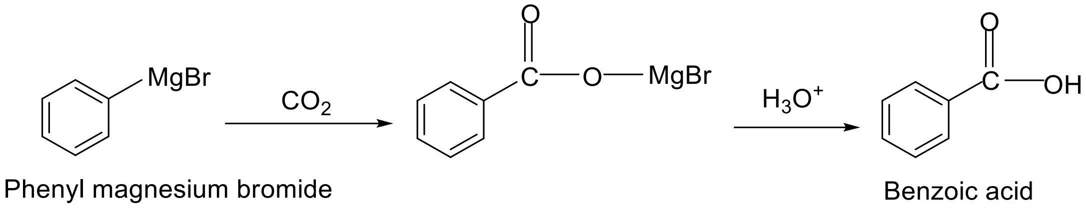
5. By Grignard's reagents

Grignard's reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on reaction with mineral acids.

$$\underset{\text{Alkyl halide}}{R{-}X} \xrightarrow[\text{Ether}]{\text{Mg}} \underset{\text{Grignard reagent}}{R{-}MgX} \xrightarrow[2.\ H^+]{1.\ CO_2} \underset{\text{Carboxylic acid}}{R{-}COOH}$$

(Where R is an alkyl or aryl group)

Benzoic acid is prepared by the action of carbon dioxide on phenyl magnesium bromide (Grignard's reagent).



6. By the hydrolysis of esters

Carboxylic acids can be prepared by the hydrolysis of esters either in acidic or alkaline medium. For example, the acetic acid is formed by the hydrolysis of ethyl acetate in acidic conditions.

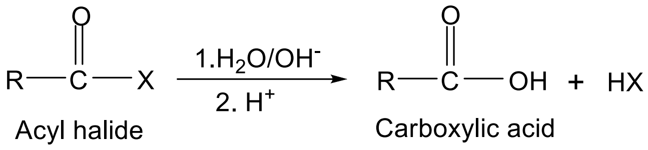
$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightleftharpoons{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

7. By the hydrolysis of acid derivatives *viz.* acyl chloride, acid anhydride, esters and amides

The acid derivatives on hydrolysis with acid or alkali form corresponding carboxylic acids.

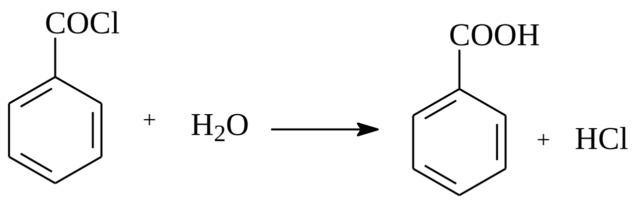
(i) By the hydrolysis of acyl halides

Acid chlorides are hydrolyzed with water to parent carboxylic acids.



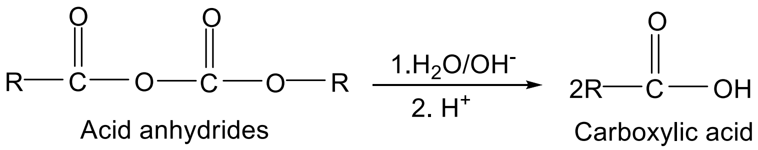
$$\underset{\text{Acyl halide}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X} \xrightarrow[2.\ H^+]{1.H_2O/OH^-} \underset{\text{Carboxylic acid}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + HX$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl + H_2O} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$$



(ii) By the hydrolysis of acid anhydride

Acid anhydrides are hydrolyzed with water to acids.

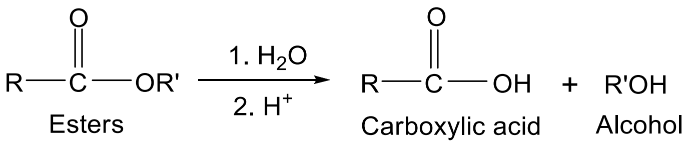


$$\underset{\text{Acid anhydrides}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-O-R} \xrightarrow[2.\ H^+]{1.H_2O/OH^-} \underset{\text{Carboxylic acid}}{2R-\overset{O}{\overset{\|}{C}}-OH}$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

(iii) By the hydrolysis of esters

Esters are hydrolyzed to carboxylic acids in the presence of an acid.

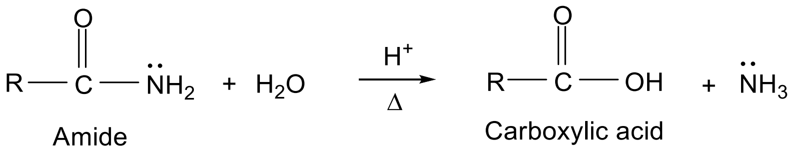


$$\underset{\text{Esters}}{R-\overset{O}{\overset{\|}{C}}-OR'} \xrightarrow[2.\ H^+]{1.\ H_2O} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alcohol}}{R'OH}$$

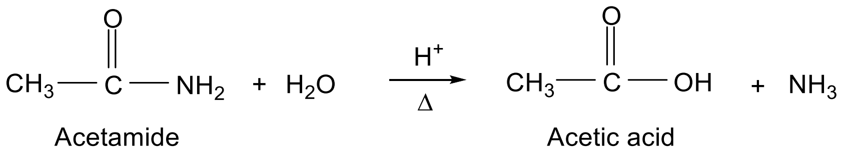
$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

(iv) By the hydrolysis of amide

Acid amides are not easily hydrolyzed with water but hydrolyzed easily on heating with dilute acids or alkalies.



$$\underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2} + H_2O \xrightarrow[\Delta]{H^+} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \ddot{N}H_3$$

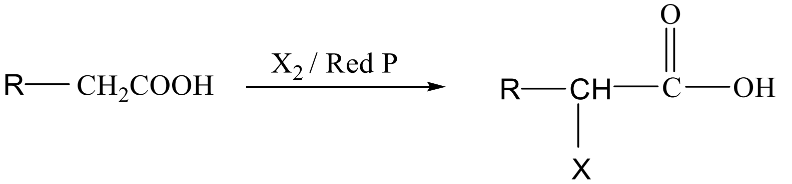


$$\underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O \xrightarrow[\Delta]{H^+} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + NH_3$$

4.8 REACTIONS OF CARBOXYLIC ACIDS

The carboxylic acids are reactive organic compounds because of the –OH and –CO group and undergo many reactions some of which are as follows.

(1) α-Halogenation of aliphatic acids: Carboxylic acids undergo halogenation with chlorine or bromine in the presence of a small amount of red phosphorus from α-halo or β-haloacids. The reaction is known as ***Hell Volhard Zelinsky's reaction.*** In this reaction, a carboxylic acid containing an α-hydrogen atom is replaced by a chlorine or bromine atom to form an α-halo carboxylic acid. The general reaction is as:

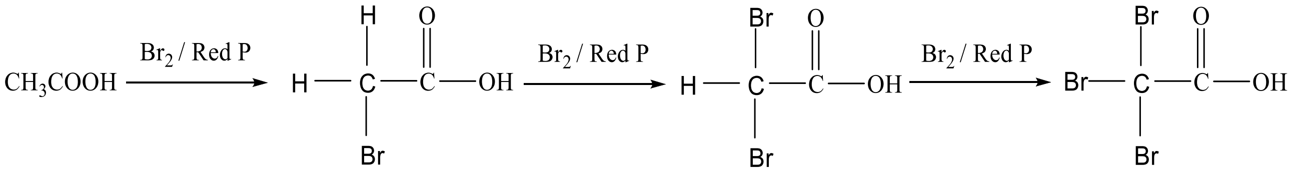


$$R-CH_2COOH \xrightarrow{X_2\,/\,\text{Red P}} R-\underset{X}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$$

Carboxylic acid α-Halocarboxylic acid

(Where, X= Cl, Br)

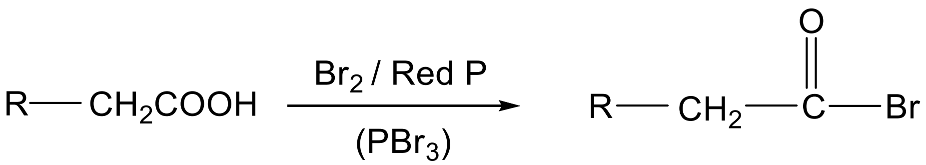
The bromination of acetic acid is a good example of this reaction.



$$CH_3COOH \xrightarrow{Br_2\,/\,\text{Red P}} H-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Br_2\,/\,\text{Red P}} H-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Br_2\,/\,\text{Red P}} Br-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$$

Mechanism: The stepwise mechanism is as follow of HVZ reaction

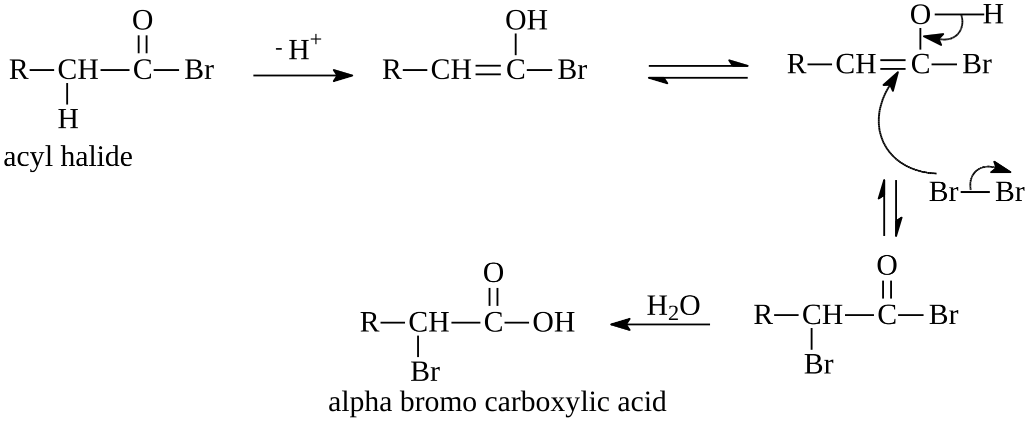
Step 1: Phosphorus reacts with bromine to form phosphorus tribromide, and in the first step this converts the carboxylic acid into an acyl bromide.



$$R-CH_2COOH \xrightarrow[(PBr_3)]{Br_2\,/\,\text{Red P}} R-CH_2-\overset{O}{\overset{\|}{C}}-Br$$

Acyl halide

Step 2: The acyl bromide then tautomerizes to the enol form which subsequently attacks the halogen molecule to form a α-halo acyl halide. Water hydrolysis yields the final α-halo carboxylic acid product.



Although the α-bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with Br_2 under acidic conditions, this reaction will generally not occur with acids, esters, and amides because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur.

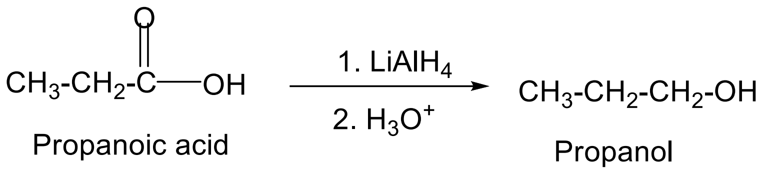
(2) Reactions of -COOH group

(i) a. Reduction of carboxylic acid to alcohols by $LiAlH_4$

The carboxylic acids are reduced to primary alcohols with a strong reducing agent like lithium aluminium hydride ($LiAlH_4$). In this reaction, the carbonyl group of a carboxyl group is reduced to $-CH_2$ group.

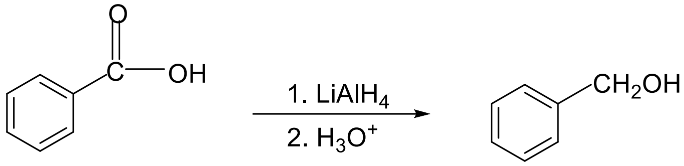
$$\text{R-COOH} \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4} \text{R-}CH_2OH$$

Propanoic acid is reduced to propanol in presence of lithium aluminium hydride ($LiAlH_4$).



$$CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{—OH} \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4} CH_3\text{-}CH_2\text{-}CH_2\text{-OH}$$

Similarly, benzoic acid is reduced to benzyl alcohol in presence of lithium aluminium hydride ($LiAlH_4$).



Benzoic acid Benzyl alcohol

Higher carboxylic acids are also reduced to alcohols by hydrogen in presence of copper chromium oxide. This reaction is used to prepare detergents such as sodium lauryl sulphate from lauryl alcohol.

$$C_{11}H_{23}COOH + 2H_2 \longrightarrow C_{11}H_{23}CH_2OH + 2H_2O$$

Lauric acid Lauryl alcohol

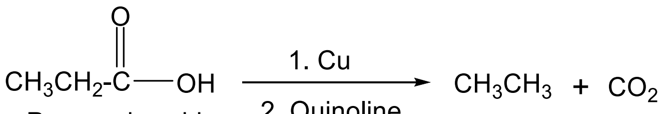
Carboxylic acids cannot be reduced by H_2/Ni, or Na/C_2H_5OH, or $NaBH_4$, or catalytic hydrogenation.

b. Reduction by HI: Carboxylic acids can be reduced to either primary alcohols or alkanes depending upon the reducing agent involved in the reaction.

(ii) Decarboxylation reaction: When an anhydrous sodium salt of a fatty acid is heated with soda lime (NaOH + CaO) or Cu/ quinoline, it loses carbon dioxide to form an alkane. This reaction is known as the decarboxylation reaction. The general reaction is as:

$$RCOONa \xrightarrow[\text{Heat}]{NaOH + CaO} R{-}H + CO_2$$

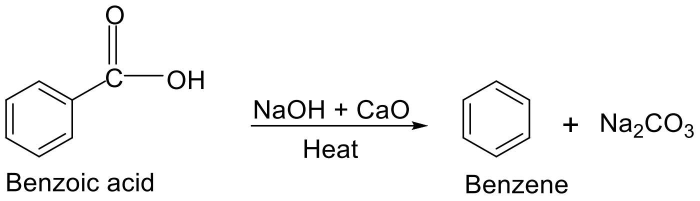
Simple copper salts such as copper chromate, copper hydroxide or copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids.



$$CH_3CH_2\text{-}\overset{\overset{\large O}{\|}}{C}\text{—}OH \xrightarrow[\text{2. Quinoline}]{\text{1. Cu}} CH_3CH_3 + CO_2$$

Propanoic acid Ethane

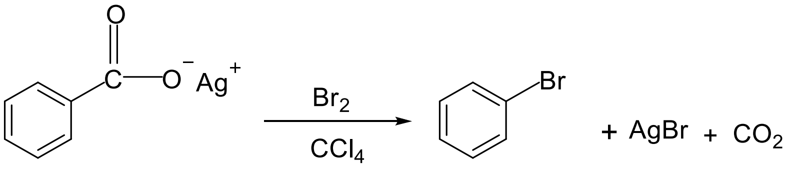
Aromatic carboxylic acids also react with sodalime to give benzene.



(iii) Hunsdiecker reaction: Silver salt of fatty acids on heating with a halogen (Cl or Br) undergo decarboxylate halogenations give alkyl or aryl halides. The general reaction is as:

$$RCOOAg + Br_2 \xrightarrow{\Delta} RBr + CO_2 + AgBr$$

For example,



(iv) Kolbe electrolysis: The electrochemical oxidation of sodium or potassium salts of fatty acids give alkanes having twice the number of carbon atoms present in the alkyl group of the acid. This process is known as *Kolbe's electrolysis*. For example; the electrolysis of potassium ethanoate forms ethane with carbon dioxide gas and hydrogen gas as side products.

$$2CH_3COOK \rightarrow 2CH_3COO^- + 2K^+$$

$$2H_2O \rightarrow 2H^+ + 2OH^-$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (at cathode)}$$

$$2CH_3COO^- \rightarrow 2CH_3COO^\cdot \text{ (at anode)}$$

$$2CH_3COO^\cdot \rightarrow 2CH_3^\cdot + 2CO_2$$

$$2CH_3\cdot \rightarrow CH_3\text{-}CH_3$$

(3) Reactions with metals and alkalies: Some reactions which show the acidic character of carboxylic compounds are as follows:

(i) Reaction with metal: Carboxylic acids react with active metals like K, Ca, Mg to form salts by releasing hydrogen gas.

$$2RCOOH + 2Na \rightarrow 2RCOONa + H_2$$

$$ {}^{2}\mathrm{CH_3COOH} + {}^{2}\mathrm{Na} \longrightarrow {}^{2}\,\mathrm{CH_3COONa} + \mathrm{H_2} $$

(ii) Reaction with alkalies: Carboxylic acids react with alkalis like sodium hydroxide to form salts and water.

$$ \mathrm{RCOOH + NaOH \rightarrow RCOONa + H_2O} $$

$$ \mathrm{CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O} $$

(iii) Reaction with sodium bicarbonate: Carboxylic acids are weaker than mineral acids like sulphuric acid or nitric acid and able to react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide with water.

$$ \mathrm{RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O} $$

$$ \mathrm{CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2}\uparrow $$

The reaction with sodium bicarbonate is also used as functional group determination of carboxylic acid

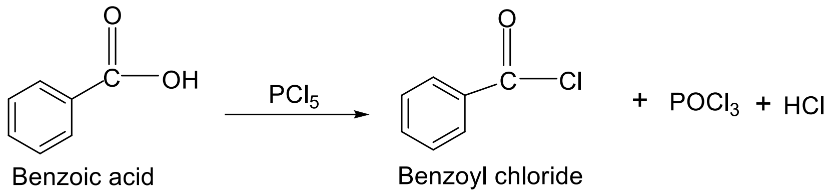
***(*4) Formation of acid derivatives:** The carboxylic acid derivatives *viz*, acyl halides (RCOCl), acid anhydrides RCOOCOR), esters (RCOOR) and acid amides ($RCONH_2$) can be derived from carboxylic acids (RCOOH) by the replacement of -OH part of a –COOH group by some other groups like -Cl, -OR, $-NH_2$.

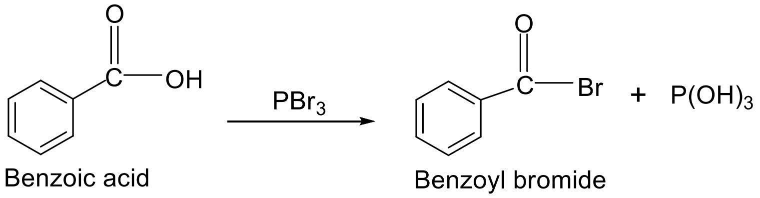
(i) Formation of acid halides: Carboxylic acids react with halide derivatives like phosphorous trichloride (PCl_3), phosphorous tribromide (PBr_3), phosphorous pentachloride (PCl_5), and thionyl chloride ($SOCl_2$) to form acyl halides. Acyl halides are formed by the replacement of –OH part of –COOH group by a -Cl or –Br group.

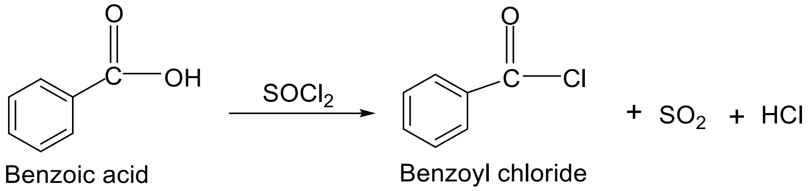
$$ \underset{\text{Acetic acid}}{\mathrm{CH_3COOH}} + \mathrm{PCl_5} \longrightarrow \underset{\text{Acetyl chloride}}{\mathrm{CH_3COCl}} + \mathrm{POCl_3} + \mathrm{HCl} $$

$$ \underset{\text{Acetic acid}}{\mathrm{3CH_3COOH}} + \mathrm{PCl_3} \longrightarrow \underset{\text{Acetyl chloride}}{\mathrm{3CH_3COCl}} + \mathrm{H_3PO_3} + \mathrm{HCl} $$

$$ \underset{\text{Acetic acid}}{\mathrm{CH_3COOH}} + \mathrm{SOCl_2} \longrightarrow \underset{\text{Acetyl chloride}}{\mathrm{CH_3COCl}} + \mathrm{SO_2} + \mathrm{HCl} $$







Acyl halides like acyl chlorides are also prepared by the reaction of sodium salts of carboxylic acids with phosphorous trichloride (PCl_3) or thionyl chloride ($SOCl_2$).

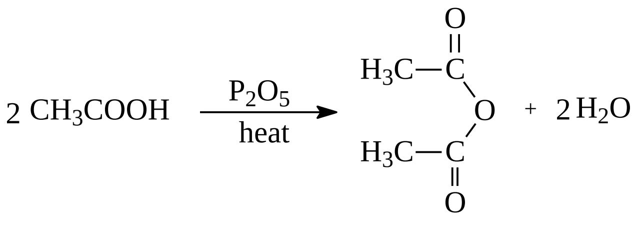
$$3CH_3COONa + PCl_3 \longrightarrow 3CH_3COCl + Na_3PO_3$$

Sodium acetate Acetyl chloride

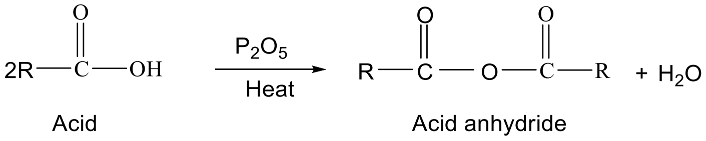
$$(CH_3COO)_2Ca + SOCl_2 \longrightarrow 2CH_3COCl + CaSO_4$$

Calcium acetate Acetyl chloride

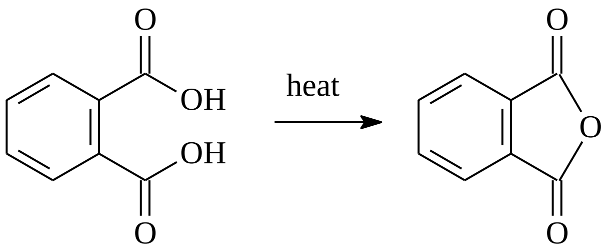
(ii) Formation of acid anhydride: The acid anhydrides can be obtained by the dehydration of the carboxylic group in the presence of strong dehydrating agents like P_2O_5 or concentrated H_2SO_4.



$$2\,CH_3COOH \xrightarrow[\text{heat}]{P_2O_5} (CH_3CO)_2O + 2\,H_2O$$



$$2R{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow[\text{Heat}]{P_2O_5} R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}R + H_2O$$



phthalic acid phthalic anhydride

(iii) Formation of esters: Carboxylic acids react with alcohols to form esters in the presence of concentrated H_2SO_4. This reaction involves the replacement of -OH group by –OR group of alcohol or phenol and also known as Fischer-speier esterification. For example, ethanoic acid reacts with ethanol to form ethyl ethanoate.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{OHC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Esters can also be prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Diazomethane}}{CH_2NH_2} \xrightarrow{\text{Ether}} \underset{\text{Methyl benzoate}}{CH_3COOC_2H_5} + N_2$$

Esters can also be prepared by the reaction of silver salt of acids on alkyl halides.

$$\underset{\substack{\text{Silver salt}\\ \text{of acid}}}{RCOOAg} + \underset{\substack{\text{Alkyl}\\ \text{halide}}}{R'X} \longrightarrow \underset{\text{Ester}}{RCOOR'} + AgX$$

$$\underset{\text{Silver acetate}}{C_6H_5COOAg} + \underset{\text{Ethyl bromide}}{C_2H_5Br} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgBr$$

(iv) Formation of amides

Carboxylic acids react with ammonia to form ammonium salts which on heating lose water molecule to form amides.

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\text{Heat}} H_2O + \underset{\text{Acetamide}}{CH_3CONH_2}$$

4.9 PREPARATION OF CARBOXYLIC ACID DERIVATIVES

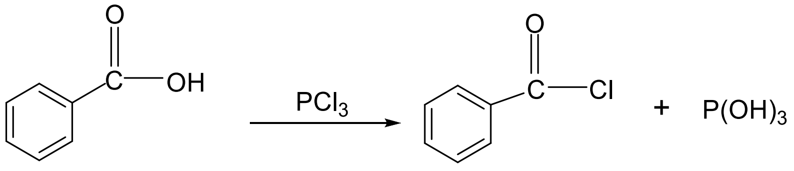
(A) ACYL CHLORIDE: Acid chlorides also known as acyl chlorides have the general formula R-COCl. They are obtained by the replacement of a –OH group by a -Cl atom. They can be formed by heating carboxylic acids or their salts with phosphorous trichloride (PCl_3), phosphorus penta chloride (PCl_5), or thionyl chloride ($SOCl_2$).

1. From acids: Acyl chlorides are prepared by heating carboxylic acids with phosphorous trichloride (PCl_3), phosphorus penta chloride (PCl_5), or thionyl chloride ($SOCl_2$).

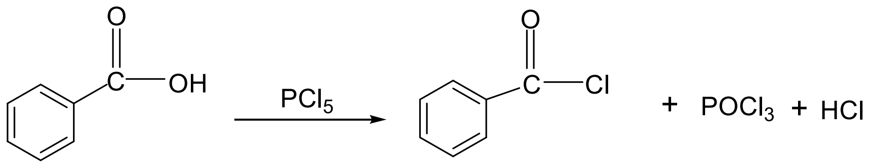
$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

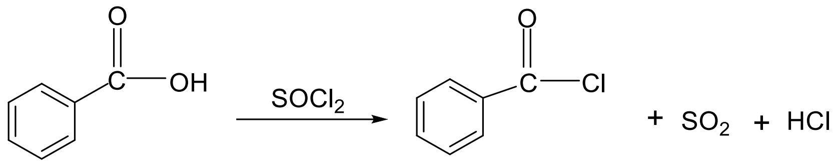
$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$



Benzoic acid Benzoyl chloride



Benzoic acid Benzoyl chloride



Benzoic acid Benzoyl chloride

2. From salts: Acyl chlorides are prepared by the treatment of sodium salts of carboxylic acids with phosphorous trichloride (PCl_3) or thionyl chloride ($SOCl_2$).

$$\underset{\text{Sodium acetate}}{3CH_3COONa} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + Na_3PO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{2CH_3COCl} + CaSO_4$$

(B) ESTERS OF ACIDS: Esters are carboxylic acid derivatives that are formed by the replacement of the hydroxyl (-OH) part of the –COOH group by an alkoxy group (-OR). They are found naturally in several plants, fruits, and flowers. Orange, banana, apple, pineapple, mango etc. are the chief source of esters. Oils, fats and waxes are also composed of the esters of higher fatty acids like stearic acid, palmitic acid, oleic acid and cerotic acid, etc. Esters can be formed by the following general methods:

1. By direct esterification: When an alcohol interacts with an acid in the presence of a suitable acid catalyst, esters are formed by the elimination of a water molecule. This process is known as esterification.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{OHC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Phenol}}{C_6H_5OH} \xrightarrow{H^+} \underset{\text{Phenyl acetate}}{CH_3COOC_6H_5} + H_2O$$

2. By the action of alcohols on acid chlorides or anhydrides: Esters are prepared by the nucleophilic substitution of acid chlorides or acid anhydrides with alcohols.

$$RCOCl + R'OH \longrightarrow RCOOR' + HCl$$

Acid chloride, Alcohol, Ester, Hydrochloric acid

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

Ethanoyl chloride, Ethanol, Ethyl ethanoate

$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

Acid anhydride, Alcohol, Ester, Acid

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Ethanoic anhydride, Ethanol, Ethyl ethanoate, Acetic acid

3. By heating silver salts of carboxylic acids with alkyl halides: Esters are prepared by the reaction of silver salt of acids on alkyl halides.

$$RCOOAg + R'X \longrightarrow RCOOR' + AgX$$

Silver salt of acid, Alkyl halide, Ester

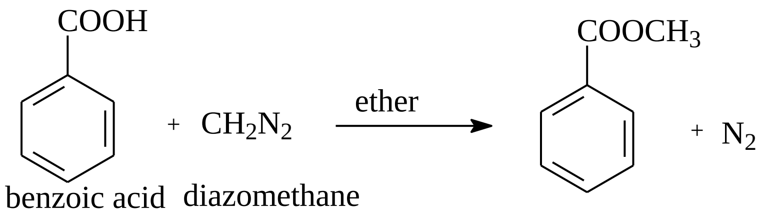
$$CH_3COOAg + C_2H_5Br \longrightarrow CH_3COOC_2H_5 + AgBr$$

Silver acetate, Ethyl bromide, Ethyl acetate

4. By the action of diazomethane on carboxylic acids: Methyl esters are prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

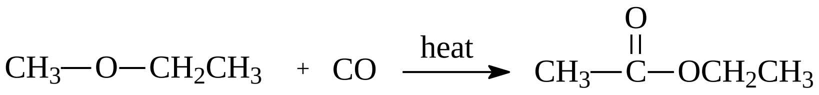
$$CH_3COOH + CH_2N_2 \xrightarrow{\text{Ether}} CH_3COOCH_3 + N_2$$

Acetic acid, Diazomethane, Methyl acetate



5. From ethers and carbon monoxide: When ether interacts with carbon monoxide at 125-180 ºC under 500 atmospheric pressures in presence of boron trifluoride catalyst, an ester is formed.

$$\underset{\text{Ether}}{R-O-R} + CO \xrightarrow{\Delta} \underset{\text{Ester}}{RCOOR}$$



$$CH_3-O-CH_2CH_3 + CO \xrightarrow{\text{heat}} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-OCH_2CH_3$$

(C) ACID AMIDES: Amides are regarded as carboxylic acid derivatives in which the hydroxyl group (-OH) is replaced by an amino group (-NH_2). For example, the most common amides are methanamide ($HCONH_2$) and ethanamide (CH_3CONH_2). They have the general formula R-$CONH_2$. The acid amides can be prepared by the following general methods:

1. Action of ammonia on acyl chloride, acid anhydride or ester: Acid amides can be prepared by the acylation of ammonia with acyl chlorides, acid anhydrides or esters.

$$\underset{\text{Acetyl chloride}}{CH_3COOCl} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + NH_4Cl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethanol}}{C_2H_5OH}$$

2. By heating ammonium salts of fatty acids: The ammonium salts of carboxylic acids on heating give amides.

$$\begin{tikzcd}
\underset{\text{Acetic acid}}{CH_3COOH + NH_3} \arrow[r] & CH_3COONH_4 \arrow[d, "\text{Heat}"] \\
 & H_2O + \underset{\text{Acetamide}}{CH_3CONH_2}
\end{tikzcd}$$

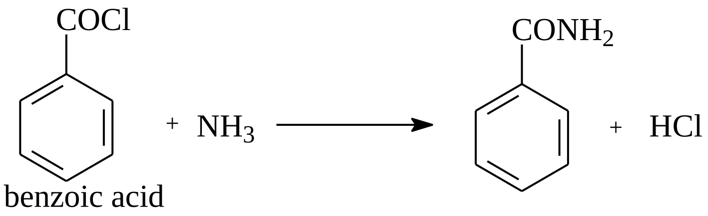
3. Partial hydrolysis of cyanides: The partial hydrolysis of cyanides with concentrated hydrochloric acid, polyphosphoric acid or alkaline peroxide produces amides.

$$\underset{\text{Acetonitrile}}{CH_3CN} + H_2O \xrightarrow[H_2O_2]{\text{Alkaline}} \underset{\text{Acetamide}}{CH_3CONH_2}$$

4. Reaction of an acid chloride with an amine: Acid chlorides are converted into primary, secondary and tertiary amides by the reaction with ammonia, primary amines and secondary amines respectively.

$$\underset{\text{Acid chloride}}{R\text{-}COCl} + \underset{\text{Ammonia}}{NH_3} \longrightarrow \underset{1^\circ\ \text{Amide}}{R\text{-}CONH_2} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl + NH_3} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$



$$\underset{\text{Acid chloride}}{R\text{-}COCl} + \underset{1^\circ\ \text{Amine}}{R'NH_2} \longrightarrow \underset{2^\circ\ \text{Amide}}{R\text{-}CONHR'} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl + C_2H_5NH_2} \longrightarrow \underset{N\text{-Ethyl acetamide}}{CH_3CONHC_2H_5} + HCl$$

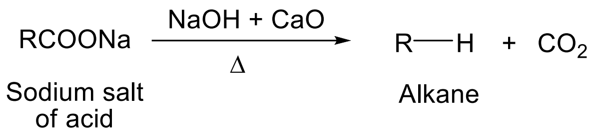
$$\underset{\text{Acid chloride}}{R\text{-}COCl} + \underset{2^\circ\ \text{Amine}}{R'_2NH} \longrightarrow \underset{3^\circ\ \text{Amide}}{R\text{-}CONR'_2} + HCl$$

4.10 MECHANISM OF DECARBOXYLATION

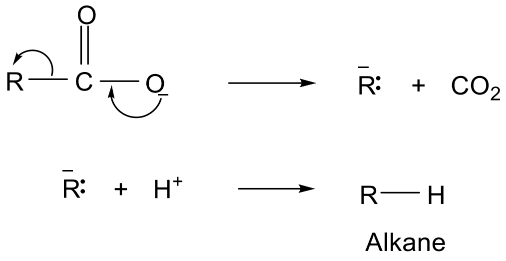
When anhydrous sodium salt of a fatty acid is heated with sodalime (NaOH + CaO) or Cu/quinine, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction.

Decarboxylation is of two types:

1. Simple carboxylic acids

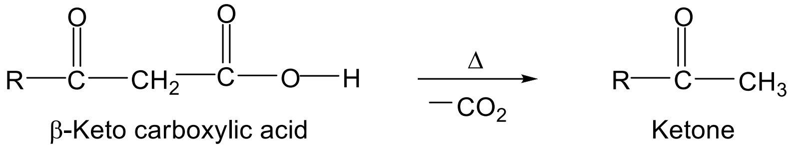


Mechanism



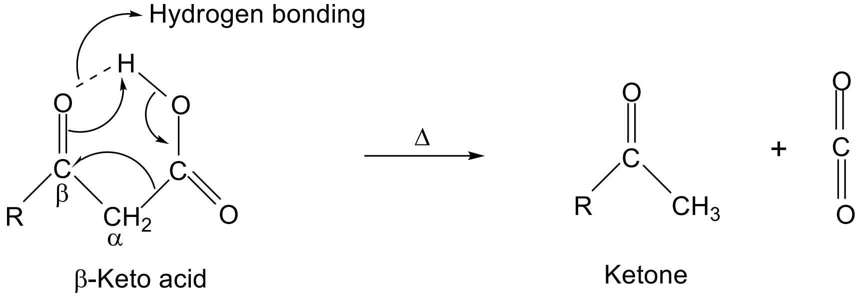
2. β-carbonyl carboxylic acids

The β-keto carboxylic acids lose CO_2 readily on heating at about 100 ºC.

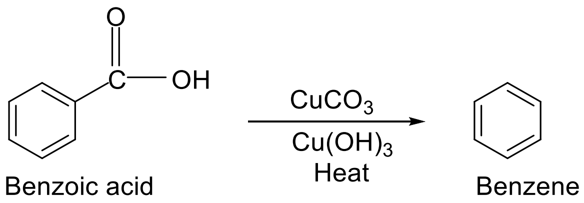


Mechanism

Decarboxylation of β-keto acid takes place via a six-membered cyclic transition state.



Note: Simple copper salts such as copper hydroxide and copper carbonate can also be used in the decarboxylation of aliphatic and aromatic acids. For example:

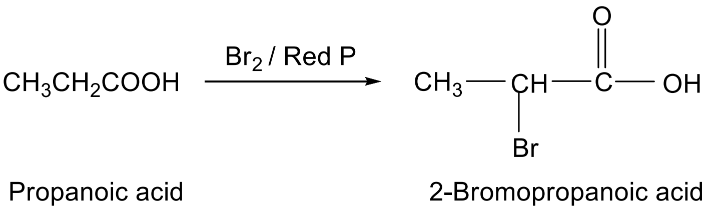


4.11 METHODS OF FORMATION AND CHEMICAL REACTIONS OF HALO ACIDS

Hydroxy acids, halo acids, amino acids and nitro acids are the derivatives of mono-carboxylic acids and known as substituted carboxylic acids.

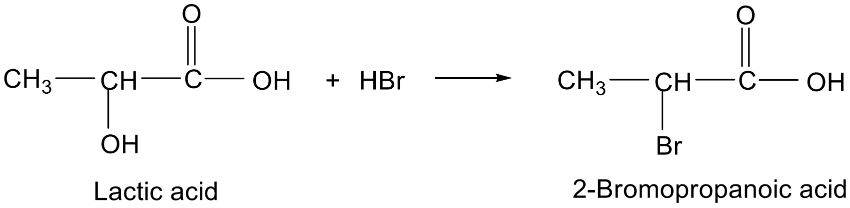
4.11.1 PREPARATION OF HALO ACIDS:

1. Hell Volhard, Zelinski reaction: Aliphatic carboxylic acids on reaction with bromine in the presence of phosphorous produce α- halo acids. This reaction is known as Hell Volhard Zelinski reaction.



$$CH_3CH_2COOH \xrightarrow{Br_2\,/\,Red\ P} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

2. By hydroxy acids: α-halo acids can be obtained by the treatment of α- hydroxy acids with HCl or HBr.



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH + HBr \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

3. By α, β-unsaturated aldehydes: α, β-unsaturated aldehydes on reaction with halogen acids followed by oxidation produce β-halo acids.

$$CH_2{=}CH-CHO + HCl \longrightarrow CH_2ClCH_2CHO \xrightarrow{[O]} CH_2ClCH_2COOH$$

Acrolein

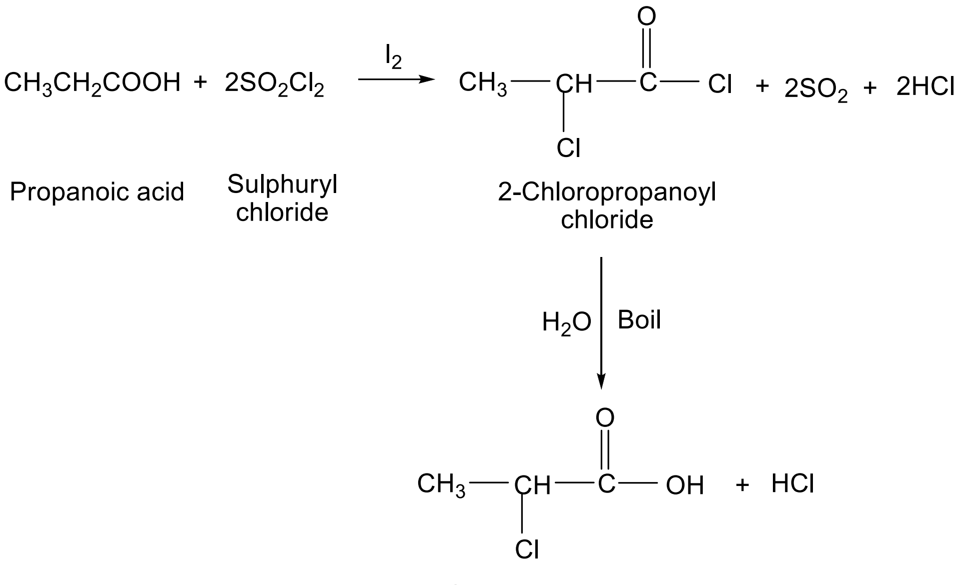
β-Chloropropionic acid

4. By α, β-unsaturated carboxylic acids: α, β-unsaturated carboxylic acids on reaction with halogen acids produce halo acids.

$$CH_3CH{=}CHCOOH + HBr \longrightarrow CH_3CHBr\,CH_2COOH$$

Crotonic acid β-Bromobutyric acid

5. By the reaction of sulphuryl chloride on carboxylic acids: Reaction with SO_2Cl_2 in presence of iodine carboxylic acid gives halo acid.

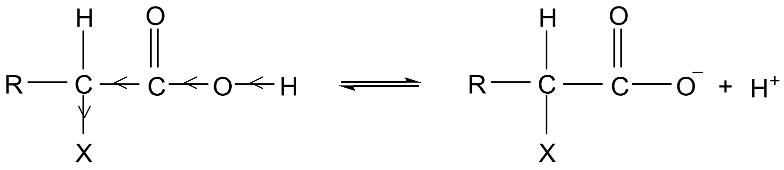


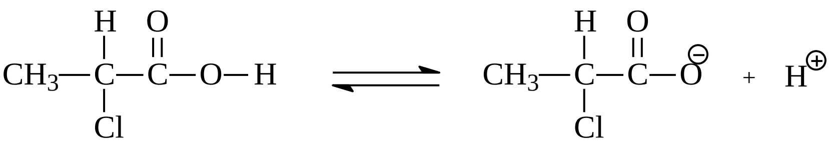
2-Chloropropanoic acid

4.11.2 CHEMICAL REACTIONS OF HALO ACIDS:

Halo acids show the similar properties as carboxylic acids. Halo acids also give the reactions of halogen groups. The main reactions of halo acids are as follows:

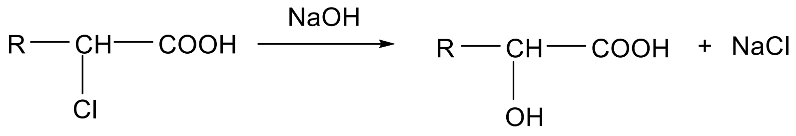
1. Acidic strength: The halo acids are more acidic than carboxylic acids because halogens are more electronegative than other atoms therefore a halogen atom withdraws the electron pairs towards it and help to release the proton; since the halo acids are more acidic than the normal acids.





2. Reaction due to halogen atom

(i) Reaction with alkali; α-halo acids undergo alkaline hydrolysis form the α-hydroxy acids.



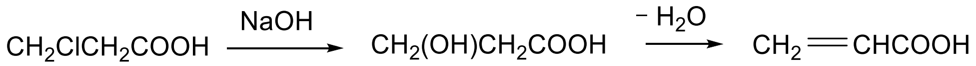
$$R-CH(Cl)-COOH \xrightarrow{NaOH} R-CH(OH)-COOH + NaCl$$

$$CH_3-CH(Br)-COOH + AgOH \longrightarrow CH_3-CH(OH)-COOH + AgBr$$

2-Bromopropanoic acid

Lactic acid

While, β-halo acids on reaction with alkali form β-hydroxy acid and α, β-unsaturated acid.



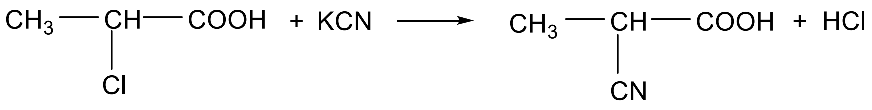
$$CH_2ClCH_2COOH \xrightarrow{NaOH} CH_2(OH)CH_2COOH \xrightarrow{-H_2O} CH_2{=}CHCOOH$$

β-Chloropropionic acid

β-Hydroxy propionic acid

Acrylic acid

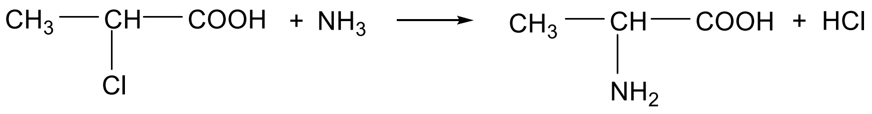
(ii) Nucleophilic substitution reactions: The halogen group present in a halo acid can be replaced by nucleophiles such as –CN, NH_3, or $–OC_2H_5$.



$$CH_3-CH(Cl)-COOH + KCN \longrightarrow CH_3-CH(CN)-COOH + HCl$$

α-Chloropropionic acid

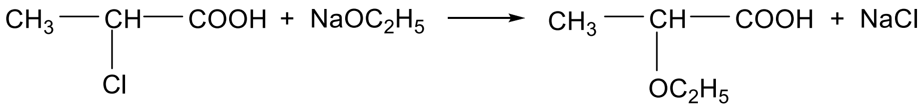
α-Cynopropionic acid



$$CH_3-CH(Cl)-COOH + NH_3 \longrightarrow CH_3-CH(NH_2)-COOH + HCl$$

α-Chloropropionic acid

α-Aminopropionic acid



$$CH_3-CH(Cl)-COOH + NaOC_2H_5 \longrightarrow CH_3-CH(OC_2H_5)-COOH + NaCl$$

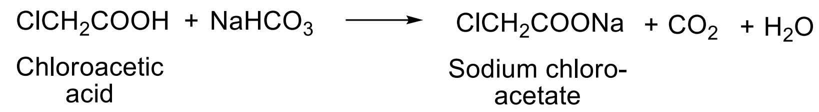
α-Chloropropionic acid

Sodium ethoxide

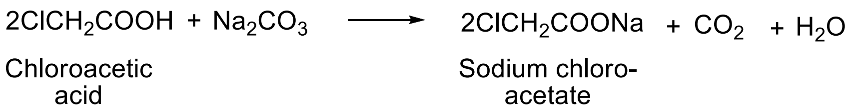
α-Ethoxypropionic acid

3. Reaction due to –COOH group

(i) Action with $NaHCO_3$ or Na_2CO_3: On reaction with $NaHCO_3$ or Na_2CO_3 halo acids decompose to release carbon dioxide.

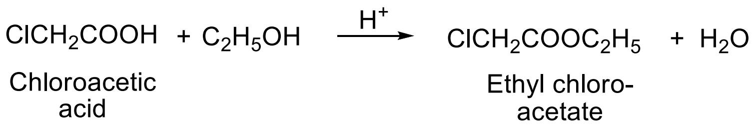


$$ClCH_2COOH + NaHCO_3 \longrightarrow ClCH_2COONa + CO_2 + H_2O$$



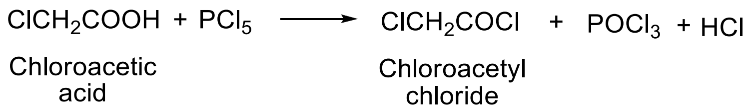
$$2ClCH_2COOH + Na_2CO_3 \longrightarrow 2ClCH_2COONa + CO_2 + H_2O$$

(ii) Reaction with alcohols: Halo acids react with alcohols to form the esters.



$$ClCH_2COOH + C_2H_5OH \xrightarrow{H^+} ClCH_2COOC_2H_5 + H_2O$$

(iii) Reaction with PCl_5: They also react with PCl_5 to form the acid chlorides.



$$ClCH_2COOH + PCl_5 \longrightarrow ClCH_2COCl + POCl_3 + HCl$$

4.12 HYDROXY ACIDS: MALIC, TARTARIC AND CITRIC ACIDS

Hydroxy acids contain a -OH group and a -COOH group. They may be mono or polybasic. The monocarboxylic acids are classified as α-hydroxy acids, β-hydroxy acids, γ-hydroxy acids and δ-hydroxy acids depending on whether the –OH group bounded to the α, β, γ and δ carbon atom of the hydrocarbon chain with respect to –COOH group (*Table-6.8*). Glycolic acid, lactic acid, tartaric acid malic acid, citric acid, mandelic acid etc. are α-hydroxyl acids while salicylic acid, β-hydroxybutanoic acid etc. are β-hydroxy acids. α-Hydroxy acids are naturally occurring carboxylic acids found in many foods including glycolic acid (sugar cane), lactic acid (milk), citric acid (citrus fruits), and malic acid (apples) among others. The most commonly used α-hydroxy acids are glycolic and lactic acids.

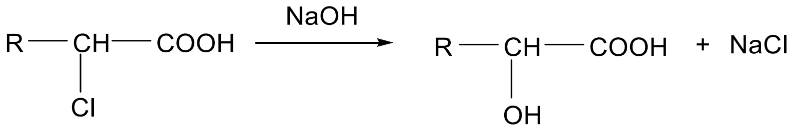
Table 4.8 – Common name of some hydroxyl acids

Chemical formula	**name**
$CH_2(OH).COOH$	hydroxyl acetic acid

$CH_3CH(OH).COOH$	α-hydroxy propionic acid
$CH_2(OH)CH_2.COOH$	β-hydroxy propionic acid
$CH_2(OH).CH_2CH_2COOH$	γ-hydroxy butric acid

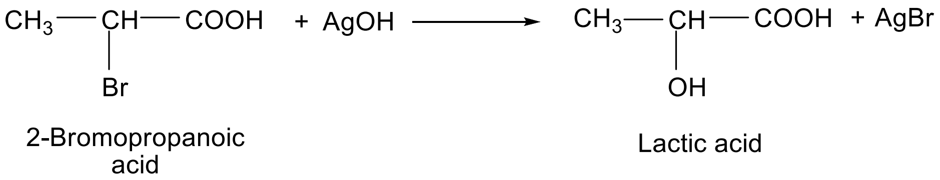
A. Preparation of α-hydroxy acids: The hydroxyl carboxylic acids are synthesized by using different methods as:

1. By the hydrolysis of α-halo acids: α-hydroxy acids can be prepared by the alkaline hydrolysis of α-halo acids.



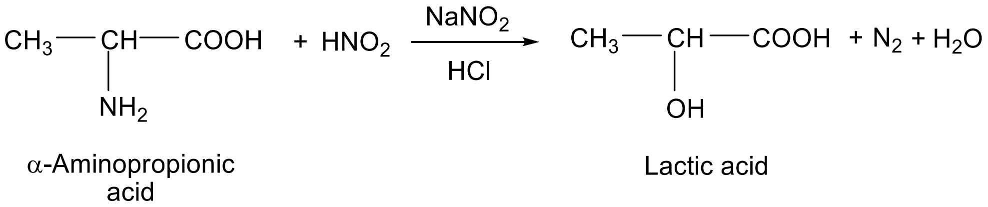
$$R-\underset{\underset{Cl}{|}}{CH}-COOH \xrightarrow{NaOH} R-\underset{\underset{OH}{|}}{CH}-COOH + NaCl$$

Lactic acid is obtained by the alkaline hydrolysis of α-bromopropionic acid.



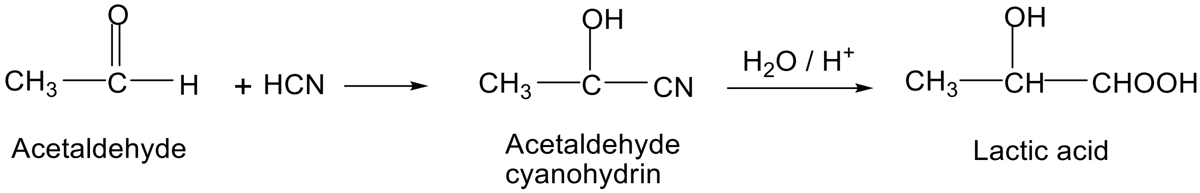
$$CH_3-\underset{\underset{Br}{|}}{CH}-COOH + AgOH \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-COOH + AgBr$$

2. By the action of nitrous acid: α-aminopropionic acid on treatment with nitrous acid in the presence of sodium nitrite and hydrochloric acid.



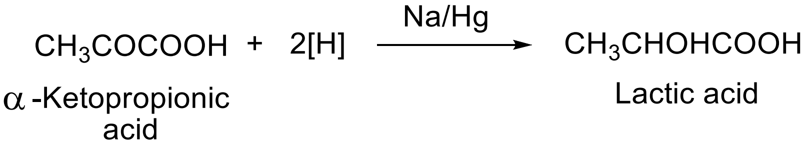
$$CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH + HNO_2 \xrightarrow[HCl]{NaNO_2} CH_3-\underset{\underset{OH}{|}}{CH}-COOH + N_2 + H_2O$$

3. By the hydrolysis of cyanohydrins: α-hydroxy acids can be obtained by the reaction of aldehydes with cyanohydrins followed by acid hydrolysis.



$$CH_3-\overset{\overset{O}{\parallel}}{C}-H + HCN \longrightarrow CH_3-\overset{\overset{OH}{|}}{C}-CN \xrightarrow{H_2O\ /\ H^+} CH_3-\overset{\overset{OH}{|}}{CH}-CHOOH$$

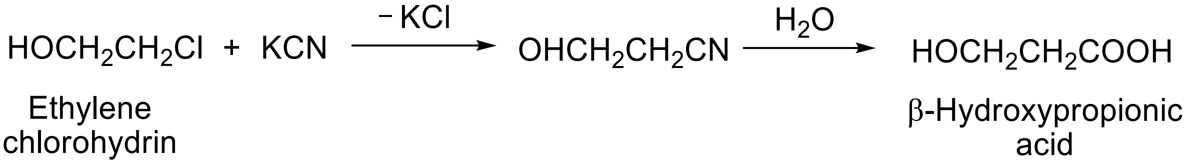
4. By the reduction of keto acids: α-hydroxy acids can be obtained by the reduction of ketonic acids in presence of Na/Hg.



$$CH_3COCOOH + 2[H] \xrightarrow{Na/Hg} CH_3CHOHCOOH$$

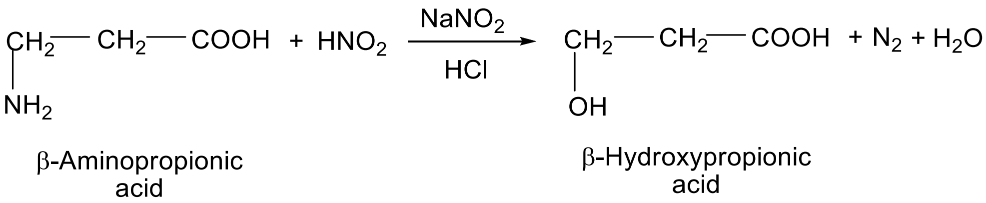
B. Preparation of β-hydroxy acids: like α-hydroxy acids, β-hydroxy acid can be synthesized using the following methods: -

1. From chlorohydrins: β-hydroxypropionic acid can be produced by the reaction of ethylene chlorohydrins with potassium cyanide followed by hydrolysis.



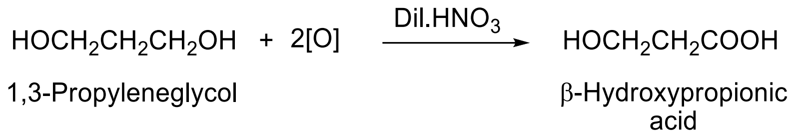
$$HOCH_2CH_2Cl + KCN \xrightarrow{-KCl} OHCH_2CH_2CN \xrightarrow{H_2O} HOCH_2CH_2COOH$$

2. By the action of nitrous acid: β-hydroxypropionic acid is prepared by the action of nitrous acid on β-aminopropionic acid in the presence of sodium nitrite and hydrochloric acid form lactic acid.



$$\underset{\underset{NH_2}{|}}{CH_2}-CH_2-COOH + HNO_2 \xrightarrow[HCl]{NaNO_2} \underset{\underset{OH}{|}}{CH_2}-CH_2-COOH + N_2 + H_2O$$

3. By the oxidation of 1,3-dihydroxy compounds: β-Hydroxypropionic acid is obtained by the reaction of 1,3-propyleneglycol with oxygen in presence of dilute nitric acid.



$$HOCH_2CH_2CH_2OH + 2[O] \xrightarrow{Dil.HNO_3} HOCH_2CH_2COOH$$

1,3-Propyleneglycol β-Hydroxypropionic acid

4.12.1 Physical Properties of Hydroxy Acids:

1. Physical state: Most of hydroxy acids occur naturally and have several important biological properties. They are colorless, crystalline solids or syrupy liquids. Hydroxy acids are more acidic than normal carboxylic acids.

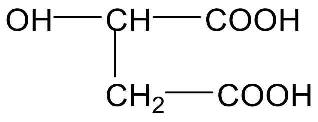
2. Solubility: The hydroxyl derivatives contain –OH and -COOH groups which form hydrogen bonds with water, therefore they are more soluble in water than the corresponding carboxylic acids.

3. Boiling points: The boiling or melting points of hydroxyl acids are also higher than the corresponding carboxylic acids.

4.12.2 Preparation and Chemical Properties of Hydroxy Acids:

The method of preparation, physical and chemical properties of some of the individual hydroxyl acids alongwith their uses are being described as follow.

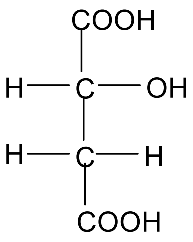
A. MALIC ACID



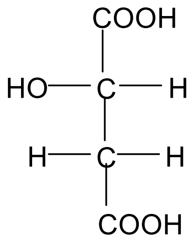
$$HO-CH(COOH)-CH_2-COOH$$

Malic acid

Malic acid is an organic compound with the molecular formula $C_4H_6O_5$. It is also known as hydroxyl butanedioic acid. It is a dicarboxylic acid that is made by all living organisms, contributes to the pleasantly sour taste of fruits, and is used as a food additive. Malic acid is a colorless crystalline solid, soluble in water and alcohol but sparingly soluble in ether, it melts at 130 ºC. Malic acid contains one asymmetric carbon, hence it exists in two optically active (two stereoisomeric forms: L- and D-enantiomers) and one inactive form, though only the L-isomer exists naturally.



D-malic acid

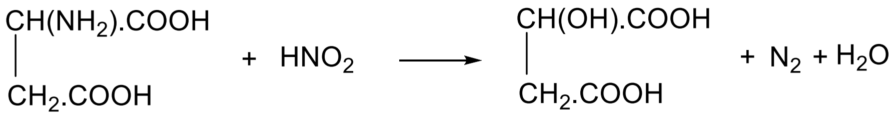


L-malic acid

Preparation of malic acid: Malic acid can be prepared by the following methods:

1. By the action of nitrous acid on α-amino succinic acid (aspartic acid).

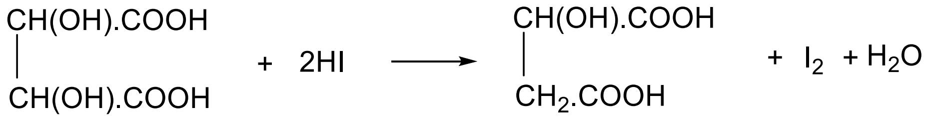
Malic acid can be obtained by the reaction of nitrous acid on Aspartic acid.



$$\begin{array}{l}CH(NH_2).COOH\\ |\\ CH_2.COOH\end{array} + HNO_2 \longrightarrow \begin{array}{l}CH(OH).COOH\\ |\\ CH_2.COOH\end{array} + N_2 + H_2O$$

Aspartic acid Malic acid

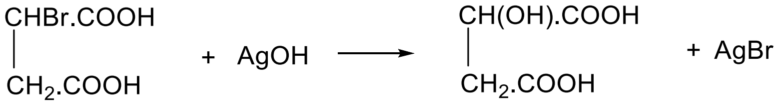
2. By the partial reduction of tartaric acid: Malic acid can be prepared by the reduction of tartaric acid with HI.



$$\begin{array}{l}CH(OH).COOH\\ |\\ CH(OH).COOH\end{array} + 2HI \longrightarrow \begin{array}{l}CH(OH).COOH\\ |\\ CH_2.COOH\end{array} + I_2 + H_2O$$

di-Tartaric acid Malic acid

3. From bromosuccinic acid: When bromosuccinic acid is treated with moist silver oxide, malic acid is obtained.

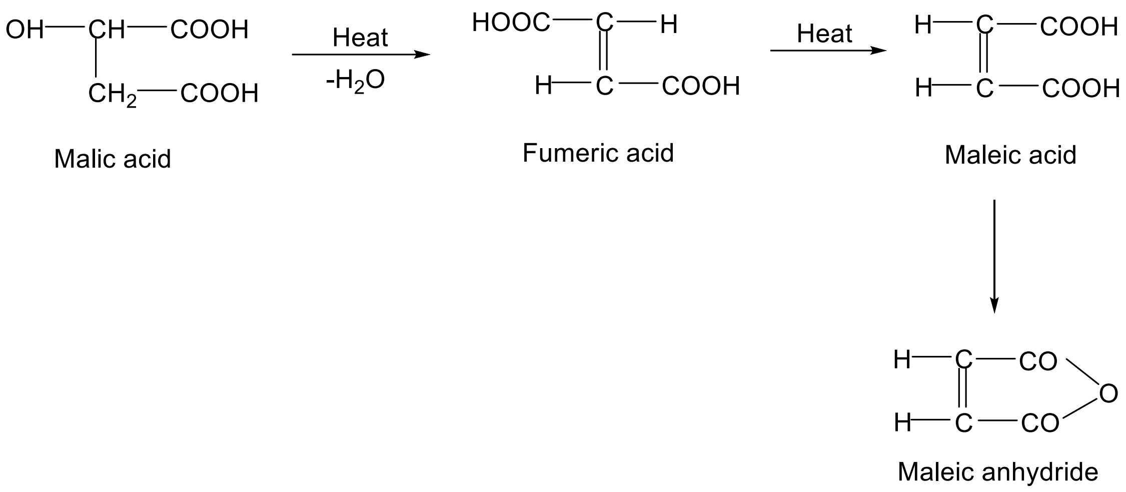


$$\begin{array}{l}CHBr.COOH\\ |\\ CH_2.COOH\end{array} + AgOH \longrightarrow \begin{array}{l}CH(OH).COOH\\ |\\ CH_2.COOH\end{array} + AgBr$$

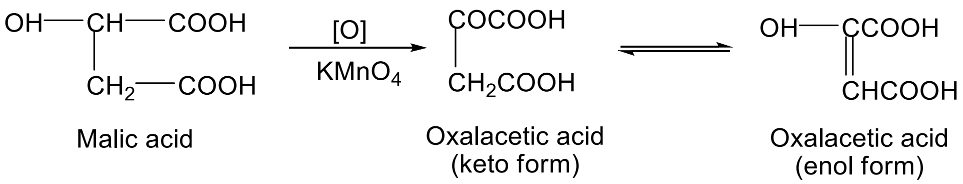
Bromosuccinic acid Malic acid

Chemical properties of malic acid: Malic acid possess following chemical properties.

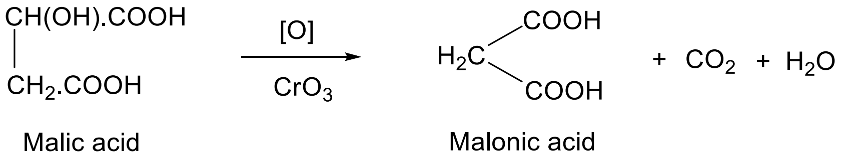
1. Action of heat: Malic acid undergoes dehydration on heating to form maleic anhydride.



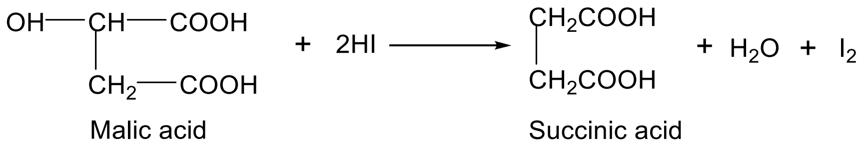
2. Oxidation with KMnO$_4$: On oxidation with KMnO$_4$ malic acid forms oxalacetic acid, which exits in keto-enol tautomerism.



3. Oxidation with H$_2$CrO$_4$: On oxidation with chromic acid, malic acid converts into malonic acid.



4. Reduction: Malic acid reduces with HI to form succinic acid.



Uses: Malic acid is used:

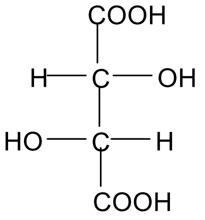
1. In the preparation of several esters and salts.
2. As a substitute of citric acid in drinks.
3. In the preparation of medicine of sore throat.

B. TARTARIC ACID

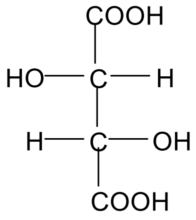
$$\begin{array}{l}\text{CHOHCOOH}\\ |\\ \text{CHOHCOOH}\end{array}$$

Tartaric acid

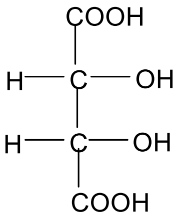
Tartaric acid, $HOOC(CHOH)_2COOH$, is a dicarboxylic acid, found in many plants, particularly tamarinds and grapes. Tartaric acid is also known as α,α′-dihydroxy succinic acid (IUPAC name: 2,3-dihydroxybutanedioic acid). It is a colorless crystalline solid, soluble in water and alcohol, and melts at 170 ºC. It has an acidic taste. Tartaric acid has two identical asymmetric carbon atoms and exists in four stereoisomeric forms dextro, laevo, meso and racemic:



D-tartaric acid



L-tartaric acid

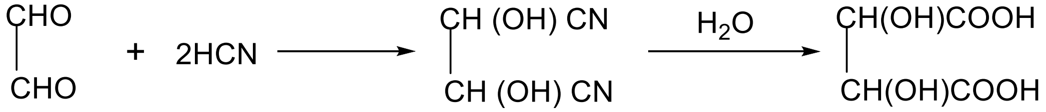


meso-tartaric acid

1. Dextrorotatory tartaric acid (d-tartaric acid) is found naturally in grapes berries, plums and several other fruits.
2. Levorotatory tartaric acid (l-tartaric acid) is obtained chiefly by resolution of racemic tartaric acid.
3. Racemic tartaric acid (an equal mixture of d- and l-tartaric acid) is prepared commercially by the molybdenum- or tungsten-catalyzed oxidation of maleic anhydride with hydrogen peroxide.

Preparation of tartaric acid: Tartaric acid can be prepared by the following general methods:

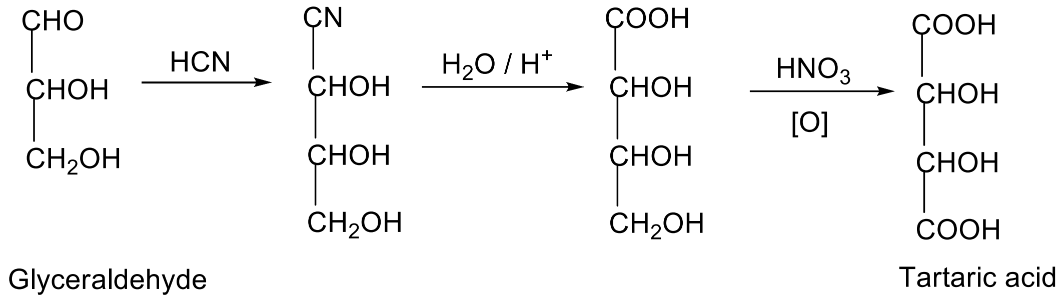
1. From glyoxal: On treatment with hydrogen cyanide, glyoxal produces glyoxal cynohydrin which on hydrolysis gives tartaric acid.



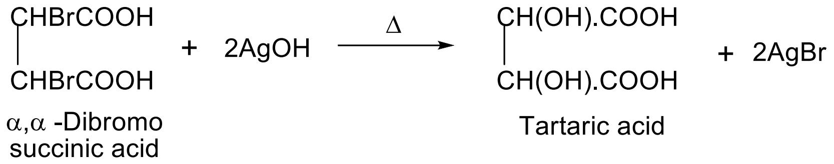
$$\begin{array}{l}\text{CHO}\\ |\\ \text{CHO}\end{array} + 2HCN \longrightarrow \begin{array}{l}\text{CH (OH) CN}\\ |\\ \text{CH (OH) CN}\end{array} \xrightarrow{H_2O} \begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array}$$

Glyoxal Tartaric acid

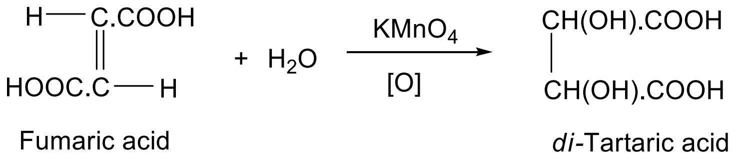
2. From Kiliani-Fisher synthesis: Kiliani-Fisher synthesis is one of the methods to increase the of carbons in compounds. Tartaric acid can also be formed from glyceraldehydes.



3. From α, α'-dibromosuccnic acid: Both (±) and meso tartaric acids are prepared by boiling α, α'-dibromosuccnic acid with moist silver oxide.

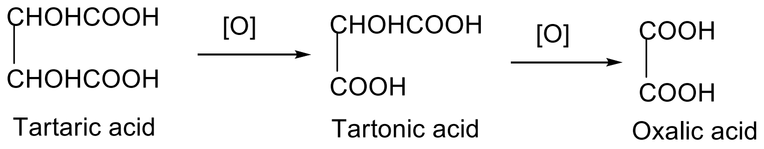


4. By the oxidation of fumeric acid: Tartatic acid can be prepared by the oxidation of fumeric acid with alkaline $KMnO_4$.

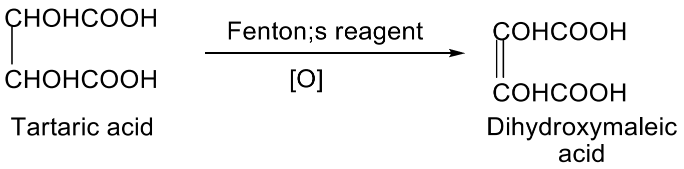


Chemical properties of tartaric acid: The chemical properties of tartaric acids are as under.

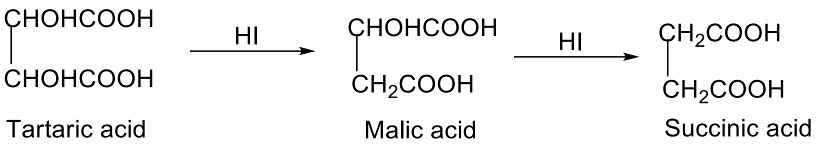
1. Oxidation: With mild oxidizing agents tartaric acid yields tartonic acid while with strong oxidizing agents, tartaric acid forms oxalic acid.



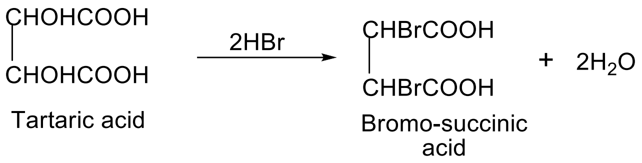
However, on oxidation with Fenton's reagent (alkaline H_2O_2 + $FeSO_4$), tartaric acid is oxidized into dihydroxy maleic acid.



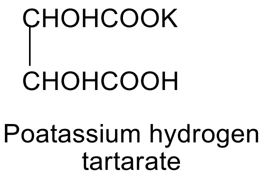
2. Reduction: Tartaric acid with HI is reduced into malic acid and then to succinic acid.

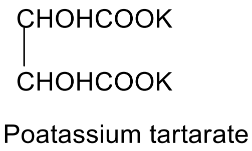


With HBr, the tartaric acid is reduced to bromosuccinic acid.

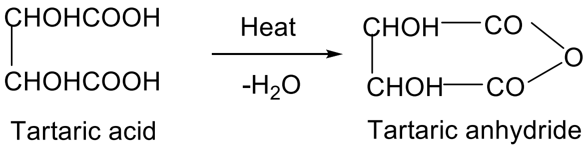


3. Salt formation: Tartaric acid forms two series of salts with the reactions of alkali.

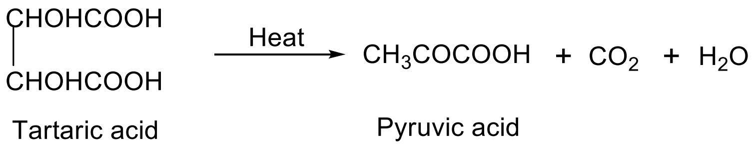




4. Action of heat: When tartaric acid is heated at 150ºC, it decomposes into tartaric anhydride.



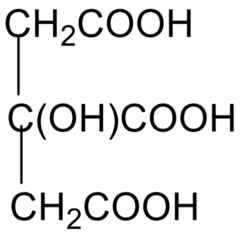
On strong heating, it decomposes into pyruvic acid with the evolution of CO_2.



Uses: Tartaric acid is used:

1. In the preparation of baking powder and effervescent beverages.
2. In mirror silvering in the form of sodium potassium tartrate.
3. As mordant in dying and calico printing.

C. CITRIC ACID



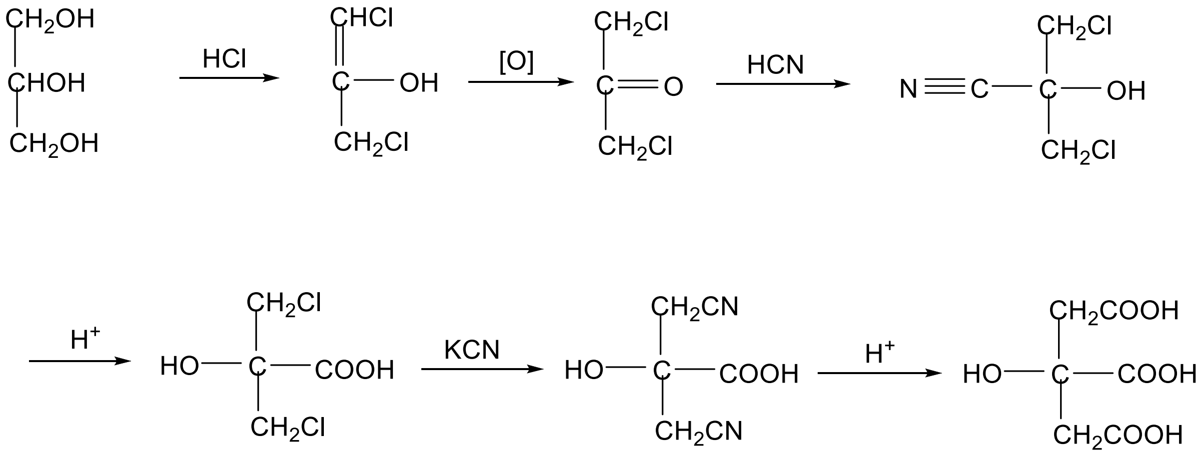
$$CH_2COOH-C(OH)(COOH)-CH_2COOH$$

Citric acid

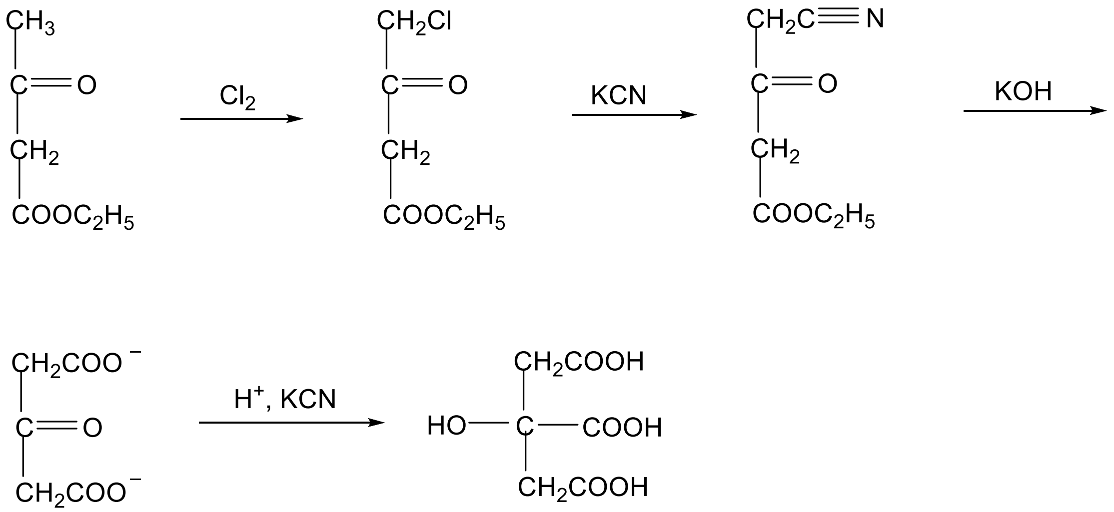
Citric acid is a weak organic tri-basic acid having the chemical formula $C_6H_8O_7$. The IUPAC name of citric acid is 2-hydroxypropane-1,2,3-tricarboxylic acid. It occurs naturally in citrus fruits like lemon, orange, tomato, etc. Citric acid is a crystalline solid containing one water molecule. It is soluble in water and alcohol but sparingly in ether. At 130 ºC it loses water molecules and the anhydrous acid melts at 153 ºC.

Synthesis of citric acid: Citric acid can be synthesized by the following methods:

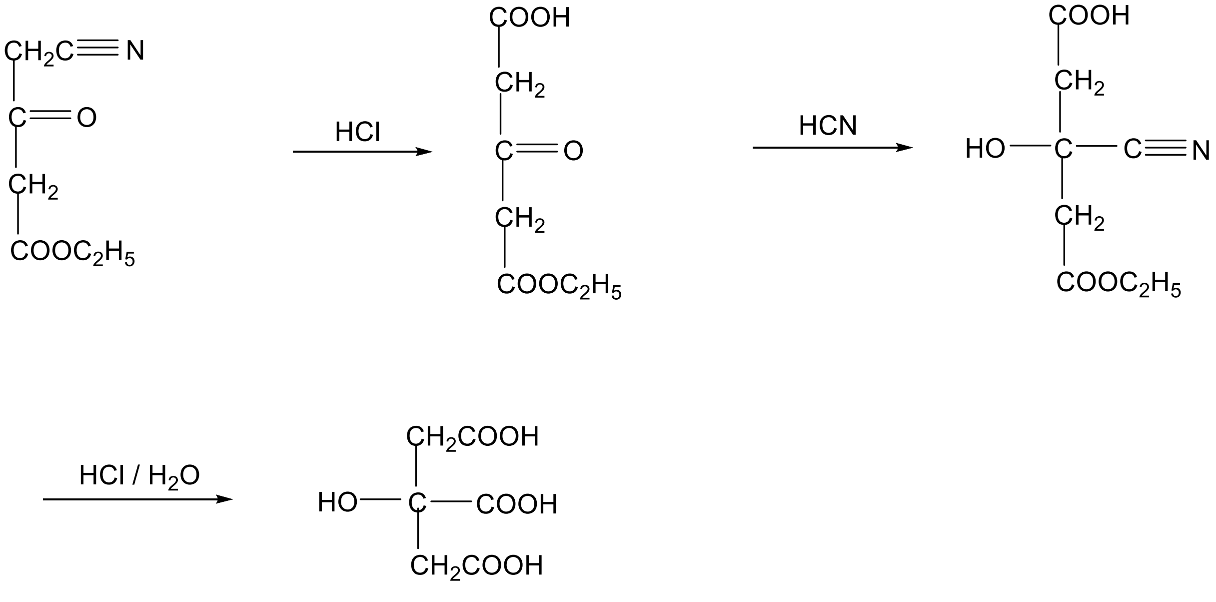
1. By Grimaux and Adam synthesis (1880): The sequential steps in this synthesis are: 1,2,3-hydroxy propane → 1,3-dichloro-2-propenol → 1,3-dichloro-2-propanone → 1,3-dichloro-2-cyno-2-hydroxypropane → α-chloromethyl-α-hydroxypropionic acid → β-cyno-α-cynomethyl-α-hydroxypropionic acid → 2-hydroxy-1,2,3-tricarboxylic acid.



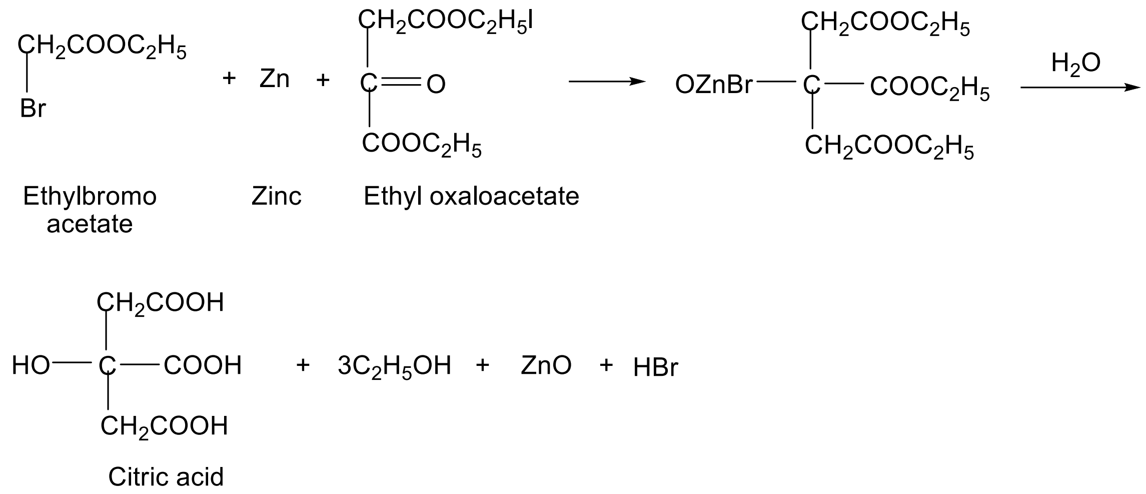
2. By Haller and Held synthesis (1890): This synthesis can be represented as: Ethyl-β-keto butyrate → ethyl-γ-chloro-β-ketobutyrate → ethyl-γ-cyno-β-ketobutyrate → β-keto glutaric acid → 2, hydroxyl-1,2,3-tricarboxylic acid.



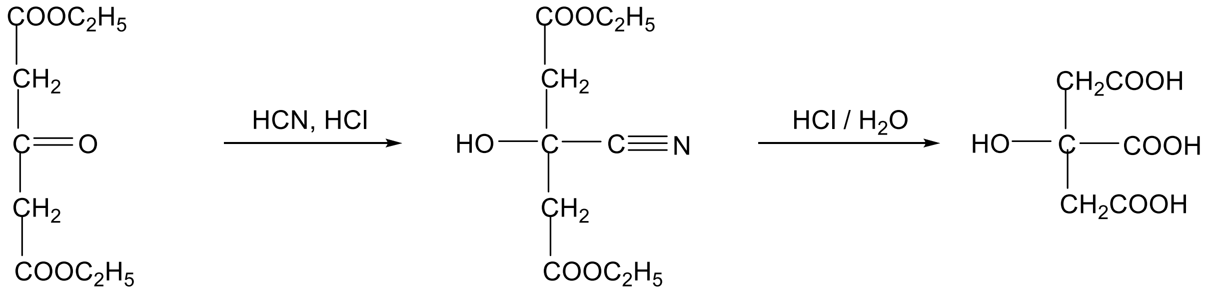
3. By Dunschmann and Pechmann synthesis (1891): This synthesis can be represented as: Ethyl-γ- chloro-β-ketobutyrate → ethyl-β-ketoglutarate → ethyl-β-cyno-β-hydroxy glutarate.



4. By Reformatsky's reaction: Citric acid is obtained by the reaction of ethylbromo acetate with oxaloacetate in the presence of zinc followed by hydrolysis.

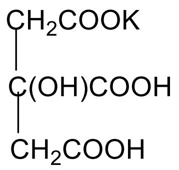


5. From diethyl β-ketoglutarate: This synthesis is progress as: Diethyl β-ketoglutarate → diethyl β-cyno-β-hydroxy glutarate.

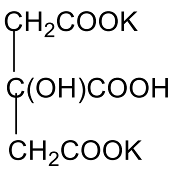


Chemical reactions of citric acid: Citric acid undergo the following types of chemical reactions

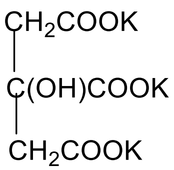
1. Citric acid forms three types of salts: Citric acid is a tricarboxylic acid therefore it forms three series of salts on reaction with alkalies *e.g.*, monopotassium citrate, dipotassium citrate and tripotassium citrate.



Monopotassium citrate

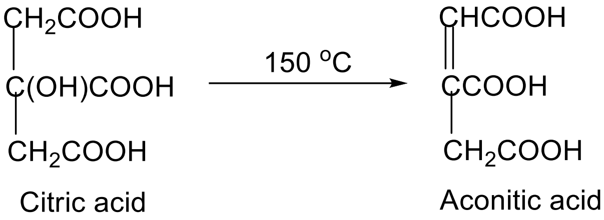


Dipotassium citrate

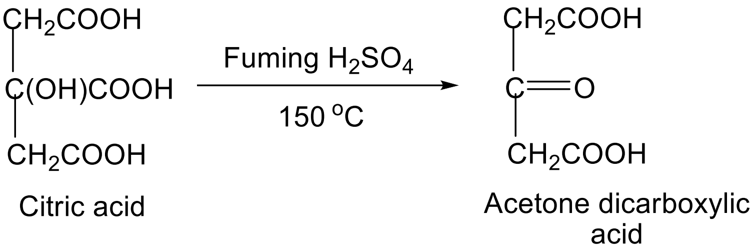


Tripotassium citrate

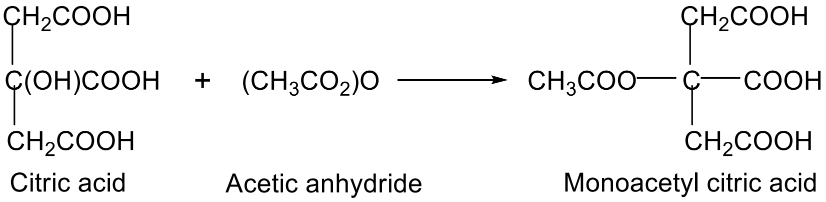
2. Action of heat: On heating at 150 ºC, citric acid undergoes dehydration as:



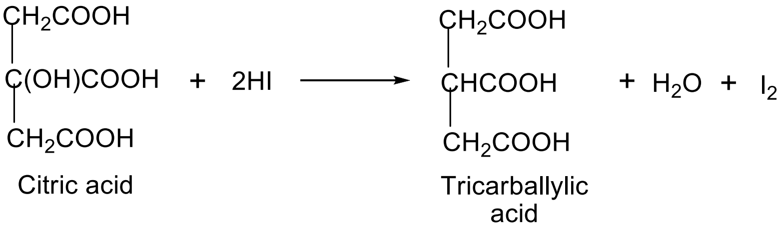
On heating with fuming sulphuric acid at 150 °C, citric acid gives acetone dicarboxylic acid.



3. Reaction with acetic anhydride: Citric acid produces monoacetyl derivative**s.**



4. Reduction: In presence of hydrogen iodide citric acid reduced to tricarballylic acid.



Uses: Citric acid is used:

1. As flavor compound in the preparation of synthetic fruit drinks.
2. As laxative in form of magnesium citrate.
3. As solvent in polymer synthesis.
4. As an iron supplement in the form of ferric ammonium citrate.
5. As mordant in printing and dying.

4.13 SUMMARY

The summary of the following chapter is:

- Carboxylic acids are compounds with one or more –COOH groups, classified as mono, di, tri, or polycarboxylic acids.
- Fatty acids, such as stearic acid and oleic acid, are long-chain monocarboxylic acids.
- They are named based on IUPAC rules and have a planar structure due to sp2 hybridization.
- Carboxylic acids form hydrogen bonds and have higher boiling points than hydrocarbons, with varying solubility in water. They are weak acids, more acidic than alcohols, and can be synthesized through methods like oxidation of alcohols and aldehydes. Functional derivatives, such as esters and amides, are also discussed.

4.14 TERMINAL QUESTIONS

Section-A

Q.1 Long answered questions: Answer the following questions

1. What are carboxylic acids? Describe the structure and nomenclature of aliphatic and aromatic carboxylic compounds.
2. What are carboxylic acids? Give the general methods of preparation of carboxylic acids.
3. Describe the reduction and decarboxylation reactions of carboxylic acids.
4. What are halo acids? Give the general methods of preparation and chemical properties of halo acids.
5. What are hydroxyl acids? Give the general methods of reparation and properties of malic acid.
6. Describe the general methods of preparation, physical and chemical properties of tartaric acid.
7. How is citric acid synthesized? Describe the important chemical properties of citric acid.
8. Describe the general methods of preparation, physical and chemical properties of acyl chlorides.

Section-B

Q.2 Short answered questions

1. How can you synthesize carboxylic acids from cyanides?
2. Write a short note on the acid strength of carboxylic acids.
3. Write the physical properties of carboxylic acids.
4. Why the monochloroacetic acid is stronger than acetic acid?
5. Explain benzoic acid is more acidic than phenol.
6. Compare the acidic strength of acetic acid and halo acids.
7. Give the mechanism of Hell Volhard Zelinsky reaction, and Decarboxylation reaction?
8. How can you obtain halo acids from Hell Volhard Zelinsky reaction?
9. Give the mechanism of decarboxylation.
10. How can you synthesize esters and amides from carboxylic acids?
11. How can you prepare succinic acid from tartaric acid?
12. Give the method of preparation of hydroxyl acids.
13. How can you convert tartaric acid into oxalic acid, and tartaric acid into malic acid?
14. How will you have obtained it?
    a) Carboxylic acids from acyl chlorides
    b) Carboxylic acids from aldehydes
    c) Carboxylic acids from alkyl benzene
    d) Carboxylic acids from nitriles
15. How can you convert?

a) Carboxylic acids into halo acids
b) Carboxylic acids into alcohols
c) Carboxylic acids into alkanes
d) Amides from acetyl chloride

Section-C

Q.3 Multiple choice questions (MCQ)

1. Which functional group is present in a carboxylic acid?

(a) -COOH (b) $–NH_2$

(c) -RCOOR’ (d) –OR’

2. Which one of the followings is a monocarboxylic acid?

(a) Oxalic acid (b) Succinic acid

(c) Formic acid (d) Citric acid

3. What is the IUPAC name of HOOC $(CHOH)_2$ COOH?

(a) 2-Hydroxypropionic acid (b) 2, 3-Dihydroxybutanedioic acid

(c) 2-Hydroxybutanedioic acid (d) Butanedioic acid

4. Carboxylic acids are more soluble in water than alcohols and ethers due to

(a) Their high molecular weight (b) Hydrogen bonding

(c) More reactive carboxyl carbon (d) Their acidic character

5. Carboxylic acid and alcohols both form hydrogen bonds with water but why do carboxylic acids have higher boiling points than alcohols?

(a) Because acids are more reactive than alcohols.

(b) Because carboxylic acids are weak acids.

(c) Because alcohols are not ionized completely.

(d) Because the two molecules of a carboxylic acid form two hydrogen bonds.

6. Which of the following is the strongest acid?

(a) $CH_2ClCOOH$ (b) $CH_2BrCOOH$

(c) CH_2FCOOH (d) CH_2ICOOH

7. The weakest acid among the following is

(a) Cl_3CCOOH (b) $Cl_2CHCOOH$

(c) $ClCH_2COOH$ (d) CH_3COOH

8. Primary alcohols are oxidized with acidic $KMnO_4$ into

(a) Carboxylic acid (b) Amide

(c) Acid anhydride (d) Alcohols

9. Derivatives of carboxylic acids are hydrolyzed into

(a) Alcohols (b) Acyl chlorides

(c) Thioethers (d) Carboxylic acids

10. With $LiAlH_4$ the carboxylic acid reduced to

(a) Acids (b) Alcohols

(c) Amines (d) Ketones

11. Anhydrides can be converted into carboxylic acids by

(a) Oxidation (b) Ammonolysis

(c) Hydrolysis (d) Decarboxylation

12. Carboxylic acids react with SO_2Cl_2 in presence of iodine to form

(a) Halo acids (b) Alcohols

(c) Hydroxy acids (d) Ketones

13. Carboxylic acids can be prepared by the S_N2 nucleophilic substitution reaction of

(a) Alkyl halide with HI (b) Alkyl halide with CO

(c) Acid anhydrides with NaCN (d) Alkyl halide with NaCN

14. Which of the following gives malic acid on reaction with α-aminosuccinic acid?

(a) Hydrogen iodide (b) Nitrous oxide

(c) Acidic $KMnO_4$ (d) Lithium aluminium hydride

15. The major product (?) of the reaction is an:

$$\text{RCOONa} \xrightarrow[\Delta]{\text{NaOH + CaO}} \text{?} + CO_2$$

(a) Alcohol (b) Amine

(c) Alkane (d) Ester

16. Malic acid on reduction with chromic acid produce

(a) Succinic acid (b) Tartaric acid

(c) Citric acid (d) Malonic acid

17. Malic acid can be reduced with HI into

(a) Succinic acid (b) Tartaric acid

(c) Citric acid (d) Malonic acid

18. Citric acid is

(a) Halo acid (b) α-Hydroxy acid

(c) β-Hydroxy acid (d) Mineral acid

19. On reduction with strong oxidizing agent tartaric acid forms

(a) Maleic acid (b) Succinic acid

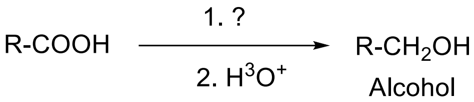
(c) Oxalic acid (d) Citric acid

20. Formation of α-chloropropionic acid to α-aminopropionic acid is an example of

(a) Electrophilic substitution (b) Ammonolysis

(c) Friedel Craft acylation (d) Nucleophilic substitution

21. What is the reagent for the following reaction?



$$R\text{-}COOH \xrightarrow[2.\ H^3O^+]{1.\ ?} R\text{-}CH_2OH$$

Alcohol

(a) $LiAlH_4$ (b) $KMnO_4$

(c) NaOH (d) HI

22. A primary alcohol can be oxidized to which of the following?

(a) An aldehyde (b) A ketone

(c) A carboxylic acid (d) A hemiacetal

23. α- bromination of carboxylic acid by a mixture of Br_2 and PBr_3 is called

(a) Michael reaction (b) Hell-Volhard Zelinskii reaction

(c) Friedel Craft acylation (d) Claisen- condensation reaction

24. Which of the following acids is used in making baking powder?

(a) Oxalic acid (b) Citric acid

(c) Tartaric acid (d) Lactic acid

25. Acid present in lemon is

(a) Oxalic acid (b) Citric acid

(c) Tartaric acid (d) Lactic acid

4.15 ANSWERS (MCQ):

1.	**(a)**	**2.**	**(c)**	**3.**	**(b)**	**4.**	**(b)**	**5.**	**(d)**
6.	**(c)**	**7.**	**(d)**	**8.**	**(a)**	**9.**	**(c)**	**10.**	**(b)**
11.	**(c)**	**12.**	**(a)**	**13.**	**(d)**	**14.**	**(b)**	**15.**	**(c)**
16.	**(d)**	**17.**	**(a)**	**18.**	**(b)**	**19.**	**(c)**	**20.**	**(d)**
21.	**(a)**	**22.**	**(c)**	**23.**	**(b)**	**24.**	**(c)**	**25.**	**(b)**

4.16 REFERENCES

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UNIT-5 ACID ANHYDRIDES

CONTENTS:

5.1 Introduction
5.2 Objectives
5.3 Structure and nomenclature of acid anhydrides
5.4 Preparation of acid anhydrides
5.5 Physical properties
5.6 Chemical reactions of acid anhydrides
5.7 Summary
5.8 Terminal Questions
5.9 Answers
5.10 References

5.1 INTRODUCTION

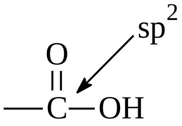
The most important functional derivatives of carboxylic acids are acid anhydrides ($(RCO)_2O$), (where R is alkyl group) which are obtained by the replacement of -OH part of the carboxyl group of acids by -OCOR, groups respectively.

5.2 OBJECTIVES

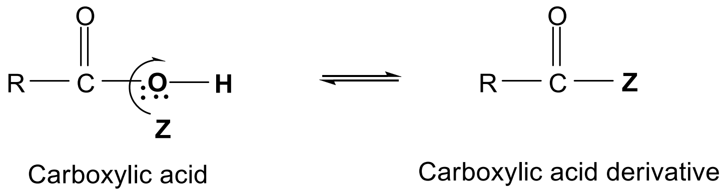
- The objectives of this unit are to study carboxylic acid derivatives *viz.* acid anhydrides, using the IUPAC naming system. Describe the structure; acid strength and reactivity of acid anhydrides ($(RCO)_2O$).
- To synthesize carboxylic acid derivatives acid anhydrides. To describe the physical and chemical properties of acid anhydrides (carboxylic acid derivatives).

5.3STRUCTURE AND NOMENCLATURE OF ACID ANHYDRIDES

A carboxylic group contains a carbonyl group (C=O) and a hydroxyl group (-OH) bonded to the carbonyl carbon. The structure of the carboxylic group is:



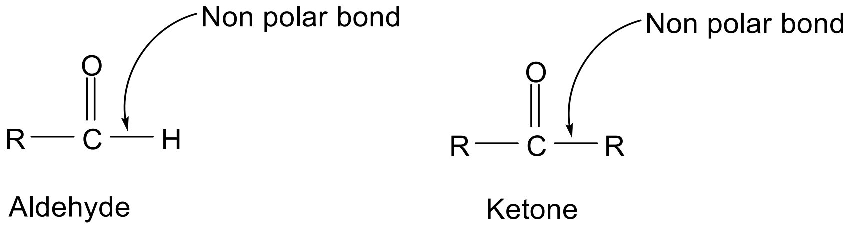
The carboxylic carbon in a carboxylic acid is bonded with three functional groups, therefore the carboxylic carbon is sp^2 hybridized and hence the carboxylic group has a planer structure with bond angles of approximately 120^o. Carboxylic acid derivatives are the organic compounds that are synthesized from the carboxylic acids by the replacement of –OH group of carboxyl group by -OCOR (acyloxy group) groups. These acid derivatives are distinguished from each other by the group attached to the carbonyl carbon atom.



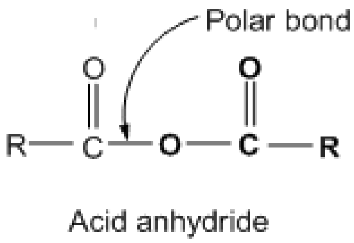
Where Z is , the acyloxy group.

Hence, the carboxylic acids and their derivatives contain a *sp*^{2} hybridized carbonyl group which consists of an O atom bonded to a C atom via a double bond in a planar model with bond angles of approximately 120^o. In carboxylic acid derivatives, the hetero atom group (-Cl, N, or O) is connected to the carbonyl carbon via a σ bond. The resonance interaction of the carbonyl group with the lone pair of the adjacent heteroatom has important implications on the reactivity.

The carbonyl carbon of the acyl group in carbonyl compounds is attached directly to a hydrogen atom or any other carbon atom. The carbon-carbon bond and carbon-hydrogen bonds are non-polar because the electronegativities of the carbon and hydrogen are almost same. For example, aldehydes and ketones are nonpolar carbonyl compounds.

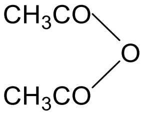
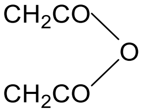
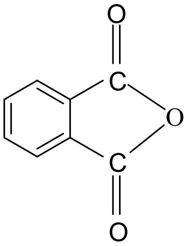


The carbonyl carbon in acyl compounds is attached directly to an oxygen, nitrogen, or halogen atom. Such bonds, C-O, C-N, and C-halogen, are polar because oxygen, nitrogen and halogen are more electronegative than that of carbon. The carboxylic acid and their derivatives are the examples of acyl compounds.



IUPAC nomenclature of acid anhydrides

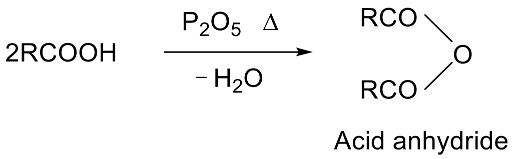
Acid anhydrides: Acid anhydrides are named by adding the word *"anhydride"* after the IUPAC name of the acid.

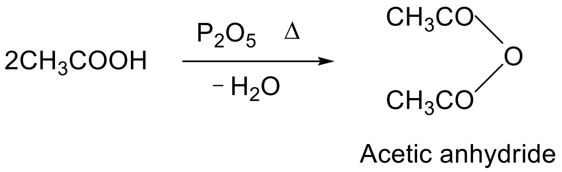
Structure	**Common name**	**IUPAC name**
	acetic anhydride	ethanoic anhydride
	succinic anhydride	butanedioic anhydride
	Phthalic anhydride	o-Benzenedioic anhydride

5.4 PREPARATION OF ACID ANHYDRIDES

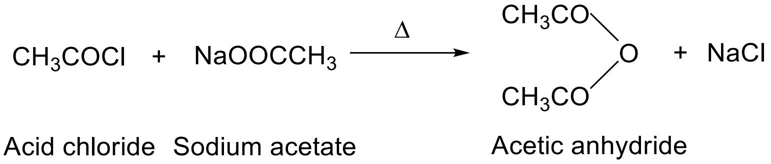
ACID ANHYDRIDE: Acid anhydrides are formed by the dehydration of carboxylic acids. They are obtained by the elimination of one water molecule from the two molecules of monocarboxylic acids. Ethanoic anhydride is the most common acid anhydride. They can be prepared by the following general methods:

1. Dehydration of anhydrous acids: Acid anhydride can be obtained by heating anhydrous acids in presence of a dehydrating agent like P_2O_5.

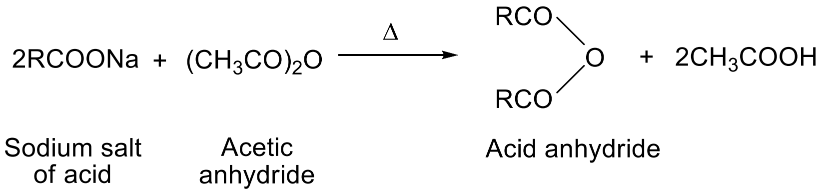




2. By heating acid chlorides with anhydrous salts of acid: Acid anhydride can be prepared by heating an acid chloride with anhydrous sodium salts of a carboxylic acid.

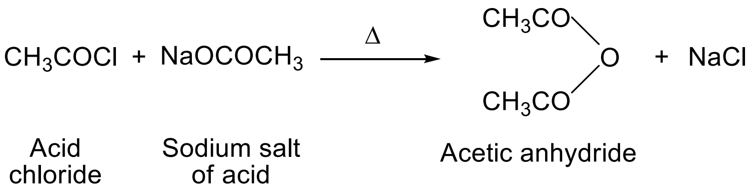


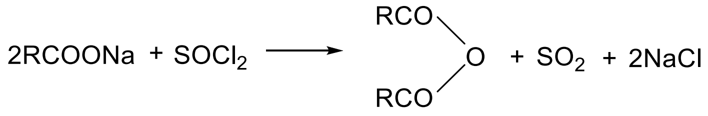
3. By heating sodium salts of carboxylic acids with acetic anhydride: Anhydrides of higher acids can be obtained by heating sodium salts of carboxylic acids with acetic anhydride.



4. By the reaction of excess amount of anhydrous sodium salts of acid with phosphorus oxy-chloride or thionyl chloride: Acid anhydrides are synthesized by treating sodium salt of carboxylic acid with $POCl_3$ or $SOCl_2$.

$$3CH_3COONa + POCl_3 \longrightarrow 3CH_3COCl + Na_3PO_4$$





$$2RCOONa + SOCl_2 \longrightarrow (RCO)_2O + SO_2 + 2NaCl$$

Acid anhydride

5.5 PHYSICAL PROPERTIES

1. Acid anhydrides are colorless liquids or solids with irritating smell.

2. They are soluble in organic solvents, although the lower members are readily soluble in water.
3. They have higher boiling points than parent acids due to their larger size.

5.6 CHEMICAL REACTIONS OF ACID ANHYDRIDES

Acid anhydrides are less reactive than acyl chlorides towards nucleophilic substitution. The most common acid anhydride is acetic anhydride. The important chemical reactions of acetic anhydride are:

1. Hydrolysis: Acid anhydrides are hydrolyzed with water to acids.

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

2. Alcoholysis: Acid anhydrides react with ethyl alcohol to produce esters.

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Acetic acid}}{CH_3COOH}$$

3. Ammonolysis: Ammonia rapidly reacts with acetic anhydrides to give acetamide.

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O + NH_3} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Acetic acid}}{CH_3COOH}$$

4. Action with primary amines: Primary amines react with acid anhydride to form amides.

$$(CH_3CO)_2O + C_2H_5NH_2 \longrightarrow CH_3CONHC_2H_5 + CH_3COOH$$

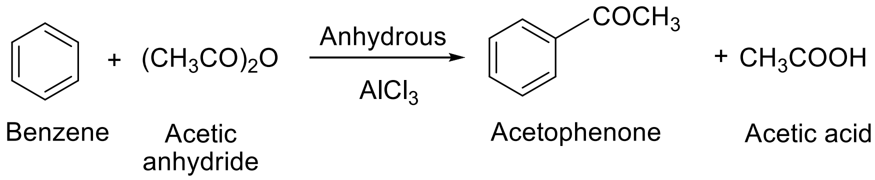
Acetic anhydride; Ethyl amine; *N*-Ethyl acetamide; Acetic acid

5. Reduction: On reduction with $LiAlH_4$, or Na and alcohol, acetic anhydrides produce alcohols.

$$(CH_3CO)_2O + 8[H] \xrightarrow[\text{or, Na/Alcohol}]{LiAlH_4} 2C_2H_5OH + H_2O$$

Acetic anhydride

6. Friedel Craft acylation: Acitic anhydrides on treatment with benzene in presence of anhydrous $AlCl_3$ form aromatic ketones.



7. Action with phosphorous pentachloride: Acetic anhydride reacts with phosphorous pentachloride to form acetyl chloride and phosphorous oxy-trichloride.

$$(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3$$

Acetic anhydride; Acetyl chloride; Phosphorous oxytrichloride

8. Action of chlorine: Acid anhydride reacts with chlorine to form acetyl chloride and monochloroacetic acid.

$$(CH_3CO)_2O + Cl_2 \longrightarrow CH_3COCl + ClCH_2COOH$$

Acetic anhydride; Chlorine; Acetyl chloride; Monohloro-acetic acid

9. Action with dry hydrogen chloride: On reaction with dry hydrogen chloride, acetic anhydride forms acetyl chloride and acetic acid.

$$CH_3CO.O.COCH_3 + HCl \longrightarrow CH_3COCl + CH_3COOH$$

Acetic anhydride; Acetyl chloride

Uses: Acid anhydrides are used in the preparation of amyl acetate, aspirin, dyes also acetate rayon. They are also used as acetylating agent.

5.7 SUMMARY:

- This unit describes the method of preparation, and physical and chemical properties of functional derivatives of carboxylic acids, viz; acid anhydride.
- Acid anhydride can be obtained by the dehydration of carboxylic acids, by heating an acid chloride with a carboxylate salt, by heating sodium salts of carboxylic acids with acetic anhydride, by the reaction of excess amount of anhydrous ammonium salts of acid with phosphorus oxy-chloride or thionyl chloride etc.
- This unit also describes the chemical properties of acid anhydride like hydrolysis, alcholysis, Friedel Craft acylation, reduction, Action with Cl_2, PCl_5, HCl, primary amine etc.

5.8 TERMINAL QUESTIONS

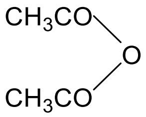
Q.1 Long answered questions

1. Give the preparation, physical and chemical properties of acid anhydrides.
2. Discuss the structure of acid anhydride.
3. How will you have obtained:

   a) Acetyl chloride from acid anhydride
   b) Ethanol from acid anhydride
   c) Acetamide from acid anhydride
   d) Primary amines from acid anhydride

Q.2 Multiple choice questions (MCQ)

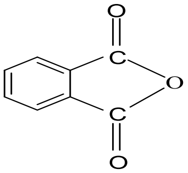
1. The given structure is for



a) Succinic anhydride b) Diethyl ether

c) Acetic anhydride d) Acetone

2. What is the IUPAC name of the given compound?



a) *o*-Benzenedioic anhydride b) Butanedioic anhydride

c) Ethanoic anhydride d) Phthalic anhydride

3. Which of the following compounds would be converted to acetic anhydride when treated with sodium acetate?

a) Acetaldehyde b) Acetyl chloride

c) Methyl acetate d) Acetamide

4. What is the formed product when acid anhydride is hydrolyzed?

a) Aldehyde b) Ketone

c) Alcohols d) Carboxylic acid C

5. The product is obtained in this reaction is:

$CH_3COCl + NaOOCCH_3 \longrightarrow$

a) Acidic acid b) Carboxylic acid

c) Acid anhydride d) Sodium acetate

6. Which functional group is present in an acid anhydride?

a) -COOH b) $–NO_2$

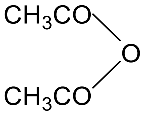
c) C-O-C d) -SH

7. Ammonia rapidly reacts with acetic anhydrides to give ………

a) Acetamide b) N- ethyl acetamide

c) Ethyl acetate d) Ammonium ion

8. IUPAC name of following compound:



a) Ethanoic anhydride	b) Butanoic oxy acid
c) Ethoxy acid	d) Butan1,2 di oxo acid

5.9 ANSWERS

1. (c)	**2**. (d)	**3.**(b)	**4.**(d)
5. (c)	**6**. (c)	**7.**(a)	**8.**(a)

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UNIT-6 ACID HALIDES

CONTENTS:

6.2 Introduction

6.2 Objectives

6.3 Structure and nomenclature of acid halides

    6.3.1 The Polarity of acyl halide

    6.3.2 IUPAC nomenclature of acid halide

6.4Relative stability of acid halides

6.5Preparation of acid anhydrides

6.6 Physical properties

6.8 Chemical reactions of acid anhydrides

6.8 Summary

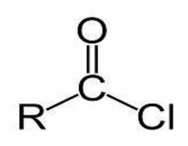
6.9 Terminal Questions

6.10 Answers

6.11 References

6.1 INTRODUCTION

An acid halide, sometimes referred to as an acyl halide, is used in organic chemistry. A halide group (−X, where X is a halogen) is substituted for a hydroxyl group (−OH) in an oxoacid to create this chemical molecule. The molecule has a −C(=O) X functional group, which is made up of a carbonyl group (C=O) singly linked to a halogen atom if the acid is a carboxylic acid (−C(=O) OH). The general formula for such an acyl halide can be written as **RCOX**,



Acid Chloride

Where, R = an alkyl group,

CO = carbonyl group,

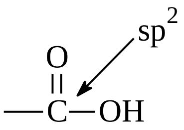
X = Halogens such as Cl, Br, I, F.

6.2 OBJECTIVES

- The objectives of this unit are to study carboxylic acid derivatives acid halides (acyl halides) using the IUPAC naming system.
- Describe the structure; acid strength and reactivity of acid halides (acyl halides). To synthesize carboxylic acid derivatives acid acid halides (acyl halides).
- To describe the physical and chemical properties of acid acid halides (acyl halides).

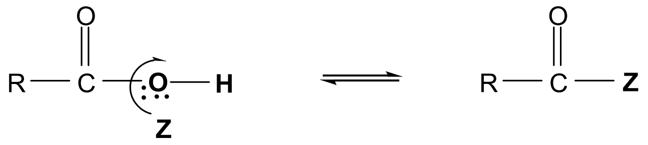
6.3STRUCTURE AND NOMENCLATURE OF ACID HALIDES

A carboxylic group contains a carbonyl group (C=O) and a hydroxyl group (-OH) bonded to the carbonyl carbon. The structure of the carboxylic group is:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carboxylic acid carbon is connected to three functional groups; it is sp2 hybridized, resulting in a planar structure with bond angles of around 120OC for the carboxylic group. Derivatives of carboxylic acids are organic compounds created by substituting the -Cl (X halogens) groups for the -OH group of the carboxyl group in carboxylic acids. The group affixed to the carbonyl carbon atom sets these acid derivatives apart from one another.



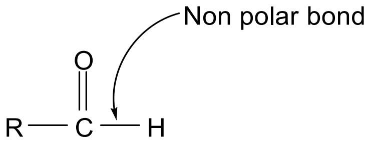
Carboxylic acid

Carboxylic acid derivative

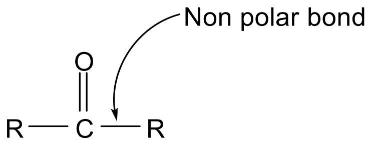
Where Z is, –Cl (X halogens) groups.

In derivatives of carboxylic acids, a σ bond connects the halogen atom group to the carbonyl carbon. Significant effects on the reactivity are caused by the carbonyl group's resonance interaction with the nearby heteroatom's lone pair. The reactivity is significantly impacted by the carbonyl group's resonance interaction with the nearby heteroatom's lone pair.

The carbonyl carbon of the acyl group in carbonyl compounds is attached directly to a hydrogen atom or any other carbon atom. The carbon-carbon bond and carbon-hydrogen bonds are nonpolar because the electronegativities of the carbon and hydrogen are almost the same. For example, aldehydes and ketones are nonpolar carbonyl compounds.



Aldehyde



Ketone

The carbonyl carbon in acyl compounds is attached directly to the halogen atom. Such bonds, C-halogen, are polar because halogen is more electronegative than that of carbon.

6.3.1 The Polarity of acyl halide

The chemical reactions of organic compounds containing an acyl group are determined by the type of bond (polar or nonpolar) formed between the acyl group’s carbonyl carbon and the substituent attached to it. Acyl compounds are organic compounds that contain an acyl group. Acyl compounds are categorized into two groups based on their polarity: nonpolar carbonyl compounds and polar acyl compounds. In acyl chlorides, the carbonyl carbon is directly attached to the chlorine. As chlorine is more electronegative than carbon, such bonds are polar.

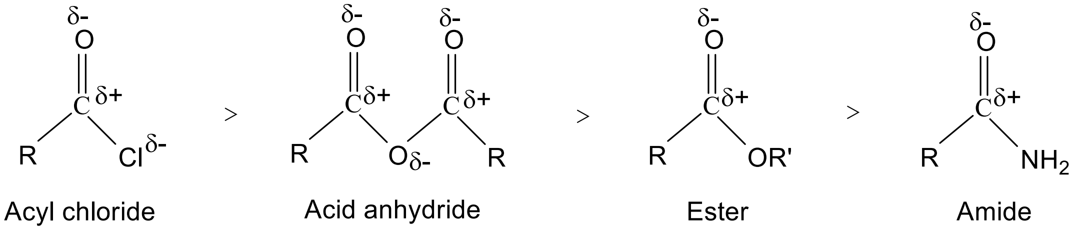
6.3.2 IUPAC nomenclature of acid halide

The functional group of an acyl halide (acid halide) is an acyl group (RCO−) bonded to a halogen atom. They are named by changing the suffix -ic acid in the name of the parent carboxylic acid to -yl halide. Because acyl chlorides are the least expensive to make and are reactive enough, the other acyl halides (bromides, iodides, fluorides) are of only minor importance. In the IUPAC system, acid chlorides are named by replacing the *"e"* ending of the parent alkane by *"-oyl chloride"*.

Structure	**Common name**	**IUPAC name**
HOCl	formyl chloride	methanoyl chloride
CH_3COCl	acetyl chloride	ethanoyl chloride
C_2H_5COCl	propionyl chloride	propanoyl chloride
C_3H_7COCl	butyryl chloride	butanoyl chloride
C_4H_9COCl	valeryl chloride	pentanoyl chloride

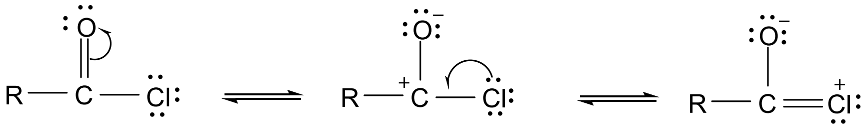
6.4 RELATIVE STABILITY OF ACID HALIDE (ACYL HALIDE)

Acid derivatives can be listed in order of their reactivity towards nucleophilic acyl substitution as:



The magnitude of the δ+ charge on the carbonyl carbon depends on the electron-releasing or electron-attracting power of the substituent. The substituent groups of acid chlorides and anhydrides can withdraw electrons from the carbonyl carbon, making these derivatives more reactive than carboxylic acids. On the other hand, in esters and amides, the substituent (Z group) releases electrons onto the carbonyl carbon which makes these derivatives less reactive. The reactivity of the carboxylic acid derivatives can be explained in details as:

For Example, Acyl chlorides: The electron-withdrawing inductive effect of an acyl chloride is not stabilized by electron pair donation; the electron-withdrawing inductive effect of chlorine makes it more electrophilic and more reactive towards nucleophilic acyl substitution.



6.5 PREPARATION OF ACID HALIDE (ACYL HALIDE)

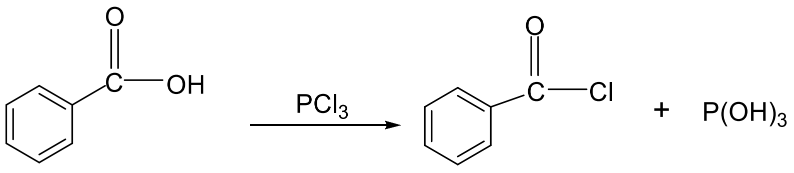
Acid chlorides also known as acyl chlorides have the general formula R-COCl. They are obtained by the replacement of a –OH group by a -Cl atom. They can be formed by heating carboxylic acids or their salts with phosphorous trichloride (PCl_3), phosphorus penta chloride (PCl_5), or thionyl chloride ($SOCl_2$).

1. From acids: Acyl chlorides are prepared by heating carboxylic acids with phosphorous trichloride (PCl_3), phosphorus penta chloride (PCl_5), or thionyl chloride ($SOCl_2$).

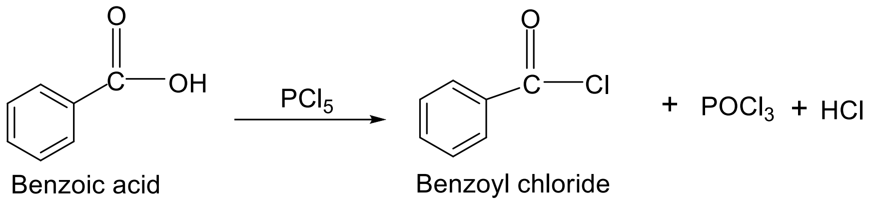
$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3 + HCl$$

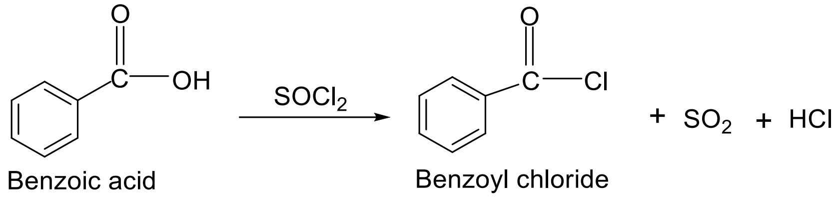
$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$



Benzoic acid Benzoyl chloride





2. From salts: Acyl chlorides are prepared by the treatment of sodium salts of carboxylic acids with phosphorous trichloride (PCl_3) or thionyl chloride ($SOCl_2$).

$$3CH_3COONa + PCl_3 \longrightarrow 3CH_3COCl + Na_3PO_3$$

Sodium acetate Acetyl chloride

$$(CH_3COO)_2Ca + SOCl_2 \longrightarrow 2CH_3COCl + CaSO_4$$

Calcium acetate Acetyl chloride

3. Industrial routes:

The industrial route to acetyl chloride involves the reaction of acetic anhydride with HCl.

$$(CH_3CO)_2O + HCl \longrightarrow CH_3COCl + CH_3COOH$$

6.6 PHYSICAL PROPERTIES

Acyl chlorides:

1. The lower members are colorless, volatile liquids having irritating smell.

2. Higher members are colorless liquids.

3. They dissolve in organic solvents such as alcohol, ether, and chloroform.

4. Because of their inability to form hydrogen bonds, acyl chlorides have lower boiling and melting points than their corresponding acids.

5. It decomposes quickly in water thus; it absorbs water vapor from the air and decomposes to produce hydrogen chloride.

6.7 CHEMICAL REACTIONS OF ACID HALIDE (ACYL HALIDE)

Acyl halides (chlorides) are the most reactive carboxylic acid derivatives. Acid halides can be converted into other acyl compounds via nucleophilic acyl substitution due to their high reactivity. The chemical characteristics of acyl halides (acyl chlorides) are as follows:

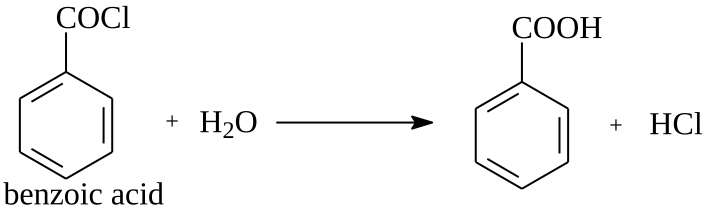
1. Basic character: Acyl chlorides are very much less basic because the chlorine atom is not effective at stabilizing a positive charge.

2. Reduction: Acid chlorides get reduced to aldehydes by the action of hydrogen in the presence of Pd/BaSO$_4$.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow[\text{Xylene}]{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

3. Hydrolysis: Acid chlorides are hydrolyzed with water to parent carboxylic acids.

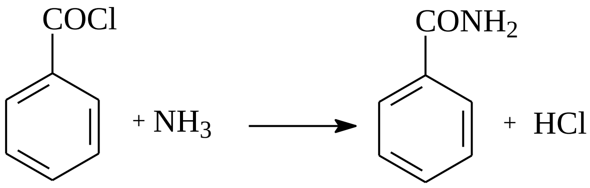
$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$$



benzoic acid

4. Action with ammonia: Acid chlorides react with ammonia to form acid amides.

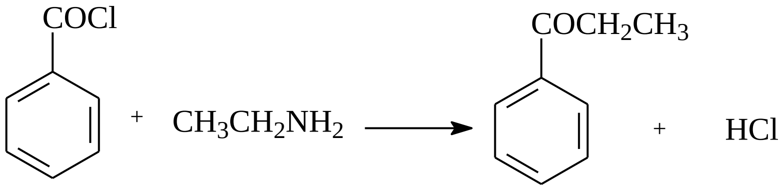
$$\underset{\text{Acetyl chloride}}{CH_3COCl} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$



5. Action of amines: Acid chlorides on reaction with primary and secondary amines give acid amides.

$$CH_3COCl + C_2H_5NH_2 \longrightarrow CH_3CONHC_2H_5 + HCl$$

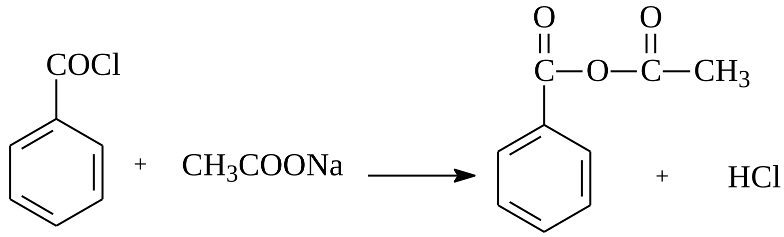
Acetyl chloride   *N*-Ethyl acetamide



6. Formation of acid anhydride: Acid chlorides by treating with sodium salts of fatty acids produce anhydrides.

$$CH_3COCl + NaOOCCH_3 \longrightarrow (CH_3CO)_2O + NaCl$$

Acetyl chloride   Sodium acetate   Acetic anhydride



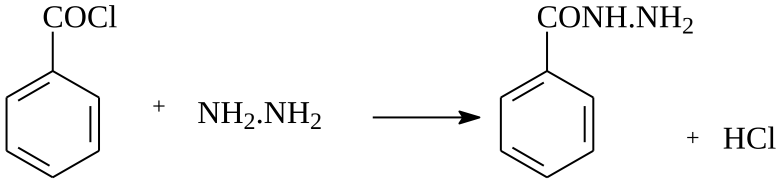
benzoyl chloride   methylphenyl anhydride

7. Action of hydrazine: On treatment with hydrazine acid chlorides form hydrazides.

$$RCOCl + H_2N.NH_2 \longrightarrow RCONH.NH_2 + HCl$$

Acid chloride   Hydrazine   Hydrazide

$$CH_3COCl + NH_2.NH_2 \longrightarrow CH_3CONHNH_2 + HCl$$



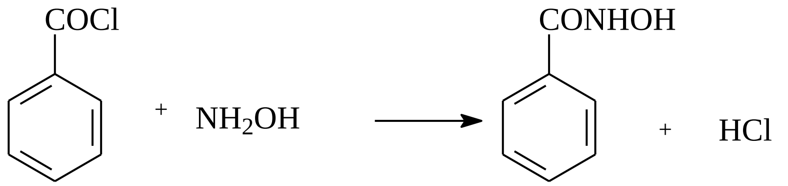
phenyl hydrazine

8. Action of hydroxyl amine: In reaction with hydroxyl amine the acid chlorides form hydroxamic acid.

$$RCOCl + H_2NOH \longrightarrow RCONH.OH + HCl$$

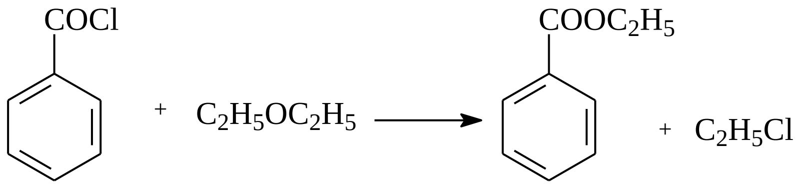
Acid chloride   Hydroxyl amine   Hydroxamic acid

$$CH_3COCl + NH_2OH \longrightarrow CH_3CONHOH + HCl$$



9. Action of ethers: Acid chlorides on reaction with diethyl ether in presence of zinc chloride form esters.

$$\underset{\text{Acid chloride}}{CH_3COCl} + \underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5} \xrightarrow{ZnCl_2} \underset{\text{Ethyl acetate}}{CH_3CO.O.C_2H_5} + \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

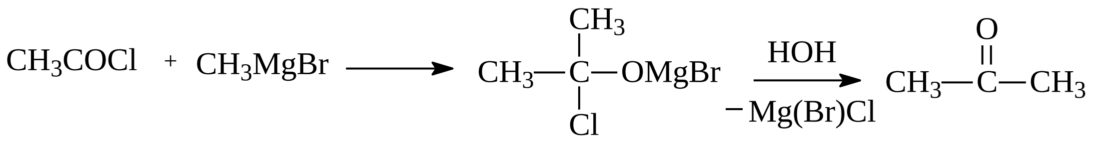


10. Action of potassium cyanide: Acid chlorides react with potassium cyanide to form acetyl cyanide which on acid-catalyzed hydrolysis gives pyruvic acid.

$$CH_3COCl + KCN \xrightarrow{-\,KCl} CH_3COCN \xrightarrow[H^+]{H_2O} \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

11. Reaction with Grignard's reagent: Acid chlorides on reaction with Grignard's reagent give tertiary alcohols.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Methyl magnisium chloride}}{ClMgCH_3} \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + MgCl_2$$



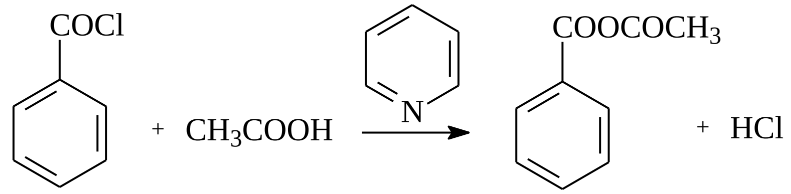
$$CH_3COCl + CH_3MgBr \longrightarrow CH_3{-}\underset{Cl}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}OMgBr \xrightarrow[-\,Mg(Br)Cl]{HOH} CH_3{-}\overset{O}{\overset{||}{C}}{-}CH_3$$

12. Action with halogens: Acid chlorides react with chlorine to form monochloroacetic acid.

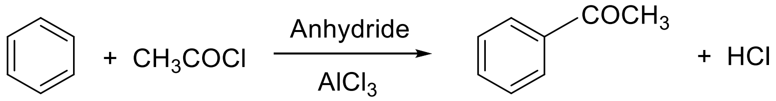
$$\underset{\text{Propionyl chloride}}{CH_3CH_2COCl} + Cl_2 \longrightarrow \underset{\text{Chloropropionyl chloride}}{CH_3CHClCOCl} + HCl$$

13. Reaction with carboxylic acid: Acid chlorides react with carboxylic acids in the presence of pyridine to form acid anhydrides.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + CH_3COOH \xrightarrow{\text{Pyridine}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + HCl$$



14. Friedel Craft's reaction: Acyl chlorides on reaction with aromatic hydrocarbons in the presence of Lewis acid (AlCl3) in Friedel Craft acylation form aromatic ketones.



Acetophenone

USES:

1. It is used in the manufacture of agrochemicals.
2. It is utilized in the synthesis of organic compounds like Acetic anhydride, acetamide, acetaldehyde, and other carbonic chemicals
3. It is used in the production of pharmaceuticals and acetylating reagents in the production of dyes.

6.8 SUMMARY

- This unit covers the preparation methods, and physical and chemical properties of carboxylic acid derivatives, specifically acyl chlorides. It explains their preparation using reagents like PCl_3, PCl_5, $SOCl_2$ and discusses their properties, including reduction, reactions with heat, halogens, carboxylic acids, and Grignard reagents, as well as industrial-scale production.

6.9TERMINAL QUESTIONS

Section-A

1.Describe the general methods of preparation, physical and chemical properties of acyl chlorides.

2.What are acid halide(chlorides) ? How can acid halide (chloride) be converted into:

a) Acetamide b) Acetic anhydride

c) Acetophenone d) Pyruvic acid

3. Explain the followings:

a) Acetyl chloride has lower boiling point than acetic acid.

b) Acetyl chloride is more reactive than acetic anhydride.

4. How will you have obtained:

a) Amides from acetyl chloride

b) Tertiary alcohol from acetyl chloride

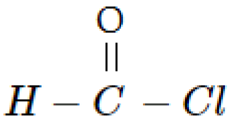
c) Acyl chlorides from esters

d) Aldehyde from acetyl chloride

Section-B

Multiple choice questions (MCQ)

1. Which of the following is the name given to the given compound?



$$H - \overset{\overset{\displaystyle O}{||}}{C} - Cl$$

a)Acetylchloride b)Formylchloride

c)Chloretone d) Oxochloromethane

2. When formic acid reacts with PCl_5 it forms which of the following?

a) Formylchloride b)Acetylchloride

c) Methylchloride d) Propionyl chloride

3. What is the product D in the given reaction?

$$C_6H_5CCl_3 + C_6H_5CO_2H \rightarrow 2\ C_6H_5COCl + D$$

a) Cl_2 b) H_2O

c) HCl d) H_2

4. Which of the following is the product B when acid chloride reacts with alcohol?

$$\mathbf{RCOCl + R'OH \rightarrow B + HCl}$$

a) Chlorophenol b) Ester

c) Ether d) Acetyl chloride

5. For synthesis of carboxylic acid, the intermediate product needed is which of the following?

a) Acyl chloride b) aryls

c) benzene d) carboxylic acid

6. Acyl chlorides are more reactive than other carboxylic acid derivatives

a) Because their boiling points are higher.

b) Because they are heavier than water.

c) Because they have a pleasant odor.

d) Due to electron withdrawing inductive effect of chlorine atom.

7. Reduction of acetyl chloride with Pd/$BaSO_4$ will produce

a) Alcohols b) Ketones

c) Acid d) Acetaldehyde

8. Which one of the following derivatives is most reactive towards nucleophilic substitution

a) Acyl chloride b) Acid anhydride

c) Ester d) Amide

9. On reaction with thionyl chloride ($SOCl_2$), Calcium acetate is converted into

a) Acid anhydrides b) Alcohols

c) Amines d) Acid chlorides

10. Acid chlorides react with carboxylic acids in the presence of pyridine to form:

a) Amines b) Acetone

c) Acid anhydrides d) Acetaldehyde

6.10 ANSWERS

1. (a)	**2. (a)**	**3. (c)**	**4. (b)**	**5.(a)**
6. (d)	**7.(d)**	**8.(a)**	**9. (d)**	**10.(c)**

6.11 REFERENCES

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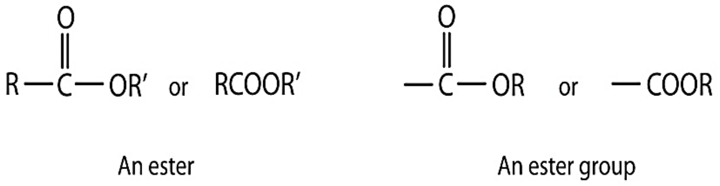
UNIT-7 ESTER

CONTENTS:

7.1Introduction
7.2 Objectives
7.3 Structure and nomenclature of Ester
7.4 Preparation of Ester
7.5 Physical properties
7.6 Chemical reactions of Ester
7.7 Summary
7.8 Terminal Questions
7.9 Answers
7.10 References

7.1 INTRODUCTION

Esters are represented by the formula RCOOR', where R and R' are hydrocarbon groups. The **ester**, which is an organic compound derived from a carboxylic acid and an alcohol in which the OH of the acid is replaced by an OR group, looks somewhat like an ether and also somewhat like a carboxylic acid. Even so, compounds in this group react neither like carboxylic acids nor like ethers; they make up a distinctive family. Unlike ethers, esters have a carbonyl group. Unlike carboxylic acids, esters have no acidic hydrogen atom; they have a hydrocarbon group in its place.



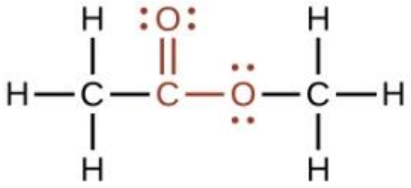
7.2 OBJECTIVES

In this unit, we have to understand Carboxylic acid derivatives esters (RCOOR'). In this unit, readers learn about:

- IUPAC name and structure of ester.
- Preparation methods of ester.
- Concise detail of Physical and chemical properties of ester.

7.3 STRUCTURE AND NOMENCLATURE OF ESTER

Esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In an ester, the second oxygen atom bonds to another carbon atom (Figure). The names for esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts. The functional groups for an ester are shown in below.



methyl ethanoate
(methyl acetate)

Esters have the general formula RCOOR′, where R may be a hydrogen atom, an alkyl group, or an aryl group, and R′ may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were a hydrogen atom, the compound would be a carboxylic acid.)

***IUPAC nomenclature of* Acid esters:**

Although esters are covalent compounds and salts are ionic, esters are named like that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion.

In the IUPAC system, esters are generally named by first naming the alkyl group followed by the name of the acid and changing the *"ic"* by *"ate"*.

Structure	**Common name**	**IUPAC name**
$HCOOCH_3$	methyl formate	methyl methanoate
$CH_3COOC_2H_5$	ethyl acetate	ethyl ethanoate
$C_2H_5COOCH_3$	methyl propionate	methyl propanoate
$CH_3COOC_6H_5$	phenyl acetate	phenyl ethanoate
$C_6H_5COOC_6H_5$	phenyl benzoate	phenyl benzoate
$C_6H_5COO\ CH_3$	methyl benzoate	methyl benzoate

7.4 PREPARATION OF ESTER

Esters are carboxylic acid derivatives that are formed by the replacement of the hydroxyl (-OH) part of the –COOH group by an alkoxy group (-OR). They are found naturally in several plants, fruits, and flowers. Orange, banana, apple, pineapple, mango, etc. are the chief source of esters. Oils, fats, and waxes are also composed of esters of higher fatty acids like stearic acid, palmitic acid, oleic acid cerotic acid, etc. Esters can be formed by the following general methods:

1. **By direct esterification:** When an alcohol interacts with an acid in the presence of a suitable acid catalyst, esters are formed by the elimination of a water molecule. This process is known as esterification.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + H_2O$$

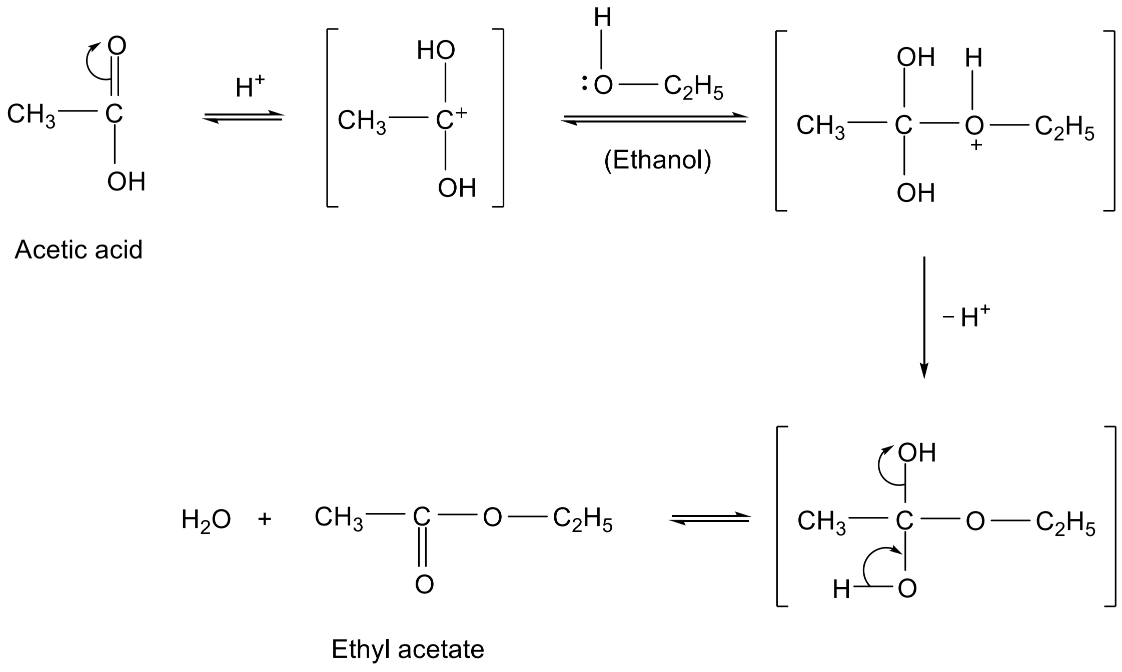
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{OHC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Phenol}}{C_6H_5OH} \xrightarrow{H^+} \underset{\text{Phenyl acetate}}{CH_3COOC_6H_5} + H_2O$$

ESTERIFICATION MECHANISM: When a carboxylic acid is treated with an alcohol in the presence of an acid catalyst, an ester is formed along with water. This reaction is known as *Fischer esterification.*

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{OHC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Mechanism: *The sequential mechanism of esterification under acidic conditions is as under:*



2. By the action of alcohols on acid chlorides or anhydrides: Esters are prepared by the nucleophilic substitution of acid chlorides or acid anhydrides with alcohols.

$$RCOCl + R'OH \longrightarrow RCOOR' + HCl$$

Acid chloride, Alcohol, Ester, Hydrochloric acid

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

Ethanoyl chloride, Ethanol, Ethyl ethanoate

$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

Acid anhydride, Alcohol, Ester, Acid

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Ethanoic anhydride, Ethanol, Ethyl ethanoate, Acetic acid

3. By heating silver salts of carboxylic acids with alkyl halides: Esters are prepared by the reaction of silver salt of acids on alkyl halides.

$$RCOOAg + R'X \longrightarrow RCOOR' + AgX$$

Silver salt of acid, Alkyl halide, Ester

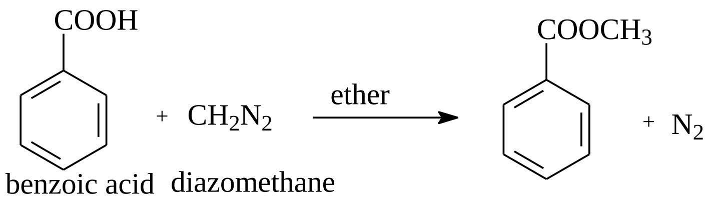
$$CH_3COOAg + C_2H_5Br \longrightarrow CH_3COOC_2H_5 + AgBr$$

Silver acetate, Ethyl bromide, Ethyl acetate

4. By the action of diazomethane on carboxylic acids: Methyl esters are prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

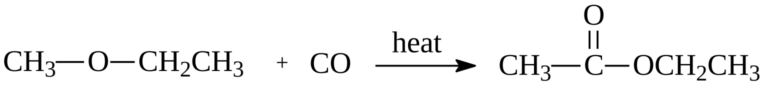
$$CH_3COOH + CH_2N_2 \xrightarrow{\text{Ether}} CH_3COOCH_3 + N_2$$

Acetic acid, Diazomethane, Methyl acetate



5. From ethers and carbon monoxide: When ether interacts with carbon monoxide at 125-180 ºC under 500 atmospheric pressures in the presence of a boron trifluoride catalyst, an ester is formed.

$$\underset{\text{Ether}}{R-O-R} + CO \xrightarrow{\Delta} \underset{\text{Ester}}{RCOOR}$$



$$CH_3-O-CH_2CH_3 + CO \xrightarrow{\text{heat}} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-OCH_2CH_3$$

7.5 PHYSICAL PROPERTIES

1. Esters are colorless liquids or solids having fruity or flowery odor.

2. Low molecular weight esters are soluble in water. The solubility of esters decreases with increases the molecular weight.

3. All esters are soluble in organic solvents like benzene, ethers etc. Esters do not form hydrogen bonding, so they have lower melting and boiling points than corresponding carboxylic acids. 4. Boiling points of normal chain esters are higher than those of branched-chain isomers.

7.6 CHEMICAL REACTIONS OF ESTER

Esters are less reactive than acyl chloride and acid anhydrides. Methyl methanoate ($HCOOCH_3$) and ethyl ethanoate ($CH_3COOC_2H_5$) are the most common esters. They can be converted into carboxylic acid by acid or base hydrolysis, into amides with ammonia and can be reduced into alcohols with $LiAlH_4$.

1. Hydrolysis: Esters are hydrolyzed to carboxylic acids in the presence of an acid whereas in presence of an alkali they produce sodium salts of carboxylic acids.

Acid hydrolysis

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

Alkaline hydrolysis:

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethanol}}{C_2H_5OH}$$

Mechanism of acid hydrolysis: The esters are hydrolyzed in the following steps.

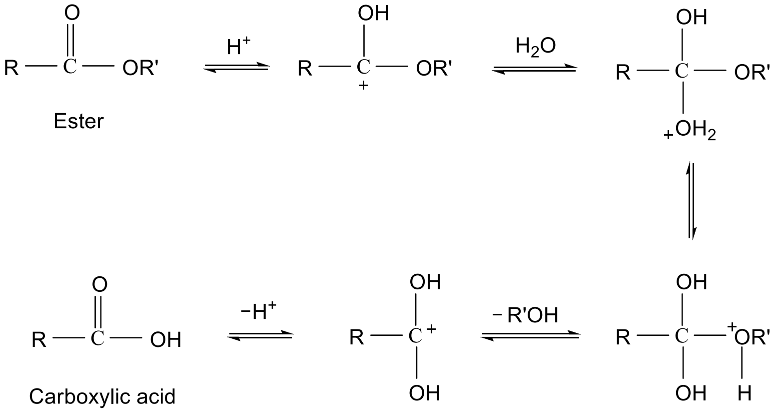
Step 1: Protonation of the ester carbonyl makes it more electrophilic.

Step 2: The ‘O’ atom of water acts as a nucleophile which attacks the electrophilic C in the C=O group, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3: Deprotonate the oxygen that came from the water molecule to neutralize the charge.

Step 4: The –OR′ group converts into a good leaving group by protonation, and R′OH is eliminated.

Step 5: Deprotonation of the oxonium ion reveals the carbonyl C=O group in the carboxylic acid product and regenerates the acid catalyst.

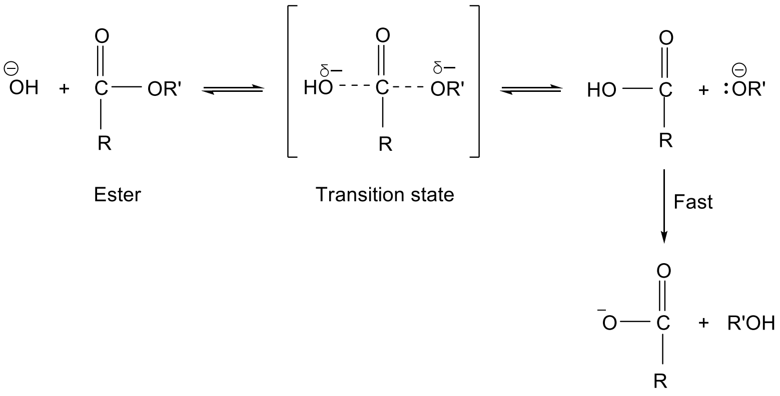


(ii) Mechanism of alkaline hydrolysis: In alkaline medium esters are hydrolyzed in ***the*** following sequential steps.

Step 1: The hydroxide nucleophile attacks at the electrophilic carbon of the ester C=O, and breaks the π bond to create a tetrahedral intermediate.

Step 2: These intermediate collapses to reform the C=O bond results in the loss of the alkoxide (RO^-) group.

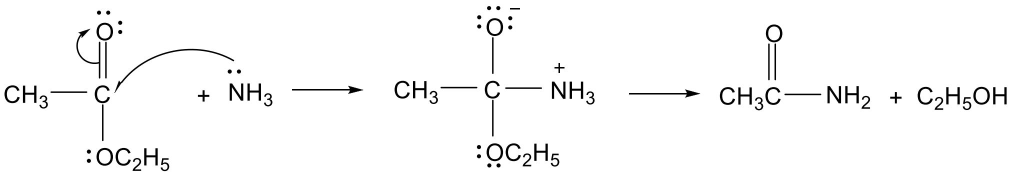
Step 3: A very rapid equilibrium coexists where the alkoxide ion (RO^-) acts as a base for deprotonating the carboxylic acid.



2. **Action of ammonia:** Esters slowly react with ammonia to form amides and alcohols. This process is called *ammonolysis.*

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethanol}}{C_2H_5OH}$$

Mechanism:



Ethyl acetate Acetamide Ethanol

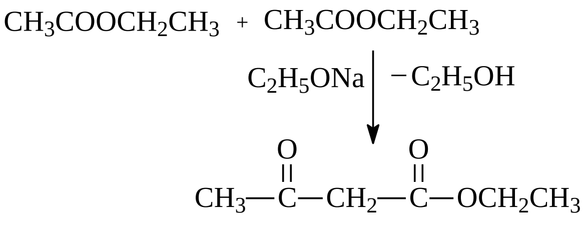
3. Reduction: On reduction with $LiAlH_4$ or Na and alcohol, esters produce alcohols.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[\text{or, Na/Alcohol}]{LiAlH_4} \underset{\text{Ethanol}}{2C_2H_5OH}$$

4. Halogenation: Esters on reaction with chlorine or bromine in the presence of red phosphorous give the α-halogenated esters (*Hell Volhard Zelinsky reaction*).

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + Br_2 \xrightarrow{\text{Red P}} \underset{\alpha\text{-Bromoethyl acetate}}{CH_2BrCOOC_2H_5} + HBr$$

5. Claisen condensation: One molecule of an ester combines with a second molecule of that ester in the presence of sodium alkoxide to give an aldehyde or a ketone. This reaction is known as Claisen condensation.



$$CH_3COOCH_2CH_3 + CH_3COOCH_2CH_3 \xrightarrow[-C_2H_5OH]{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

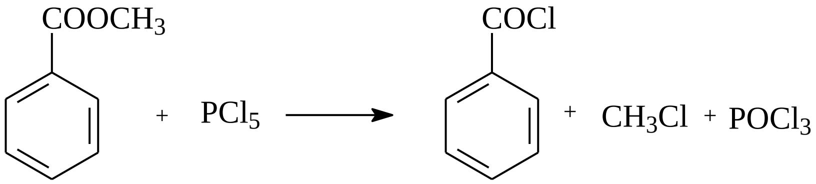
ethylacetoacetate

6. Action of phosphorous pentachloride or thionyl chloride: On reaction with phosphorous pentachloride or thionyl chloride, esters are converted into acid chlorides and alkyl halides.

$$\underset{\text{Ester}}{RCOOR'} + PCl_5 \longrightarrow \underset{\text{Acid chloride}}{RCOCl} + POCl_3 + R'Cl$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} + SO_2$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3$$



7. Trans-esterification:

Trans-esterification is the conversion of a carboxylic acid ester into a different carboxylic acid ester. When an ester is treated with an excess amount of alcohol in the presence of either an acid or a base there can be an exchange of alkoxy groups.

$$RCOOR' + R''OH \xrightarrow[\text{or alkali}]{\text{Acid}} RCOOR'' + R'OH$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Butyl alcohol}}{C_4H_9OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Butyl acetate}}{CH_3COOC_4H_9} + \underset{\text{Ethanol}}{C_2H_5OH}$$

8. Reaction with hydrazine: Esters react with hydrazine to form acid hydrazides.

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Hydrazine}}{NH_2NH_2} \longrightarrow \underset{\text{Acid hydrazide}}{RCONH.NH_2} + R'OH$$

Uses: Esters are used as solvents in perfumes, plasticizers, gums, resins, cellulose, paints, varnishes, oils and fats. They are commercially used in making artificial flavors and essences.

7.7 SUMMARY

- This unit provides a detailed overview of esters, which are carboxylic acid derivatives with the general structure RCOOR'.
- It explains the preparation methods, such as esterification with alcohols and acids, and nucleophilic substitution of acid chlorides or anhydrides with alcohols.
- The unit also delves into the chemical properties of esters, including hydrolysis in both acidic and alkaline media, esterification mechanisms, trans-esterification, and reactions with

reagents like PCl_3, PCl_5, $SOCl_2$, and hydrazine. Additionally, it highlights the various applications of esters in different fields.

7.8 TERMINAL QUESTIONS

Section-A

1. How are acid esters prepared? Describe the important chemical properties of esters.
2. Describe the mechanism of the acid and alkaline hydrolysis of esters.
3. Give the mechanism of esterification.
4. How can you convert:
   a) Acyl chlorides into esters
   b) Esters into amides
   c) Esters into alcohols
5. What is *ammonolysis*? Discuss its mechanism.
6. Give the mechanism of acid-catalyzed and basic-catalyzed hydrolysis of esters.

Section-B

1. Which one of the following is an ester?

a) RCOCl b) RCOOR’

c) RCOOH d) $RCONH_2$

2. Esters undergo acid-hydrolysis form

a) Carboxylic acids b) Acyl chlorides

c) Thioethers d) Alcohols

3. The major product (?) of the reaction is:

$$CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{Red P}} \ ? + HBr$$

a) $CH_3COOC_2H_5Br$ b) $CH_2CHBrCOOC_2H_5$

c) $CH_2BrCOOC_2H_5$ d) $CH_3BrCOOC_2H_5$

4. Esters on reduction with alkali produce:

a) Carboxylic acids b) Primary amines

c) Sodium salts of carboxylic acids d) Amides

5. Ester is obtained by the reaction between:

a) Acid chloride and alcohol b) Acid anhydride and phenol

c) Acid chloride and phenol d) All the above

6. The IUPAC name of $HCOOC_6H_5$ is:

a) Phenyl formate b) Phenyl methanoate

c) Benzyl methanoate d) None of the above

7. What is the characteristic odour of an ester?

a) Alcoholic odour b) Fruity like odour

c) Rotten egg odour d) None of the above

8. What will be the product for the given reaction?

$$CH_3OH + CO \rightarrow ?$$

a) Ethyl formate b) Methyl formate

c) Ethyl acetate d) Methyl acetate

9. Which of the following is used as catalyst for the esterification of carboxylic acid and alcohol?

a) Nitrous acid b) Sulphuric acid

c) Sulphurous acid d) Nitric acid

10. In the hydrolysis of ester what are the products formed:

a) Alcohol and carboxylic acid b) Ketone and water

c) Alkane and acid d) Aldehyde and alcohol

7.9 ANSWERS

1. (b)	**2. (a)**	**3. (c)**	**4. (c)**	**5.(d)**
6. (b)	**7.(b)**	**8.(b)**	**9. (b)**	**10.(a)**

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BLOCK-III: NITROGEN-CONTAINING COMPOUNDS

UNIT 8: NITRO COMPOUNDS

CONTENTS:

8.1 Introduction

8.2 Objectives

8.3 Nomenclature of nitro compounds

8.4 Preparation of Nitroalkanes (Aliphatic nitro compounds)

8.5 Chemical reactions of Nitroalkanes

8.6 Preparation of Nitroarenes (Aromatic nitro compounds)

8.7 Chemical reactions of Nitroarenes

    8.7.1 Mechanism of nucleophilic substitution in nitroarenes

    8.7.2 Reduction of nitroarenes in different conditions

8.8 Picric acid (2, 4, 6- trinitrophenol)

    8.8.1 Physical properties of picric acid

    8.8.2 Chemical properties of picric acid

8.9 Summary

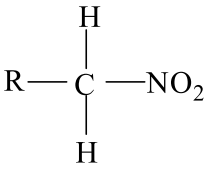
8.10 Terminal questions

8.11 Answers (MCQ)

8.12 References

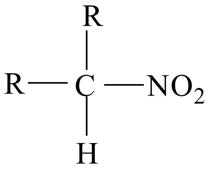
8.1 INTRODUCTION

Nitro-compounds are those organic compounds which contain at least one nitro (-NO2) functional group in the molecule. These compounds are obtained by replacing one or more hydrogen in the hydrocarbon with nitro (-NO_2) group. Nitro-compounds may be aliphatic or aromatic according to the nitro group attached to an alkyl or aryl group. The organic compounds where nitro group (-NO_2) is directly attached to the carbon of hydrocarbon chain are known as aliphatic nitro compounds *e.g.* nitromethane (CH_3NO_2), nitroethane ($C_2H_5NO_2$), 1-nitropropane ($NO_2CH_2CH_2CH_3$), whereas the compounds where nitro group (-NO_2) is directly attached to an aromatic ring are known as aromatic nitro compounds or nitroarenes such as nitrobenzene ($C_6H_5NO_2$), *m*-dinitrobenzene, 2-nitroethylbenzene, *p*-nitrotoluene, *o*-nitroaniline, 2,4,6-trinitrophenol etc. The aliphatic nitro compounds may be further classified into primary, secondary or tertiary nitro compounds as the nitro group is attached to primary, secondary or tertiary carbon atom respectively.



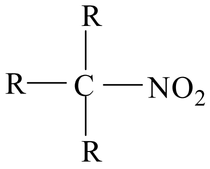
$R-\overset{H}{\underset{H}{C}}-NO_2$

Primary



$R-\overset{R}{\underset{H}{C}}-NO_2$

Secondary



$R-\overset{R}{\underset{R}{C}}-NO_2$

Tertiary

Nitro compounds are found naturally in plants and animals, and can be synthesized. These compounds are associated in many hormones, vitamins, and amino acids and proteins. These compounds possess wide chemical reactivity and used in the synthesis of several important products like drugs, agrochemicals, polymers (nylon), dyes and explosives. There are many functional groups, which contain one or more nitrogen atoms includes nitro compounds, amines, cyanides, isocyanides, diazo compounds etc.

8.2 OBJECTIVES

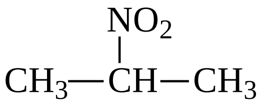
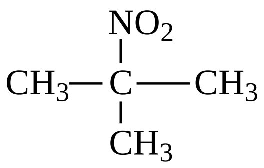
- The main objectives of this unit are: To make the students aware of the organic compounds containing nitrogen particularly the aliphatic and aromatic nitro compounds, the chemical properties of nitroalkanes, the mechanism of nucleophilic substitution in nitroarenes.

- To explain the reduction of nitroarenes in different media and to describe the preparation, chemical properties and uses of picric acid.

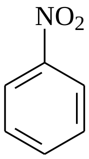
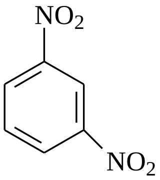
8.3 NOMENCLATURE OF NITRO COMPOUNDS

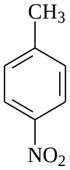
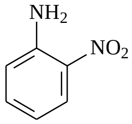
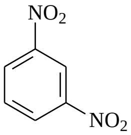
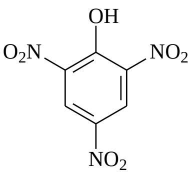
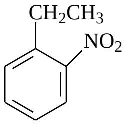
In IUPAC system, nitro compounds are named by prefixing "nitro" before the name of hydrocarbon in which the nitro group is substituted. Arabic numerals are used to indicate the position of nitro group and other substitutes if any.

Aliphatic nitro compounds:

COMPOUNDS	IUPAC NAME
CH_3NO_2	nitromethane
$CH_3CH_2NO_2$	nitroethane
$CH_3CH_2CH_2NO_2$	1– nitropropane
 $CH_3-CH(NO_2)-CH_3$	2 – nitropropane
 $CH_3-C(NO_2)(CH_3)-CH_3$	2 – methyl – 2 – nitropropane

Aromatic nitro compounds

COMPOUNDS	IUPAC NAME
	nitrobenzene
	m– nitrobenzene

COMPOUNDS	IUPAC NAME
	p– nitrotoluene
	o–nitroaniline
	m - dinitrobenzene
	2, 4, 6 - trinitrophenol
	2 - nitroethylbenzene

7.4 PREPARATION OF NITROALAKANES (ALIPHATIC NITRO COMPOUNDS)

1. **Action of Silver nitrite on alkyl halide:**

   This method is commonly used in the laboratory to prepare nitroalkanes. When alkyl halides are heated with silver nitrate, nucleophilic substitution occurs, to yield nitroalkanes Nitro compounds are formed when iodo alkanes combine with silver nitrate. Nitroethane is produced when iodoethane is treated with silver nitrate.

$$CH_3 - CH_2 - I + AgNO_2 \rightarrow CH_3 - CH_2 - NO_2 + AgI$$

Nitroethane

2. **From Chloroacetic acid:**

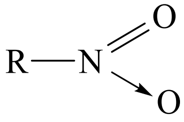
   Lower nitroalkanes, specifically nitromethane, are produced by reacting chloroacetic acid with sodium nitrite or potassium nitrite. Nitroacetic acid, which is generated as an intermediate product, decarboxylates to produce nitromethane.

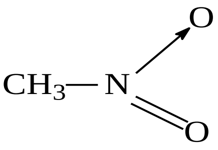
$$ClCH_2COONa + NaNO_2 + H_2O \rightarrow CH_3NO_2 + NaCl + NaHCO_3$$

3. **Hydrolysis of α- nitroalkenes:** An α- nitroalkene on hydrolysis in the presence of an acid or alkali produce nitroalkane.

$$CH_3 - C(CH_3) = CHNO_2 + H_2O \rightarrow CH_3 - C(CH_3) = O + CH_3 - NO_2$$

8.5 CHEMICAL PROPERTIES OF NITROALKANES

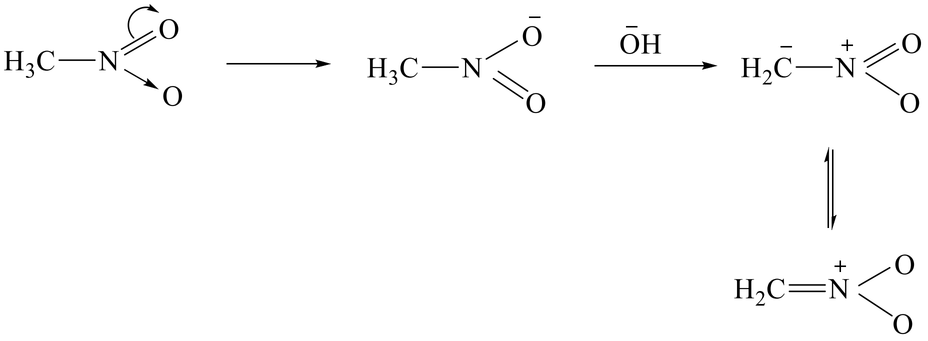




Nitroalkanes are nitro derivatives of alkanes obtained by the replacement of a hydrogen atom by a nitro group. They are isomeric with alkyl nitriles. Nitroalkanes are named by prefixing 'nitro' to the name of the parent hydrocarbon *e.g.*, $C_2H_5NO_2$ (nitroethane), $C_3H_7NO_2$ (nitropropane), etc.

Nitroalkanes may be primary, secondary, or tertiary according to the nitro group attached to a primary, secondary, and tertiary carbon. They are colorless liquids that have a pleasant odor. Nitromethane is sparingly soluble in water while higher nitroalkanes are insoluble in water but soluble in organic solvents. They have high boiling points. They are highly polar organic compounds.

1. Acidic character: The nitroalkanes containing α-hydrogen atoms exhibit an acidic character due to the electron-withdrawing nature of the nitro group.



Nitroalkanes containing α-hydrogen react with a strong alkali to form salts.

$$R\text{—}CH_2NO_2 + NaOH \longrightarrow [R\text{-}CHNO_2]^- + Na^+ + H_2O$$

2. Reduction: Nitro compounds can be reduced to primary amines under a variety of conditions. Various reduction stages of the nitro group are given below: The final product depends upon the pH of the reaction medium and the nature of the reducing agent.

(i) Reduction in acidic medium: Nitroalkanes can be reduced to the corresponding primary amines by a combination of active metals (Zn, Fe or Sn) and concentrated hydrochloric acid (HCl).

$$R{-}NO_2 + 6[H] \xrightarrow{Fe/HCl} RNH_2 + 2H_2O$$

$$CH_3CH_2CH_2NO_2 \xrightarrow{Fe/HCl} CH_3CH_2CH_2NH_2$$

(ii) Reduction in neutral medium: Reduction with zinc dust and ammonium chloride solution in neutral medium, nitroalkanes are converted into corresponding *N*-alkyl hydroxyl amines.

$$R{-}NO_2 + 4[H] \xrightarrow{Zn/NH_4Cl} RNH.OH + H_2O$$

Nitromethane on reduction with zinc dust and ammonium chloride solution in neutral medium converted into *N*-methylhydroxy amine.

$$\underset{\text{Nitromethane}}{CH_3{-}NO_2} + 4[H] \xrightarrow{Zn/NH_4Cl} \underset{\text{N-Methylhydroxy amine}}{CH_3{-}NHOH} + H_2O$$

(iii) Catalytic reduction: The nitro group of an aliphatic and aromatic nitro compound is easily reduced to corresponding primary amines with hydrogen using raney Ni, Pt or Pd catalyst.

$$\underset{\text{Nitroalkane}}{R{-}NO_2} + 3H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{Primary amine}}{RNH_2} + 2H_2O$$

The nitroethane is reduced to ethylamine with Pt or Ni catalyst.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 3H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + 2H_2O$$

(iv) Reduction with metal hydrides: Nitroalkanes are easily reduced to corresponding primary amines with $LiAlH_4$.

$$\underset{\text{Nitromethane}}{CH_3{-}NO_2} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Methylamine}}{CH_3{-}NH_2}$$

3. Hydrolysis: When primary nitroalkanes are heated with boiling HCl or H_2SO_4 undergo hydrolysis to form carboxylic acid and corresponding salt of hydroxyl amine. This reaction is used for the manufacturing of hydroxylamine.

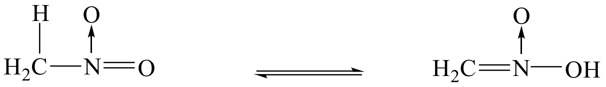
$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O \xrightarrow{HCl} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Hydroxylamine}}{NH_2OH}$$

Secondary nitroalkanes hydrolyze with boiling HCl to give ketones and nitrous oxide.

$$\underset{\text{Nitroalkane}}{2R_2CHNO_2} \xrightarrow{HCl} \underset{\text{Ketone}}{2R_2CO} + N_2O + H_2O$$

Tertiary nitroalkanes, however, do not generally undergo hydrolysis with hydrochloric acid.

4. Tautomerism: Nitroalkanes containing α-hydrogen atoms, *i.e.*, primary and secondary nitroalkanes, show tautomerism. For example, nitromethane exists in two tautomeric forms, nitro form and isonitro form.

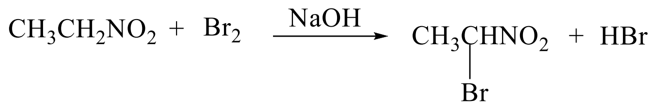


$$\underset{\substack{\text{Nitromethane}\\\text{(Nitro form or pseudo acid form)}}}{H_2\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\uparrow}{N}}=O} \rightleftharpoons \underset{\substack{\text{Nitronic acid}\\\text{(Aci form or isonitro form)}}}{H_2C=\overset{O}{\overset{\uparrow}{N}}-OH}$$

The nitro form is often called *pseudo acid form* whereas the aci-form is called *nitronic acid*. Similarly, nitroethane, 1-nitropropane, and 2-nitropropane show tautomerism whereas aromatic nitro compounds like nitrobenzene, *m*-dinitrobenzene, etc., and tertiary nitro compounds do not show tautomerism due to the absence of α-hydrogen atom on α-carbon atom.

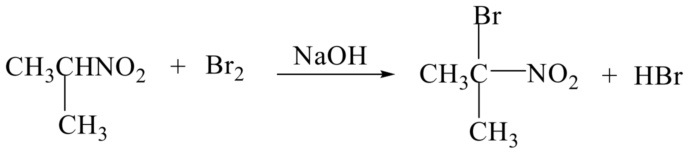
5. Halogenation: Primary and secondary nitroalkanes on treatment with halogen (chlorine or bromine) in the presence of alkali form halo nitroalkanes. During this reaction, all three hydrogen atoms of nitroalkanes are replaced by the halogen atoms.

$$\underset{\text{Nitromethane}}{CH_3NO_2} + Cl_2 \xrightarrow{NaOH} \underset{\text{Chloropicrin}}{CCl_3NO_2}$$



$$CH_3CH_2NO_2 + Br_2 \xrightarrow{NaOH} CH_3\underset{Br}{\underset{|}{C}}HNO_2 + HBr$$

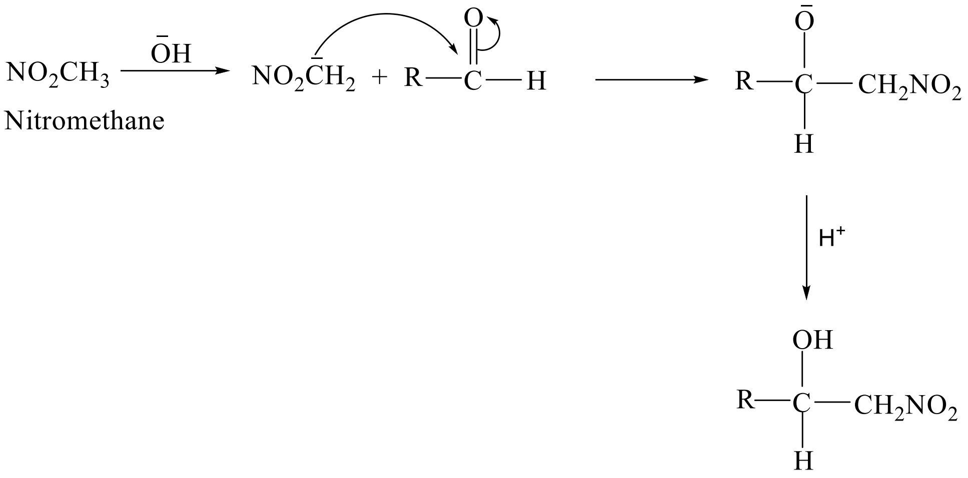
α-Bromonitroethane



$$CH_3\underset{CH_3}{\underset{|}{C}}HNO_2 + Br_2 \xrightarrow{NaOH} CH_3\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-NO_2 + HBr$$

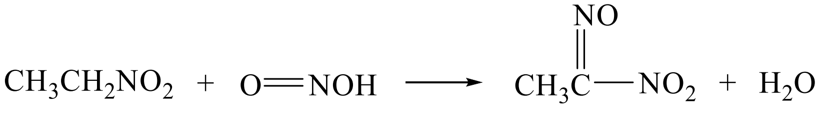
2-Bromo-2-nitropropane

6. Reaction with aldehydes: Nitroalkanes having α-hydrogen can undergo nucleophilic addition reaction with aldehydes similar to aldol type addition reaction.



7. Action with nitrous acid: Nitroalkanes on reaction with nitrous acid give different products depending upon the type of nitro compound.

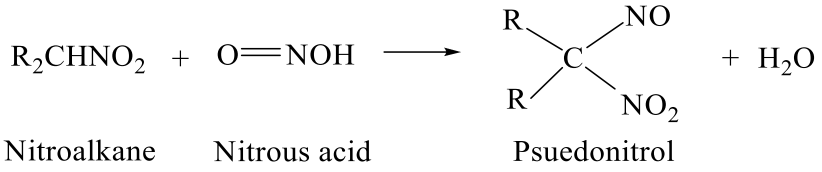
Primary nitroalkanes on reaction with nitrous acid give nitrolic acids which dissolve in alkalies to form a red solution.



$$CH_3CH_2NO_2 + O{=}NOH \longrightarrow CH_3\overset{NO}{\overset{\|}{C}}-NO_2 + H_2O$$

Nitroethane Nitrous acid Nitrolic acid

Whereas, secondary nitroalkanes on reaction with nitrous acid give blue colored pseudo-nitroles which do not dissolve in alkali.



Tertiary nitroalkanes do not react with nitrous acid since they do not have α-hydrogen atoms.

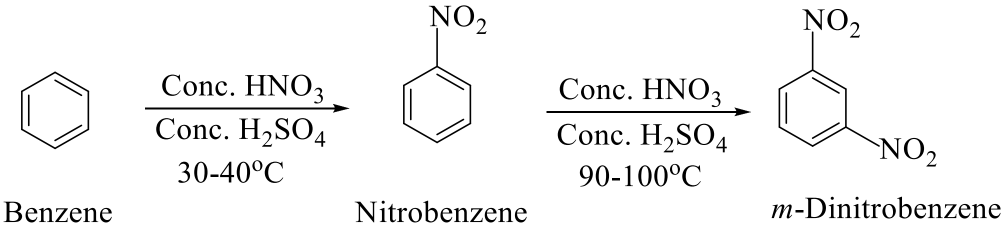
Uses of nitro compounds: Nitroalkanes *e.g.* nitromethane, nitroethane, etc., and nitrobenzene are extensively used as solvents in industry.

1. Nitroarenes are important intermediates in the manufacture of polymers detergents, dyes, and pharmaceuticals.
2. Nitroarenes are also used for the preparation of explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and research and development explosives (RDX).
3. Chloropicrin is used as an insecticide.

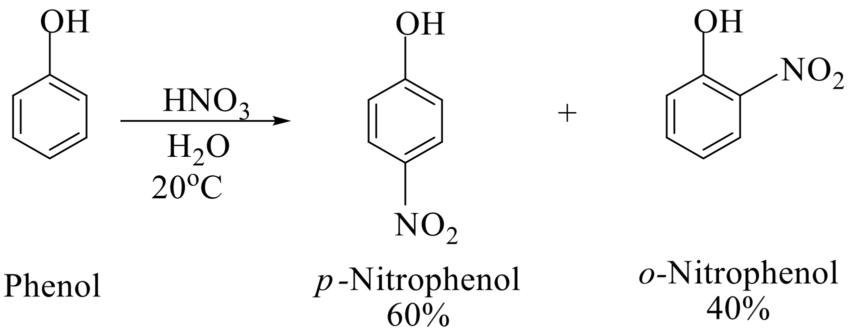
8.6 PREPARATION OF NITROARENES (AROMATIC NITRO COMPOUNDS)

Nitroarenes can be prepared by the following general methods:

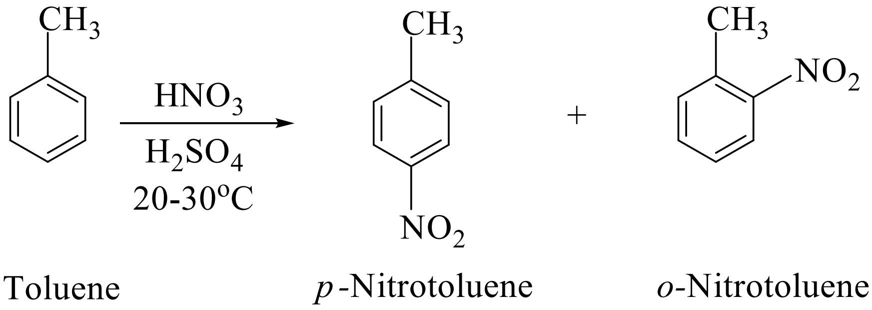
1. By the nitration of aromatics: The aromatic nitro compounds can be prepared by the direct nitration of aromatics. The formation of nitroarene depends upon the temperature, nature of the nitrated aromatic compound and nature of reagent used. For example, nitrobenzene is prepared by the direct nitration of benzene using concentrated HNO_3 and H_2SO_4 at about 30-40°C.



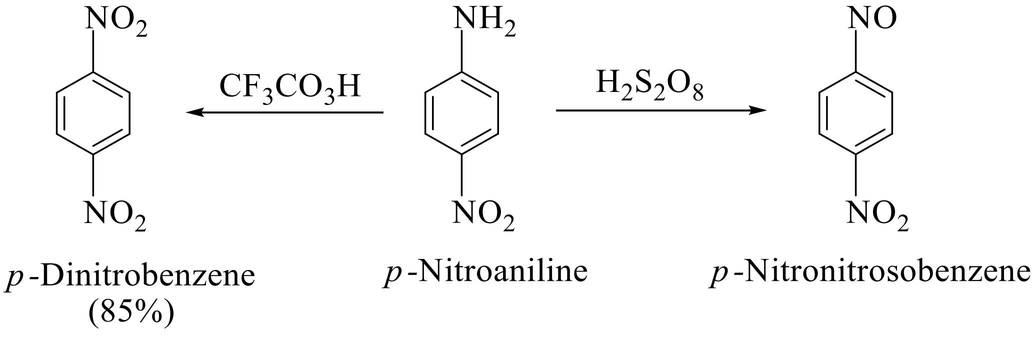
The nitrophenol is prepared by the nitration of phenol in presence of HNO_3 and H_2O at 20°C.



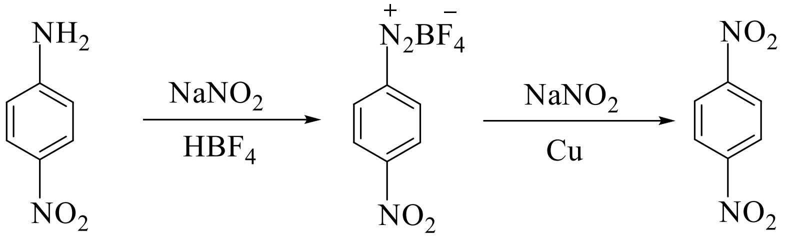
Nitrotoluene can be prepared by the nitration of toluene with concentrated HNO_3 and H_2SO_4 at about 20-30°C.



2. By the oxidation of the amino group to nitro group: *p*-dinitrobenzene can be prepared by the oxidation of the amino group into a nitro group with per-acids such as persulphuric acid ($H_2S_2O_8$) and peroxy trifluoroacetic acid (CF_3CO_3H).



3. By the replacement of amino group by nitro group: The $–NH_2$ group in aromatic group can bereplaced by treating the compound with $NaNO_2/HBF_4$ as follow



p-Nitroaniline *p*-Dinitrobenzene

8.7 CHEMICAL REACTIONS OF NITROARENES

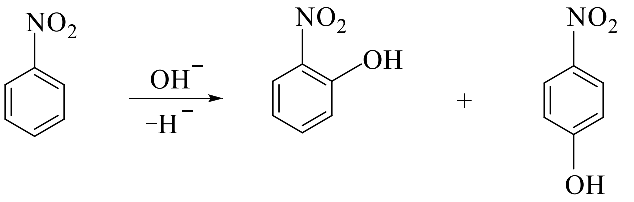
8.7.1 Mechanism of nucleophilic substitution in nitroarenes

Nucleophilic aromatic substitution occurs with a variety of strong nucleophiles, including –OH, –OR, $–NH_2$, –SR, and neutral nucleophiles such as NH_3 and RNH_2. The mechanism of nucleophilic aromatic substitution is an addidtion-elimination type; therefore, the mechanism of these reactions has two important steps:

1. Addition of the nucleophile to form a resonance-stabilized carbanion
2. Elimination of hydrogen or halogen leaving group.

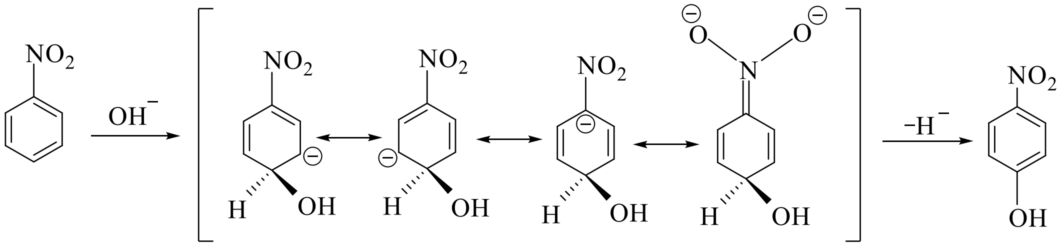
For example: 1. Nucleophilic aromatic substitution in nitrobenzene

Nitrobenzene reacts with –OH nucleophile to form the *o*-nitrophenol and *p*-nitrophenol.

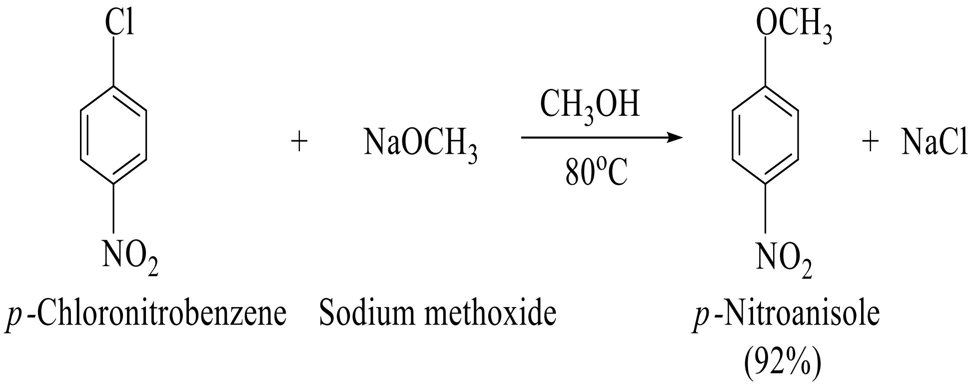


Nitrobenzene *o*-Nitrophenol *p*-Nitrophenol

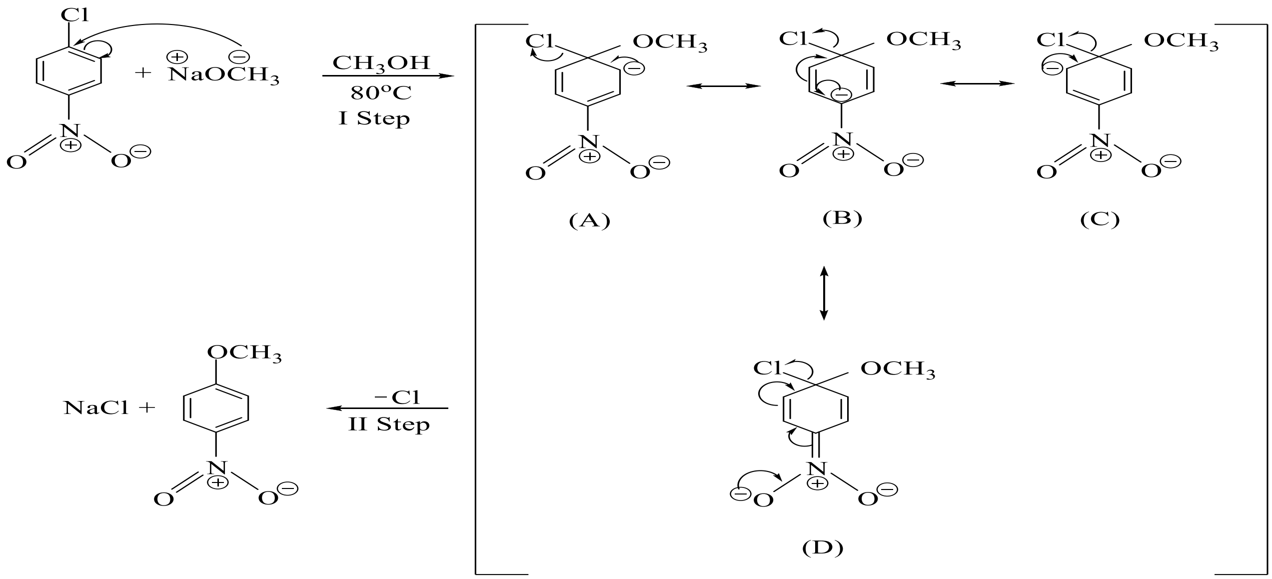
Mechanism: The mechanism for the formation of *p*-nitrophenol from nitrobenzene is as follows:



2. Addition elimination mechanism of nitro chlorobenzene: The nitro substituted aryl halides undergo reaction with nucleophiles such as ammonia and hydroxide, where the chlorine is eliminated/substituted *e.g.* *p*-chloronitrobenzene reacts with sodium methoxide at 85 ºC to form the *p*-nitroanisole.



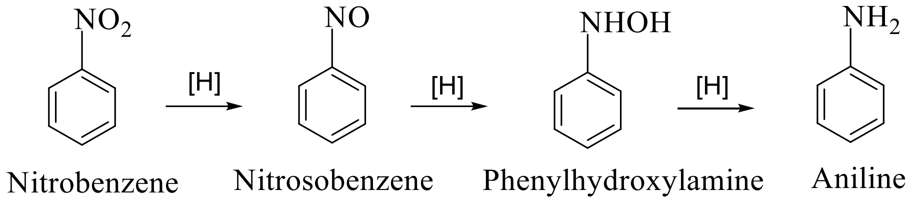
The mechanism of the formation of *p*- nitroanisole from *p*-chloronitrobenzene is as follows:



8.7.2 Reduction of nitroarenes in different conditions

The nitroarenes give different products while reduced in different reaction conditions such as nature of reducing agents and the pH of the reaction medium as follow

(i) Reduction of nitroarenes in acidic medium: Nitroarenes can be easily reduced to corresponding primary aryl amines by tin metal and hydrochloric acid. For example, the reduction of nitrobenzene with tin metal and hydrochloric acid gives aniline.

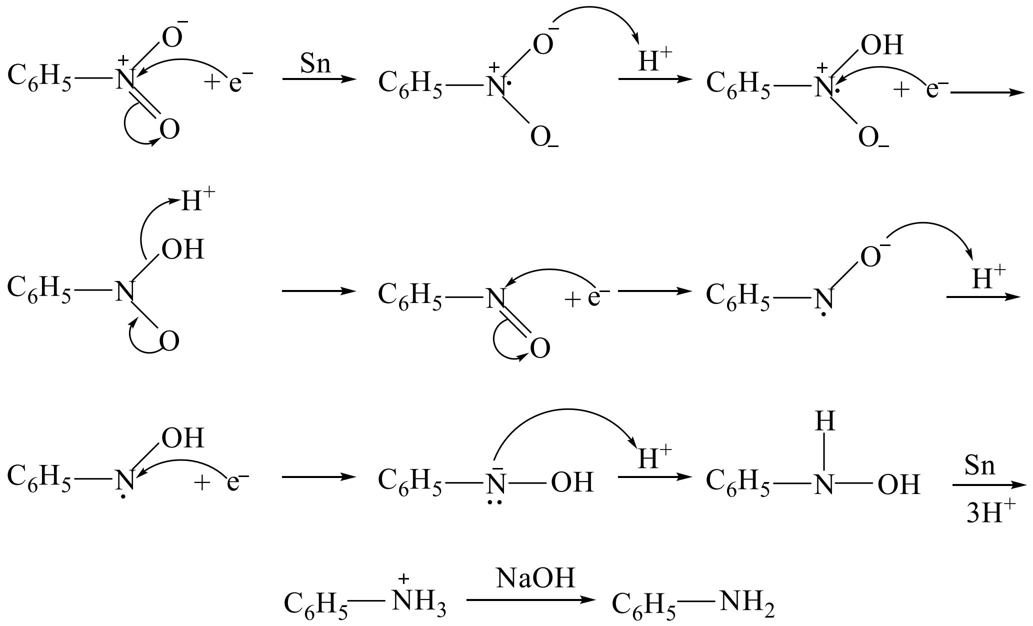


Mechanism:

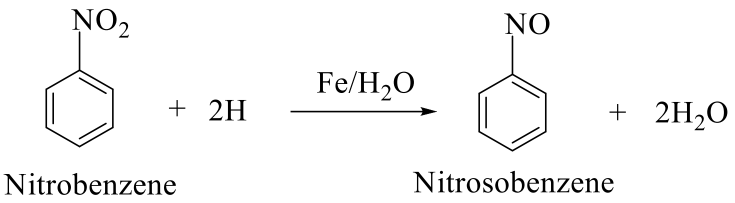
1. The reduction of nitrobenzene to aniline is an example of oxidation reduction reaction in which the Sn^0 is oxidized to stannic ion Sn^{4+} by the donation of four electrons to substrate to form an intermediate.

2. This intermediate radical is then ion protonated, the protons are provided by the acid.

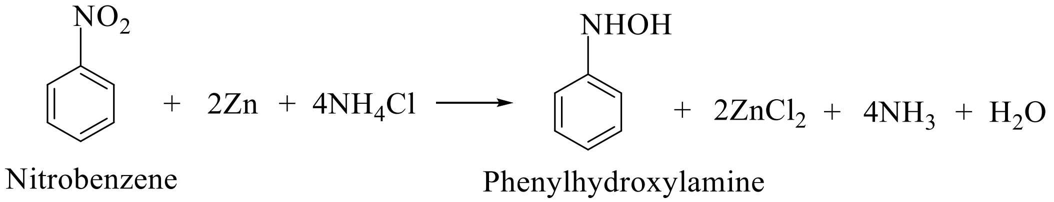
3. The oxygen atom from the nitro group is removed as water molecule. The scheme of this reaction mechanism is as:



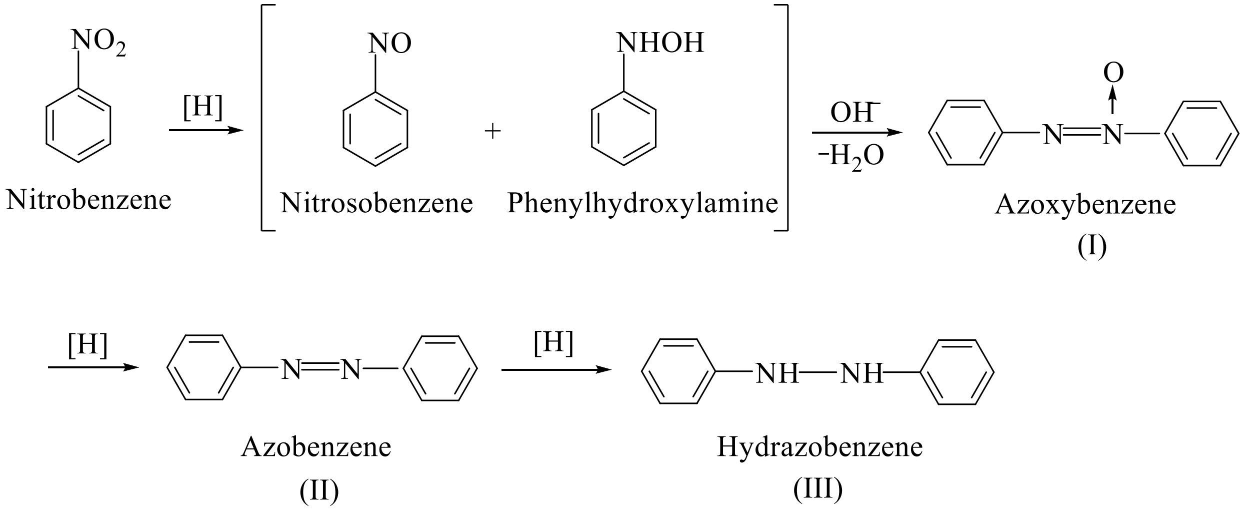
(ii) Reduction of nitroarenes in neutral medium: With iron and steam a nitro compound gets reduced to nitroso compounds.



The reduction of nitrobenzene with zinc metal and ammonium chloride or calcium chloride gives only *N*-phenylhydroxylamine. The hydroxylamines are reducing agents and can reduce *Tollen's reagent.*



(iii) Reduction of nitroarenes in alkaline medium: Whilst acidic and neutral reduction result in the formation of mono-nuclear compounds, reaction in alkaline medium yields a variety of binuclear compounds due to the interaction of nitroso- and hydroxylamine derivatives formed during the reduction. The reduction of nitrobenzene yields different products depending upon the nature of reducing agent used. The scheme of alkaline reduction is given below:

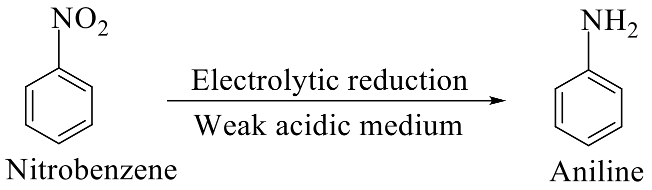


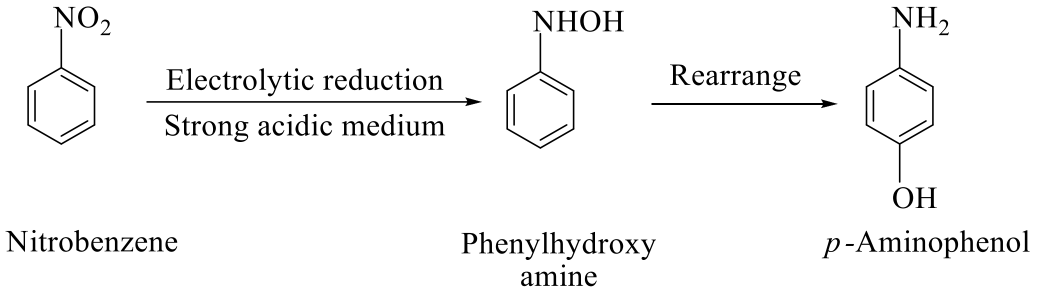
(i) The product-I, azoxybenzene is formed by the reduction of nitrobenzene with alkaline sodium arsenite (Na_3AsO_3/NaOH).

(ii) The product-II, azobenzene is formed, when nitrobenzene is reduced with zinc dust and methanolic caustic soda solution, or by alkaline stannite.

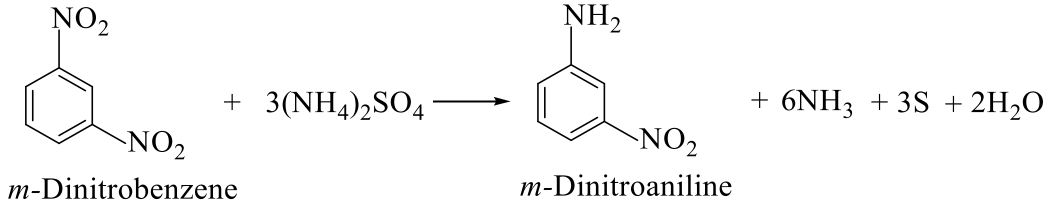
(iii) The product-III, hydrazobenzene is obtained by reduction of nitrobenzene with zinc dust and aqueous sodium hydroxide (Zn/NaOH).

(iv) Electrolytic reduction: Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium, it gives *p*-aminophenol obviously through the acid catalyzed rearrangement of initially formed phenyl hydroxyl amine.

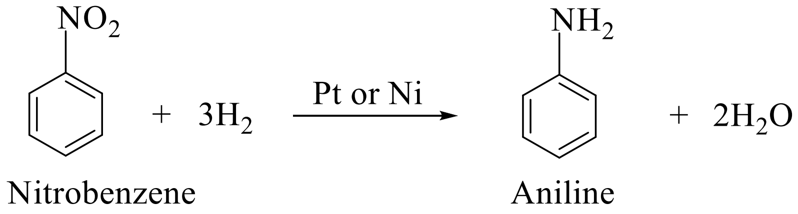




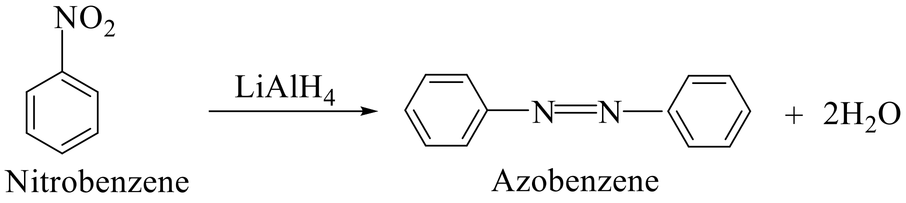
(v) Selective reduction: If two or more nitro groups are present in the benzene ring, it is possible to reduce one of them without affecting the others. Such reductions are called selective reductions. For example, reduction of *m*-dinitrobenzene with sodium or ammonium sulphide gives *m*-nitroaniline. This reduction of nitro compounds with sulphides and polysulphides is called **Zinin reduction**.



(vi) Catalytic reduction: Nitrobenzene is reduced to aniline with hydrogen using Pt or Ni catalyst.

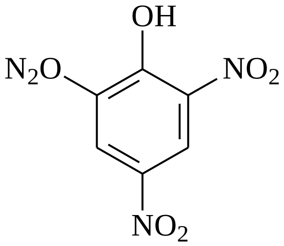


(vii) Reduction with metal hydride: Aromatic nitro compounds on reduction with $LiAlH_4$ give azo compounds.



8.8 PICRIC ACID (2, 4, 6-TRINITROPHENOL)

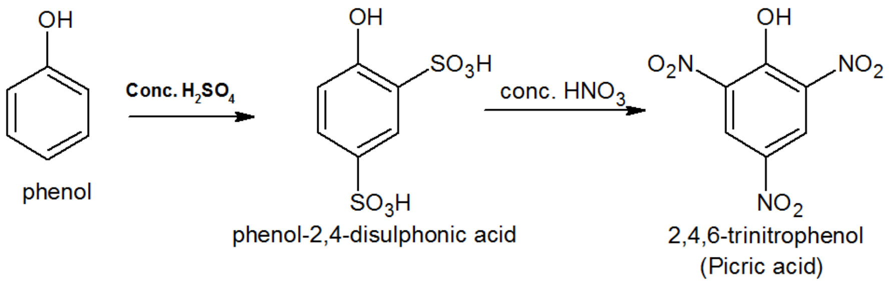
Picric acid is the chemical compound formally called 2, 4, 6-trinitrophenol (TNP). It has a chemical formula $C_6H_3N_3O_7$. Its name comes from a Greek word *pikros* means "bitter", reflecting the bitter taste of picric acid.



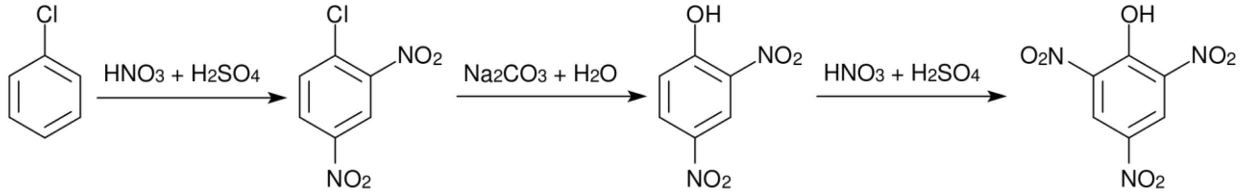
picric acid
(TNP)

Preparation of picric acid: TNP can be synthesized by various methods as:

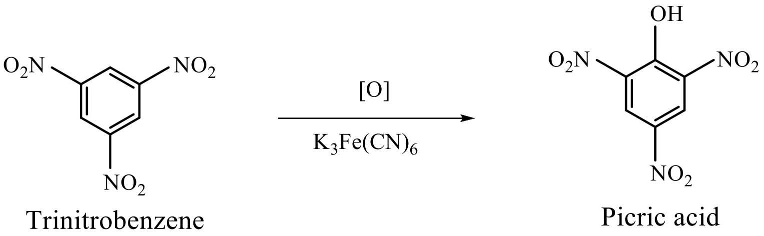
1. From phenol: Picric acid can be prepared from phenol by sulphonation followed by the nitration.



2. From chlorobenzene: Picric acid can be obtained by the reaction of nitric acid followed by hydrolysis and followed by nitration.



3. From trinitro benzene: Picric acid can be prepared by the oxidation of sym-trinitrobenzene with potassium ferricyanide.



8.8.1 Physical properties of picric acid

1. Picric acid is a yellow crystalline solid and one of the most acidic phenols.

2. It is volatile, flammable, highly toxic and bitter in taste.

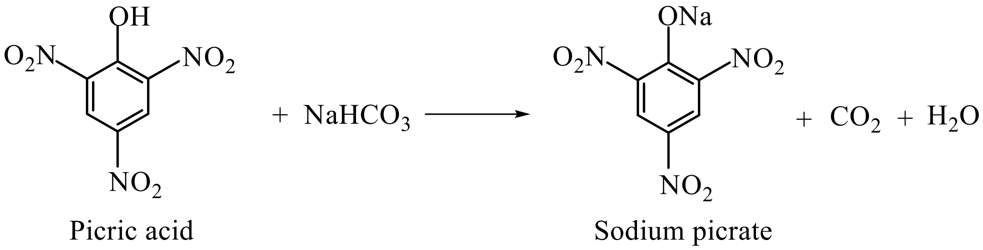
3. Its melting point is 122ºC. It is sparingly soluble in water, but soluble in hot water, alcohols and ethers.

4. It is explosive when dry and forms picrates when exposed with metals.

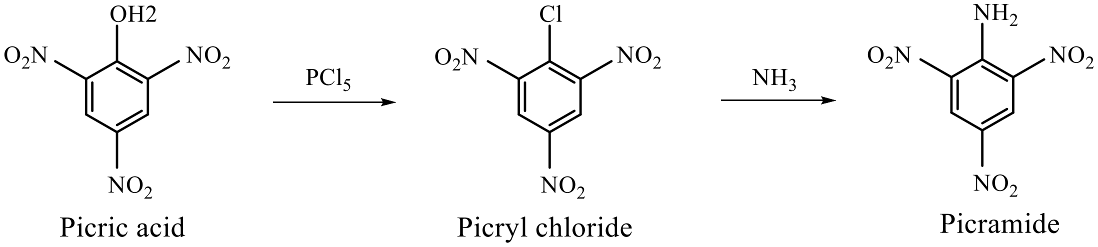
5. Picric acid is especially hazardous because it is volatile and slowly sublimes even at room temperature.

8.8.2 Chemical properties of picric acid

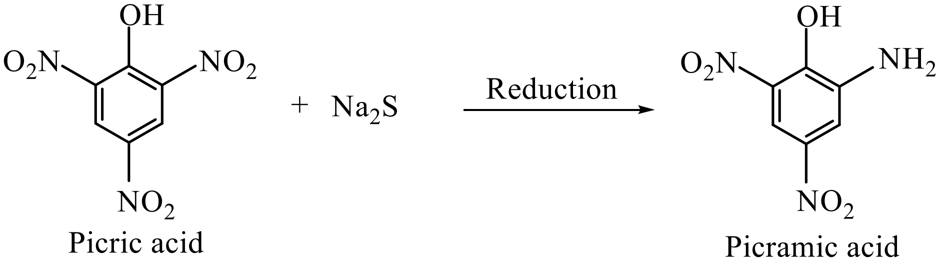
1. Picric acid is much stronger acidic than phenol due to $-NO_2$ functional group. Picric acid reacts with $NaHCO_3$ to liberate CO_2.



2. Picric acid on reaction with phosphorus pentachloride forms picryl chloride.



3. On reduction with sodium sulphide (Na_2S) in the presence of water, picric acid gives picramic acid.



Uses: Picric acid is used in electric batteries, the leather industry, dyes, pigments, inks, and paints, the manufacture of colored glass and textile mordents, as a laboratory reagent, and in matches and explosives.

8.9. SUMMARY

- This unit focuses on organic compounds containing nitrogen covalently bonded to carbon, specifically nitro compounds.

- It covers aliphatic and aromatic nitro compounds, including their preparation methods, such as direct nitration or oxidation of amino groups. Aromatic nitro compounds, or nitroarenes, feature a nitro group attached to a benzene ring, while aliphatic nitro compounds can be primary, secondary, or tertiary.
- The unit also discusses the reduction of nitro compounds and provides detailed information on picric acid (2,4,6-trinitrophenol), including its synthesis, properties, and uses.

8.10 TERMINAL QUESTIONS

Section-A

Long answered questions

1.What are nitro compounds? Describe the nomenclature and general methods of preparation of nitroarenes.

2. Describe the chemical properties of nitroalkanes.

3.How can you prepare nitroarenes from: (i) the nitration of aromatics (ii) from *p*-nitrobenzene (iii) from *p*-nitroaniline?

4. Describe the mechanism of

a) Nucleophilic aromatic substitution in nitroarenes.

b) Reduction of nitrobenzene in acidic medium.

5. Describe the general methods of preparation, chemical properties, and uses of picric acid.

6. What are nitro compounds? Describe the nomenclature and general methods of preparation of nitroalkanes.

Section-B

Short answered questions

1. What are nitro compounds? Explain the structure of nitro compounds.
2. How can you distinguish between alkyl and aryl nitro compounds?
3. Write a short note on nitroarenes.
4. Write the physical properties of nitro compounds.
5. Describe the reduction of nitrobenzene in acidic, neutral, and alkaline medium.
6. Give the mechanism of nucleophilic substitution in nitroarenes.

7. Explain the following:

(a) Acidic character of nitroalkanes

(b) Halogenation of nitroalkanes

8. How can you convert?

(a) Primary nitroalkanes into carboxylic acids

(b) Secondary nitroalkanes into ketones

(c) Nitroalkane into primary amine

(d) Nitromethane to chloropicrin

9. How will you obtain:

(a) Nitrobenzene from benzene

(b) *p*-Nitronitrosobenzene from *p*-dinitrobenzene

(c) Picric acid from chlorobenzene

(d) Picramide from picric acid

Section-C

Multiple choice questions (MCQ)

1. Which functional group is present in a nitro compounds?

(a) -COOH (b) $-NO_2$

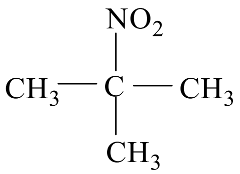
(c) C-O-C (d) -SH

2. Which one of the followings is a nitroalkane?

(a) CH_3SH (b) CH_3OH

(c) $CH_3CH_2NO_2$ (d) CH_3SCH_3

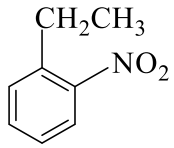
3. What is the IUPAC name of the given compound?



$$(CH_3)_3C-NO_2$$

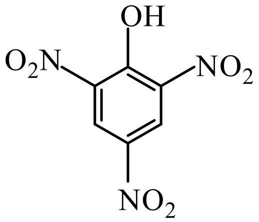
(a) 2-Methyl-2-nitropropane	(b) Ethanethiol
(c) Triethyl nitro	(d) Ethyl hydrogen sulphide

4. What is the IUPAC name of the given nitroarene?



(a) 2-Methyl-2-nitropropane	(b) 2-Nitroethyl benzene
(c) *p*-Nitrotoluene	(d) 2-Nitroethyl toluene

5. The given structure is for



(a) Asprin	(b) RDX
(c) Picric acid	(d) Trinitrotoluene

6. Nitroarenes can be obtained

(a) By heating haloalkanes with potassium sulphide.

(b) By the oxidation of alcohols with $KMnO_4$.

(c) By heating alkyl halide with alcoholic $AgNO_2$.

d) By the nitration of benzene.

7. Nitroalkanes are more acidic than corresponding hydrocarbons

(a) Because their boiling points are higher.

(b) Because they are heavier than water.

(c) Because they have a pleasant odor.

(d) Due to the electron withdrawing nature of nitro group.

8. The reduction nitroalkanes with Fe and concentrated HCl give

(a) Hydroazobenzene (b) Primary amines
(c) Hydroxylamine (d) Azobenzene

9. Secondary nitroalkanes undergo hydrolysis with boiling HCl give

(a) Ketones (b) Carboxylic acids
(c) Thioethers (d) Alcohols

10. Reduction in which the nitroalkanes are reduced to corresponding N-alkyl hydroxyl amines with zinc dust and ammonium chloride solution is conducted in

(a) Acidic medium (b) Alkaline medium
(c) Neutral medium (d) None of these

11. Nitrobenzene is converted into azobenzene by reduction with

(a) Alkaline sodium stannite
(b) Alkaline sodium arsenite
(c) Zinc and ammonium chloride
(d Zinc metal and aqueous sodium hydroxide

12. Reduction of nitrobenzene with $LiAlH_4$ will produce

(a) Azoxybenzene (b) p-Aminophenol
(c) *m*-Dinitrobenzene (d) Aniline

13. Nitroethane reacts with nitrous acid (HNO_2) to form

(a) Nitrolic acid (b) Nitrous oxide
(c) Hydroxylamine (d) Ethanamide

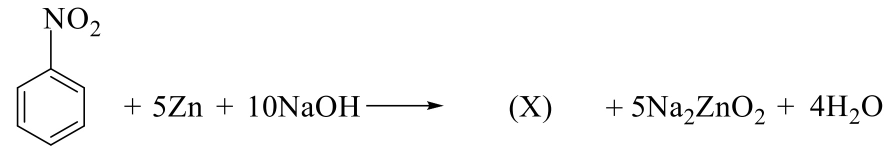
14. Tertiary nitroalkanes cannot tautomerise because they

(a) Are stable (b) Are not stable
(c) Are saturated hydrocarbons (d) Do not contain α-hydrogen

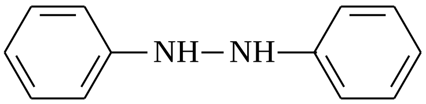
15. Which of the following gives a ketone when boiled with concentrated HCl?

(a) Primary nitroalkanes (b) Secondary nitroalkanes
(c) Tertiary nitroalkanes (d) All of the above

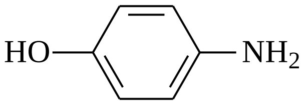
16. The major product (X) of the reaction is:



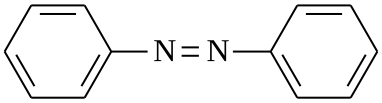
Nitrobenzene

(a)


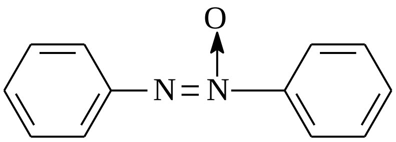
hydrazobenzene

(b)


p–aminophenol

(c)


azobenzene

(d)


azoxybenzene

17. Nitromethane on reduction with Zn and NH_4Cl gives:

(a) Methanamide (b) Ethylamine

(c) *N*-Methylhydroxy amine (d) Methylamine

18. Which compound is obtained at the end of the following reaction?

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O \xrightarrow{HCl} ? + \underset{\text{Hydroxylamine}}{NH_2OH}$$

(a) Acetic acid (b) Formaldehyde

(c) Methanethiol (d) Methyl chloride

19. Chloropicrin is formed by the halogenation of nitromethane with

(a) Bromine (b) Chlorobenzene

(c) Chlorine (d) Toluene

20. The reduction of nitrobenzene with zinc and sodium hydroxide gives

(a) Azobenzene (b) Azoxybenzene

(c) Nitrosobenzene (d) Hydrazobenzene

21. Picric acid can be obtained from

(a) Hydrolysis of picryl chloride

(b) Phenol by sulphonation followed by the nitration

(c) Nitration of benzoic acid

(d) Nitration of toluene

22. On reduction with $NaHCO_3$, picric acid gives

(a) Picramide (b) *m*-Dinitrobenzene

(c) Sodium picrate (d) Picramic acid

23. The reduction of picric acid with sodium sulphide (Na_2S) in presence of water gives

(a) Picramic acid (b) Picramide

(c) Sodium picrate (d) Trichlorobenzene

24. The reduction of nitrobenzene with Sn and HCl gives

(a) Azoxybenzene (b) Hydroazobenzene

(c) Primary aryl amines (d) *p*-Aminophenol

25. Primary nitroalkanes are upon hydrolysis with concentrated hydrochloric acid gives

(a) Primary amines (b) Ketones

(c) Alcohols (d) Carboxylic acids

8. 11 ANSWERS (MCQs)

1. (b)	**2. (c)**	**3. (a)**	**4. (b)**	**5. (c)**
6. (d)	**7. (d)**	**8. (b)**	**9. (a)**	**10. (c)**
11. (a)	**12. (d)**	**13. (a)**	**14. (d)**	**15. (b)**
16. (a)	**17. (c)**	**18. (a)**	**19. (c)**	**20. (d)**
21. (b)	**22. (c)**	**23. (a)**	**24. (c)**	**25. (d)**

8. 12 REFERENCES

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UNIT 9: AMINES

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9.2 Objectives

9.3 Structure and nomenclatures of amines

- 9.3.1 IUPAC Nomenclature of aliphatic amines
- 9.3.2 IUPAC Nomenclature of aromatic amines

9.4 Physical properties of amines

9.5 Stereochemistry of amines

9.6 Separation of a mixture of primary, secondary and tertiary amines

9.7 Structural features affecting basicity of amines

9.8 Preparation of alkyl and aryl amines

9.9 Reductive amination of aldehydic and ketonic compounds

9.10 Summary

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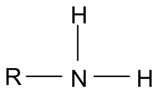
9.12 Answers (MCQ)

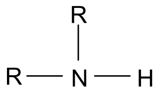
9.13 References

9.1 INTRODUCTION

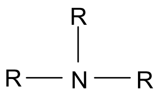
Amines are aliphatic and aromatic derivatives of ammonia which are obtained by the replacement of one, two or all three hydrogen atoms of ammonia by alkyl or aryl groups. Amines are described as primary (1°), secondary (2°) or tertiary (3°) depending on how many alkyl or aryl substituents are attached to the nitrogen atom. The tetra alkyl derivatives of ammonium salts are known as quaternary ammonium salts *e.g.*, tetramethyl ammonium chloride, $(CH_3)_4N^+Cl^-$.


$R-\overset{\displaystyle H}{\overset{|}{N}}-H$

Primary amine


$R-\overset{\displaystyle R}{\overset{|}{N}}-H$

Secondary amine


$R-\overset{\displaystyle R}{\overset{|}{N}}-R$

Tertiary amine

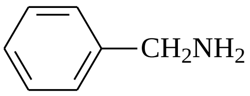
Primary amines: Primary amines are obtained by the replacement of one hydrogen atom of ammonia by an alkyl or aryl group. For example: Methyl amine, ethyl amine, phenyl amine etc.

CH_3NH_2

methylamine

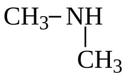
$CH_3CH_2NH_2$

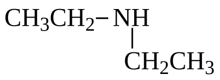
ethylamine

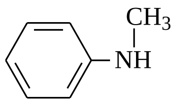


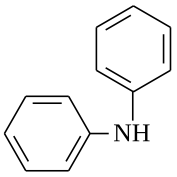
benzylamine

Secondary amines: Secondary amines are obtained by the replacement of two hydrogen atoms of ammonia by the two alkyl or aryl groups. For example: Dimethyl amine, ethyl methyl amine, methyl phenylamine, diphenylamine, etc.

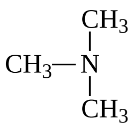

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{NH}$

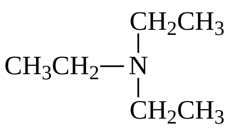

$CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{NH}$

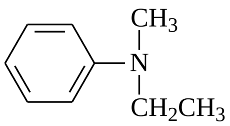


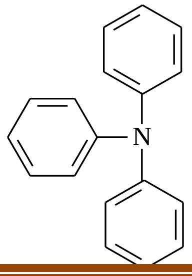


Tertiary amines: Tertiary amines are obtained by the replacement of all three hydrogen atoms of ammonia by the three alkyl or aryl groups. Examples: Trimethyl amine, tri ethyl amine, ethyl methyl phenylamine, triphenylamine, etc.

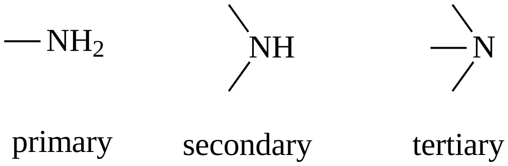

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{N}}$


$CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}}$

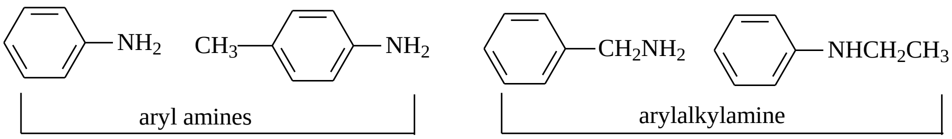




The characteristic functional groups for primary, secondary and tertiary amines are:



Aromatic amino compounds are of two types, aryl amines and arylalkyl amines. Aryl amines are those compounds in which the –NH_2 group is directly attached to the nucleus *e.g.,* aniline, *p*-tolidine etc. whereas in arylalkyl amines the –NH_2 group is attached to a carbon atom of the side chain *e.g.,* benzylamine, β-phenylethylamine etc.

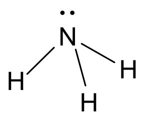


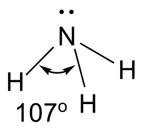
9.2 OBJECTIVES

- In continuation to unit 8 (organic compounds containing nitrogen) this unit aims to describe amines as derivatives of ammonia having a pyramidal structure, classify them as primary, secondary, and tertiary amines, and describe their common and IUPAC names.
- To explain how we can distinguish between primary, secondary, and tertiary amines.
- To describe some of the important methods of preparation of amines, to explain their physical and chemical properties and to study the mechanism of the reductive amination of aldehydes and ketonic compounds, Gabriel's phthalimide synthesis and Hofmann's bromamide reaction etc.

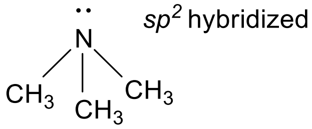
9.3 STRUCTURE AND NOMENCLATURE OF AMINES

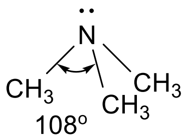
Amines are ammonia derivatives; the shape of the amine functional group is similar to its parent molecule ammonia. The nitrogen in ammonia forms three σ bonds and also carries one lone pair of electrons. The nitrogen in ammonia as well as aliphatic amines is sp^3 hybridized. Therefore, the shape of ammonia is trigonal pyramidal which can be represented as





The amino compounds are obtained by replacing hydrogen atom by alkyl or aryl groups, their shape can be represented as:

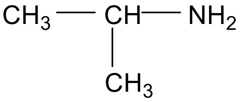




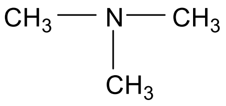
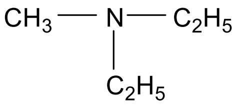
The bond angle between H-N-H in ammonia is 107°, the bond angle in amine is *assumed almost the same as in ammonia.*

9.3.1 IUPAC Nomenclature of aliphatic amines

Usually, amines are named after the alkyl group attached to the nitrogen atom. In IUPAC nomenclature, the primary amines are named as amino alkanes; secondary amines are named as *N*-alkylaminoalkanes and tertiary dialkylamino alkanes.

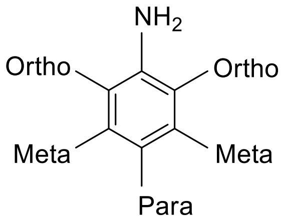
Compound	**Common name**	**IUPAC name**
Primary amines		
CH_3NH_2	methyl amine	aminomethane
$CH_3CH_2NH_2$	ethyl amine	aminoethane
$CH_3CH_2CH_2NH_2$	propyl amine	aminopropane
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-NH_2$	isopropyl amine	*2*-methylaminoethane
Secondary amines		
CH_3NHCH_3	dimethyl amine	*N*-methylaminomethane
$CH_3NHC_2H_5$	ethyl methyl amine	*n*-methylaminoethane
$CH_3NHC_3H_7$	methyl propyl amine	*N*-methylaminopropane

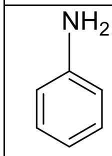
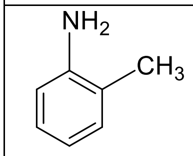
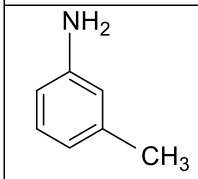
Tertiary amines

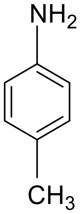
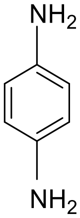
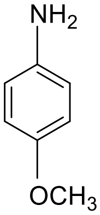
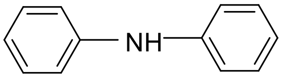
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$	trimethyl amine	*N*,*N*-dimethylaminomethane
 $CH_3-\underset{\displaystyle C_2H_5}{\underset{\vert}{N}}-C_2H_5$	diethyl methyl amine	N-ethyl-N-methyl aminoethane

9.3.2 IUPAC Nomenclature of aromatic amines

The simplest member of aromatic amines is aminobenzene (aniline). Amines containing a –NH_2 group, first identified the position of the amino group and counted this position as position-1 of the ring. Then give numbers to all positions (as 2, 3, 4, 5, 6, etc.) in a clockwise direction. They are named as *o, m or p* substituted. The next position to the amino group is *ortho* (*o*), the third position to the amino group is *meta* (*m*) and the vertically opposite position to the amino group is *para* (*p*).



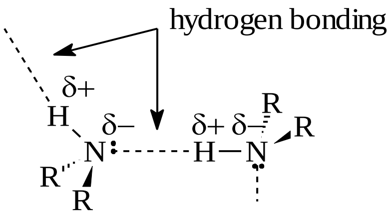
Compound	**Common name**	**IUPAC name**
	aniline	aminobenzene
	*o*-toluidine	*2*-methyl aniline
	*m*-toluidine	*3*-methyl aniline

	*p*-toluidine	*4*-methyl aniline
	*p*-phenylene diamine	*p*-iaminobenzene
	anisidine	*p*-methoxy aniline
	diphenyl amine	*N*-phenyl amine

9.4 PHYSICAL PROPERTIES OF AMINES

1. Physical state: Lower amines are combustible gases at room temperature, C_3-C_{11} members of amines are volatile liquids, while the higher amines are solids. The lower members of amines have fishi ammoniacal odour,

2. Hydrogen bonding: Amines are polar compounds and both primary and secondary amines form intermolecular hydrogen bonds. The boiling points and solubility of amines are associated with the intermolecular hydrogen bonding involved in these molecules.

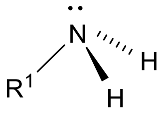


3. Boling points: An N-H---N hydrogen bond is weaker than O-H---O hydrogen bond because the electronegativity difference between nitrogen and hydrogen (0.9) is less than between oxygen and hydrogen (1.4). Therefore, amines have lower boiling points than the corresponding alcohols. Tertiary amines cannot form hydrogen bond because they have no hydrogen therefore the boiling point of tertiary amines will be even lower than primary or secondary amines.

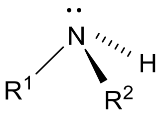
4. Solubility of amines: Primary and secondary amines form hydrogen bonds with water and are more soluble in water than hydrocarbons of comparable molecular weight. Low molecular weight amines are completely soluble in water while higher molecular weight amines are moderately soluble or insoluble in water.

9.5 STEREOCHEMISTRY OF AMINES

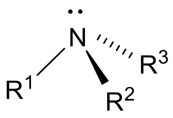
Amines are classified into primary, secondary and tertiary based on the number of hydrogen atom (s) are replaced by the alkyl or aryl groups. Tertiary amines have three different groups *i.e.* R^1, R^2, and R^3 attached to the nitrogen atom, they are asymmetric or chiral, and therefore they do not form superimposable mirror image. Tertiary amines exist in two enantiomeric forms. This is due to the inability of unshared pair of electrons present in fourth sp^3 orbital of nitrogen to serves as a fourth group to keep configuration.



1° amine



2° amine



3° amine

In contrast, quaternary ammonium salts, in which the nitrogen atom is attached to four different groups. In quaternary ammonium salts, the groups may also be chiral and able to show enantiomeric as well as optical activity. This is because the nitrogen in these salts is tetrahedral and all its sp^3 orbitals are involved in the bond formation.

Amines display different characteristic infrared absorption peaks based on the degree of amines.

a) Primary amines contain two N-H bonds which display two peaks around 3300 cm^{-1} The shape of IR peak is similar to the molar teeth, hence also known as the "molar peak"

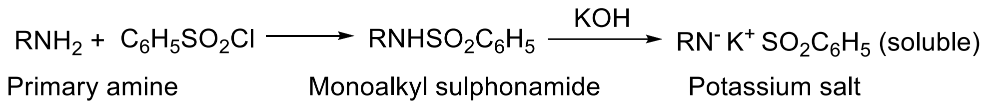
b) Secondary amines contain one N-H bond which displays a single peak around 3300 cm^{-1}

c) Tertiary amines contain no N-H bonds and do not show up in infrared spectroscopy.

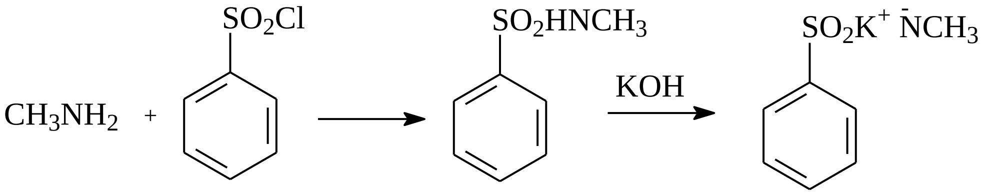
9.6 SEPARATION OF A MIXTURE OF PRIMARY, SECONDARY AND TERTIARY AMINES

Two methods are used to distinguish the primary, secondary, and tertiary amines *i.e.* Hinsberg,s method and Hofmann's method.

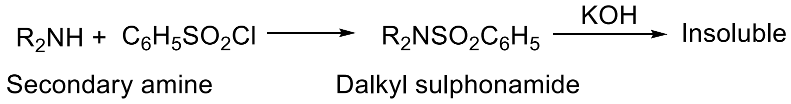
1. Hinsberg, 's method: Hinsberg's reagent is benzene sulphonyl chloride ($C_6H_5SO_2Cl$). The primary, secondary and tertiary amines can be separated by Hinsberg's reagent test. Primary amine reacts with Hinsberg's reagent to form a precipitate of *N*-alkyl benzene sulphonamide which is soluble in strong alkali like KOH.



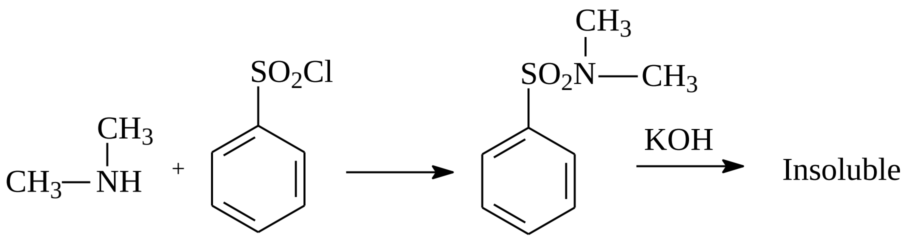
$$\underset{\text{Primary amine}}{RNH_2} + C_6H_5SO_2Cl \longrightarrow \underset{\text{Monoalkyl sulphonamide}}{RNHSO_2C_6H_5} \xrightarrow{KOH} \underset{\text{Potassium salt}}{RN^- K^+ SO_2C_6H_5 \text{ (soluble)}}$$



Secondary amine reacts with Hinsberg's reagent to form a precipitate of *N*, *N*-dialkyl benzene sulphonamide which is insoluble in alkali.

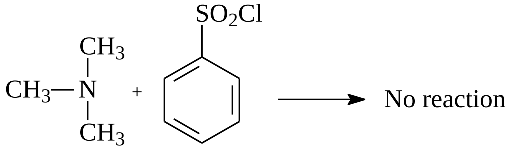


$$\underset{\text{Secondary amine}}{R_2NH} + C_6H_5SO_2Cl \longrightarrow \underset{\text{Dalkyl sulphonamide}}{R_2NSO_2C_6H_5} \xrightarrow{KOH} \text{Insoluble}$$

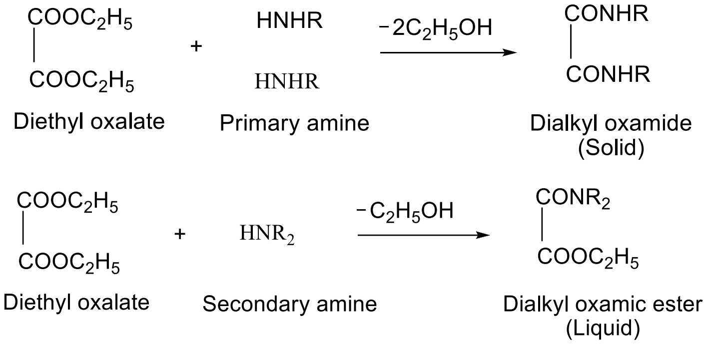


Tertiary amines do not react with Hinsberg's reagent.

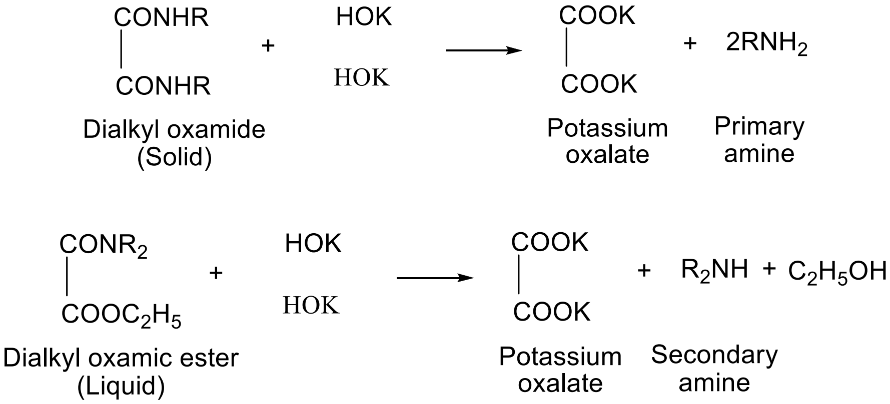
$$R_3N + C_6H_5SO_2Cl \longrightarrow \text{No reaction}$$



2. Hofmann's method: The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide; a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

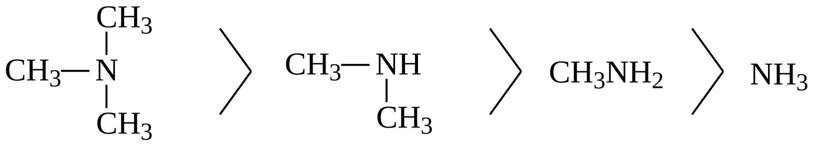


Now, the mixture containing primary, secondary and tertiary amines is subjected to fractional distillation, when tertiary amine, which is highly volatile, distils over. The remaining residue mixture containing solid oxamide and liquid oxamic ester are separated by the simple filtration. Both solid oxamide and liquid oxamic ester are separately treated with a strong alkali like KOH to recover and purified by the distillation.



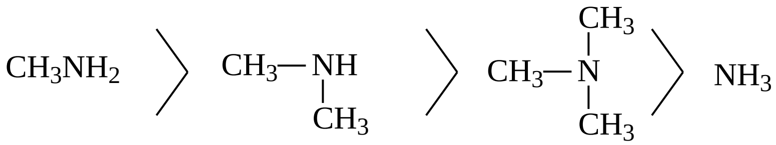
9.7 STRUCTURAL FEATURES AFFECTING BASICITY OF AMINES

Amines, like ammonia, are weak bases ($K_b = 10^{-4}$ to 10^{-6}). The basicity of amines is due to the presence of an unshared pair of electrons on the nitrogen atom which can share with other atoms. This unshared pair of electrons creates an electron density around the nitrogen atom. The greater the electron density, the more basic is the amine. Electron-releasing groups (e.g., methyl, ethyl, and other alkyl groups) increase the basicity of aromatic amines whereas electron-withdrawing groups (e.g., halogen, nitro, carbonyl groups) decrease the basicity of aromatic amines. Thus, the basicity of aliphatic amines increases with increases alkyl substitutions as given below:



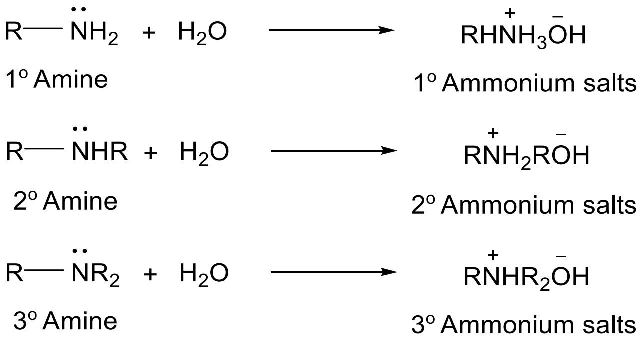
$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

However, in aqueous solutions, the order of basicity changes.



$$CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N > NH_3$$

The differences in the basicity order in the gas phase and aqueous solutions are the result of solvation effects. Amines in water solution exist as ammonium ions.



$$R—\ddot{N}H_2 + H_2O \longrightarrow RH\overset{+}{N}H_3\overset{-}{O}H$$

1° Amine 1° Ammonium salts

$$R—\ddot{N}HR + H_2O \longrightarrow R\overset{+}{N}H_2R\overset{-}{O}H$$

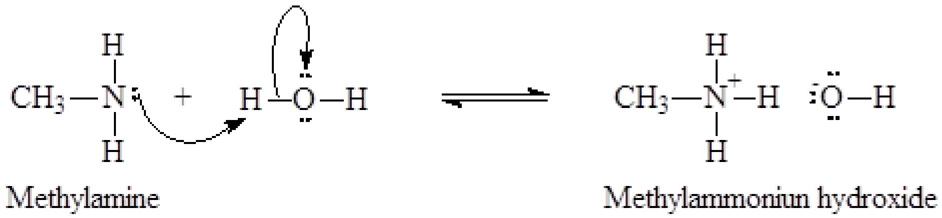
2° Amine 2° Ammonium salts

$$R—\ddot{N}R_2 + H_2O \longrightarrow R\overset{+}{N}HR_2\overset{-}{O}H$$

3° Amine 3° Ammonium salts

In water, the ammonium salts of primary and secondary amines undergo solvation effects (due to hydrogen bonding) to a much greater degree than ammonium salts of tertiary amines. These solvation effects increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups.

Amines act as nucleophiles in most circumstances; the unshared pair of electrons on nitrogen form a new covalent bond with hydrogen and displaces hydroxide ions.



The equilibrium constant for this reaction is as follows:

$$K_{eq} = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]\,[H_2O]}$$

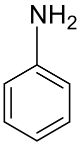
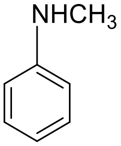
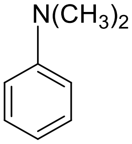
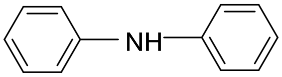
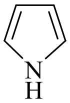
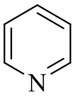
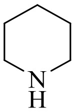
The base ionization constant $K_b = K_{eq}\,[H_2O]$. The value of K_b for methylamine is 4.37 x 10^{-4} ($pK_b = 3.36$).

$$K_b = K_{eq}\,[H_2O] = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]}$$

Amines are basic in nature (Lewis base) the basic strength in terms of their pK_b values is given in table 1. The smaller the pK_b value stronger the base.

Table -1: Basic strength of amines (pK_b):

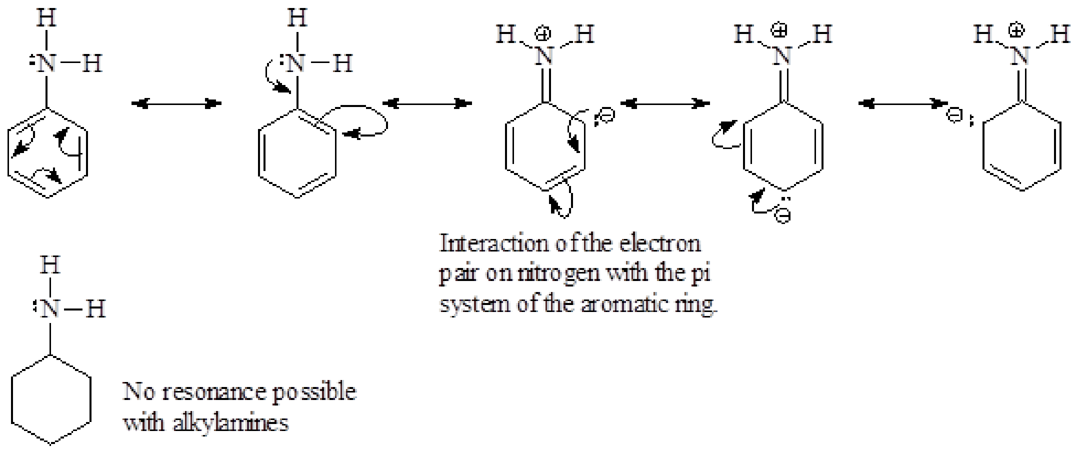
Compound	**Structure**	pK_b
ammonia	NH_3	4.74
Primary amines		
methylamine	CH_3NH_2	3.36
ethylamine	$CH_3CH_2NH_2$	3.34
n-propyl amine	$CH_3CH_2CH_2NH_2$	3.42

Secondary amines		
dimethylamine	$(CH_3)_2NH$	3.29
diethylamine	$(CH_3CH_2)_2NH$	3.02
dipropylamine	$(CH_3CH_2CH_2)_2NH$	3.1
Tertiary amines		
triethylamine	$(CH_3)_3N$	4.3
triethylamine	$(CH_3CH_2)_3N$	3.26
Aromatic amines		
aniline		9.38
N-methylaniline		9.15
N, *N*-dimethylaniline		8.95
diphenyl aniline		13.15
Heterocyclic aromatic amines		
pyrrole		~14
pyridine		~8.7
piperidine		2.7

All aliphatic amines have about the same base strength, pK_b 3.0 - 4.0 and are slightly stronger bases than ammonia. The increase in basicity compared with ammonia can be attributed to the greater stability of an alkyl ammonium ion, as, $RCH_2NH_3^+$, compared with the ammonium ion, NH_4^+. This greater stability arises from the electron releasing effect of alkyl groups and the resulting partial delocalization of the positive charge from nitrogen onto carbon in the alkyl ammonium ion.

Aromatic amines are weaker bases than ammonia and aliphatic amine. The less basic character of anilines can be explained on the following bases:

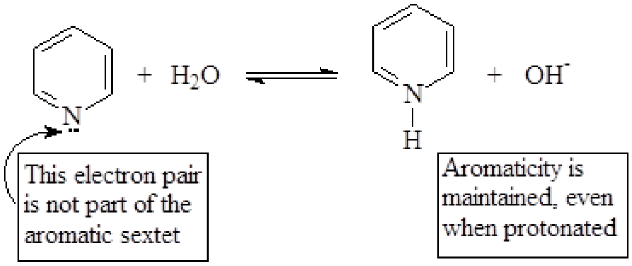
1. Delocalization of the unshared electron pair on nitrogen atom: The resonance stabilization of the free base form of aromatic amines. For aniline and other aryl amines, this resonance stabilization is a result of interaction of the unshared pair on nitrogen with the π-system of the aromatic ring. Due to this interaction the electron pair on nitrogen is less available for reaction with acid. No such resonance stabilization is possible for alkyl amines and therefore the electron pair on the nitrogen of an alkyl amine is more available for reaction with acid; alkyl amines are stronger bases than aryl amines.



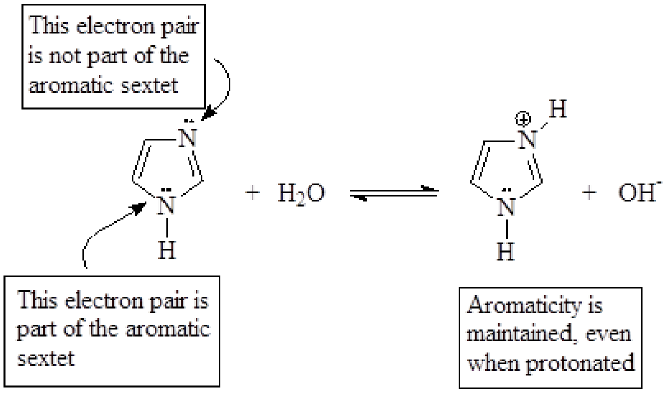
2. Substituent effect: The second factor contributing to the decreased basicity of aromatic amines is the electron withdrawing effect of the sp^2-hybridized carbons of the aromatic ring compared with the sp^3-hybridized carbons of aliphatic amines. The unshared pair of electrons on nitrogen in an aromatic amine is pulled toward the ring and, therefore, less available for protonation to form the conjugate acid of the amine.

Electron releasing groups (e.g., methyl, ethyl, and other alkyl groups) increase the basicity of aromatic amines whereas electron withdrawing groups (e.g., halogen, nitro, carbonyl groups) decrease the basicity of aromatic amines.

The decrease in basicity of halogen substitution is due to the electron-withdrawing inductive effect of the electronegative halogen. The decrease in basicity on nitro substitution is due to a combination of inductive and resonance effects, as can be seen by comparing the base ionization constants of 3-nitroaniline (pK_b *11.53*) and 4-nitroaniline (pK_b *13.0*). Note that the conjugate acid of 4-nitroaniline (pK_a *1.0*) is a stronger acid than phosphorous acid (pK_a *2.0*). Heterocyclic aromatic amines are weaker bases than aliphatic amines. When a nitrogen atom is incorporated directly into an aromatic ring, its basicity depends on the bonding context. For example, in the pyridine ring, the nitrogen lone pair occupies an sp^2 orbital which is not a part of the aromatic sextet.



Proton transfer from water or other acid to pyridine does not involve the electrons of the aromatic sextet. Pyridine is a weaker base than aliphatic amines because the unshared pair of electrons of the pyridine nitrogen lies in sp^2 hybrid orbital, whereas in aliphatic amine, the unshared pair lies in sp^3 orbital. Electrons in sp^2 hybrid orbital (33% s character) are held more tightly by the nucleus than electrons in sp^3 hybrid orbital (25% s character). It is this effect that decreases the basicity of the electron pair on sp^2 hybridized nitrogen compared with that on sp^3 hybridized nitrogen.



There are two nitrogen atoms in imidazole, each with an unshared pair of electrons. One shared pair lies in a 2*p* orbital and is an integral part of the (4n+2) pi electrons of the aromatic system. The other unshared pair lies in an sp^2 hybrid orbital and is not part of the aromatic sextet. It is the pair of electrons not part of the pi system that functions as the proton acceptor.

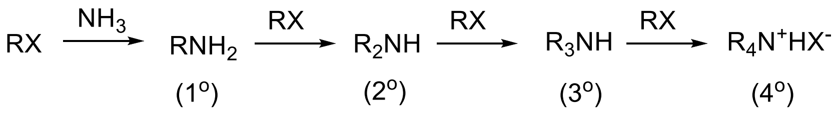
In pyridine, the unshared pair of electrons functions as the proton acceptor and imidazole lies in the sp^2 hybrid orbital and has decreased basicity compared with an unshared pair of electrons in the sp^3 hybrid orbital. The positive charge on the imidazolium ion is delocalized on both nitrogen atoms of the ring and, therefore, imidazole is a stronger base than pyridine.

9.8 PREPARATION OF ALKYL AND ARYL AMINES

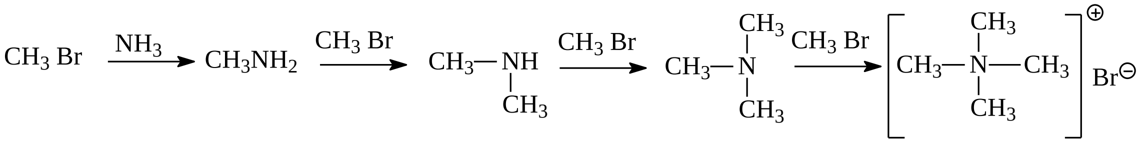
The alkylation of ammonia, Gabriel's phthalimide synthesis, Hofmann's bromamide synthesis, reduction of nitriles, reduction of oximes and acid amides, reduction of nitroarenes, and reductive amination of aldehydes and ketones are methods commonly used for preparing amines.

A. Methods for the preparation of all three types of amines along with quaternary ammonium salts.

1. From alkyl halides (Hoffmann method): When alkyl halides are heated with an aqueous or alcoholic solution of ammonia in a closed reaction vessel at about 100ºC, a mixture of primary, secondary and tertiary amines along with a quaternary ammonium salt is obtained. The primary amine (1º) is obtained by the replacement of halogen as halide by ammonia. Now this primary amine acts as a nucleophile and attaches itself to the alkyl halide molecule to produce the secondary amine (2º). Again, this secondary amine acts as a nucleophile and attaches itself to the alkyl halide molecule to give the tertiary amine (3º). At last, the tertiary amine attaches itself to the alkyl halide molecule to form the quaternary ammonium salts (4º). The process is as:

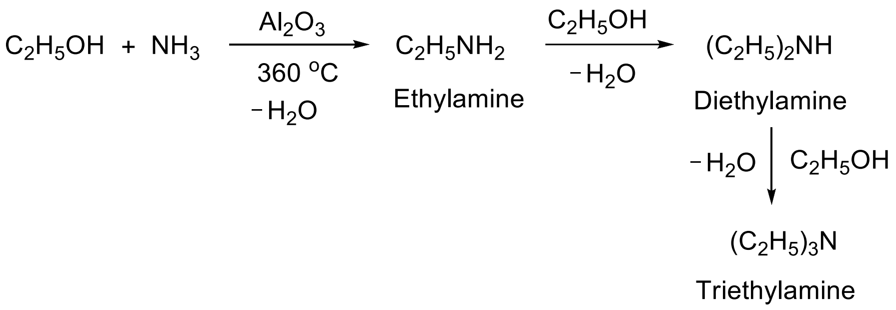


$$RX \xrightarrow{NH_3} \underset{(1^o)}{RNH_2} \xrightarrow{RX} \underset{(2^o)}{R_2NH} \xrightarrow{RX} \underset{(3^o)}{R_3NH} \xrightarrow{RX} \underset{(4^o)}{R_4N^+HX^-}$$



$$CH_3Br \xrightarrow{NH_3} CH_3NH_2 \xrightarrow{CH_3Br} CH_3-\underset{\underset{CH_3}{|}}{NH} \xrightarrow{CH_3Br} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} \xrightarrow{CH_3Br} \left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^{\oplus} Br^{\ominus}$$

2. By the action of ammonia on alcohol (Sabatier and Mailhe method): When alcohol vapours with ammonia are passed over a bed of Al_2O_3, W_2O_3, ThO_2 or silica gel at about 360ºC, a mixture of amines along with the quaternary ammonium salt are obtained.



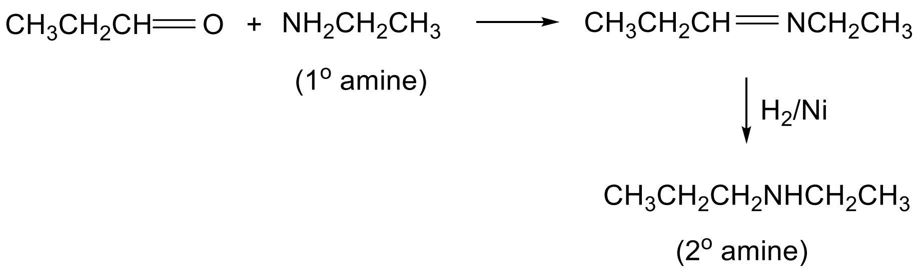
$$\begin{tikzcd} C_2H_5OH + NH_3 \arrow[r, "Al_2O_3", "360\,^{o}C\ -H_2O"'] & \underset{\text{Ethylamine}}{C_2H_5NH_2} \arrow[r, "C_2H_5OH", "-H_2O"'] & \underset{\text{Diethylamine}}{(C_2H_5)_2NH} \arrow[d, "C_2H_5OH", "-H_2O"'] \\ & & \underset{\text{Triethylamine}}{(C_2H_5)_3N} \end{tikzcd}$$

This method yields a mixture of 1º, 2º, and 3º amines along with 4º salts which are separated from each other by means of Hinsberg's method or Hofmann's method. However, primary amines can be prepared in good yield by using excess ammonia.

3. From carbonyl compounds: On heating with an acidic solution of ammonia or amine, carbonyl compounds are converted into amines.

$$CH_3CH{=}O + NH_3 \longrightarrow \underset{\text{Imine}}{CH_3CH{=}NH} \xrightarrow{H_2/Ni} \underset{\text{Amine}}{CH_3CH_2NH_2}$$

This reaction is called the ***reductive amination of aldehydes***. Using this reductive amination the 1° amine to 2° amines can be formed.



$$\begin{tikzcd} CH_3CH_2CH{=}O + \underset{(1^{o}\ \text{amine})}{NH_2CH_2CH_3} \arrow[r] & CH_3CH_2CH{=}NCH_2CH_3 \arrow[d, "H_2/Ni"] \\ & \underset{(2^{o}\ \text{amine})}{CH_3CH_2CH_2NHCH_2CH_3} \end{tikzcd}$$

4. By the reduction of amides: Amides yield primary amines on reduction by lithium aluminum hydride, while *N*-substituted and *N, N*-disubstituted amides produce secondary and tertiary amines, respectively.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

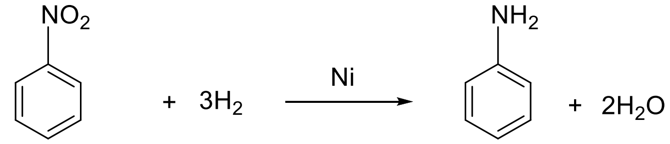
$$\underset{\text{N-methyl acetamide}}{CH_3CONHCH_3} \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} \underset{\text{N-methyl ethylamine}}{CH_3CH_2NHCH_3}$$

$$\underset{\text{N,N-dimethyl acetamide}}{CH_3CON(CH_3)_2} \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} \underset{\text{N,N-dimethyl ethylamine}}{CH_3CH_2N(CH_3)_2}$$

B. Additional methods for the preparation of primary amines:

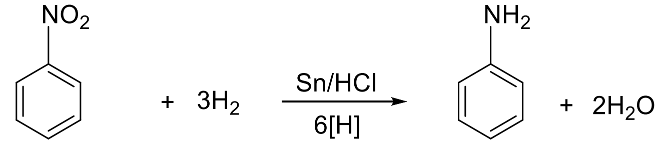
1. By the reduction of nitroarenes: Aromatic amines are normally prepared by the reduction of corresponding nitroarenes in presence of hydrogen and Raney nickel, tin and hydrochloric acid, iron and hydrochloric acid, zinc and acetic acid, or ammonium hydrogen sulphide.

(i) Catalytic reduction: Nitro compounds are reduced to amines with hydrogen gas in the presence of powdered nickel.



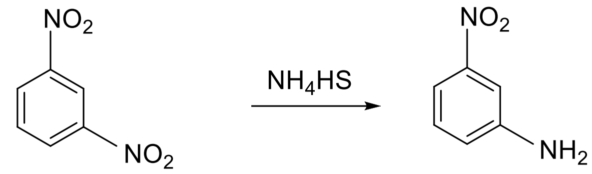
Nitrobenzene Aniline

(ii) Reduction with Sn/HCl, or Fe/HCl, or Zn/CH₃COOH: Nitro compounds are also reduced with metal and concentrated hydrochloric acid like Sn/HCl, Fe/HCl, or Zn/CH_3COOH into amines.



Nitrobenzene Aniline

(iii) Partial reduction with NH₄HS: By partial reduction, one of two nitro groups in a dinitro compound is reduced into the amino group by using ammonium hydrogen sulphide as a reducing agent.



m-Dinitro benzene *m*-Nitro aniline

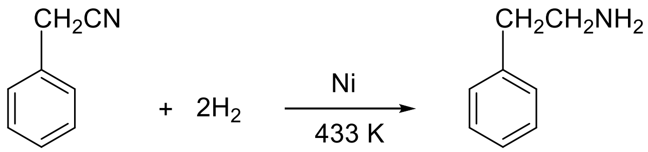
2. By the reduction of nitriles or cyanides: The carbon-nitrogen triple bond in a nitrile or cyanide can be reduced by the reaction of hydrogen gas in the presence of a metal catalyst like nickel, palladium or lithium aluminium hydroxide.

For example, methyl nitrile is reduced by hydrogen and nickel to ethyl amine.

$$CH_3CN + 2H_2 \xrightarrow[433\ K]{Ni} CH_3CH_2NH_2$$

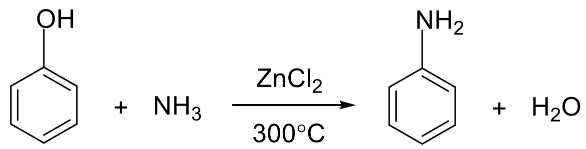
Methyl nitrile Ethyl amine

Phenyl methyl cyanide is reduced by hydrogen and nickel or by lithium aluminium hydroxide to phenyl ethyl amine.



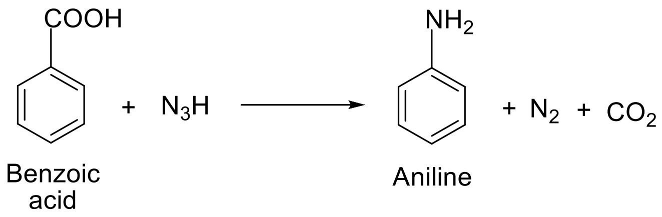
Phenyl methylcyanide Phenyl ethylamine

3. By the action of ammonia on phenol: Mono aryl amines are prepared by the reaction of ammonia on phenols in presence of zinc chloride at 300 ºC.

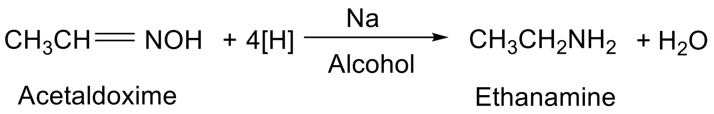


Phenol Aniline

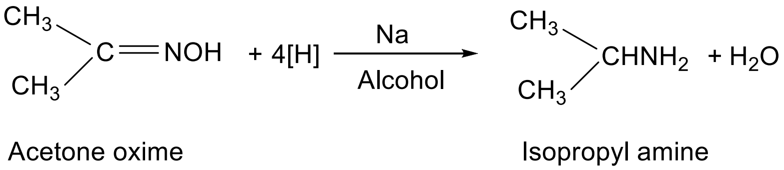
4. By Schmidt reaction: Aromatic amines can be obtained by the treatment of aromatic carboxylic acid in concentrated sulphuric acid with chloroform solution of hydrazoic acid.



5. By the reduction of oximes: Oximes yield primary amines on reduction by sodium and ethanol or by lithium aluminium hydroxide ($LiAlH_4$).

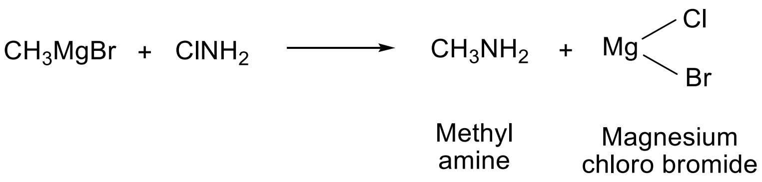


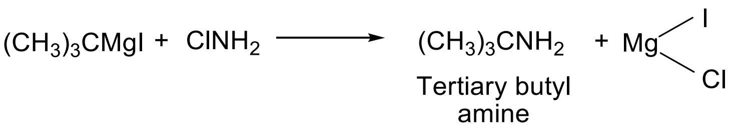
$$CH_3CH{=}NOH + 4[H] \xrightarrow[\text{Alcohol}]{\text{Na}} CH_3CH_2NH_2 + H_2O$$



6. By the action of chloramine with Grignard's reagent: The primary amines can be obtained by the action of chloramines on Grignard's reagent.

For example, methyl amine is prepared by the action of chloramines on methyl magnesium bromide.

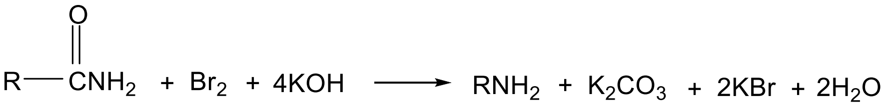




7. By the decarboxylation of amino acids: When an amino acid is heated with $Ba(OH)_2$, it loses CO_2 to form a primary amine. For example:

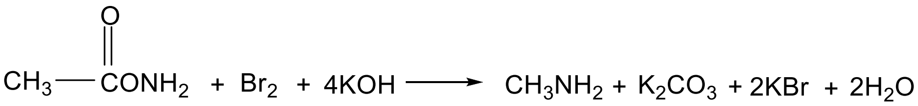
$$\underset{\text{Glycine}}{H_2NCH_2COOH} \xrightarrow{Ba(OH)_2} \underset{\text{Methylamine}}{H_2NCH_3}$$

8. By Hofmann's bromamide synthesis: Hofmann bromination reaction is an organic reaction used to convert a primary amide to a primary amine using bromine in an aqueous or ethanolic solution of sodium hydroxide. This reaction is as:



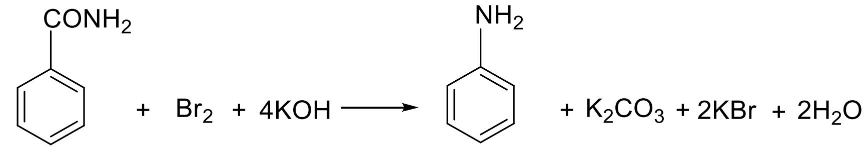
$$\underset{\text{Amide}}{R-\overset{\overset{O}{\|}}{C}NH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Amine}}{RNH_2} + K_2CO_3 + 2KBr + 2H_2O$$

For example, acetamide reacts with bromine and potassium hydroxide to form methyl amine.



$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}ONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

Similarly,

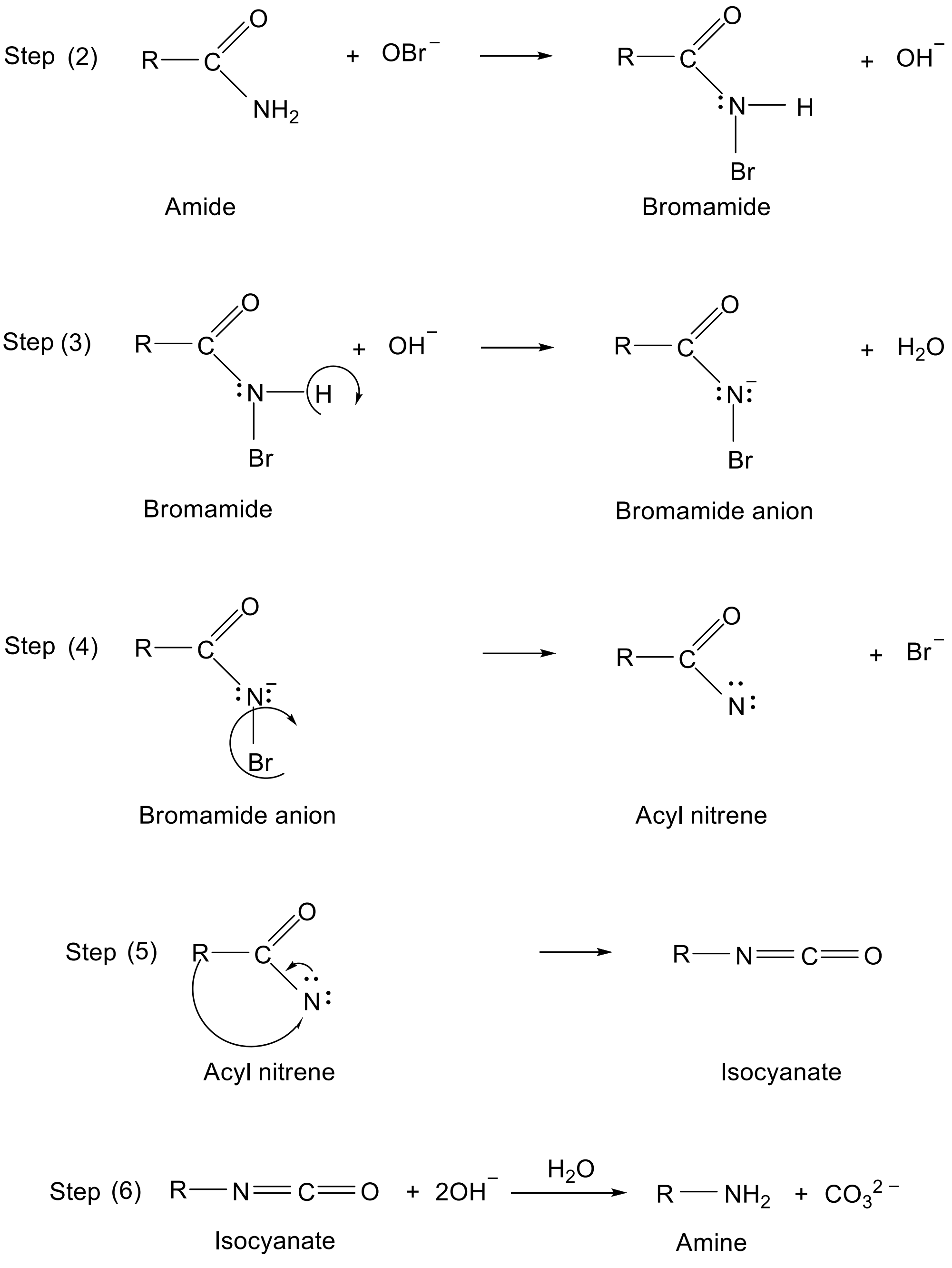


Benzamide Phenyl amine

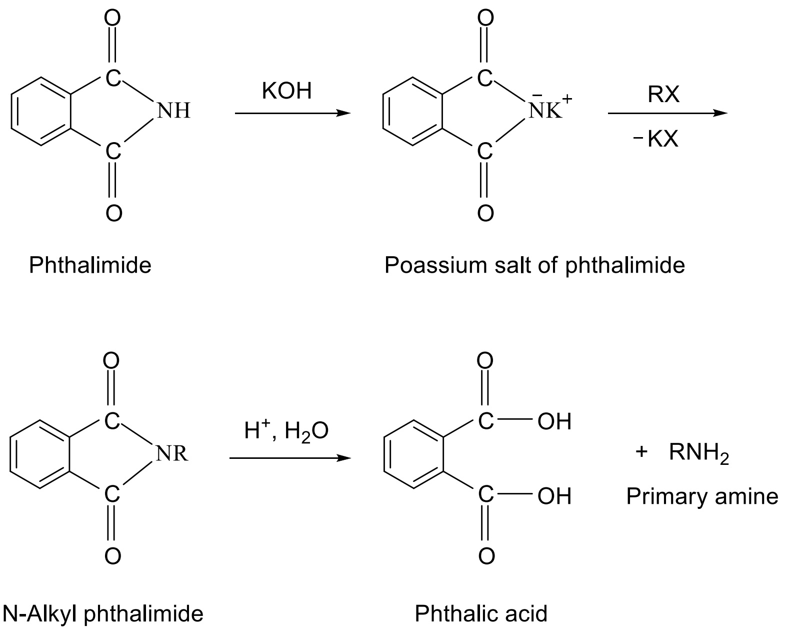
Mechanism: The reaction mechanism involves several steps:

1. The hypobromite ion OBr- anion is produced by the reaction of alkali with bromine.
2. The anion reacts with amide to give bromamide.
3. Base abstraction of the remaining amide proton gives a bromoamide anion.
4. The bromoamide anion rearranges as the R group attached to the carbonyl carbon migrates to nitrogen at the same time the bromide ion leaves, giving an isocyanate (steps 4 and 5).
5. The isocyanate adds water in a nucleophilic addition step to yield a carbamic acid after that carbamic acid spontaneously loses CO_2 to yield amine.

Step (1) $2KOH + Br_2 \longrightarrow 2KBr + KBrO + H_2O$



9. By Gabriel's phthalimide reaction: This method is used for the preparation of primary amines. Phthalimide on reaction with ethanolic potassium hydroxide gives potassium salt of phthalimide, which on heating with alkyl halide followed by alkaline hydrolysis forms the corresponding primary amine.



Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

10. By Wurtz reaction: Primary amines can be obtained by the hydrolysis of isocynide or isocyanate.

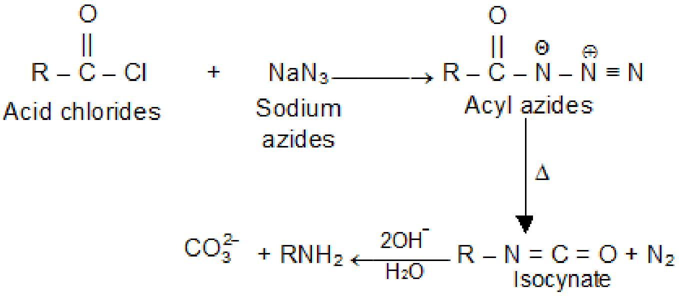
$$CH_3-N\equiv C + 2H_2O \xrightarrow{HCl} CH_3NH_2 + HCOOH$$

Methyl isocyanide Methylamine

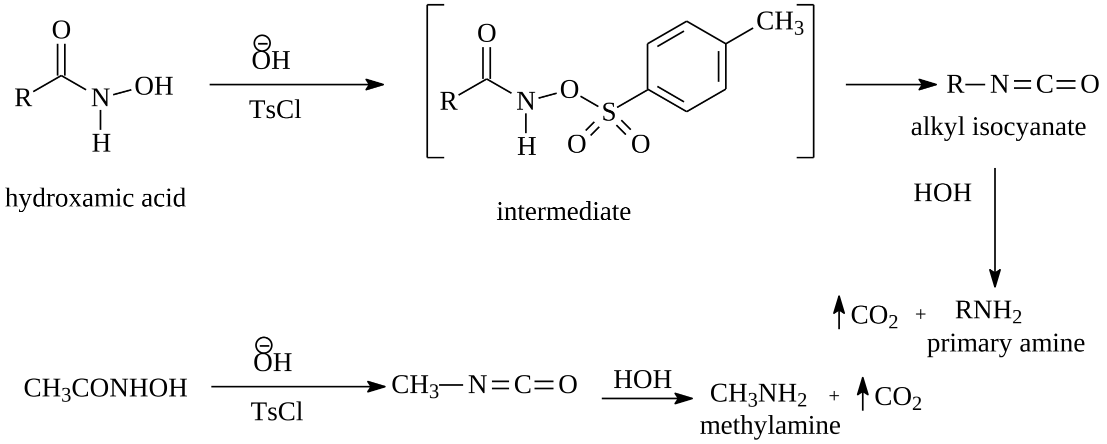
$$CH_3-N=C=O + 2KOH \longrightarrow CH_3NH_2 + K_2CO_3$$

Methyl isocyanate Methylamine

11. By Curtius reaction: Acid chlorides on reaction with sodium azides give isocyanate which is decomposed with water into amines.



12. Lossen reaction: Lossen rearrangement is a conversion of hydroxamic acid to isocyanate through the formation of O- acyl sulphonyl or phosphoryl intermediate hydroxamic acid O-derivative. This rearrangement is used for the synthesis of primary amines from hydroxamic acid.



C. Additional methods for the preparation of secondary amines

1. By reduction of alkyl isocyanide or isocyanates: Isocyanide or isocyanates are reduced to secondary amines with hydrogen gas in presence of Na/C_2H_5OH.

$$R—NC + 2H_2 \xrightarrow{Na/C_2H_5OH} R\text{-}NHCH_3$$

Alkyl isocynide

Methyl alkyl amine

$$CH_3NC + H_2 \xrightarrow{Na/C_2H_5OH} CH_3NHCH_3$$

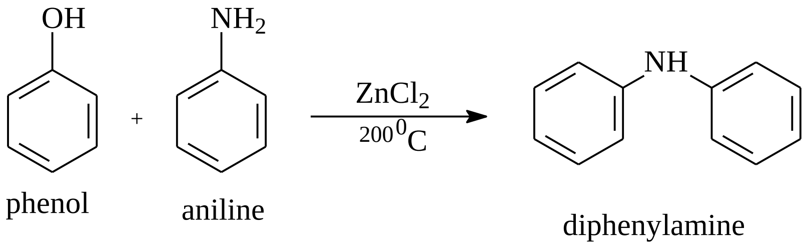
2. By reduction of *N*-substituted amides: Secondary amides can be reduced to amines by a strong oxidizing agent like lithium aluminum hydroxide by the conversion of C=O group to –CH_2. Amides cannot be reduced by the less reactive $NaBH_4$.

$$CH_3CONHCH_3 \xrightarrow{LiAlH_4} CH_3CH_2NHCH_3$$

N-methyl acetaminde

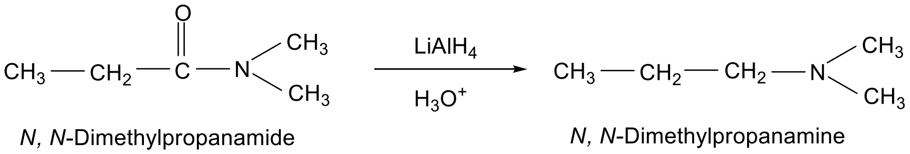
Ethyl methyl amine

3. By heating phenol with aniline: Secondary aromatic amines are prepared by heating phenol with aniline in presence of anhydrous zinc chloride at 200 ºC.

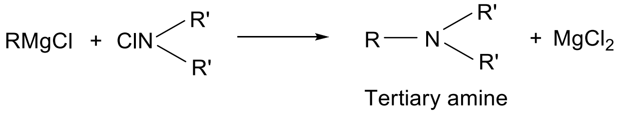


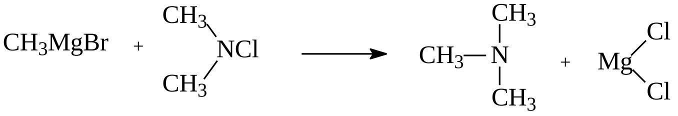
D. Additional methods for the preparation of tertiary amines

1. By reduction of *N,N*-disubstituted amides: *N*, *N*-disubstituted amides yield tertiary amines on reduction by lithium aluminum hydride.

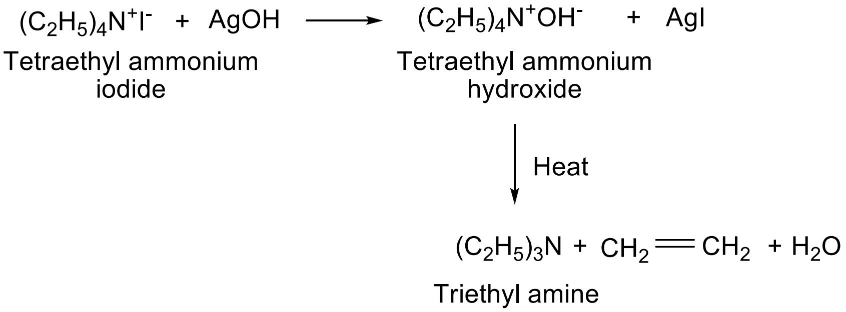


2. From Grignard's reagent: Grignard reaction can be used to synthesize tertiary amines as follow

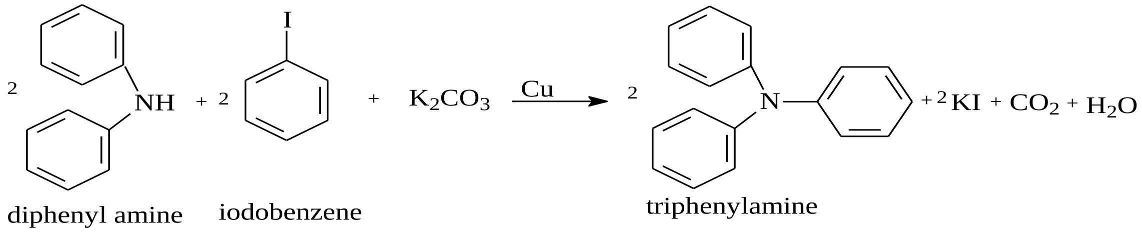




3. By the decomposition of tetra alkyl ammonium hydroxide: A quaternary ammonium salt is hydrolyzed with moist silver oxide into quaternary ammonium hydroxide which on strong heating gives tertiary amine.

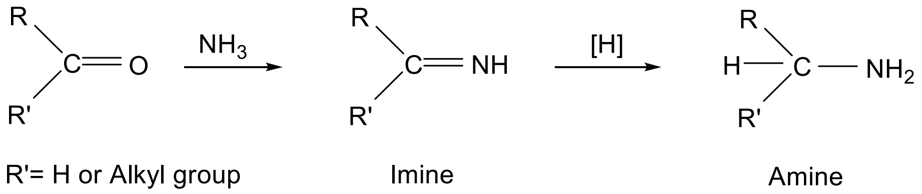


4. By Ullmann's reaction: Tertiary aromatic amines are obtained by heating diphenylamine with iodobenzene, potassium carbonate and a small amount of copper as catalyst in nitrobenzene solution.

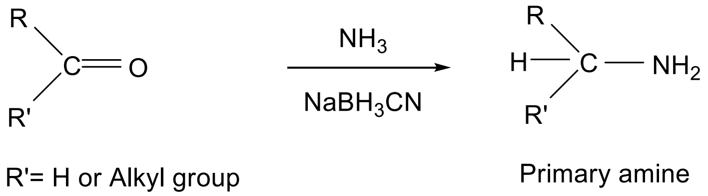


9.9 REDUCTIVE AMINATION OF ALDEHYDIC AND KETONIC COMPOUNDS

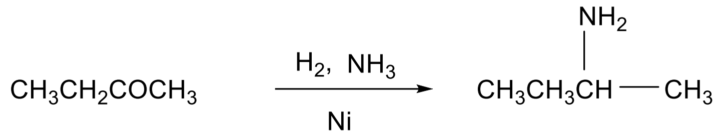
Aldehydes and ketones can be converted into primary, secondary and tertiary amines using reductive amination in presence of ammonia or amine. The reaction is completed in two steps. The first step is the nucleophiic addition of the carbonyl group to form an imine. The second step is the reduction of the imine to an amine using a reducing agent. A reducing agent employed commonly includes hydrogen and a catalyst such as Ni, $NaBH_3CN$ (sodium cyanoborohydride), $LiBH_3CN$ (liyhium cyanoborohydride) etc. The general reductive reactions of aldehydes and ketones are as:



Conversion of aldehyde or ketone into primary amine:



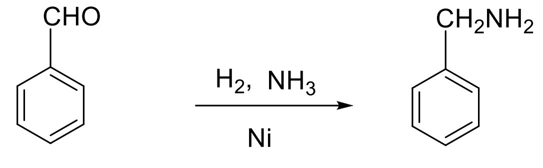
For example, methyl ethyl ketone is reduced by ammonia in the presence of nickel into 2-amino butane.



$$CH_3CH_2COCH_3 \xrightarrow[Ni]{H_2,\ NH_3} CH_3CH_3\overset{\overset{NH_2}{|}}{C}H-CH_3$$

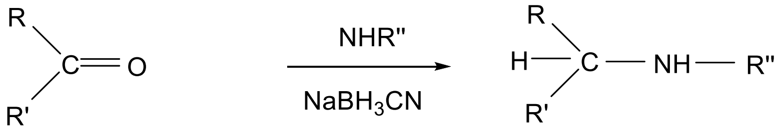
Methyl ethyl ketone 2- Amino butane

Similarly, benzaldehyde is reduced with ammonia in the presence of hydrogen and nickel into benzylamine.



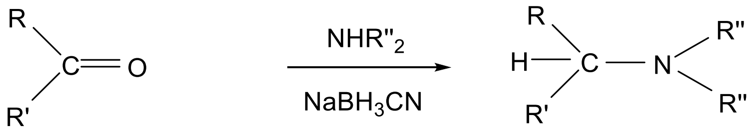
Benzaldehyde Benzylamine

Conversion of aldehyde or ketone into secondary amine:



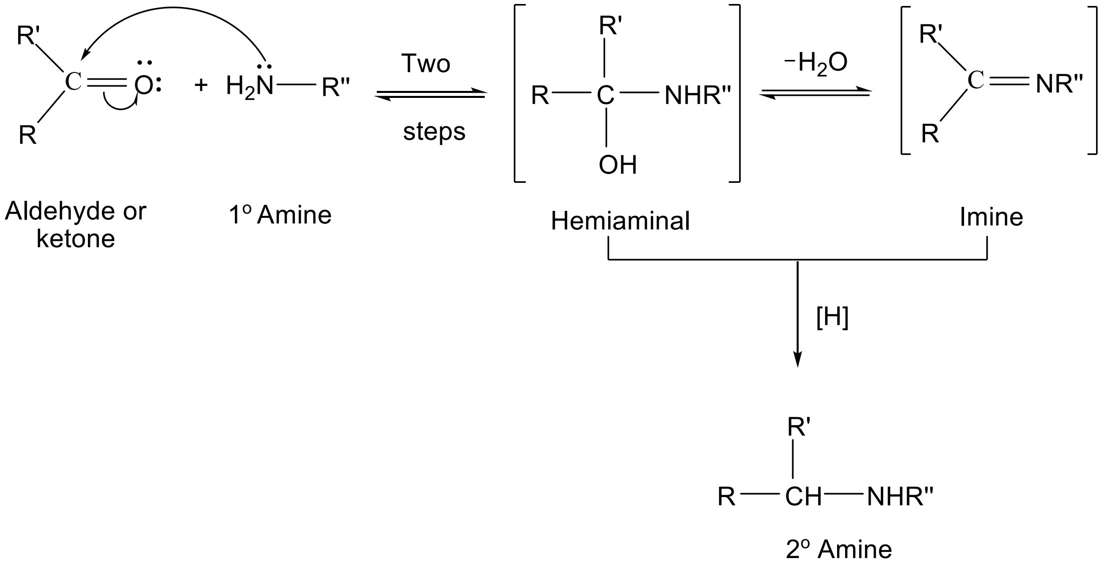
R'= H or Alkyl group Secondary amine

Conversion of aldehyde or ketone into tertiary amine:



R'= H or Alkyl group Tertiary amine

Mechanism:The sequential mechanism is as follow:



9.10 SUMMARY

- This unit focuses on the study of amines, including aliphatic and aromatic derivatives of ammonia, formed by replacing hydrogen atoms with alkyl or aryl groups.
- It covers their classification into primary, secondary, and tertiary amines, as well as aromatic amino compounds like aryl and aryl alkyl amines.
- The unit also explains IUPAC nomenclature, physical and chemical properties, basic character, and methods of preparation, along with the stereochemistry and reactions of aliphatic and aromatic amines.

9.11 TERMINAL QUESTIONS

Section -A

Q.1 Long answered questions:

5. What are amines? Describe the general methods of preparation of alkyl and aryl amines.
6. Give the preparation, physical and chemical properties of acid anhydrides.
7. How can you prepare primary amines from: (i) Gabrial’s phthalimide reaction (ii) Wurtz reaction (iii) Hofmann’s bromamide method (iv) Curtius reaction.
8. Describe the general methods of preparation and physical and chemical properties of amides.

9. Describe the mechanism of the acid and alkaline hydrolysis of esters.

Section -B

Q.2 Sort answered questions

10. How can you distinguish between primary, secondary and tertiary amines?
11. Why amines are basic in nature? Explain the role of substituents on the basicity of amines.
12. Compare the reactivity of carboxylic acid derivatives towards nucleophilic substitution.
13. How can you prepare secondary amines from isocynides?
14. How can you prepare tertiary amines from tetra alkyl ammonium hydroxide?
15. How can you synthesize primary and secondary amines by reductive amination of aldehydes?
16. Give the mechanism of reductive amination of aldehyde and ketones.
17. Explain the followings:

(c) Acetyl chloride has lower boiling point than acetic acid

(d) Acetyl chloride is more reactive than acetic anhydride

18. How can you convert?

(e) Acyl chlorides into esters

(f) Esters into amides

(g) Amides into amines

(h) Amides into carboxylic acids

19. How will you obtain:

(e) Primary amine from primary amide

(f) Primary amine from phthalimide

(g) Benzylamine from benzaldehyde

(h) Methylamine from methylisocyanate

Section –C

Q.3 Multiple choice questions (MCQs)

26. Which functional group is present in a primary amine?

(a) -COOH (b) $–NH_2$

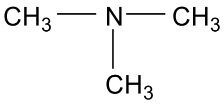
(c) C-O-C (d) -SH

27. Which one of the followings is an amino compound?

a) CH_3SH (b) $CH_3NHC_2H_5$

(c) $CH_3CH_2NO_2$ (d) CH_3SCH_3

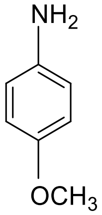
28. What is the IUPAC name of the given compound?



(a) *N*, *N*-Dimethylaminomethane (b) N-ethyl-N-methyl aminoethane

(c) Triethyl nitro (d) N- methylaminopropane

29. The given structure is for



(a) *p*-Toluidine (b) *o*-Toluidine

(c) *p*-Methoxyaniline (d) *p*-Diaminobenzene

30. All three amines can be obtained

(a) By Hofmann’s bromamide method.

(b) By Curtius reaction.

(c) By the decarboxylation of amines.

(d) By reductive amination of aldehydes and ketones.

31. Amines are weak bases

(a) Because their boiling points are higher.

(b) Because lower members are water soluble.

(c) Because they are volatile.

(d) Due to the presence of unshared pair of electrons on nitrogen atom.

32. The reduction of nitroalkane with Sn/HCl gives

(a) Tertiary amines (b) Primary amines

(c) Secondary amines (d) All of these

33. All three amines can be prepared by the reductive amination of

(a) Aldehydes and ketones (b) Carboxylic acids

(c) Ethers and thioethers (d) Alcohols and thiols

34. Aromatic amines are less basic than ammonia and aliphatic amines because

(a) They have (4n+2) π electrons.

(b) They are more reactive.

(c) The lone pair of electrons on nitrogen is partially shared with benzene ring.

(d) Nitrogen does not have lone pair of electrons in aromatic amines.

35. Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis because

(a) Aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.

(b) Aromatic amines are less basic than aliphatic amines.

(c) Aryl halides are decomposed with phthalimide.

(d) None of the above.

36. Reduction of nitrobenzene with Ni will produce

(a) Azoxybenzene (b) p-Aminophenol

(c) *m*-Dinitrobenzene (d) Aniline

37. Hofmann's bromamide reaction is used to convert

(a) Primary amide to primary amines

(b) Alkyl halide to primary amine

(c) Aldehyde to primary amines

(d) Glycine to primary amines

38. Tertiary amines cannot form hydrogen bonding because they

(a) Are stable (b) Are unstable

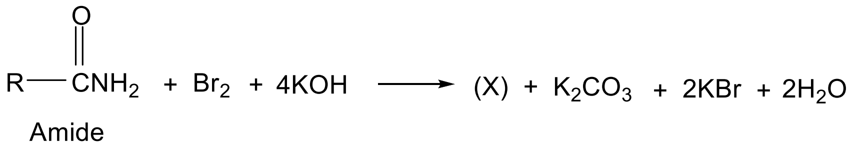
(c) Are saturated hydrocarbons (d) Do not have hydrogen

39. Which of the following gives a tertiary amine when treated with AgOH?

(a) N-Methyl acetamide (b) Tetraethyl ammonium iodide

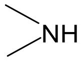
(c) Acetone oxime (d) Phenyl methylcynide

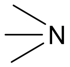
40. The major product (X) of the reaction is:



$$\underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}NH_2} + Br_2 + 4KOH \longrightarrow (X) + K_2CO_3 + 2KBr + 2H_2O$$

(a) RNH_2

(b) 

(c) 

(d) $(CH_3)_4N^+Cl^-$

16. Methanol has the higher boiling point than methylamine because

(a) Methylamine is more basic than methanol.

(b) Methylamine does not show hydrogen bonding.

(c) Hydrogen bonding is stronger in methanol than in methylamine.

(d) An unshared pair of electrons is present on nitrogen atom in amines.

17. Amines which are bonded in one alkyl group are

(a) Primary amine (b) Secondary amine

(c) Tertiary amine (d) Quaternary amines

18. Aniline reacts with phenol in presence with zinc chloride at 200ºC to form

(a) Primary amine (b) Secondary amine

(c) Tertiary amine (d) Quaternary amines

19. Chloramine reacts with methyl magnesium bromide to form

(a) Tertiary butyl amine (b) Ethyl methyl amine

(c) Acyl amides (d) Methyl amine

20. Quaternary ammonium salts on hydrolysis with most silver produce

(a) Primary amine (b) Secondary amine

(c) Tertiary amine (d) Azo compounds

9.12 ANSWERS (MCQs)

26. (b)	**27. (b)**	**28. (a)**	**29. (c)**	**30. (d)**
31. (d)	**32. (b)**	**33. (a)**	**34. (c)**	**35. (a)**
36. (d)	**37. (a)**	**38. (d)**	**39. (b)**	**40. (a)**
41. (c)	**42. (a)**	**43. (b)**	**44. (d)**	**45. (c)**

9.13 REFERENCES

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BLOCK–IV THERMOCHEMISTRY AND ELECTROCHEMISTRY

UNIT 10: THERMOCHEMISTRY

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10.1 Introduction
10.2 Objectives
10.3 Standard state
10.4 Standard enthalpy of formation
10.5 Hess's law of constant heat summation
    10.5.1. Application of Hess's law
10.6 Heat of reaction
10.7 Enthalpy of neutralization
10.8 Bond dissociation energy
10.9 Temperature dependence of enthalpy: Kirchoff's equation
10.10 Summary
10.11 Terminal questions
10.12 Answer's
10.13 References

10.1 INTRODUCTION

The chemical reactions are invariably accompanied by energy changes which, ordinarily, appear in the form of evolution or absorption of heat. Thermochemistry is the branch of physical chemistry that deals with the thermal or heat changes caused by chemical reactions. The energy change that occurs in a chemical reaction is largely due to a change of bond energy, i.e., a change of potential energy that results from the breaking of bonds in reactants and the formation of new bonds in products.

This unit of chemistry qualitatively and quantitatively describes the energy changes that occur during chemical reactions. This unit is also helpful to the heat summation states that if two or more thermochemical equations can be added together to give a final equation explain Hess's law. Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. As we have discussed the energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds. Thus, thermochemistry provides useful information regarding bond energies.

10.2 OBJECTIVES

The objective of this unit learners can:

- Define In Standard state, Standard enthalpy of formation.
- Define Hess's law with Application.
- Define Heat of reaction, Bond dissociation energy, and Enthalpy of neutralization.
- Temperature dependence of enthalpy: Kirchoff's equation

10.3 STANDARD STATE

The standard molar enthalpy of every element at 1 atm pressure and 298.15 K in the most stable state is taken as zero. These conditions of 1 atm pressure and 298.15 K are called standard state conditions. It is not possible to determine the absolute value of molar enthalpy, but we can use the above convention to find out the standard molar enthalpy of a substance. The molar standard enthalpies are taken as zero at 1 atmospheric pressure and 298.15 K temperature. The term standard state is used to describe a reference state for substances and is a help in thermodynamical calculations (such as enthalpy, entropy and Gibbs free energy calculations). The superscript degree symbol (°) indicates that substances are in their standard states. ($\Delta H°$, $\Delta G°$, $S°$.....)

10.4 STANDARD ENTHALPY OF FORMATION

The standard enthalpy of formation, also known as the heat of formation, is the enthalpy change when 1 mole of a pure substance in the standard state from its elements is also taken in the standard state (i.e., 298 K and 1 atmospheric pressure). The standard enthalpy of formation is denoted by the symbol $\mathbf{\Delta H_f^o}$. Its unit is kilojoule per mole or kJ/mol.

In ΔH_f^o f subscript indicates that one mole of the compound has been forming in a standard state from its elements in their most stable states of aggregation. The reference state of elements is its most stable state of aggregation 1 atmospheric pressure and 298.15 K temperature.

For Example:

$$C(s) + O_2\,(g) \rightarrow CO_2\,(g)\ , \qquad \Delta H_f^o = -393.5\ kJ$$

When 1 mole of CO_2 (g) is formed from its elements C (s) and O_2 (g) 393.5 kJ of heat is produced. Hence, the heat of formation of CO_2 is 393.5 kJ mol^{-1}.

$H°_f$. change in enthalpy that accompanies the formation of 1 mol of that substance from its elements, with all substances in their standard states.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_f\ (products) - \sum m\Delta H°_f\ (reactants)$$

Where, $\sum$ = the sum of

m and n = stoichiometric coefficients of the chemical reaction

Example: Enthalpies of the formation of CO_2 (g) and H_2O (l) under standard conditions are

394.65kJ and 285.84 kJ per mole. If the standard enthalpy of combustion of acetaldehyde (CH_3CHO) is 1167.62 kJ per mole, find its enthalpy of formation.

Solution: From the equation:

$$CH_3CHO \; + \; 5/2O_2 \; \rightarrow \; 2\,CO_2 \; + \; 2\,H_2O$$

$$-1167.62 = [\,2 \text{ x } \Delta H°_f\,(CO_2) + 2 \text{ x } \Delta H°_f\,(H_2O)\,] - [\Delta H°_f\,(CH_3CHO) + 5/2 \text{ x } \Delta H°_f\,(O_2)]$$

$$= 2x(-394.65) + 2 \text{ x } (-285.84) – (\Delta H°_f\,(CH_3CHO) + (5/2 \text{ x } 0)$$

$$= -789.30 – 571.68 - (\Delta H°_f\,(CH_3CHO)$$

$$\Delta H°_f\,(CH_3CHO = -193.36 \text{ kJ}.$$

10.5 HESS'S LAW OF CONSTANT HEAT SUMMATION

The energy changes accompanying chemical processes are governed by a general principle known as Hess's law. This law states that the amount of heat involved or absorbed in a process is the same whether the process occurs in two or more different ways in one step or several steps.

Let us suppose that substance A can be changed to Z directly.

$$A \qquad Z+Q_1 \;:\; \longrightarrow \qquad \Delta H_1= -Q_1$$

Where Q_1 is the heat involved in the direct change.

When the same change is brought about in stages:

$$A \longrightarrow B+q_1 \qquad \Delta H_2= -q_1$$

$$B \longrightarrow C+q_2 \qquad \Delta H_2 = -\,q_2$$

$$C \longrightarrow Z + q_3 \qquad \Delta H_3 = -\,q_3$$

The total evolution of heat $q_1+q_2+q_3 = Q_2$

According to Hess's law $Q_1=Q_2$. If it is not so, let $Q_2>Q_1$. Then by transforming A to Z through stages and transforming directly back to A, there would be a gain of heat energy= Q_2-Q_1. By repeating the process again and again unlimited heat energy will be developed in an isolated system. This goes against the first law of thermodynamics. Hence Q_1 must be equal to Q_2

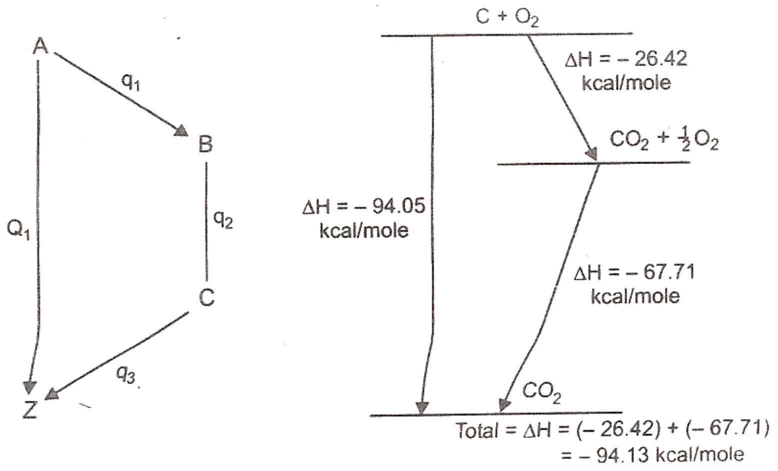

Fig 10.1 Illustration of Hess's law

Examples of Hess's:

Burning of carbon-to-carbon dioxide:

Carbon can be burnt to carbon dioxide directly or it may first change to carbon monoxide which may then be oxidized to carbon dioxide.

Ist way $C_s + O_2(g) \longrightarrow CO_2(g)\ \Delta H = -94.05$ kcal

2nd way $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)\ \Delta H = -26.42$ kcal

$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)\ \Delta H = -67.71$ kcal

Overall change $C(s)+O_2(g) \longrightarrow CO_2(g)\ \Delta H = -94.1$ k cal

It is shown in Fig 10.1

10.5.1 Application of Hess's Law

(i) Calculation of enthalpy of reaction:

With the help of Hess's law, it is possible to calculate the enthalpies of many reactions which cannot be determined experimentally. For example, measuring the heat evolved when carbon burns in oxygen to form carbon monoxide is extremely difficult.

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g): \Delta H = ?$$

From Hess's law, it is known that the heat evolved in the combustion of one-mole carbon dioxide is the same, viz whether the reaction takes place in a single step as

$$C_{(S)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.05$$

or in two steps as

$$C_{(S)} + 1/2\ O_2(g) \longrightarrow CO(g) \qquad \Delta H = x \text{ kcal (say)}$$

$$CO(g) + 1/2\ O_2(g) \longrightarrow CO_2(g) \quad \Delta H = y \text{ kcal (say)}$$

Although x, the heat change involved in the combustion of carbon monoxide cannot be determined easily, y, the heat change involved in the combustion of carbon monoxide to give carbon dioxide can be measured and is -67.71 kcal. According to Hess's law

$$x + y = -94.05 \text{ kcal}$$

or, $x = -94.05 - 67.71 = -26.34$ kcal

Thus, ΔH heat of combustion of carbon to give carbon monoxide is – 26.34 kcal.

(ii) Determination of enthalpy changes of slow reactions:

Hess's law is extremely useful in determining enthalpy changes of those reactions which take place extremely slowly for example, the transformation of rhombic sulphur into monoclinic sulphur is so slow that direct measurement of enthalpy change is not possible. But the enthalpy of combustion of rhombic sulphur is known to be respectively, i.e.,

(i) $S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g); \qquad \Delta H = -297.5 \text{ kJ}$

(ii) $S(\text{monoclinic}) + O_2(g) \rightarrow SO_2(g); \qquad \Delta H = -300.0 \text{ kJ}$

Substracting (i) from (ii) and rearranging, we get

$S(\text{monoclinic}) \quad - \quad S(\text{rhombic}) \; ; \qquad \Delta H = -2.5 \text{ kJ}$

or S(rhombic) - S(monoclinic) $\Delta H = 2.5$ kJ

Thus the transformation of one mole of rhombic sulphur into monoclinic sulphur is accompanied by absorption of kcal of heat.

(iii) Calculation of enthalpy of formation:

The enthalpy of the formation of compounds can be calculated by the application of Hess's law when it is not possible to determine these experimentally. For example, it is impossible to determine experimentally the enthalpy of the formation of benzene from its elements: carbon and hydrogen. However, it can be calculated from the enthalpy of combustion of benzene and the enthalpy of formation of water and carbon dioxide. The solution is carried out in two steps

Step I

(i) $C_6H_6(l) + 15/2\ O_2(g) \longrightarrow 6CO_2 + 3H_2O\ (l)$ $\Delta H = -781.74$ kcal

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.14$ kcal

(iii) $H_2O\ (g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O\ (l)$ $\Delta H = +\ 68.40$ kcal

Step-II

(iv) $6\ C(s) + 6O_2\ (g) \longrightarrow 6CO_2(g);$ $H = -564.84$ kcal

(v) $3H_2(g) + 3/2\ O_2(g) \longrightarrow 3H_2O(l)$ $\Delta H = -205.20$ kcal

Adding (iv) and (v) and subtracting (1) we get

$6C(s) + 3H_2(g) \longrightarrow C_6H_6\ (l);$ $\Delta H = 11.70$ kcal

Thus, enthalpy of formation of benzene is 11.72 Kcal.

10.6 HEAT OF REACTION

Thermochemical reactions are studied either at (a) constant volume or at (b) constant pressure. The magnitude of changes observed under the two conditions is different. The change in internal energy (ΔE)is the heat change accompanying a chemical reaction at constant volume because no external work is performed. But at constant pressure, there is a change in the internal energy, and work is also involved because of expansion or contraction. In the laboratory, most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume. To study heat changes for reactions taking place at constant pressure and constant temperature, a new term enthalpy has been introduced.

The enthalpy of a system is defined as the sum of the internal energy and the product of its volume with pressure. That is

$$H = E + PV$$

Where H is enthalpy, E is internal energy, P is the pressure and V is the volume of the system. The term H is also called heat content.

Like internal energy, enthalpy is also a state function and it is not possible to measure its absolute value. However, a change in enthalpy (ΔH) accompanying a process can be measured accurately and is given by the expression.

$$\Delta E = H_{products} - H_{reactants}$$

$$= H_P - H_r$$

At constant pressure and temperature, the change in the enthalpy ΔH will be equal to a change in the internal energy ΔE and the work done in the expansion or contraction $P\Delta V$

Hence $\Delta H = \Delta E + P\Delta V$ ……………10.1

Therefore, while heat change in a process is equal to its change in internal energy ΔE at constant volume, it gives at constant pressure the enthalpy change ΔH.

ΔE= heat change at constant volume

ΔH= heat change at constant pressure

For reactions involving solids and liquids only, the change in volume (ΔV) is very small and hence the term $P \times \Delta V$ is so small that it is neglected. For such reactions ΔE is equal to ΔH. In case of gases, we have to specify whether the reaction is taking place at constant pressure or at constant volume, because the value of $P \times \Delta V$ is appreciable. Most of such reactions are however, studied at constant pressure and change in enthalpy ΔH is involved.

10.7 ENTHALPY OF NEUTRALIZATION

The change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralized by one gram equivalent of base or vice versa in a dilute solution is known as the heat of neutralization.

Following are some examples of the heat of neutralization

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(l)$ $\Delta H = -13.68$ kcal

$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{3(aq)} + H_2O(l)$ $\Delta H = -13.69$ kcal

$HNO_{3(aq)} + KOH_{aq)} \longrightarrow KNO_{3(aq)} + H_2O(l)$ $\Delta H = -13.87$ kcal

From these equations written above it is observed that heat of neutralization of a strong acid and strong base is – 13.7 kcal. This can be explained with the help of the theory of ionization. If HA and BOH represent any strong acid and strong base respectively and an equivalent amount of these in a dilute solution is mixed, we have

$H^+ (aq) + A(aq) + B(aq) + OH(aq) \longrightarrow A(aq) + B(aq) + H_2O(l)$ $\Delta H = -13.7$ Kcal

Hence $H^+_{(aq)} + OH_{(aq)} \longrightarrow H_2O$ (l) $\Delta H = -13.7$ kcal

Thus the heat of neutralization of an acid and a base is merely heat of formation of water from hydrogen and hydroxyl ions.

If, however, the acid or alkali is weak, the enthalpy of neutralization is different because the reaction now involves the dissociation of a weak acid or weak alkali as well the neutralization of acetic acid with sodium hydroxide, for example, involves the dissociation of the acid as well as the usual neutralization of H^+ and OH^- ions as represented below.

(i) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

(ii) $H+ (aq) + OH (aq) \longrightarrow H_2O$ (l)

As H^+ ions are neutralized by OH^- ions furnished by the completely dissociated sodium hydroxide, more H^+ ions are formed by the dissociation of acetic acid to re-establish the equilibrium. Thus, both reactions proceed side by side till acetic acid is completely neutralized. The enthalpy of neutralization of acetic acid by sodium hydroxide is -13.2 kcal. Since the average value for the combination of H^+ and OH^- ions is taken as -13.7 kcal, the enthalpy of dissociation of acetic acid may be taken as 0.5 kcal. The heat of dissociation of a weak acid or weak base may be defined as the change in enthalpy of the system when one mole of it is dissociation into ions.

10.8 BOND DISSOCIATION ENERGY

Bond energy for any particular type of bond in a compound may be defined as the average amount of energy required to dissociate (i.e., break) one mole, Avogadro number of bonds of that type present in the compound. This is also called the enthalpy of the formation of the bond.

Thus the bond energy of H-H bond is the energy required to break all the bonds in one mole of the gas. It is expressed in kcal per mole or kJ per mole. For example, the bond energy of the H-H bond is 433 kJ per mole or 103.58 kcal per mole.

Bond energies of some common bonds are given below.

(i) $H_2(g) \longrightarrow 2H_g(g)$; $\Delta H=433.1$ kJ

(ii) $O_2(g) \longrightarrow 2O(g)$; $\Delta H=489.5$ kJ

(iii) $N_2(g) \longrightarrow 2N(g)$; $\Delta H=937.4$ kJ

(iv) $C(s)\ C(g)$; $\longrightarrow$ $\Delta H=719.6$ kJ

Suppose we have to determine the enthalpy of the formation of the C-H bond in methane. We should know the enthalpy of the formation of methane. This had been calculated from the enthalpy of combustion of methane to be – 74.9 kJ. Thus

(v) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta H= - 74.9$ kJ

Multiplying equation (i) by 2 we have

(vi) $2H_{2(g)} \longrightarrow 4H_{(g)}$; $\Delta H= 866.2$ kJ

Adding equation (iv) and (vi) and subtracting from equation (v) we have

$C(g) + 2H_2(g) \longrightarrow CH_4(g)$; $H= -1660.7$ kJ

It follows from above that -1660.7 kJ of energy is required to break four moles of C-H bonds in methane. Therefore, the average bond energy per mole of C-H bond is -1660.7/4 = 415.2 kJ. This is also the enthalpy of the formation of the C-H bond.

10.9 TEMPERATURE DEPENDENCE OF ENTHALPY

The heat of a reaction changes with a change in the temperature of a gas due to variations in its specific heat. The equation representing the variation of heat change of reaction with temperature is known as **Kirchoff's equation**.

At constant volume, the heat of the reaction, ΔE, is given by the relation

$$\Delta E = E_2 - E_1$$

Where E_2 is the internal energy of products and E_1 is the internal energy of reactants.

Differentiating this equation concerning temperature keeping volume constant we get

$$\left[\frac{\partial}{\partial T}(\Delta E)\right]_v = (\partial E_2/\partial T)_v - = (\partial E_1/\partial T)_v \quad \text{........10.2}$$

But we know $\frac{\partial E}{\partial T} = C_v$

Hence $\left[\frac{\partial}{\partial T}(\Delta E)\right] = (C_v)_2 - (C_v)_1$ ….. …...10.3

$= \Delta C_v$

Here $(C_v)_2$ is heating capacity of products and $(C_v)_1$ is heat capacity of reactants.

On integrating the above equation between the limits T_1 and T_2 and keeping in view that when the temperature is T_1 heat of reaction is ΔE_1 and when the temperature is T_2 heat of reaction is ΔE_2

$$\int_{\Delta E_1}^{\Delta E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v dT$$

Or $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$ …………. 10.4

Similarly, heat of reaction at constant pressure is given by the relation.

$$\Delta H = H_2 - H_1 \quad \text{.......... 10.5}$$

Where H_2 aw H_1 are heat content or enthalpy of products and reactants respectively.

Differentiating equation 10.5 concerning temperature at constant pressure.

$$\left[\frac{\partial}{\partial T}(\Delta H)\right]p = (\partial H_2/\partial T)\, p - \partial H_1/\partial T)\, p$$

We have

$$= (C_P)_2 – (C_P)_1 = \Delta C_p \qquad ....10.6$$

Here $(C_P)_2$ and $(C_P)_1$, are the heat capacities of products and reactants respectively.

or $$d\,(\Delta H) = \Delta C_p dT$$

integrating the equation between temperature T_1 and T_2

we have

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta CpdT$$

$$= \Delta C_p\,(T_2 - T_1) \qquad ..... \quad 10.7$$

The relations (10.3), (10.4), (10.6), and (10.7) were first derived by Kirchoff and are called Kirchoff’s equations.

These equations are used to calculate the heat of reaction at a given temperature provided heat of reaction at some other temperature and when the heat capacities of products and reactants are known.

10.10 SUMMARY

- In this unit we have studied different definitions associated with thermochemistry. As we know thermochemistry is the study of energy changes involved in chemical reactions.
- This study is very useful in determining enthalpy changes in various reactions.
- Kirchoff’s equation is very useful in calculating the change of enthalpy with temperature. Hess’s law and bond energy calculations are utilized for various transformations.

10.11 TERMINAL QUESTIONS

(A) Objective type questions:

Q.1 Which of the following relations holds good for the reaction?

$$CO_{(g)} + ½\,O_2(g) \longrightarrow CO_2(g)$$

(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$

(c) $\Delta H=\Delta E+\frac{1}{2}RT$ (d) $\Delta H=\Delta E-\frac{1}{2}RT$

Q.2 The change in internal energy with temperature at constant volume is given by the relation.

(a) $\Delta E = \Delta C_v(T_1-T_2)$ (b) $\Delta E = \Delta C_P(T_2-T_1)$

(c) $\Delta E = \Delta C_v(T_2-T_1)$ (d) $\Delta E = \Delta C_P(T_1-T_2)$

Q.3 Which of the following always has a negative value?

(a) Heat of reaction (b) Heat of formation

(c) Heat of combustion (d) Heat of solution

Q.4 The change in enthalpy that takes place when one mole of a compound is formed from its elements is called:

(a) Heat of combustion (b) heat of formation of compound

(c) Heat of synthesis (d) standard heat of formation

Q.5 The heat of neutralization of strong acid and strong base is always:

(a) Zero (b) constant (c) positive (d) changing

Q.6 Standard state refers to:

(a) One-atmosphere pressure and 25^0C temperature.

(b) One-atmosphere pressure and 100^0C temperature.

(c) One-atmosphere pressure and 0^0C temperature.

(d) None of these.

Q.7 Thermochemistry is the study of:

(a) Heat changes accompanying chemical reaction

(b) Net entropy changes in a reaction

(c) Net free energy change in a chemical reaction

(d) None of these.

Q.8 The equation showing the effect of temperature change on the heat of reaction is known as:

(a)Arrhenius equation (b) Kirchoff's equation

(c) Ostwald's equation (d) None of these

Q.9.The enthalpies of elements in their standard state are taken as zero. Thus, the enthalpy of formation of a compound

(a)Will always be positive (b) Will always be negative

(c)may be positive or negative (d) will always be zero

Q. 10 Which of the following is not an application of Hess's law?

(a) determination of heat of formation
(b) determination of heat of transition
(c) determination of Gibb's energy
(d) determination of heat of hydration

(B) Short answer type questions:

Q.1. Define the following terms:

(a) Thermochemistry

(b) Heat of formation

(c) Thermochemical equation

Q.2. What is meant by heat of formation?

Q.3. Show that the temperature dependence of heat of a reaction is given by the relation.

$$\left[\frac{\partial}{\partial T}(\Delta H)\right] = \Delta C_P$$

Q.4 Define heat of neutralization?

C) Long answer type questions:

Q.1. State Hess's law of constant heat summation. Calculate the heat of formation of acetylene from the following data:

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta n = -94.052$ kcal

$H_2(g) + ½ O_2(g) \longrightarrow H_2O; \quad \Delta H = -68.317$ kcal

$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2CO_{2(g)} + H_2O(l); \Delta H = -310.615$ kcal

Q.2. (a)Explain what is meant by the term bond energy.

(b)Define heat of neutralization. Why heat of neutralization of a strong acid and strong base is 13.69 kcal?

Q.3. Define 'Bond Energy'. How is the bond energy of a bond calculated for a polyatomic molecule? How is it used to calculate the enthalpy change of a reaction?

10.12 ANSWER'S

1. (d)	**2.(**c)	**3.** (c)	**4.** (b)	**5.**(b)
6. (a)	**7.** (a)	**8.** (b)	**9.** (d)	**10.**(c)

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UNIT 11: ELECTROCHEMISTRY-I

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11.1 INTRODUCTION

Substances like mica, wax, glass ebonite, etc. strongly resist the flow of electricity and practically do not allow any current to flow through them. These substances are called non-conductors. On the other hand, there are substances such as copper, silver, mercury, water solutions of salts acids, etc. through which electric current can easily pass; these are called conductors. The conductors are broadly classified into two categories: (i) electric conductors or metallic conductors and (ii) electrolytic conductors or electrolytes.

Electronic conductors include metals, alloys, graphite, etc. in which the electricity is carried exclusively by the transport of electrons. The electrons flow from a higher negative potential to a lower one; there is no transport of matter during the passage of electricity. In electrolytes, the flow of current is accompanied by the actual transfer or migration of matter. Such transfer of matter leads to the decomposition of matter at the points where electricity enters or leaves the electrolyte and, in the process, helps in the transfer of electrons. The electrolytes are solutions of salts, acids, and bases usually in water.

11.2 OBJECTIVES

- The objective of this chapter is to explore the behavior of solutes in different solvents, emphasizing the principle of "like dissolves like." It aims to explain the solubility of polar and non-polar substances in their respective solvents, and the concept of electrolytes and non-electrolytes.
- The chapter will also focus on the ability of electrolytes, such as sodium chloride and copper sulfate, to conduct electricity when dissolved in water or a molten state, and the importance of these principles in understanding chemical reactions in solution.

11.3 ELECTRICAL TRANSPORT:

11.3.1 Conduction in metal and electrolyte solution:

Metal in general allows an electric current to pass through and is called a conductor of electricity. The phenomenon of an electrolyte passing electric current through its solution is termed electrolysis. The process of electrolysis is carried out in an apparatus called the electrolytic cell. The cell contains a solution of an electrolyte in which two metallic rods, Electrodes. These rods are connected to the two terminals of a battery which is the source of electricity. The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called the anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called the cathode.

11.3.1.1 Mechanism of electrolysis:

The process of electrolysis taking place is shown in Fig 11.1. The cations migrate to the cathode and form a neutral atom by accepting electrons.

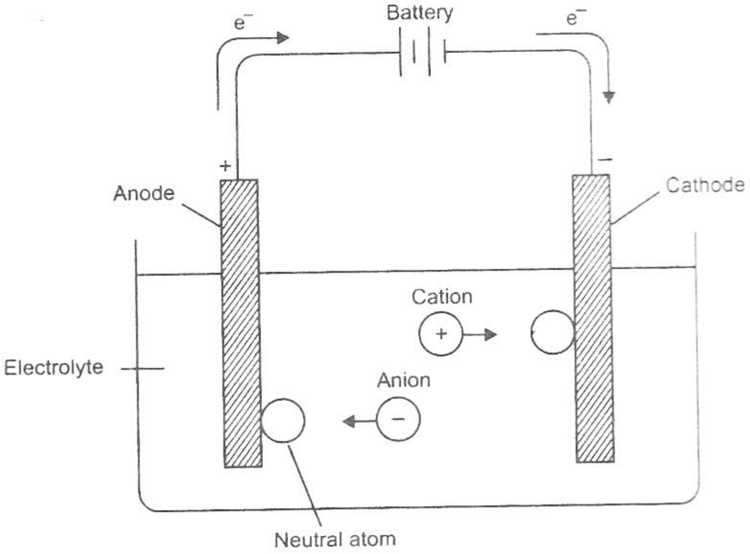


Fig 11.1 The mechanism of electrolysis

The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes, chemical reaction takes place.

Let us consider the electrolysis of hydrochloric acid. In solution hydrochloric acid is ionised.

$$HCl \longrightarrow H^+ + Cl^-$$

In the electrolytic cell Cl^- ions will move towards the anode and the H^+ ions will move toward the cathode. At the electrode, the following reaction will take place.

At cathode:

$$H^+ + e^- \longrightarrow H \text{ (reduction)}$$

You see each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Paris of hydrogen then unites to form a molecule of hydrogen gas H_2.

At anode

$$Cl^- \longrightarrow Cl + e^- \text{ (oxidation)}$$

After the chloride ion loses its electron to the anode, pairs of chlorine atoms unite to form chlorine gas, Cl_2.

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction i

$$2\,HCl \longrightarrow H_2 + Cl_2$$

	Cathode	Anode
Ions attracted	Cations	Anions
Direction of electron	Into cell	Out of cell
Movement		
Half reaction	Reduction	Oxidation
Sign	-ve; since it is attached	+ve; since it is attached
	to the –ve end of battery	to the +ve end of the battery

Table 11.1 Description of the cell

Electrolytes obey Ohm's law, to the same extent as the metallic conductors. According to this law the current I flowing through a conductor is given by the relation I=E/R, where E is the electromotive force i.e., the difference of potential at the two ends of the conductor, and R is resistance

$$I = E / R$$

Electric units:

There are a few electrical units that you should understand before taking up the study of quantitative aspects of electrolysis. These are:

Amperes: Current strength is generally expressed in amperes. The ampere is defined as the current that deposits 0.00118 grams of silver per second from a 15 percent solution of silver nitrate in a coulometer. Or we can say an ampere is a current of one coulomb per second.

Coulomb: The quantity of electricity passing through a conductor is the product of current strength and time and is generally expressed in coulombs. A coulomb is a unit quantity of electricity. It is the amount of electricity that will deposit 0.001118 grams of silver from a 15 percent solution of silver nitrate in a coulometer.

Ohm: The unit of electrical resistance is ohm. It is the resistance offered at 0^0C to a current by a column of mercury 106.3 centimeters long of about one square millimeter cross-sectional area and weighing 14.454521 grams.

Volt: A volt is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

Faraday’s law of electrolysis:

Faraday discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. He formulated two laws in 1834, which are known as Faraday’s law of electrolysis. The laws are as follows

Faraday’s first law of electrolysis:

The amount of a given product liberated at an electrode during electrolysis is directly proportioned to the quantity of electricity that passes through the electrolytic solution.

Faraday’s second law of electrolysis:

When the same amount of electricity passes through solutions of different electrolytes, the amount of substance liberated at the electrodes is directly proportional to their chemical equivalents. These two laws have been shown to hold very rigidly provided the passage of electricity takes place entirely by electrolytic conduction. It applies to molten electrolytes as well as to the solution of electrolytes and is independent of temperature, pressure, or nature of the solvent.

If m is the mass of substance deposited on the electrode by passing Q coulombs of electricity, then

$$m \propto Q$$

But $$Q = I x t$$

Where I, is the strength of the current in amperes and t is time in seconds for which current has been passed.

Therefore, $$m \propto I x t$$

or $$m = z x I x t$$

Here z is the constant known as the electrochemical equivalent of the electrolyte. If I=1 ampere and t=1 second then

$$m = z$$

from this, it follows that the electrochemical equivalent is the amount of substance deposited by one ampere current passing for one second (i.e., one coulomb)

It has been found that the quantity of electricity required to liberate one gram equivalent of substance is 96,500 coulombs. This quantity is known as Faraday and is denoted by the symbol F.

It is clear that the quantity of electricity to deposit one mole of a substance is given by the expression,

Quantity of electricity = nxF

Where n is the valence of the ion. Thus, the quantity of electricity required to discharge.

one mole of Ag^+ = 1xF = 1F

one mole of Cu^{2+} = 2xF = 2F

one mole of Al^{3+} = 3xF = 3F

We can represent the reaction on the cathode as:

$$Ag^+ + e^- = Ag$$

$$Cu^{2+} + 2e^- = Cu$$

$$Al^{3+} + 3e^- = Al$$

The moles of electrons required to discharge one mole of ions Ag^+, Cu^{2+} and Al^{3+} are one, two, and three respectively. It means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say

1 Faraday = 96500 coulombs= 1 mole electrons

Verification of the second law of electrolysis:

Faraday's second law states that when the same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.

To verify this law, let us take the arrangement of the type shown in Fig. 11.2. Now pass the same amount of electricity through the three coulometers containing solutions of dilute sulphuric acid (H_2SO_4), copper sulphate ($CuSO_4$) and silver nitrate ($AgNO_3$) respectively. These coulometers are fitted with platinum, copper and silver electrodes as shown in Fig. 11.2. The masses of hydrogen, copper, and silver liberated/ deposited at the respective cathodes are in the ratio of their equivalent weights. That is

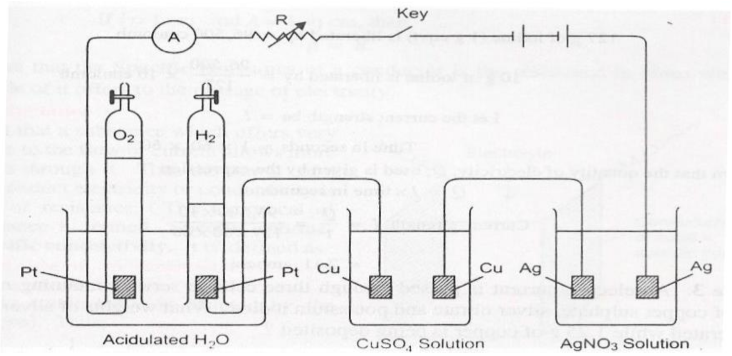


Fig. 11.2 Verification of Faraday's second law of electrolysis

$$\frac{\text{mass of hydrogen liberated}}{\text{mass of copper deposited}} = \frac{\text{equivalent weight of hydrogen}}{\text{equivalent weight of copper}}$$

and $\frac{\text{mass of copper deposited}}{\text{mass of silver deposited}} = \frac{\text{equivalent weight of copper}}{\text{equivalent weight of silver}}$

From this experiment, we can calculate the mass of hydrogen, copper and silver liberated at their respective cathodes by one coulomb of electricity. We find these are always

Hydrogen = 0.00001036 g

Copper = 31.78x0.00001036 = 0.0003292 g

Silver = 107.88x0.00001036 = 0.001118 g

Since the equivalent weights of hydrogen, copper and silver are 1. 31.78 and 107.88 g respectively, it follows that the electrochemical equivalents are proportional to chemical equivalents (or equivalent weights).

Faraday's second law of electrolysis helps to calculate the equivalent weights of metals, the unit of electrical charge and the Avogadro number.

Examples:

(i) 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Solution: Given t= 50x60 = 3000 seconds, I= 0.2 amperes, quantity of electricity used Q= Ixt = 3000x0.2 = 600 coulombs

Amount of copper deposited by 600 coulombs = 0.1978 g

Amount of copper deposited by one coulomb = 0.1978/600

= 0.0003296 g

This is the chemical equivalent of copper

(ii) Calculate the current strength in amperes required to liberate 10 g iodine from potassium iodide solution in one hour. The equivalent weight of iodine in 127.

Solution:

127 g of iodine is liberated by 96500 coulombs

1 g of iodine will be liberated by $\frac{96500}{127}$ coulombs

10 g of iodine will be liberated by $\frac{96500}{127}$ x10 coulombs

Let the current strength be I

Time in seconds = 60x60 seconds

The quantity of electricity is given by Q=Ixt

$$I = Q/t = \frac{96500 \times 10}{127 \times 60 \times 60}$$

$$= 2.11 \text{ amperes}$$

11.3.2 Electrolytic conduction:

From the above discussion, it is clear that the flow of electricity through solutions of electrolytes is due to the migration of ions when a potential difference is applied between the two electrodes. The power of electrolytes to conduct electrical currents is formed by conductivity or conductance. It is defined as the reciprocal of resistance (R) of solution. Like metallic conductors, electrolytes obey Ohm's law. According to this law the current I flowing through a metallic conductor is given by the relation.

$$I = E/R$$

Where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resitance R of a conductor is directly proportional to the length l and inversely proportional to the area of cross-section, A. That is

$$R \propto \frac{l}{A}$$

$$\text{or } R = \rho \frac{l}{A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11.1)$$

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. Its value depends upon the material of the conductor. From (11.1) we can write

$$\rho = Rx\frac{A}{\rho}$$

If $\rho = 1\ cm\ \ and\ A = 1\ sq.cm,\ then$

$$\rho = R$$

It means that the specific resistance of a conductor is the resistance in ohms that a one-centimeter cube of it offers to the passage of electricity. The reciprocal of specific resistance, i.e., 1/ ρ is called specific conductance.

Specific conductance:

A substance that offers very little resistance to the flow of current allows more current to pass through it. Thus, the power of a substance to conduct electricity is the converse of resistance. The reciprocal of specific resistance is termed specific conductance or specific conductivity. Hence,

The conductance of a one-centimeter cube (cc) of a solution of electrolyte is specific conductance (fig. 11.9). It is denoted by the symbol κ (kappa). Thus

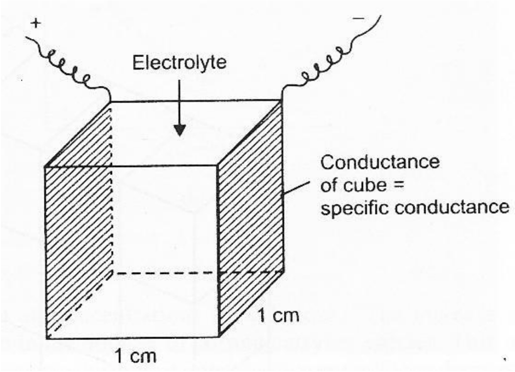


Fig. 11.3 specific conductance

$$\kappa = \frac{1}{\rho} = \frac{1}{R} x \frac{l}{A}$$

Unit of specific conductance:

Specific conductance is generally expressed in reciprocal ohms (r.o.) or mhos or ohm^{-1}. Its unit can be derived as follows:

$$= \frac{1}{A} \cdot \frac{R}{R} = \frac{1}{cm^2} x \frac{cm}{ohm}$$

$$= \text{ohm}^{-1}\ \text{cm}^{-1}$$

The internationally recommended unit for ohm^{-1}(or mho) is Siemens. When s is used the conductance is expressed as s cm^{-1}. The Siemens unit is named after Sir Willian Siemens, who was a noted electrical engineer.

The specific conductance increases with: (i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of the aqueous solution of an electrolyte, the volume of water in which a certain amount of water-electrolyte is dissolved is always measured in cubic centimeters and is known as dilution. If the volume of the solution is VCC, the specific conductance of the solution is written as κv.

Equivalent conductance:

Specific conductance, although a suitable property for characterizing metallic conductance, is not so for characterizing electrolytic conductance where the value, amongst other things, depends upon the concentration of the solution of the electrolyte as well. While measuring conductance of electrolytes in solutions, another quantity of much greater significance, known as equivalent conductance, is frequently used.

Equivalent conductivity is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by Λ. It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolytes at the dilution V.

Thus $\Lambda = \kappa$.V

This is shown in fig 8.4. A solution having one gram-equivalent water between electrode placed 1 cm apart has $\Lambda = \kappa$ x 9

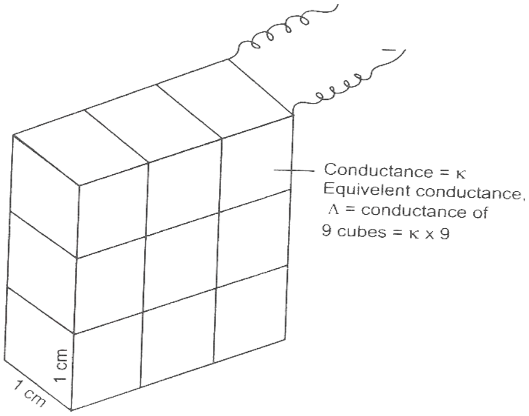


Fig 11.4 solution of 1 g-equivalent dissolved in 9cc of the electrolyte dissolved in, say, 9cc water be placed between two electrodes. 1 cm. apart.

The solution could be considered as consisting of nine cubes, each of which has a conductance κ (specific conductance). Thus, the total conductance of the solution will be 9 x κ. Similarly, Vcc of solution will form V cubes and the total conductance will be κ xV.

If an electrolyte solution contains N gram equivalents in 1000cc of the solution, the volume of the solution containing 1 gram-equivalent will be 1000/N. Hence

$$\Lambda = \frac{\kappa\, 1000}{N}$$

The unit of equivalent conductance may be deduced as follows

$$\Lambda = \kappa x V$$

$$= \frac{1}{R} . \frac{l}{A}\ x\ V$$

$$= \frac{1}{ohm} x \frac{cm}{cm_2} x \frac{cm_3}{eqvt}$$

$$= ohm^{-1}\ cm^2\ eqvt.$$

Molar conductance:

Sometimes molar conductance helps compare the conductances of electrolytes. It is defined as:

The conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume Vcc is known as molecular conductance. It is denoted by μ. the value of molecular conductance is obtained by multiplying the specific conductance, κ by the volume in κ containing one mole of electrolyte.

Molar conductance $\mu = \varkappa x V$. Here V is the volume of the solution in cc which contains one mole of the electrolyte Since,

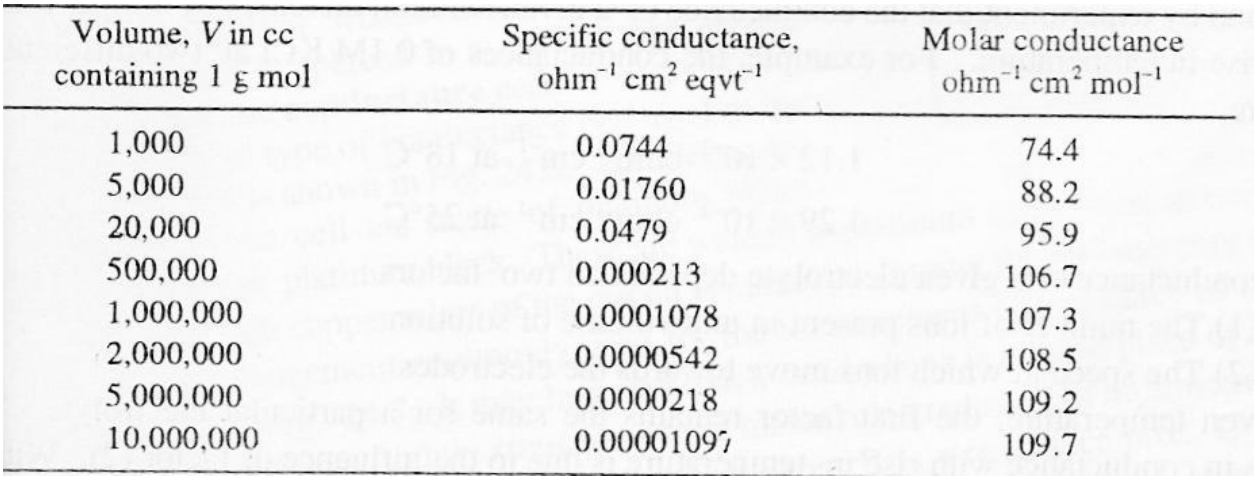
$$\varkappa = \frac{1}{R} x \frac{l}{A}$$

$$\mu = \frac{1}{R} x \frac{l}{A} x\ V$$

$$= \frac{1}{ohm} x \frac{cm}{cm2} x \frac{cm3}{mol}$$

$$= ohm^{-1}\ cm^2\ mol^{-1}$$

Effect of dilution on specific conductance, equivalent conductance and molecular conductance:



Volume, V in cc containing 1 g mol	Specific conductance, $ohm^{-1}\ cm^2\ eqvt^{-1}$	Molar conductance $ohm^{-1}\ cm^2\ mol^{-1}$
1,000	0.0744	74.4
5,000	0.01760	88.2
20,000	0.0479	95.9
500,000	0.000213	106.7
1,000,000	0.0001078	107.3
2,000,000	0.0000542	108.5
5,000,000	0.0000218	109.2
10,000,000	0.00001097	109.7

Table 11.2 specific and molar conductance of NaCl solution at 18^0C Strong and weak electrolytes:

Specific conductance is the conductance of a one-centimeter cube of a solution of an electrolyte. If we dilute the solution the specific conductance decreases. On diluting the solution, the concentration of ions per cc decreases. Hence the specific conductance decreases. But the equivalent conductance and molar conductance increase with dilution. This is because equivalent conductance and molar conductance are the product of specific conductance and the volume of the solution containing one gram-equivalent or one mole of the electrolyte respectively. With dilution specific conductance decreases while volume increases. The increase in the second factor is much more than the decrease in the first factor. Also, on dilution more and more electrolytes dissociate into ions, and hence equivalent conductance and molecular conductance increase.

Strong and weak electrolytes:

There are two classes of electrolytes, depending upon their ionization

(i) Strong electrolytes
(ii) Weak electrolytes

Strong electrolytes:

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionized. Strong electrolytes have a high value of equivalent conductance even at low concentrations. HCl, H_2SO_4, HNO_3, $HClO_4$, HI, HB_r, NaOH, KOH, Ca $(OH)_2$, Mg $(OH)_2$ and almost all salts are examples of some strong electrolytes.

Weak electrolytes:

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionized. Such solution is called a weak electrolytic solution. That has low value of equivalent conductance.

All organic acids such as acetic acid, oxalic acid; most organic bases and a few salts such as mercury chloride and lead acetate are some examples of weak electrolytes.

11.3.3Measurement of electrolytic conductance:

As you know that conductance is the reciprocal of resistance, hence it can be determined by measuring the resistance of the electrolytic solution. This can be measured with the help of a Wheatstone bridge. The solution whose conductance is to be determined is placed in a special type of cell known as the conductivity cell.

Conductivity cell and cell constant:

The vessel in which the measurement of the conductivity of the solution is to be made is known as the conductivity cell. They are of various shapes and sizes depending upon the nature of the solution taken. A simple type of conductance cell used in the laboratory is shown in Fig 8.5. The electrodes fitted in the cell are made of platinum plates coated with platinum black. These are welded to platinum wires fused in two thin glass tubes. The contact with the copper wires of the circuit is made by dipping them in mercury contained in the tube.

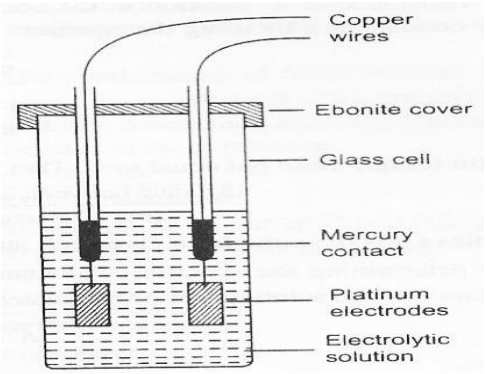


Fig 11.5 conductivity cell

The arrangement commonly used for the measurement of resistance of the conductivity cell is shown in fig 11.6. When a direct current is passed through a solution, the following two difficulties arise:

(i) The electrodes are polarized i.e. the product of the electrolysis accumulate on them.

(ii) The passage of current involves the decomposition of a portion of the solute so the concentration of this substance changes during passage electric current.

In order to remove these difficulties, we use alternating current in place of direct current. In this case galvanometer is replaced by head-phone. AB is a manganin wire tightly stretched over a meter rule graduated in millimeters. A sliding contact G moves along this wire. R is resistance box. S is induction coil from which alternating current is led as shown in the fig 11.6. A conductivity cell containing the experimental electrolyte is attached in the bridge as shown.

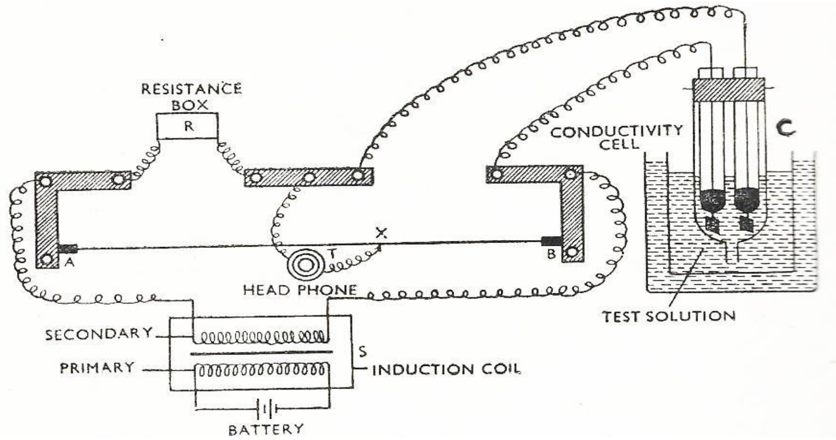


Fig 11.6 Apparatus for measuring conductivity

The sliding contact is moved slowly along the wire AB, till a point x is reached at which the potential becomes equal to that of R. Under such conditions, no current will flow through the headphones and it will be silent. At all other points, a buzzing sound can be heard in the headphones. In actual practice, it is not usually possible to obtain complete silence in the headphones, so the point of minimum sound is taken as the null point of the experiment. When this occurs, we have

$$\frac{resistance\ of\ C}{Resistance\ of R} = \frac{resistance\ of\ BX}{resistance\ of\ AX} = = \frac{length\ BX}{length\ AX}$$

or Resistance of c = $\frac{length\ of\ BX}{length\ of\ AX}$ x resistance of R

The resistance of a solution in the conductivity cell as measured above can be converted to specific conductance by using the equation

$$\kappa = \frac{1}{R}.\frac{l}{A}$$

$$= \frac{1}{R}.x$$

The ratio $\frac{l}{A}$ has been put equal to x, that is,

$$\frac{distance\ between\ the\ electrodes}{area\ of\ the\ electrodes} = x\ (cell\ constant)$$

The value of x is the same for a given cell and is called the cell constant.

After determining the specific conductance, κ the equivalent conductance, Λ and the molar conductance μ of the solution can be calculated by using the expression

$$\Lambda = \frac{\kappa\ x\ 1000}{N}$$

and $$\mu = \frac{\kappa\ x 1000}{M}$$

where N is the gram-equivalent and M is the gram-mole do the electrolyte.

Determination of cell constant:

The exact value of the cell constant (l/A) can be determined by measuring the distance between the electrodes (l) and the area of the cross-section (A). Actual measurement of these dimensions is very difficult. Therefore, an indirect method is employed to determine the value of the cell constant.

We know that:

Specific conductance $\kappa = \frac{1}{R} x \frac{l}{A}$

κ= observed conductance x cell constant

Hence cell constant = $= \frac{specific\ conductance}{observed\ conductance}$

To determine the cell constant, a standard solution of KCl whose specific conductance at a given temperature is known, is used. Then a solution of KCl of the same strength is prepared and its conductance is determined experimentally at the same temperature. Substituting the two values in the above expression, the cell constant can be calculated.

Examples:

(i) Specific conductance of a decimolar solution of potassium chloride at 18^0C is 1.12 mho. The resistance of a conductivity cell containing the solution at 18^0C was found to be 55 ohm. Calculate the cell constant.

Solution:

R= 55 ohm, conductivity= 1/55 mho, κ=1.12 mho

Cell constant = $= \frac{1.12}{1/55}$ = 61.6

(ii) The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 om^2 in area was found to be 320 ohms. Calculate the equivalent conductance of the solution.

Solution:

Given l=1.80 cm and A=5.4 cm^2

Hence cell constant $\kappa = \frac{l}{a} = \frac{1.80}{5.4} = \frac{1}{3}$

Observed conductance = $\frac{1}{32}$ mhos

Since the solution is $\frac{N}{10}$, V= 10,000 ml

Specific conductance = κ x observed conductance

$= \frac{1}{3} x \frac{1}{32} = \frac{1}{96}$ mhos

$\Lambda = \kappa$ x V = $\frac{1}{96}$ x 10,000 = 104.1 mhos cm^2 $equiv^{-1}$

11.4 KOHLRAUSH'S LAW

From the study of the equivalent conductance of electrolytes at infinite dilution, Kohlrausch discovered an interesting relationship between conductivity and transport number. At 25^0 the value of equivalent conductivity at infinite dilution λ_∞ for some electrolytes are given below:

Electrolyte	$\lambda_{\alpha\ 25}{}^oC$	Difference	Electrolyte	$\lambda_{\alpha\ 25}{}^oC$	Difference
NaBr NaCl	128.51 126.45	2.06	KBr NaBr	151.92 128.51	23.41
KBr KCl	151.92 149.86	2.06	KCl NaCl	149.86 126.45	23.41
LiBr LiCl	117.09 115.03	2.06	KNO_3 $NaNO_3$	144.96 121.55	23.41
NH_4Br NH_4Cl	151.80 149.74	2.06	KOH NaOH	271.52 248.11	23.41

Table 11.3 Equivalent conductivity at infinite dilution of some electrolytes

It is clear from the above table that when the bromine ion is replaced by the chloride ion, a constant difference of 2.06 is produced in the value of the conductivity at infinite dilution. Similarly, when potassium ion is replaced by sodium ion a difference of 23.41 is observed, anion remaining the same. In other words, each ion makes a certain definite contribution to the conductivity of the solution. Hence in 1875, Kohlrausch's enunciated a law, known as Kohlrausch's law. It states that:

The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductance of the component ions.

Mathematically the law may be expressed

$$\lambda_\infty = \lambda^0{}_a + \lambda^0{}_c$$

The values of $\lambda^0{}_a$ *and* $\lambda^0{}_c$ are called the ionic conductance of the anion and cation respectively at infinite dilution.

11.4.1 Application of Kohlaruch's law:

(i) Calculation of molar ionic conductance:

For each ion, the ionic conductance possesses a constant value at a fixed temperature and is the same no matter of which electrolyte it forms a part. It is directly proportional to the speed of the ions.

$$\lambda_a \alpha u_{-} \qquad \text{or } \lambda_a = ku_{-}$$

$$\lambda_c \alpha u_{+} \qquad \text{or } \lambda_c = ku_{+}$$

Where k is the proportionality constant

Also $\lambda\infty \ \alpha \ (\lambda_a + \lambda_c) = k(u_{-} + u_{+})$

$$\frac{\lambda a}{\lambda\infty} = \frac{u-}{u-+u-} = t_{-}$$

And $$\frac{\lambda c}{\lambda\infty} = \frac{u+}{u\pm u} = t_{+}$$

Also $$\frac{\lambda a}{\lambda c} = \frac{t_-}{t_+} = \frac{t-}{1-t_-}$$

Hence from experimental values of transport number of the ions we can determine ionic conductance.

11.4.1.1 Ionic conductance of weak electrolytes:

Weak electrolytes do not ionize to a sufficient extent in solution and are far from being completely ionized even at very great dilution. The experimental value of $\lambda\infty$ in such cases is, therefore not possible. However, it can be calculated with the help of Kohlraushs law.

$$\frac{\lambda a}{\lambda c} = \frac{t_-}{1-t_-}$$

$$\lambda_a - \lambda_a t_{-} = t_- \lambda_c$$

$$\lambda_a = t_{-}(\lambda_a + \lambda_c)$$

$$= t_- \lambda\infty$$

Thus, the ionic conductance of an ion is obtained by multiplying the equivalent conductance at infinite dilution of any strong electrolyte containing that ion by its transport number.

In this manner, the ionic nobilities of the two ions present in the weak electrolyte can be calculated. Thus, we can get the equivalent conductance of the electrolyte at infinite dilution by adding up two values also we can apply indirect method for evolution of equivalent conductance of week electrolyte.

Suppose equivalent conductance of acetic acid is to be determined at infinite dilution. For this we should know the equivalent conductance at infinite dilution of hydrochloric acid solution acetate and sodium chloride all strong electrolytes as shown below:

$$\lambda_{CH3COOH} = \lambda\ CH_3COO^- + \lambda_{H+}$$

$$= (\lambda_{HCl} + \lambda_{CH3COONa}) - \lambda_{Nacl}$$

The molar conductance at infinite dilution of a sparingly soluble substance, like silver chloride, can also be obtained from similar considerations. Thus:

$$\lambda_{AgCl} = \lambda_{NH4Cl} + \lambda_{AgNO3} - \lambda_{NH4NO3}$$

11.4.1.2 Calculation of the solubility of sparingly soluble salts:

Substances like $PbSO_4$ or AgCl which are ordinarily called insoluble possess a definite value of solubility in water. This can be determined from the conductance measurement of their saturated solution. Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solution so that the equivalent conductance at infinite dilution. This according to Kohlrausch`s law is the sum of the ionic conductance.

So $\kappa v = \lambda\infty = \lambda_a + \lambda_c$

Knowing κ and $\lambda\infty$, we can find out which is the volume in ml containing one g-equivalent of the electrolytes.

Example: The specific conductance of saturated solution of silver chloride at 18^0c is $1.24 x 10^{-6}$ mhos after subtracting that of water. The mobilities of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively, calculate the solubility of silver chloride in grams per liter.

Solutions:

Given $\kappa = 1.24 x\ 10^{-6}$ mhos

$$\lambda\infty = \lambda_{Ag+} + \lambda_{Cl^-} = 53.8 + 65.3 = 119.1$$

$$\lambda\infty = \kappa . V$$

$$V = \frac{\lambda\infty}{\kappa} = \frac{119.1}{1.24x10} \text{ ml}$$

Hence $\frac{119.1}{1.24x10}$ ml contains AgCl =1 g equivalent = 143.5

1000ml contains AgCl $= \frac{143.5 \ x \ 1.24}{119.1} x10^{-6}x1000$

$=1.494x10^{-3}$ g

11.4.1.3 Calculation of degree of dissociation or conductivity ratio:

The apparent degree of dissociation α of an electrolyte at the dilution v is given $\alpha = \lambda_v / \lambda\infty$ where λ_v is the equivalent conductance of the electrolyte at the dilution v and $\lambda\infty$ is the equivalent conductance at infinite dilution and this according to kohlrausch is the sum of λ_α and λ_c.

11.5 ARRHENIUS THEORY OF IONIZATION OF ELECTROLYTE DISSOCIATION

Arrhenius studies the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. In 1884 he put forward his theory of ionization. Arrhenius's theory of ionization may be stated as:

(i) When dissolved in water neutral electrolyte molecules are split up into two types of charged particles. These particles are called ions and the process is termed ionization. The positively charged particles are called cations and the negatively charged ions were called anions.

The theory in modern form assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic forces. When placed in water these neutral molecules to form separate anions and cations. Thus,

$AB \longrightarrow A^+ + B^-$ old view

$A^+B^- \longrightarrow A^+ + B^-$ modern view

(ii) The ions present in the solution constantly unite to form neutral molecules. Thus, there is state of equilibrium between the undissociated molecules and the ions

$$AB \rightleftharpoons A^{+}+B^{-}$$

Applying to law of Mass Action to the ionic equilibrium we have,

$$\frac{[A^{+}][B^{-}]}{[AB]} = K$$

Where K is called the dissociation constant

(iii)The fraction of the total number of molecules of the electrolyte that dissociates into io is called the degree of ionization or dissociation. It is usually denoted by α, i.e.

$$\text{Degree of ionization or dissociation } (\alpha) = \frac{\text{No of molecules dissociated}}{\text{Total No.of molecules taken}}$$

(iv)The degree of dissociation increases with dilution and becomes maximum at the infinite dilution.

(v)These charged particles are free to move through the solution to the oppositely charged electrode. This movement of ions constitutes the electric current through electrolytes. The explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

(vi)The conductivity of an electrolyte solution depends on the number of ions present in the solution. Thus, the degree of dissociation of an electrolyte determines whether it is a stron electrolyte or a weak electrolyte.

11.5.1. Factors that govern the degree of dissociation of an electrolyte:

The degree of dissociation of an electrolyte in the solution depends upon the following factors:

(i) **Nature of the solute:** Some electrolytes like mineral acid, alkali, and most of the salts are almost completely ionized in water. These are called strong electrolytes. On the other hand, some electrolytes like organic, inorganic, acids, and bases ionize only to a small extent and are called weak electrolytes.

(j) **Nature of the solvent:** The nature of the solvent defines the value of the dielectric constant. The dielectric constant is defined as the electrolyte's ability to reduce the forces of attraction between its ions. Like water has the highest dielectric constant, thus the dissociation of an electrolyte is maximum in water.

(iii) **Temperature:** Higher temperatures cause more molecules to divide into ions, increasing the degree of dissociation.

(iv) **Concentration:** When an electrolyte is diluted, its degree of dissociation increases and reaches its maximum at infinite dilution, or zero concentration.

Limitations: Arrhenius's theory limitations are:

(i) According to Arrhenius, the electrolyte will ionize when dissolved in water. X-ray research, however, has revealed that a large number of these electrolytes are already ionized.

(ii) The failure of the Arrhenius hypothesis when applied to strong electrolytes was the most significant criticism leveled against it.

(iii) Since an electrolyte may transmit electricity while it is molten, this indicates that the electrolyte dissociates while it is molten. Therefore, the Arrhenius hypothesis was unable to describe how water functioned.

(iv)The degree of dissociation (α) of strong electrolytes calculated from conductance measurements was found to be different from that calculated from colligative properties.

(v) Strong electrolytes exhibit near-total dissociation even at low doses ($\alpha = 1$) or 100% dissociation at all concentrations. Thus, in the case of strong electrolytes, Arrhenius's theory which holds that conductance increases with dilution because dissociation increases are invalid.

11.6 OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolyte dissociation, the molecule in an electrolyte in aqueous solution undergo spontaneous dissociation into positive and negative ions and that there is a dynamic equilibrium between ions and undissociated molecules. Ostwald noted that law of mass action can be applied to the ionic equilibrium in the case of chemical equilibrium in such systems.

Let us consider a electrolyte AB which dissociates in solution to form A^+ ion and B^- ions.

$$AB \rightleftharpoons A^+ + B^-$$

Let c be the concentration of the electrolyte per liter and α be the degree of dissociation, i.e., the fraction of total concentration of the electrolyte which exists in dissociated state. Then the concentration terms at equilibrium may be written as:

Initial state c o o

$$AB \rightleftharpoons A^+ + B^-$$

Equilibrium concentration $c(1-\alpha)$ $c\alpha$ $c\alpha$

Applying law of mass action:

Rate of dissociation = $K_1c(1-\alpha)$

Rate of combination = $K_2c\alpha \times c\alpha$

or $$\frac{c\alpha x c\alpha}{c(1-\alpha)} = \frac{K_1}{K_2} = K$$

or

$$k = \frac{\alpha^2}{1-\alpha}c \quad \text{mol liter}^{-1} \text{ …………………(11.1)}$$

Equation (1) is mathematical representation of Ostwald`s dilution law. The constant K is called the dissociation constant or ionization constant. It is a constant value at constant temperature.

If one mole of electrolyte is dissolved in V liter of solution, then

$$c = \frac{1}{V}$$

Here V is known as dilution of the solution. Then equation (11.1) can be written as:

$$K = \frac{\alpha^2}{(1-\alpha)v} \text{ ……………………………..(11.2)}$$

For weak electrolytes, the value of α is very small as compared to 1, so in most of the calculations we can take $1-\alpha \cong 1$. Thus Oswald`s dilution formula can be expressed as

$$K = \frac{\alpha^2}{v} \text{ ……………………………………..(11.3)}$$

This law can be verified by determining the value of α and v. the value of α can be determined from conductivity measurements. $\alpha = \lambda_V/\lambda\infty$, λ_V and $\lambda\infty$ are the equivalent conductance at the dilution v and infinite dilution. their values are found from Kohraush`s law. The value of α at various dilution thus determined are inserted in the expression

$$K = \frac{\alpha^2}{(1-\alpha)v}$$

If, K comes out to be constant, the Ostwald`s law stands verified.

However, the law failed completely when applied to strong electrolytes. The value of K far from remaining constant rapidly falls with dilution.

11.6.1 Factor that explain the failure of Ostwald`s law in case of strong electrolytes:

(i) The Oswald`s law is based on Arrhenius theory, which assumes that only a fraction of the electrolyte is dissociated at ordinary dilution and complete dissociation occurs only at infinite dilution. This is true for weak electrolytes. Strong electrolytes are almost completely ionized at all dilutions. The value of $\lambda_V/\lambda\infty$, does not give the accurate value of α. In this case it is only a conductivity ratio.

(ii) Ostwald`s law is derived on the assumption that the law of mass action holds for ionic equlibria as well. But the concentration of ions is very high; the presence of charge affects the equilibrium. Thus, the law of mass action cannot be applied in simple form.

(iii) The ions obtained by dissociation may get hydrated and may affect the concentration terms.

11.7 DEBYE- HUCKEL –ONSAGER'EQUATION FOR STRONG ELECTROLYTES

A number of theories have put forward by different workers in order to explain the high conductance of strong electrolytes. In 1923 Debye and Huckle put forward their well-known theory of strong electrolytes in which account is taken of the electrostatic force between the ions. A brief outline of the main ideas of the theory is given below,

(i) The strong electrolytes are completely ionized at all dilutions. The present position as it has ensured from the Raman spectra, X ray analysis of crystals, distribution coefficients and vapour pressures are that there is a very small amount of unionized substance also present and that instead of saying completely ionized we should say almost completely ionized.

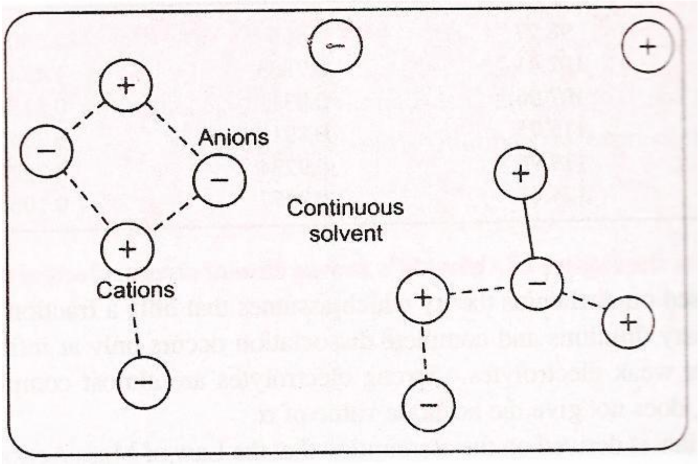


Fig 11.7 Charge distribution in ionic solutions of strong electrolytes

(ii) The oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to found in the vicinity of anions and vice- versa Fig 11.7 though the solution is on the whole neutral, there is vicinity of any ion of predominance of ions of oppositely charge which we called counter ions.

(iii) The ions are all the time on the move in all directions but on average, more counter ions than like ions pass by any given ion. This spherical haze of opposite charge is called ionic atmosphere.

(iv) A decrease in equivalent conductivity with increasing concentration is due to fall inmobilities of the ions due to greater interionic effect and vice-versa.

(v) The ratio $\lambda v/\lambda\infty$ does not correctly give the degree of dissociation α for strong electrolytes but only conductance coefficient f_c.

(vi) Despite complete ionization, the value of λv is much than $\lambda\infty$ because of the two effects, namely the electrophoretic effect and the relaxation effect.

(a) Asymmetry or relaxation effect:

Suppose there is a central negative ion fig 11.8 This is surrounded by several positively charged ions which form its ionic atmosphere. This ionic atmosphere is symmetrically situated in the absence of any electrical field. When an electrical field is applied, the negative ion moves towards the anode and the positive ionic atmosphere toward cathode. This leaves a large number of positive ions behind it than there are at front of the negative ion with the result that the symmetry of the atmosphere about the central ion is distorted. Initially the force of attraction exerted by the ionic atmosphere on the central ion was uniform. It becomes greater now behind the ion than in front. As a result of this the negative ion experiences a force which tends to drag it backward and this slows down its movement in the forward direction. This behavior is known as asymmetry effect. It may be said that the negative ion which leaves the ionic atmosphere of positive ions behind to die away would build a new ionic atmosphere and the symmetry would be corrected.

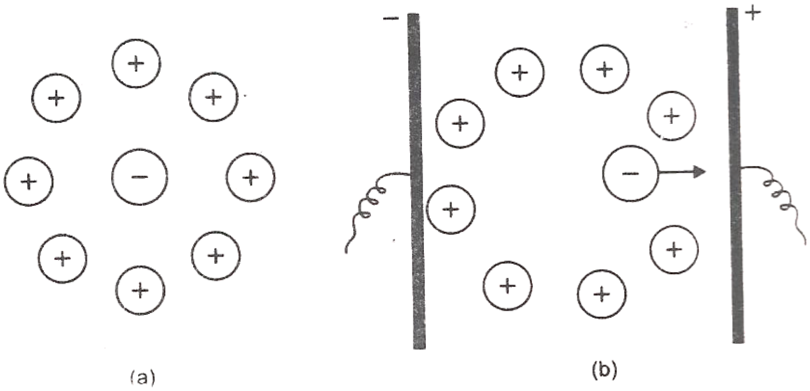


Fig 11.8 symmetric and asymmetric ionic atmospheres

If this process of building up and dying away were instantaneous there would be no cause of symmetry and the atmosphere would always be symmetrically placed about the ions. But the formation of the new ionic atmosphere does not take place at the same rate at which the old one decays and the latter lags behind or take more time known as relaxation time. For this reason, asymmetry effect is relaxation effect.

(b) Electrophoretic effect:

Another factor which acts as a drag tends to retard the motion of the ion is the tendency of the applied field to move the ionic atmosphere (to which the solvent molecules are attached) in a direction opposite to that in which the central ion associated with solvent molecules is moving. Thus the central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecule which is moving in the opposite direction i.e. , towards cathode. This causes a retarding influence on the movements of the ion. This effect is called electrophoretic effect.

Both the above causes reduce the velocity of the ion and operate in solutions of strong electrolytes with the result that a value of equivalent conductance (λ_v) lower than the value at infinite dilution ($\lambda\infty$) obtained. At infinite dilution since the electrical effects are practically absent the two values tend to approach each other.

Debye- Huckel –Onsager conductance equation:

In 1926, Debye- Huckel and Onsager worked out mathematically the magnitude of asymmetry and electrphoretic effects in term of such factors as valency of ion concentration and dielectric constant and viscosity of the medium. For univalent electrolytes such as, KCl, which furnish two univalent ions, the following equation was derived.

$$\lambda_v = \lambda\infty \ -(A+B\ \lambda\infty)\sqrt{c}$$

Where A and B are constants and c is concentration in gm-equivalent per litre. These constants depend only on the nature of the solvent and the temperature and are given by the relationship.

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad \text{and} \quad B = \frac{8.20x10^5}{(DT)^{3/2}}$$

Where D and η are the dielectric constant and coefficient of viscosity of the medium respectively at the absolute temperature T.

11.8 TRANSPORT NUMBER

11.8.1Definition: From the above discussion of the Hittorf's theoretical device as discussed above, it is evident that the number of ions discharged at each electrode depends upon the sum of the speeds or nobilities of the two ions.

Since according to Faraday's first law of electrolysis the number of ions discharged at an electrode is proportional to the total quantity of electricity passed through the solution, hence it follows that the quantity of electricity carried by a particular ion is proportional to the mobility of that particular ion. The fraction of the total current carried by the cation or anion is termed its transport number or Hittorf's number.

The transport number of cation $t_+ = \frac{v_+}{v_+ + v_-}$

The transport number of anion $t_- = \frac{v_-}{v_+ + v_-}$

Or $\frac{t_+}{t_-} = \frac{v_+}{v_-}$ and $t_+ + t_- = 1$

if the ratio $\frac{v_+}{v_-}$ is denoted by r we have, and

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and $t_- = \frac{1}{1+r}$

11.8.2 Determination of transport number:

There are two methods for determination of transport number of an ion

(i) Hittorf's method

(ii) Moving boundary method.

(i) Hittorf's method:

This method is based on the concentration changes observed in the vicinity of the electrodes. According to Hittorf's rule, the loss of concentration around any electrode is proportional to the speed of the ion moving away from it. The apparatus used in this method consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stopcocks at the bottom. The U-tube is also provided with the stopcocks at the top of the two limbs fig 11.9. By closing these stopcocks, the communication between the solution in the cathode and anode limb can be stopped. The silver anode is sealed in a glass-tube and the cathode is a piece of freshly silvered foil. The apparatus is filled with a solution of silver nitrate and a steady current of about 0.01 ampere is passed for two to three hours. It is an important precaution and the current is passed only for a short time so that too large a change in connection does not take place. The apparatus is connected with a silver or copper voltmeter (coulometer) as shown in the fig 11.9. This shows the circuit of the experiment.

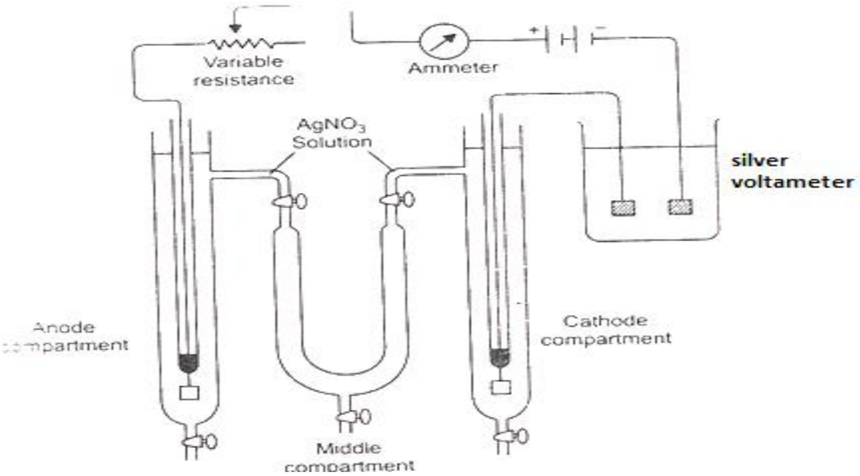


Fig 11.9 Hittorf's apparatus for determining transport number

When the current has been passed for about three hours, the stopcocks at the top of the U-tube are closed. The whole of the liquid in the anode compartment is carefully drained into a weighing flask and its weight determined. Its silver content is determined by titrating against a standard solution of potassium thiocynate. The weight of silver deposited in the silver coulometer is also noted if a copper coulometer is used in place of silver coulometer. The weight of silver equivalent to the copper deposited is calculated by multiplying it with 108/31.5. There should be no change in the concentration of the solution in the U-tube if the experiment has been successfully performed.

If the above experiment has been performed by using silver electrode, in this case nitrate ions attack the silver anode. Consequently, there is increase in concentration of Ag^+ ions rather than decrease. The same experiment can be performed by using platinum electrodes to avoid the attack of ions on the anode.

Calculations:

Two different cases may arise:

Case I: When electrodes are un-attackable (Pt electrodes are used) after passing electric current;

Let weight of anodic solution taken out = a g

Weight of $AgNO_3$ present in it by titration = b g

Weight of water = (a-b) g

Before passing electric current:

Let weight of $AgNO_3$, in (a-b) g of water before passing the electric current be = c g

Hence fall in concentration

$$= \text{(c-b) g of } AgNO_3$$

$$= \frac{c-b}{170} \text{ g eqvt of } AgNO_3$$

$$= \frac{c-b}{170} \text{ g equivalent of Ag = d (say)}$$

Let the silver deposited in the silver voltameter be

$= w_1$ g

$= \frac{w_1}{108}\, g$ eqvt of Ag

= W g eqvt of Ag (say)

Transport number of Ag^+ (Ag+) $= \frac{Fall\ in\ concentration\ around\ anode\ in\ g\ eqvt}{Amt\ of\ Ag\ deposited\ in\ g\ eqvt} = \frac{d}{w}$

And transport number of NO_3^- ion (t NO_3) = $1 - \frac{d}{w}$

Case II: When electrodes are attackable (Ag electrodes are used)

increase in concentration of anodie solution = (b-c) g of $AgNO_3$

$$= \frac{b-c}{170}\ x\ 108\ g \text{ of Ag}$$

$$= \frac{b-c}{170} \text{ g eqvt of Ag}$$

= e say

If no Ag^+ ions had migrated from the anode, the increase in concentration of Ag^+ ions would have been equal to w

Hence fall of concentration due to migration of Ag^+ ions=w-e

Hence transport number of Ag^+ ion (t_{Ag+}) = $\frac{w-e}{w}$

And transport number of ${NO_3}^-$ ion (1- $\frac{w-e}{w}$)

(ii) Moving boundary method:

The moving boundary method is based on the direct observation of migration of ions in an electric field. This method is very accurate and has been used in recent years for precision measurement

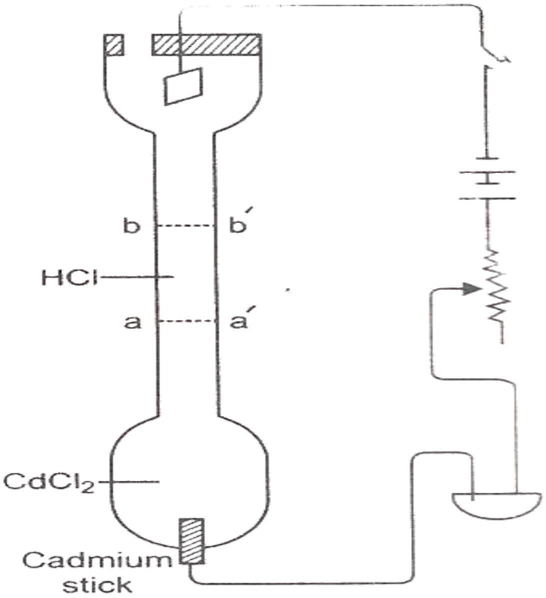


Fig 11.10 The moving boundary method for determination of transport number

The apparatus used consists of a long vertical tube fitted with two electrodes at the two ends, as shown in fig 11.10. The tube is filled with a solution of cadmium chloride ($CdCl_2$) at the lower end and hydrochloric acid at the upper end in a way that there is a sharp boundary between the two. Here we have to determine the transport number of H^+ ions, hence HCl solution is taken. The selection of indicator electrolyte is chosen in such a way (in this case $CdCl_2$) that the cation should not move faster than the cation whose transport number is to be determined. The platinum cathode dipped in HCl solution is inserted at the top and the anode (cadmium stick) is introduced at the bottom. On passing electric current through the apparatus, hydrogen gas is evolved at the cathode and H^+ ions move toward the cathode. The H^+ ions are replaced by Cd^{2+} ions and hence the boundary line moves in the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell the transport number of H^+ ion can be calculated.

In general, if the transport number of cation A^+ is to be determined, the electrolyte AX solution is taken in the upper part of the apparatus and a layer of another electrolyte BX (known as indicator electrolyte) is selected so that the velocity of B^+ ion is less than A^+ ion. In such a case, the solution is described in Fig 11.11.

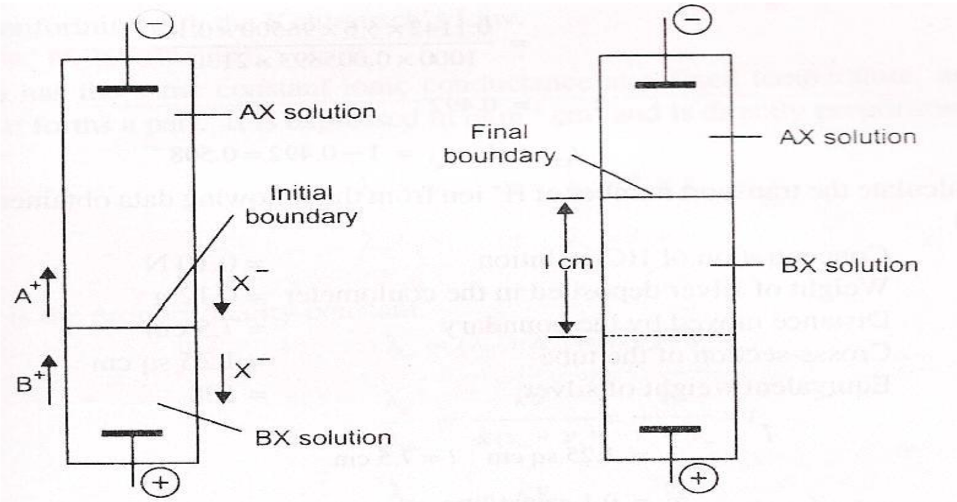


Fig 11.11 Moving boundary experiment for determining the transport number of A^+ ion.

Calculation:

Let c be the original concentration of A^+ ion in gram-equivalents per ml of the solution. If the distance through which the boundary moved = l cm, the area of the cross-section of the tube= s sq cm.

Then the number of equivalents of A^+ moving upward = $s x l x c$

Let the number of faradays of current passed = n

The fraction of current carried by A^+ ions = $n \; x \; t_{A+}$

Here $n \; x \; t_{A+} = s \; x \; l \; x \; c$

and $t_{A+} = (s \; x \; l \; x \; c \; x \; F)/Q$

Where n=Q/F, Q being the quantity of current passed and F stands for Faraday (=96500 coulombs)

Example:

Calculate the transport number of H^+ and Cl^- ions from the following data obtained by moving boundary method:

Concentration of HCl solution = 0.10N

Weight of silver deposited in the coulometer = 0.12g

Distance moved by the boundary =7.5 cm

Cross-section of the tube = 1.25 sq cm

Equivalent weight of silver = 108

Solution:

s = 1.25 sq cm , l =7.5 cm

c = 0.1 g eqvt/litre

= 0.1/1000 g eqvt/ml

108 g silver = 1 Faraday

0.12 g silver = $\frac{.12}{108}$ = .00111

Now $t_{H^+} = s \, x \, l \, x \, c/n$ = 1.25x7.5x0.1/1000x0.0011

= 0.852

And transport number of Cl^- =1-0.852

= 0.148

11.9APPLICATION OF CONDUCTIVITY MEASUREMENTS

11.9.1 Determination of degree of dissociation:

Degree of dissociation of a weak electrolyte (α) is given by

$$\alpha = \frac{\Lambda c}{\Lambda 0}$$

Where, Λ_c = Equivalent conductance at the concentration c.

Λ_0 = Equivalent conductance at the zero concentration (infinite dilution)

Knowing the value of Λ_c and Λ_0 , α can be calculated.

11.9.2 Determination of K_a of acids:

Relation between dissociation constant K_a and degree of dissociation α is given by:

$$K_a = C \frac{\alpha 2}{1-\alpha}$$

Knowing the degree of dissociation, dissociation constant can be calculated.

α can be calculated by: $\alpha = \frac{\Lambda c}{\Lambda 0}$

and, Λ_c can be obtained by using the formula, $\Lambda_c = (\kappa \times 1000) / c$

Where, κ is specific conductance.

11.9.3 Calculation of the solubility products of sparingly soluble salts:

Conductance measurement can be used for measurements of solubility of slightly soluble substances like $BaSO_4$, $PbSO_4$, AgCl etc. The method is based on the difference in the conductance of the ions of the salts. When a sparingly soluble salt is placed in water, a very little amount of the salt dissolves in the water and a solution is created. The solubility of such salts can be calculated by the application of Kholrausch's law and conductance measurements. The molar conductance (Λ_m) of a saturated solution as given by equation-

$$\Lambda_m = (\kappa \times 1000)/c$$

where κ is the specific conductance and 'c' is the concentration of the solution in mol L^{-1}. 'c' is the concentration of the salt in eq/l and hence the solubility of the salt. Since the salt is sparingly soluble, the solution is very dilute and Λ_m may be considered to be equal to Λ^0_m i.e., the molar conductance at infinite dilution. The value of Λ^0_m tor AgCl can be found by applying Kohlrausch's law of independent ionic migration.

According to this law, $\Lambda^0_{m(AgCl)} = \lambda^0_{Ag^+} + \lambda^0_{Cl^-}$ Substituting Λ^0_m in the above equation 'c' can be calculated provided κ is known. This will give the value of 'c' in mol L^{-1} from which the solubility in g L^{-1} may be calculated. Since the salt dissolves very little, the solutions are very dilute, and since the salt are strong electrolyte. Conductance offers a very easy and suitable means for determining the solubility of a sparingly soluble salt such as AgCl, $BaSO_4$, $PbSO_4$, etc. dissolved in H_2O to a very small level. That is why these salts are called sparingly soluble salts.

11.10 CONDUCTOMETRIC TITRATIONS

Titrations in which conductance measurements are made in determining the endpoint are called conductometric titrations. These are acid-alkali reactions, precipitating reactions some displacement reactions. In these measurements, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volumes of titratent. This way two linear curves are obtained, the point of intersection of which is the endpoint. The shape of curves obtained in certain types of titrations is discussed below.

11.10.1 Titration of strong acid against a strong base:

Let us consider, for example, the titration of a strong acid (HCl) with a strong base (NaOH). Take 20 ml of acid solution in the conducting cell placed in a constant temperature bath and determine its conductance. Now add 1ml of sodium hydroxide solution from the burette at a time. As the alkali is added gradually, the hydrogen ions are replaced by slow moving sodium ions as represented below,

$$H^+(aq) + Cl^-(aq) + [Na^+(aq) + OH^-(aq)] \rightarrow Na^+(aq) + Cl^-(aq) + H_2O (l)$$

Hence on continued addition of sodium hydroxide, the conductance will go on decreasing until the acid has been completely neutralized, any further addition of alkali will result in introducing fast moving hydroxyl ion, the conductance therefore, after reaching a certain minimum value will begin to increase, on plotting conductance against the volume of alkali added, the point of minimum conductance, therefore concides with the end- point of the titration fig.11.12

11.10.2 Titration of weak acid against a strong alkali:

When a weak acid is titrated against a strong alkali, we get a curve of the type Fig.11.13 (CH_3COOH /NaOH). The initial conductance of the solution is low because of the weak acid. On addition of alkali, highly ionized sodium acetate is formed

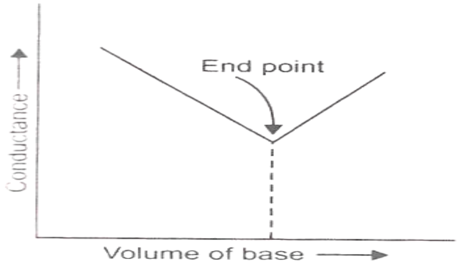


Fig. 11.12 Conductometric titration curve strong acid and strong base

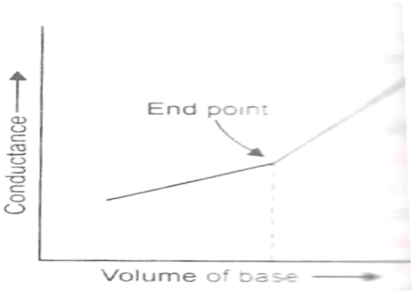


Fig. 11. 13 Curve for titration of weak acid against a strong base

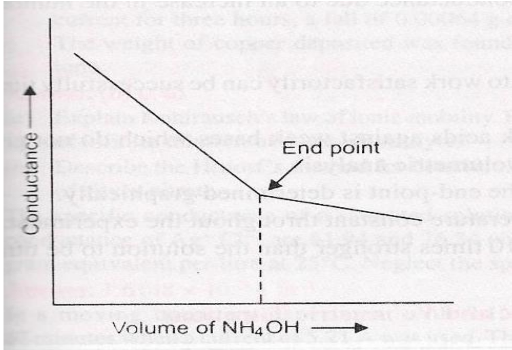
The acetate ions at first tend to suppress the ionization of acetic acid still further due to the common ion effect, but after a while the conductance begin to increase because the conducting power of highly ionized salt exceeds that of the weak acid.

$CH_3COOH \quad +Na^+ + OH^- \rightarrow CH_3OO^- + \quad Na^+ + H_2O$ **(Feebly ionized)**

Immediately after the end point, further addition of sodium hydroxide introduces the fast-moving hydroxyl ion. Thus, the conductance value shows a sharp increase the point of intersection of the two curves gives the end point fig.11.13

11.10.3 Titration of a strong acid against a weak base:

The curve obtained for the titration of a strong acid against a weak base (HCl /NH_4OH) is shown in Fig 11. 14. In this case the conductance of the solution first decreases due to the fixing up of fast-moving H^+ ion and their replacement by slow moving NH_4^+ ions.



Fog 11.14 Titration curve of strong acid against weak bas

After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small, compared to that of acid or its salt, the slope of the curve is as shown in fig.11.14.

11.10.4 Titration of weak acid and weak base:

Suppose we have to study titration of weak acid (CH_3COOH) against weak base (NH_4OH). The complete titration curve is shown in fig.11.15. The initial conductance of the solution in this case is low due to the poor dissociation of the weak acid. But it starts increasing as the salt CH_3COONH_4 is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte, the end point is quite sharp.

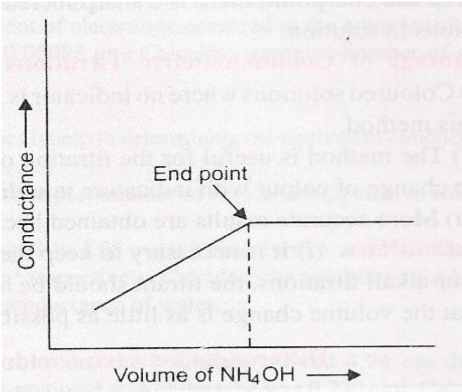


Fig11.15 Titration curve of weak acid and weak base

11.10.5 Precipitation Titrations:

The end point in precipitation reactions can be accurately determined by conductometric titration. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of potassium ion and the silver ion is of the same order. Thus, the curve is nearly horizontal fig.11.16

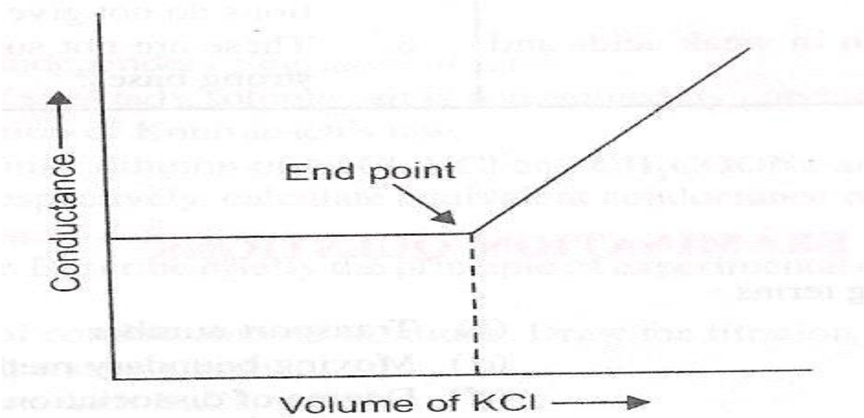


Fig 11.16 Curve for titration of KCl against AgNO

$$Ag^+ + NO_3^- + K^+ + Cl^- \rightarrow K^+ + NO_3^{--} + AgCl \text{ (ppt)}$$

After the endpoint, there is a sharp increase in conductance due to an increase in the number of free ions in the solution.

For better results, the titrations should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

11.10.6 Applications of conductometric titrations:

There are several advantages of conductrometric titrations over ordinary volumetric titrations.

(i) Colored solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(ii) The method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with an indication in ordinary volumetric analysis.

(iii) A more accurate result is obtained because the endpoint is determined graphically

Differences between conductometric and volumetric titration.

Conductometric Titrations	Volumetric Titrations
1. Conductance measurements are done to check endpoints.	1. Volume measurements are done to check endpoints.
2. Titration can be carried out even with a colored solution.	2. These titrations fail in colored solutions as suitable indicators are not available sometimes.
3. Accurate results are obtained.	3. Results are not so accurate.
4. The endpoint is determined graphically.	4. The endpoint is determined by the change in color of the indicator.
5. In the case of polybasic acids conduct metric titrations can be used.	5. In the case of polybasic acids volumetric titrations do not give correct endpoints.
6. These are successful even in weak acids and strong bases.	6. These are not successful even in weak acids and strong bases.

11.11SUMMARY

- This unit covers electrolysis, where the flow of current leads to the transfer of matter and the decomposition of substances, aiding in electron transfer.
- Key topics include transport number, Arrhenius's theory, Ostwald's law, and the theory of strong electrolytes. A significant focus is on conductometric titrations, effective for reactions where colored solutions or precipitation do not provide a sharp endpoint.

- For accurate results, titrants should be ten times stronger than the solution in the conductance cell to minimize volume changes.

11.11*TERMINAL EQUATIONS*

A. Objective type questions:

Q.1. The units of specific conductance are:

(a) ohm cm (b) ohm cm^{-1} (c) ohm^{-1} (d) ohm^{-1} cm^{-1}

Q.2. The distance between two electrodes of a cell is 3.0 cm and area of each electrode is 6.0 cm^{2}, the cell constant is

(a) 2.0 (b) 1.0 (c) 0.5 (d) 18

Q.3. When a strong acid is titrated against a strong base the endpoint is the Point of:

(a) Zero conductance (b) maximum conductance

(c) Minimum conductance (d) none of these

Q 4. The sum of the transport number of anion and cation is equal to:

(a) 1 (b) 0 (c) 0.5 (d) ∞

Q.5. The fraction of total current carried by the cation or anion is termed as:

(a) Fractional number (b) transport number

(c) Speed number (d) carrier number

Q.6. The effects that tend to retard the mobilities of ions in solution is:

(a) asymmetry effect (b) relaxation effect

(c) electrophoretetic effect (d) all of these

Q.7. During titration of weak acid against a weak base, there is a sharp increase in ________ at the end point :

(a) conductivity (b) equivalent conductance

(c) specific conductance (d) none of these

Q.8. Kohlrausch's law states that at:

(a) Infinite dilution, the equivalent conductivity of an electrolyte is equivalent to the sum of the conductances of the cations and anions

(b) Finite dilution, the equivalent conductivity of an electrolyte is equivalent to the sum of the conductances of the cations and anions.

(c) Both (a) and (b)

(d) None of the above

Q.9 Which of the following statements is correct concerning electrolytic solutions?
(a) Its conductance increases with dilution
(b) Its conductance decreases with dilution
(c) Its conductivity increases with dilution
(d) Its equivalent conductance decreases with dilution
Q.10. Which of the following solutions cannot conduct electricity?
(a) NaCl in water (b) $MgCl_2$ in water
(c) Sugar in water (d) KCl in water

B. Short Answer type questions:

Q.1 Define the terms:

(a) Electrolysis

(b) Specific conductance

(c) Transport number

(d) Equivalent conductivity

Q.2 Define and explain the following terms:

(a) Degree of dissociation

(b) Kohlrausch law

(c) Arrhenius theory

(d) Precipitation titrations

C. Long answer type questions:

Q. 1 What is the Ostwald's dilution law? How it is verified? What are its limitations?

Q. 2 (a) State and explain Faraday`s law of electrolysis

(b) On dilution, specific conductance of an electrolyte decreases and equivalent conductance increases. Discuss

Q.3. State and explain Kohlrauschs`s law of independent migration of ions. How does it help in determining the equivalent conductivity at infinite dilution of weak electrolytes?

Q.4.Explain Relaxation effects as used in Debye- Huckel theory.

Q.5.Define 'Transport number'. Briefly describe 'moving boundary method' for the determination of transport number.

11.13. ANSWERS

1.(d)	**2.** (c)	**3.** (c)	**4.** (a)	**5.**(b)
6.(d)	**7.**(a)	**8.**(a)	**9.** (a)	**10**.(c)

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UNIT 12: ELECTROCHEMISTRY-II

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12.13 References

12.1 INTRODUCTION

Electrochemistry is the branch of physical chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice-versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus, electrochemistry deals with the interaction between electrical energy and chemical change.

When a chemical reaction is caused by an externally supplied current, as in electrolysis, or if a spontaneous chemical reaction produces an electric current as in a battery, it is called an electrochemical reaction. Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

12.2 OBJECTIVE

- In the previous unit much has been discussed about electrolysis, electrical transport, conduction, Ohm’s law factors affecting electrolysis, electrolytic dissociation, Arrhenius's theory of electrolyte dissociation, transport number, determination of transport number by different methods, Conductance, etc.
- Ostwald’s dilution law, its failure in the case of strong electrolytes, and the theory of strong electrolytes have been discussed in detail. Much emphasis has been given to Kohlrausch’s law and its applications, particularly conductometric titration.

12.3 TYPES OF REVERSIBLE ELECTRODES

For thermodynamic treatment of galvanic cells, these cells must operate in a thermodynamically reversible manner. To find out if a given cell is reversible or not, it is connected to an external source of EMF acting in the opposite direction. The cell will be reversible if it satisfies the following conditions:

(i) If the opposing EMF is exactly equal to that of the cell itself, no current is given out by the cell and no chemical reaction takes place in the cell.

(ii) If the opposing EMF is infinitesimally smaller than that of the cell itself, an extremely small current is given out by the cell and a correspondingly small amount of the chemical reaction takes place in the cell.

(iii) If the opposing EMF is infinitesimally greater than that of the cell itself, an extremely small current flows through the cell in the opposite direction and a small amount of the chemical reaction also takes place in the reverse direction.

Some common types of reversible electrodes are given below: -

12.3.1 Gas electrode:

Hydrogen electrode:

Hydrogen gas bubbling at one-atmosphere pressure in a solution of hydrochloric acid constitutes hydrogen electrode Fig 12.1 It is represented as:

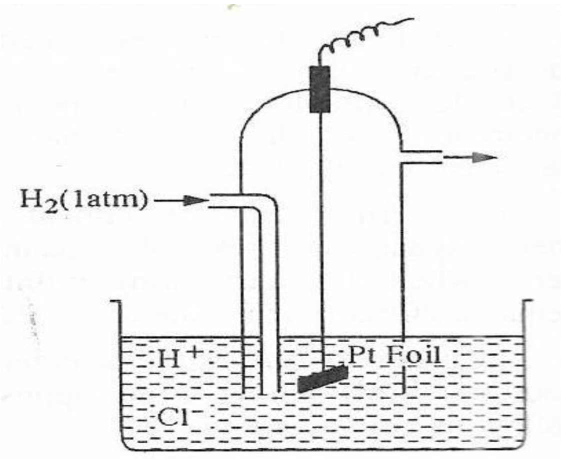


Fig 12.1 Hydrogen Electrod

Pt/H_2 (1 atm.)/H^+ (a=1) or Pt; H_2(g), H^+.

On account of hydrogen being a gas, a special device is made to make the potential difference between the gas and the solution measurable. This device consists of placing a small strip of platinized platinum foil such that it is half immersed in the solution and half surrounded by the gas. The finely divided platinum on platinum foil absorbs hydrogen and, in that condition, behaves as if, it was a solid electrode of the gas. It freely permits the change from the gaseous state to the ionic state and vice versa.

12.3.2 Metal-metal ion electrode:

An electrode of this type consists of a metal rod dipping in a solution containing its ions. For example, zinc rod dipping in zinc sulphate solution or copper rod dipping in copper sulphate solution as you have studied in 12.1 above. The electrode reaction may be represented in general as

$$M^+ (aq) + e^- \longrightarrow M(s)$$

If the metal rod behaves as a positive electrode (i.e., the reaction at the electrode involves reduction), the equilibrium will shift towards the right. The concentration of M^+ ions in solution will, therefore, decrease.

If on the other hand, the metal rod behaves as a negative electrode (i.e., the electrode reaction involves oxidation), the above equilibrium shifts towards the left. The concentration of the M^+ ion in the solution will, therefore, increase fig 12.1.

12.3.3 Metal-insoluble metal salt electrodes:

This electrode consists of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. An important electrode of this type is the calomel electrode. Calomel electrode consists of mercury, solid mercurous chloride, and a solution of potassium chloride. The electrode is represented as Hg, Hg_2Cl_2 (5); KCl (solution).

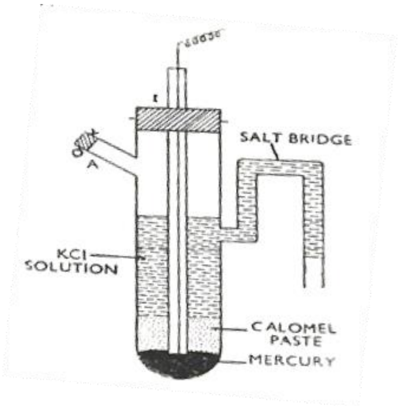


Fig 12.2 The calomel elec.

It can be easily setup in the laboratory as follows:

Mercury of high-grade purity is placed at the bottom of a glass tube having a side tube on each

side; it is known as a calomel vessel fig 12.2 Mercury is covered by a paste of mercurous chloride (calomel), as shown. A solution of potassium chloride is introduced above the paste through the

side tube. The concentration of the solution is either decinormal, or normal, or else the solution is fully saturated. A tube t containing mercury and with fused in platinum wire at its lower end to serve as contact with the mercury of the electrode is then introduced. The tube should contain sufficient mercury to sink the platinum contact to rest on the base of the tube. The side tube is filled with a jelly of agar-agar and KCl. This tube is connected with the help of this tube through a salt bridge with the other electrode, the potential of which is to be determined.

12.3.4 Oxidation-reduction electrodes:

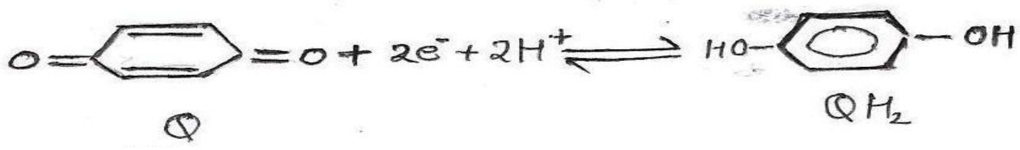
The term, oxidation-reduction electrode is used for those electrodes in which the potential is developed from the presence of ions of the same substance in two different valance (i.e., oxidation) states. Such an electrode is set up by inserting an unattackable metal such as platinum into an appropriate solution. Thus, when a platinum wire is inserted in a solution containing Fe^{2+} and Fe^{3+} ions it is found that the wire acquires potential. The potential at the electrode arises from the tendency of the ions in one oxidation state to change into a more stable oxidation state.

The electrode reaction may be represented as follows:

$$Fe^{3+} (aq) + e^{-} \rightleftharpoons F_{e}^{2+} (aq)$$

The function of the platinum wire is to pick up the electrons and provide electrical contact to the electrode.

Another important type of oxidation reduction is the quinhydron electrode. This electrode consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equimolar amounts. The electrode reaction in this case is represented as follows



This electrode may be represented as:

Pt, Q, QH_2; H^+ (aq), is reversible concerning H^+ ions.

12.4 ELECTRODE REACTIONS

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the cell reaction. Thus, as a simple voltaic cell, we have

(a) Half reactions:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(ag) + 2e^- \longrightarrow Cu(s)$$

(b) Cell reaction by adding up the half-reactions:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2}(aq) + Cu(s)$$

In the Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electric repulsions. The copper electrode gets a positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted to this electrode. The flow of current through is determined by the ‘push’ of electrons at the anode and the ‘attraction’ of electrons at the cathode. These two forces constitute the driving force or electrical pressure that sends electrons through the circuit. This driving force is called the electromotive force (e.m.f.) or cell potential. The e.m.f. or cell potential is measured in units of volts (V) and is also referred to as cell voltage.

12.4.1Cell diagram or representation of a cell:

A cell diagram is a depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of the metal electrode in contact with metal ions in solution.

In 1953 **IUPAC (International Union of Pure and Applied Chemistry)** recommended the following conventions for writing cell diagrams. Let us illustrate these concerning zinc-copper cell.

(i) A single vertical line:

In this representation (/) represents a phase boundary between the metal electrode and ion solution. These the two half cells in a voltaic cell are indicated as

Zn / Zn^{2+} Cu^{2+} / Cu phase boundary

Anode half-cell Cathode half-cell

It may be noted that the metal electrode in the anode half-cell is on the left, while in the cathode half-cell, it is on the right of the metal ion.

(ii) A double vertical line:

The double vertical line represents the salt bridge, porous partition, or any other means of permitting ion flow while preventing the electrolyte from mixing.

(iii) Anode half-cell is written on the left and cathode half-cell on the right.

(iv) In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

$Zn/Zn^{2+} \parallel Cu^{2+}/Cu$ salt bridge

Anode half-cell cathode half-cell

(v) The symbol of an inert electrode like a platinum electrode is often enclosed in a bracket. For example:

$Mg/Mg^{2+} \parallel H^{+}/H_2\ (Pt)$ inert electrode

12.4.2 Convention regarding the sign of e.m.f. value:

The magnitude of e.m.f. of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in the case of Daniel's cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the e.m.f. of the cell is given the +ve sign. If the e.m.f. acts in the opposite direction through the cell circuit it is quoted as –ve value. For, Daniell cell has an emf of 1.1V and the coper electrode is positive. This can be expressed in two ways:

$Zn /ZnSO_4 \| CuSO_4 |Cu \qquad E=1.1V$

$Cu/CuSO_4 \| ZnSO_4/Zn \qquad E=-1.1V$

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

12.4.3 Calculating the emf of a cell:

The e.m.f. of a cell is calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= E_R - E_L$$

Where E_R and E_L are the reduction potentials of the right-hand and left-hand electrodes respectively. It may be noted that the absolute values of these reduction potentials cannot be determined. These are found by connecting the half-cell with a standard electrode whose reduction potential is known.

12.5 NERNST EQUATION: EFFECT OF ELECTROLYTE CONCENTRATION ON ELECTRODE POTENTIAL

Suppose the reaction occurring in a galvanic cell is represented as:

$$aA + bB \rightleftharpoons cC + dD$$

Suppose in a particular cell reaction, n is the number of electrons liberated at one electrode (or taken up at the other electrode) then evidently, n faradays (nF) of electricity will be generated in the complete cell reaction. If, for the sake of simplicity, the emf of the cell is denoted by E, then, the electrical energy produced by the cell = nFE Hence $-\Delta G = nFE$

Then from Van`t Hoff isotherm, we know that the thermodynamic potential change would be

$$\Delta G = \Delta G^0 + RT \ln K$$

Since $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$

The other equation becomes

$$E = E^0 - \frac{RT}{nF} \ln K$$

Where, E^0 =standard electrode potential

R = gas constant,

T = absolute temperature,

n = number of electrons transported in the half reaction,

F = faraday of electricity,

K = equilibrium constant,

For oxidation hall-cell reaction when metal electrode M gives M^{2+} ions:

$$M \longrightarrow M^{2+} + 2e^-$$

$$E = E^0 - \frac{RT}{2F} \ln\left(\frac{M}{M^{2+}}\right) \quad \text{For solids M = 1}$$

Then $E = E^0 + \frac{RT}{2F} \ln(M^{2+})$ ……………..……………….(12.1)

This equation (1), which gives the effect of concentration of M^{2+} ion on the potential of M^{2+}, M electrode is known as the Nernst equation.

In the case of the hydrogen electrode, the equation is represented as:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Hence $E = E^0 + \frac{RT}{F} \ln[H^+]$ ……………………………………….(12.2)

Because the activity of H_2 gas at one-atmosphere pressure is taken as unity. Here E^0 for the hydrogen electrode is arbitrarily taken as zero, we have

$$E = \frac{RT}{F}\ln(H^+) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(12.3)$$

In the case of Fe^{3+}, Fe^{2+} electrode, the equilibrium is represented as

$$Fe^{3+}(aq) \ + \rightleftharpoons Fe^{2+}(aq)$$

Here

$$E = E^0 - \frac{RT}{F}\ln\left[\frac{Fe^{2+}}{Fe^{3+}}\right]$$

$$= E^0 - \frac{RT}{F}\ln\left[\frac{Fe^{3+}}{Fe^{2+}}\right]$$

It follows from the above discussion that if we write the electrode reaction, in general as:

$$\text{Oxidized state} \ + \ ne^- \ \rightleftharpoons \ \text{reduced state}$$

$$E = E^0 - \frac{RT}{F}\ln\left[\frac{\text{reduced state}}{\text{oxidised state}}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(12.4)$$

12.6 DERIVATION OF CELL E.M.F. AND SINGLE ELECTRODE POTENTIAL

EMF of a Cell: The electromotive force of a cell is known as EMF of a Cell (EMF). It refers to the utmost potential difference between the two electrodes within the cell. Another way to express it is as the overall voltage generated by the oxidation and reduction of half-reactions. The primary application of the EMF of a Cell is to determine the galvanic or non-galvanic nature of an electrochemical cell.

Considering the nature of potential in this context, the potential of a single half-cell or a single electrode can't be measured; the "transfer" of electrons requires both a donor and recipient, in this case, a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called **cell potentials, E_{cell},** defined as

$$E_{cell} = E_{cathode} - E_{anode}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0.0 V. This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see Fig12.3**).**

This approach to measuring electrode potentials is illustrated in Figure 12.3, which depicts a cell comprised of an SHE connected to a copper (II) /copper (0) (Cu^{+2}/ Cu) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections ensure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V (standard reduction potential) is measured, and so,

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = +0.337\ V - 0.00V$$

$$E°_{cell} = E°_{Cu+2/\ Cu} = +0.337\ V$$

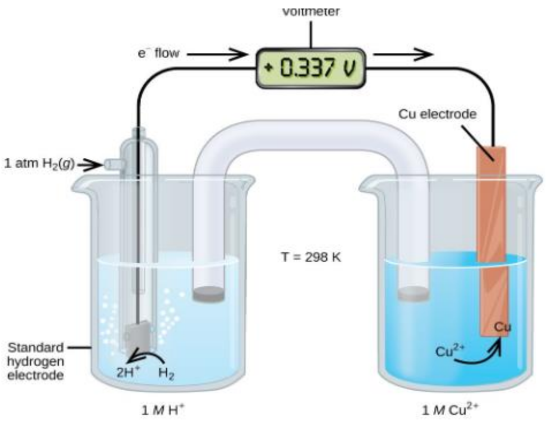


Fig. 12.3 Measurement of the standard electrode potential for the half-reaction

Cu^{+2}/ Cu electrode using hydrogen electrode as the reference electrode.

A cell permitting experimental measurement of the standard electrode potential for the half-reaction $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

12.7 STANDARD HYDROGEN ELECTRODE

The potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity (or, to be approximate, 1M concentration) has been fixed as zero. This electrode is known as standard hydrogen electrode (fig 12.4) and is represented

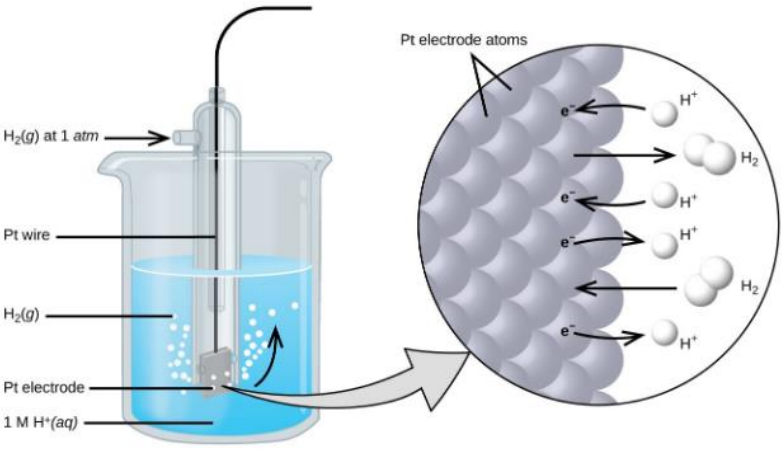


Fig 12.4 Standard hydrogen electrode

as: Pt; $H_2(g)$ (1atm), $H^+(aq)$ (c=1M)

All other single electrode potentials measured with respect to standard hydrogen electrode are referred to as potentials on the hydrogen scale.

If it is required to find the electrode potential of, say, zinc electrode dipping in a solution of zinc sulphate (i.e., Zn, Zn^{2+} electrode), all that is needed is to combine it with the hydrogen electrode so as to have a complete cell represented as:

Zn, Zn^{2+} (aq)/H_2 (g) (1 atm); H^+(aq) (C=1M) ; Pt

The e.m.f. of the cell determined potentiometrically, is then equal to potential of the zinc electrode (on the hydrogen scale) since potential of the standard hydrogen electrode is taken as zero.

In this case, reduction occurs at the hydrogen electrode and oxidation takes place at the zinc electrode shown below:

Hydrogen electrode:

$$2H^{+} (aq) + 2e^{-} \rightleftharpoons H_2 (aq)$$

Zinc electrode:

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^{-}$$

∴ The net reaction is

$$Zn(s) + 2Hg^{+} (aq) \rightleftharpoons Zn^{2+} + H_2 (g) (1atm)$$

If copper electrode is connected with the hydrogen electrode the oxidation takes place at the hydrogen electrode and reduction occurs at the copper electrode. The net reaction is then

$$H_2 (g) + Cu^{2+} (aq) \rightleftharpoons Cu(s) + 2H^{+}(aq).$$

12.8 STANDARD ELECTRODE POTENTIAL

The potential of an electrode at a given temperature we have discussed above, depends upon the concentration of the ion in the surrounding solution, if the concentration of the ions is unity and temperature 25^{0}C, the potential of the electrode is termed as the standard electrode potential. Thermodynamic quantities, the **standard cell potential, $E°_{cell}$**, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

Significance of Standard Electrode Potential

- All electrochemical cells are based on redox reactions, which are made up of two half-reactions.

- The oxidation half-reaction occurs at the anode and it involves a loss of electrons.Reduction half-reaction reaction takes place at the cathode, involving a gain of electrons. Thus, the electrons flow from the anode to the cathode.
- The cell potential of an electrochemical cell can be measured with the help of a voltmeter.
- In order to obtain the individual reduction potential of a half-cell, the need for standard electrode potential arises.It is measured with the help of a reference electrode known as the standard hydrogen electrode (abbreviated to SHE). The electrode potential of SHE is 0 Volts.
- The oxidation potential of an electrode is the negative of its reduction potential. Therefore, the standard electrode potential of an electrode is described by its standard reduction potential.
- Good oxidizing agents have high standard reduction potentials whereas good reducing agents have low standard reduction potentials.

12.9 ELECTROCHEMICAL SERIES AND ITS SIGNIFICANCE

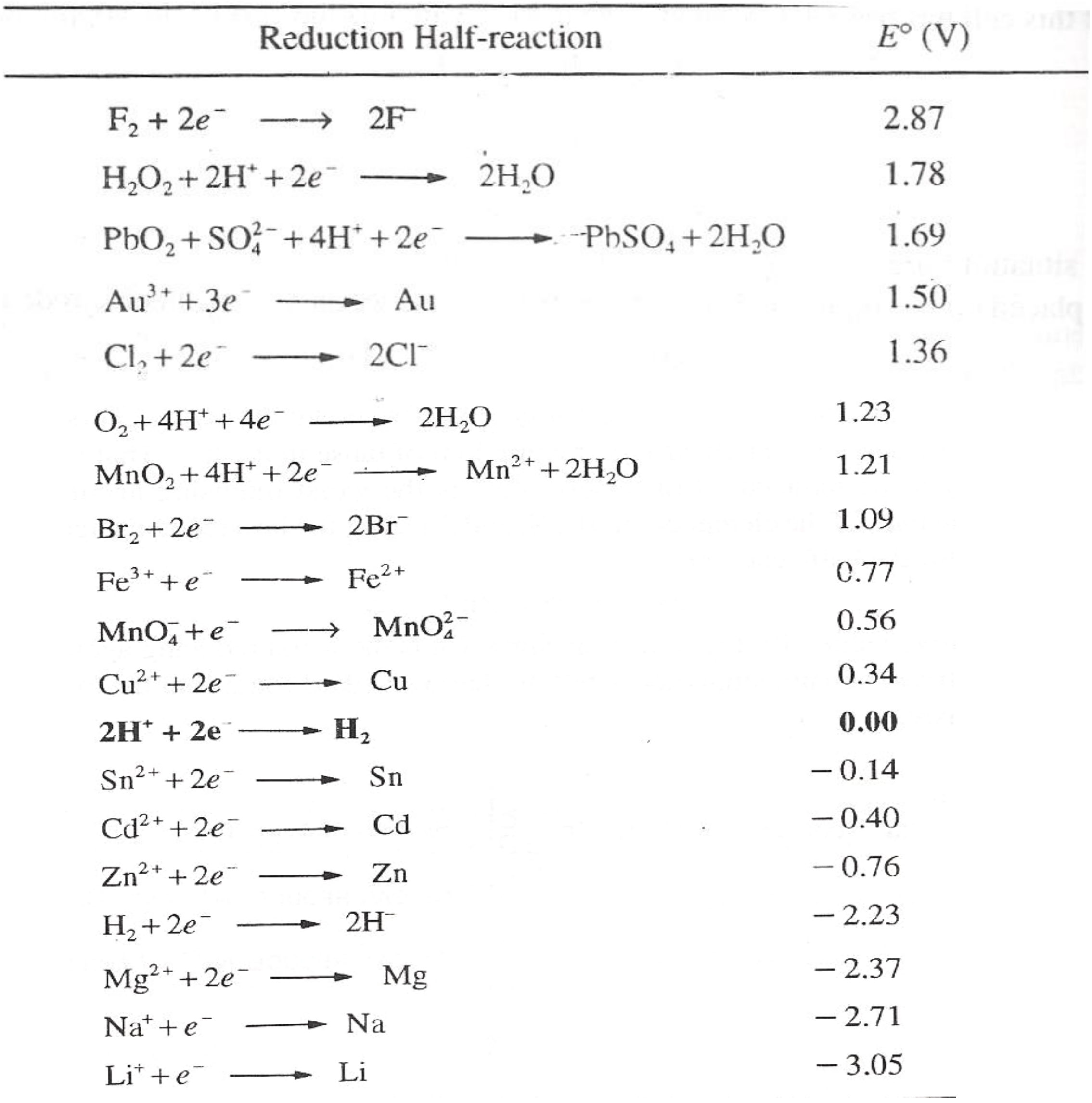
The standard electrode potential of a number of electrodes is given in the table 12.1. These values are said to be on hydrogen scale since in these determinations the potential of a standard hydrogen electrode used as a reference electrode, has been taken as zero. The values of standard electrode potentials arranged in a decreasing order constitute what is called the electrochemical series.

This table includes a large variety of electrodes (half-cell) along with their electrode reaction and standard electrode potential. The higher its positive value the greater is the tendency of the oxidized form to get reduced by accepting electrons. And, conversely, the greater the negative value, the greater is the tendency of the reduced form to get oxidized by donating electrons.

Now any two suitable half- cells can be combined to form a galvanic cell. The emf of the cell and the feasible cell reaction can be easily determined with the help of the information given in this table. For this the following rules have been suggested:

Representation of cell. The electrode on the right is written in the order: ion, electrode (e.g., Cu^{++}, Cu) and the electrode on the left is written in the order: electrode, ion, (e.g., Zn, Zn^{2+}). In the galvanic cell formed by the combination of two electrodes, oxidation occurs at the left-hand electrode and reduction at the right-hand electrode so that the electric current (electrons) in the external circuit flow from the left-hand electrode (L.H.E.) to the right-hand electrode (R.H.E.).

Table 12.1 electrochemical series, standard electrodes potential at 25^{0}C.



Reduction Half-reaction	$E°$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$\mathbf{2H^+ + 2e^- \longrightarrow H_2}$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	− 0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	− 0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	− 0.76
$H_2 + 2e^- \longrightarrow 2H^-$	− 2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	− 2.37
$Na^+ + e^- \longrightarrow Na$	− 2.71
$Li^+ + e^- \longrightarrow Li$	− 3.05

Determination of cell the potential and the emf of the cell reaction:

According to the latest convention, both the half reactions are written as reduction reaction along with their standard electrode potentials in the form of chemical equations. After balancing the number of electrons, if necessary, the half-cell reaction equation with a lower electrode potential is subtracted forms the one with a higher electrode potential. The result gives the cell potential as well as the feasible cell reaction.

The two-half-cell reaction in Daniell Cell are written a

(i) Cu^{2+} (as) + $2e^-$ $\rightleftharpoons$ Cu(s): E^0 = +0.34 V

(ii) Zn^{2+} (aq) + $2e^-$ $\rightleftharpoons$ zn(s): E^0 = -0.76

Subtracting eq. (ii) from eq. (i) we get

Cu^{2+} (aq) + Zn(s) $\rightleftharpoons$ Cu(s) + Zn^{2+}(aq) as the feasible cell reaction and

0.34– (-0.76) =1.10 V as cell potential.

12.10 SUMMARY

- In this unit the functioning of the cells has been discussed in detail. The voltaic cell also known as galvanic cell is one in which electrical current is generated by a spontaneous redox reaction.
- Different types of reversible electrodes and their functioning the functioning of hydrogen electrode and calomel electrode have been discussed in detail. Different cell reaction has also been discussed.

12.11TERMINAL QUESTION

A. Multiple choice /objective type questions:

Q.1 For the half-cell reaction O_2 (g) +$2H_2O$ (l) +$4e^-$ $\rightarrow$$4OH^-$(aq) -$\Delta G^0/FE^0$ is equal to

(a) 1, (b) 2 (c) 3 (d) 4

Q.2 In any electrochemical cell, the cathode is always…….

(a) A non-metal (b) attached to battery

(c) the electrode at which some species gain electron

(d) the electrode at which some species lose electron.

Q.3 The site of oxidation in an electrochemical cell is

(a) The anode (b) the cathode (c) the electrode (d) the salt bridge

Q.4 In the electrochemical cell, flow of electrons is from;

(a) cathode to anode in the solution

(b) cathode to anode through external supply

(c) cathode to anode through internal supply

(d) anode to cathode through internal supply

Q.5 What is the unit of EMF?

(a)Watts (b)Radians

(c)Volt (d)Seconds

Q.6 Why is Standard hydrogen electrode called as the primary reference electrode?

(a) It has a known output potential

(b) It has a constant output potential

(c) Its output potential is independent of the composition of the solution

(d) Its output potential is zero volts

Q.7 In Hydrogen electrode, the electrode is placed in a solution of ____ M Hcl. Fill in the blank.

(a) 0.0 (b) 1 (c) 2 (d) 3

Q.8 Hydrogen electrode which is the reference electrode can be used as which of the following?

(a) Anode only (b) Cathode only

(c) Anode or Cathode (d) Salt bridge

Q.9 Which of the following is not the advantage of glass electrodes?

(a) It gives accurate results for high as well as low pH values

(b) It is simple to operate

(c) It has no salt error

(d) Modern electrodes can withstand severe treatment

Q.10. In the electrochemical cell:

(a) Potential energy decreases

(b) Kinetic energy decreases

(c) Potential energy changes into electrical energy

(d) Chemical energy changes into electrical energy

B. Short answers type questions:

Q.1 Define electrochemical cell.

Q.2 What do you mean by electrode potential.

Q.3 Write a short note on redox reactions.

C. Long answer type questions:

Q.1 Describe the construction and working of calomel electrode.

Q.2. Explain the term electrode potential. Derive Nernst equation for describing the effect of concentration of electrolyte on electrode potential. What is meant by standard electrode potential?

Q.3. What is Electrochemical series. Discuss its important uses?

Q.4 Derive the cell EMF and single electrode potential of cell?

12.12ANSWERS

1.(d)	**2.** (c)	**3.** (a)	**4.**(c)	**5.** (c)
6.(d)	**7.**(b)	**8.**(c)	**9.**(a)	**10**.(d)

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BLOCK –V: LABORATORY WORK

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 Introduction
13.2 Objective
13.3 Purpose of laboratory & chemical safety
13.4 Types of hazards in the laboratory and their prevention
13.5 Laboratory safety
13.6 Assess and minimize the risk of the hazards
13.7 Summary
13.8 Bibliography

13.1 INTRODUCTION

In the laboratory, it requires great care and attention to avoid safety hazards occurring due to delicate lab instruments, open flames, hazardous chemicals etc. Negligent handling of dangerous/harmful chemicals can result in both short-term (acute) and long-term (Chronic) health issues. Burns, eye injuries, lung diseases, asphyxiation, and suffocation are some of these potential issues. Chemicals cause adverse reactions in the body through ingestion, inhalation, skin contact, and percutaneous exposure. No matter how much is being used or how it is used, a substance, operation, or activity has intrinsic hazardous characteristics or properties. Various risks to human health and physical injury can be posed by chemicals given below:

Health Hazards	Physical Hazards
Toxic	Combustible
Carcinogenic	Flammable
Mutagenic	Explosive

Reproductive toxins	Reactive or pyrophoric
Sensitizers	Oxidizers
Irritants and Corrosives	Corrosive
Asphyxiants	Compressed Gas and Liquid

The chemistry practical could involve a minor incident. Inform your teacher or the lab attendant right away, remain calm, do not panic, and use the first aid provided in the laboratory.

However, if any of these symptoms occur, you should immediately stop working, take off your protective equipment, wash your hands, and contact your healthcare provider.

- Unusual taste or odor,
- Respiratory irritation, coughing, choking, or shortness of breath,
- Sudden headache, dizziness, blurred vision, or loss of consciousness,
- Burning or painful sensation,
- Swelling, reddening, or itching skin.

13.2 OBJECTIVE

After completing this unit learners will be able

- To know 'What is a laboratory hazard'? The physical hazards and the chemical hazards in the laboratory.
- How to prevent chemical hazards in the laboratory.
- To know the effect of laboratory incidents on learner's health, such as heat burns, glass cuts, and the inhalation of gas.
- To assess and reduce the risks associated with chemical hazards in the laboratory.

13.3 PURPOSE OF LABORATORY & CHEMICAL SAFETY

- To promote safety awareness and encourage safe working practices in the laboratory.
- Safety guidelines should serve as a reminder of things you can do to work more safely and apply to all users of the laboratory.

- All learners are expected to adhere to safety guidelines and maintain safety standard strictly.

13.4 TYPES OF HAZARDS IN THE LABORATORY AND THEIR PREVENTION

Chemical and physical hazards in the laboratory fall into five major categories. Now discuss each category in details with their prevention in the laboratory.

- Chemical burns
- Heat burns
- Eyes injuries
- Injury from glassware
- Inhaling dangerous gases

13.4.1 Chemical burns

Acids, bases, etching solutions and solvents are commonly used in chemistry lab and classified as corrosive substance, and also present a serious health hazards such as chemical burns, tissue damage, organ damage, asphyxiation, corneal damage, which can lead to blindness and genetic damage if used improperly.

(Burns are a common type of hazard when dealing with harmful substances).

- Wear the gloves when working in lab.
- If the skin burns with acid, wash it with ammonium hydroxide, while in case of concentrated H_2SO_4 wash affected part with Barium chloride solution and then with cold water and apply burnol.

- If the skin burns due to the concentrated/ strong alkali (base), washed it with acetic accident finally with cold water and apply burnol. If the injury is deep then immediately contact with the health consultant/doctor.

13.4.2 Heat burns

Burners and other heating devices are frequently used in laboratories to expedite chemical reactions and processes. As with any activity that involves fire, it is important to be aware of the potential risks associated with heat-related injuries. If exposed to temperatures higher than 70°C, it is likely that a burn will occur, even if the skin is only exposed for a split second.

It is essential to maintain a safe distance away from open flames and heating devices in order to reduce the likelihood of heat-related burn injuries in the laboratory.

(The heat generated by Bunsen burners can create a range of serious physical hazards for laboratory learner who are using the equipment)

- Skin clothing and protective equipment should be kept away from any other combustible materials in the vicinity. Furthermore, it is imperative to ensure that burners are not left on after use.
- If a heat-related burn occurs while in the laboratory, it is recommended to immediately put the affected area in cold running water and hold it for a few minutes before allowing the burning sensation to subside. After that apply coconut oil or burned on the burnt part.

13.4.3 Eye injuries

In the laboratory at the time of working, you need to be aware of the chemicals that can be harmful to your eyes. You can be exposed to chemicals if you accidentally release liquids or gases that can damage your eyes. The severity of your injury depends on hazardous properties of chemical are and how much you have been exposed to it. For instance, if you get a mild eye injury from exposure to a chemical, it could just cause redness and irritation. But if you get a really bad eye injury, it could lead to permanent blindness. To prevent eye injuries in the lab, you need to wear the right protective eyewear.

- If the eyes injuries occur due to some pungent vapors in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still etching persists consult an eye doctor immediately.
- If a chemical solution or dust particle enters into eye then wash your eye with cold water until you feel relief.
- If acid has been entered into the eye, then the eye must be washed with a dilute solution of alkali sodium bicarbonate solution a few times and after that with cold water till you feel relief. an eye doctor.
- If base/alkali has been entered into eye then eye must be washed with dilute boric acid solution and finally washed with cold water till irritation persists. If still problem exist immediately consult an eye doctor.

13.4.4 Injury from glassware

The use of laboratory glassware for the storage and mixing of hazardous chemicals is a common practice; however, there is a risk of laboratory glassware breaking. If the glass is broken, it can expose sharp edges, particularly if it is very thin, which can cause severe eye and skin damage. Therefore, it is important to take steps to reduce the risk of glass breaking in laboratories.

- In order to prevent cuts from glassware, it is important to handle the glassware with caution. It is recommended to hold the glassware in a secure grip and to avoid handling the glassware with wet or wet hands.
- It is important to ensure that when glassware is not in use, it is stored in a safe and secure place where there is no potential for it to fall and shatter. If glassware is not stored in an accessible cupboard with a well-maintained and even surface, it is likely to fall and break, potentially exposing to physical injury.

- If the is due to the breakage of some glassware, glass apparatus, wound washed with sprit and then aqueous alum solution because alum is antiseptic in nature and can also help in stop bleeding by coagulation.
- It is essential to take prompt action in the case of a glass cut in order to avoid the development of an infection. If a cut is sustained from glassware, the first aid officer/doctor should be contacted so that they will dress the wound.

13.4.5 Inhaling dangerous gases

A wide variety of hazardous chemicals emit toxic vapors and gases that pose a risk to human life. The health consequences associated with exposure to these hazardous vapors can be classified as acute, chronic, or both. Acute consequences are those that occur immediately after exposure to the vapors. Chronic consequences are those that do not occur immediately but occur months and even years after exposure. Heath effects of gas inhalation can include symptoms such as:

Irritation to mucous membranes in the nose, throat, respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing etc.

- If you feel any symptoms occurs due to the inhalation of gas first go away from the working place (lab) in the open place. If still feel some problems consult with doctor immediately.

13.5 LABORATORY SAFETY

In the laboratory following safety will be taken while working in the lab.

(i) Laboratory hygiene
(ii) Fire safety
(iii) Chemical safety
(iv) Personal safety

(i) Laboratory hygiene

- Scrub hands thoroughly when finished.
- Avoid cross contamination
- Do not touch self, faucets, doorknobs, notebooks, pens etc. with gloves on.
- Keep a pen or two in your drawer for lab use only.

- Clean and disinfect your workspace

(ii) Fire safety

- Never leave flames unattended.
- Do not use flammables near ignition sources.
- Fire Extinguishers
- Fire Blanket
- Fire alarm pulls

(iii) Chemical Safety

- Wear gloves and glasses where appropriate.
- Follow instructor's directions.
- Dispose of waste properly-Do Not pour down the drain.

(iv) Personal Safety

- Lab coat to be worn all the time.
- Safety goggles must be worn all the time while working in the lab.
- Wear sensible clothing and Wear shoes.
- Appropriate gloves while handling chemicals.
- Working of alone student is not allowed

13.6 ASSESS AND MINIMIZE THE RISK OF THE HAZARDS

When you are working in a chemical lab, there is a risk associated with every chemical and glassware you use. Once you have evaluated the risks, your next step is to consider how you can reduce exposures. There are following step to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant steps you can take to reduce the risk in any laboratory environment. While incidents can occur even in the well-prepared environment, meticulous attention to detail can reduce the risk.

(I). Know what you are working with. It is important to always recognize the substance that is being used and to consider how to reduce the exposure to that substance during the experiment. For example, sodium hydroxide is commonly known as lye or caustic soda. If you are unsure, look for the Chemical.

(II). Ensure that the proper concentrations are prepared. In laboratory should not routinely work with basic (NaOH) or acidic (HCl) solutions at concentrations greater than 1 M.

(III). Ensure that all chemical bottles are properly labeled. For example, sodium hydroxide, the bottle should have the chemical name ("sodium hydroxide") spelled out, not just the formula ("NaOH"), and the concentration of the solution should also be listed.

- The signal words "Danger", "Warning", and "Caution" are used to describe the level of the hazard.
- Words such as "Caustic", "Corrosive", and "Flammable" are used to describe specific hazards.

I. Write down all the chemicals you are going to use and how much you will need for the experiment.
II. Consider the physical arrangement and the facilities available in your laboratory.

13.6.2 During an experiment

It is essential that learners are monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students throughout.

I. Use the lowest concentrations and smallest volumes possible for all chemicals. Do not allow learners to handle solids that are classified as fatal or toxic if swallowed.

II. Wear appropriate eye protection that offers both impact and splash protection. This is not only for your safety but also as a precaution in the event that an accident is caused by someone else in the laboratory.

III. Wear appropriate protective clothing (laboratory apron, coat, and gloves).

IV. Long hair must be pulled back, and clothing must be tucked in.

V. After transferring a chemical (solid or liquid) from a reagent bottle into a secondary container, be certain that the reagent bottle and the container are properly closed.

VI. Students should take only the amount required of each reagent. If there is excess, it must be disposed of properly and not returned to the reagent container.

VII. No mixing of chemicals should be allowed, other than that specified in an experimental procedure.

13.6.3 What if an emergency occurs?

I. If the chemical is in the eye: Flush water using an eyewash station for at least 15 minutes. Medical attention must be summoned as soon as possible.

II. If the chemical is swallowed or ingested: Do not induce vomiting unless the SDS recommends vomiting. Medical attention must be summoned as soon as possible.

III. If the chemical comes into contact with the skin: Rinse the affected area for 15 minutes with tap water. It may be necessary to use a safety shower. If the safety shower is used, all contaminated clothing should be removed while the person is under the safety shower, and medical attention must be summoned as soon as possible.

13.6.4 After an experiment

I. Return any chemicals (excess reagent, product, or waste) to the appropriate location, or dispose of them as instructed.

II. Clean any used glassware and return the items to the appropriate location.

III. Ensure that all chemicals are properly stored. Make sure that the caps on the reagent bottles are tightly secured.

IV. Ensure that the benches are clean before the next class comes in. One of the major causes of accidents is carelessness on the part of someone else.

V. All gas outlets are closed; especially burners were used during the experiment.

13.7 SUMMARY

- Keep tabletops clean. Return all equipment to its original location before leaving the lab.

- Report all accidents, no matter how minor, to the instructor. If you break something made of glass, be sure to use dustpan and hand broom to sweep it up and dispose of it in the glass waste receptacle.
- In case of an emergency where we have to evacuate, proceed out the nearest exit.
- Both the door should remain open all the time while working in the lab.
- Never put anything in your mouth while in the lab (including chemicals, solutions, food and drink)

- All food and drinks should be restricted to the sitting area only.

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BLOCK-VI: EXPERIMENT

UNIT 14: INORGANIC EXERCISE: VOLUMETRIC EXERCISES (DOUBLE TITRATION)

CONTENT:

14.1 Introduction

14.2 Objectives

14.3 Volumetric exercises (double titration) based on redox reactions involving internal as well as external indicators.

14.3.1 Oxidation-reduction (redox) titrations

14.3.2 Potassium dichromate method

14.3.3 External and Internal Indicators

14.4 Exercise: 1

14.4.1 To determine the strength of a given solution of ferrous ammonium sulphate by titrating it against $K_2Cr_2O_7$ solution and using potassium ferricyanide as an external indicator.

14.5 Exercise: 2

14.5.2 To determine the strength of a given solution of ferrous ammonium sulphate by titrating it against $K_2Cr_2O_7$ solution and using N- phenyl anthranilic acid as an internal indicator.

14.6 Summary

14.7 Terminal questions

14.8 References

14.1 INTRODUCTION

Chemical analyses are of two types; qualitative and quantitative. Qualitative analysis involves the identification of the constituents, *e.g.*, elements, ions or functional groups, present in a substance whereas quantitative analysis involves the determination of the quantities of particular constituents present in a substance. Volumetric analysis is the term used for quantitative chemical analyses which involve measurement of volumes of substances or their solutions to determine the particular constituents of the substance of interest. A term, titrimetric analysis is also often used to describe such experiments. Thus, titrimetric analysis or titrimetric is a common laboratory method of quantitative chemical analysis. It is used to determine the unknown concentration of a known analyte by treating a certain volume of it with a known concentration and volume of a reagent called titrant. You must bear in mind that volume measurement plays the most vital role in titrimetric or volumetric analysis, hence such measurements should be performed with utmost care.

14.2 OBJECTIVES

- The objective of these laboratory exercises is to equip you with the knowledge and skills to design, understand, and perform volumetric analyses, specifically titrations.
- You will learn to standardize solutions, perform various titrations, and identify endpoints using indicators or colour changes.
- Additionally, the exercises emphasize the importance of safe laboratory practices while handling hazardous reagents and equipment.

14.3VOLUMETRIC EXERCISES (DOUBLE TITRATION) BASED ON REDOX REACTIONS

14.3.1 Oxidation – Reduction (redox) titrations: Redox –titrations include all those varieties of titrations where one is oxidized and the other is reduced. The indicator is so chosen as to give the colour in either of the conditions. Oxidation is defined as the process of loss of one or more electrons and reduction, is the gain of one or more electrons by atoms or ions. Both oxidation and reduction take place simultaneously, i.e. one cannot take place without the other.

- The reagent undergoing reduction is called an oxidizing agent (oxidant) and it is reduced to a lower-valency state.
- The reagent undergoing oxidation is called a reducing agent (reductant) and it is oxidised to a higher-valency state.
- The reducing agents are generally used: Sodium oxalate, ferrous sulphate, ferrous ammonium sulphate, oxalic acid etc.
- The oxidants are $KMnO_4$, $K_2Cr_2O_7$, (both are acidified) I_2 etc.

In redox, titration, the estimation are generally done by the following methods:

(a) Potassium permanganate method
(b) Potassium dichromate method
(c) Iodine method

In this chapter, we discuss the Potassium dichromate method as follows:

14.3.2 Potassium dichromate method:

In the presence of dil HCl /dil H_2SO_4 (an acid) $K_2Cr_2O_7$ acts as an oxidizing agent and each molecule loses 3 molecules of oxygen available for oxidation of the reducing agent as shown below:

$$K_2Cr_2O_7 + 4\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3O$$

$$K_2Cr_2O_7 + 8HCl \longrightarrow 2\,KCl + 2CrCl_3 + 4\,H_2O + 3O$$

$$[Cr_2O_7]^{2-} + 8H^+ \longrightarrow 2Cr^{+3} + 4\,H_2O + 3O$$

That is in the presence of H^+ ions, each Cr atom by gaining 3 electrons and is reduced to +6 to +3 (Cr^{+3}). Hence the cell reaction is:

$$[Cr_2O_7]^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{+3} + 7\,H_2O$$

14.3.3 External and Internal indicator:

External indicator: About 0.1% solution of potassium ferricyanide acts as an external indicator. A drop of the titration mixture should be placed on one of the indicator drops on the plate at the endpoint. Using a glass rod, make a series of drops on the plate and observe the colour change. If ferrous ions (Fe^{2+}) are present, a strong blue colour will be developed due to the formation of a blue complex, according to the following equation;

$$2K_3Fe(CN)_6 + 3FeSO_4 \longrightarrow Fe[Fe(CN)_6]_2 + 3\,K_2SO_4$$

Ferrous ferricyanide (Dark blue complex)

Repeating this process, the blue colour becomes fainter. When a drop of solution first fails to produce a blue colour on the indicator's drop, this will be the endpoint i.e. all Fe^{+2} ions are oxidized to Fe^{3+}ions. At the endpoint, the colour of the indicator's drop becomes light brownish yellow due to the reaction of indicators with Fe^{+3} ions to produce a brown colour ferric ferrocyanide complex.

$$Fe_2(SO_4)_3 + 2K_3[Fe(CN)_6] \longrightarrow 3\,K_2SO_4 + 2Fe[Fe(CN)_6]_2$$

Brown

Internal Indicators: The most common internal indicators used are:

(a) 1% solution of diphenylamine in chemically pure conc. H_2SO_4. The endpoint is obtained as: Take 25 ml of a solution of ferrous ions, add about 25 ml dil H_2SO_4, 6-8 drops of indicator and then 5 ml phosphoric acid. Now add $K_2Cr_2O_7$ solution from burette until the last drop causes a change from green to blue – violet, this is the end point.

b) N-phenyl anthranilic acid is also used as an indicator. Take 25 ml of solution of reducing agent in a conical flask and acidified with 25ml H_2SO_4, then add few drops of the indicator solution. When the solution is titrated against $K_2Cr_2O_7$, the end point is indicated by a sudden shift in color from yellowish green to purple red. Oxidized from of this indicator is purple –red and reduced from is colourless.

14.4 EXERCISE :1

14.4.1 To determine the strength of a given solution of ferrous ammonium sulphate by titrating it against $K_2Cr_2O_7$ solution and using potassium ferricyanide as an external indicator

Theory: Acidic $K_2Cr_2O_7$ is a strong oxidizing agent. When it is added to ferrous ammonium sulphate solution containing dil H_2SO_4/ dil HCl only $FeSO_4$ is oxidized. The reaction taking place are as follows:

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + 3Cr_2(SO_4)_3 + 7H_2O$$

Ionic equation:

$$(Cr_2O_7)^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

When a drop of the titration mixture is applied to the indicator at the end point, it stops producing blue color.

Procedure:

a) Preparation of N/30 ferrous ammonium sulphate solution (Known solution)

To prepare standard FAS solution prepares N/10 solution in 250 mL volumetric flask as per your convenience. To prepare N/30 ferrous ammonium sulphate solution in 250 mL weight desired weight of FAS by using following equation:

$$w = \frac{ENV}{1000}$$

w = weight needed, E = equivalent weight, N = normality, V= desired volume

The equivalent weight of ferrous ammonium sulphate is =392. 12

The weight of ferrous ammonium sulphate is $w = \frac{392.12 \text{ x } 1\text{x } 250}{30 \text{ x} 1000} = 3.267$ gm.

Transfer the 3.267 gm. of ferrous ammonium sulphate to a volumetric flask of 250 mL capacity and add half test tube of dil. H_2SO_4 (avoid hydrolysis) of ferrous ammonium sulphate, shake the flask well till all the particles of ferrous ammonium sulphate are dissolved. Add additional distilled water to make-up the volume of 250mL which represent N/30 ferrous ammonium sulphate solution.

b) Standardization of $K_2Cr_2O_7$ solution with known ferrous ammonium sulphate solution:

Rinse a clean burette with distilled water and fill it with $K_2Cr_2O_7$ solution. Record the initial reading of the burette. Pipette out 25 ml of standard ferrous ammonium sulphate in a conical flask and add equal volume of dil. 2N - H_2SO_4 solution. Put a series of drops of indicator (potassium ferricyanide) with the help of a glass rod on a plate. Titrate the two solutions until a permanent strong blue colour is obtained. Continue the titration and repeat the process at different intervals and when the colour of the indicator drop does not give a blue colour the end point is reached. Record the final burette reading in the observation table. Repeat the titrations to get at least two concordant readings and record all readings in observation table 1. Titration with given ferrous ammonium sulphate solution: Use the same standardized $K_2Cr_2O_7$ solution to fill the burette, and then proceed as in step (b) above with 25 mL of the ferrous ammonium sulphate unknown solution in a conical flask. To obtain two readings that agree, repeat the titrations. Make note of every measurement in the observation table 2.

Observations:

Table: 1. Titration with known solution of ferrous ammonium sulphate

S.N.	Volume of standard FAS taken in the conical flask (mL)	Burette readings		Volume of $K_2Cr_2O_7$ used (mL)
		Initial(mL)	Final(mL)	
1	25.0	0.0	....	....
2	25.0	0.0	....	....
3	25.0	0.0	....	.... (say V_1 ml)

Table Titration with unknown solution of ferrous ammonium sulphate

S.N.	The volume of FAS solution taken in the conical flask (mL)	Burette readings		Volume of $K_2Cr_2O_7$used, (mL)
		Initial(mL)	Final(mL)	
1	25.0	0.0	....	....
2	25.0	0.0	....	....
3	25.0	0.0	....	.... (say V_2 ml)

Calculations:

Let, V_1 = Volume of $K_2Cr_2O_7$ used against known solution.

V_2 = Volume of $K_2Cr_2O_7$ used against unknown solution.

N_1 = Normality of $K_2Cr_2O_7$ solution

According to the Normality equation

Vol. x normality of known solution = Vol. x normality of $K_2Cr_2O_7$ solution

$$25 \times \frac{4 \times w}{392.12} = V_1 \times N_1$$

$$N_1 = \frac{25}{V1} \times \frac{4 \times w}{392.12}$$

Hence, In titration against the given solution.

$$25 \times N = V_2 \times N_1$$

Where N is the normality of the given solution.

$$N = \frac{v2}{25} \times \frac{25}{V1} \times \frac{4 \times w}{392.12}$$

$$\text{Strength of given solution} = 392.12 \times \frac{V2}{V1} \times \frac{4 \times w}{392.12}$$

$$= \frac{4 \times w \times V2}{V1} \text{ gm/litre}$$

Result:

The strength of the given ferrous ammonium sulphate solution is………… gm/litre

Precautions:

1. Use clean and dry glassware for titration.
2. Take the $K_2Cr_2O_7$ solution in the burette and handle it carefully as it is corrosive.
3. Add sufficient sulphuric acid in a conical flask before titration.
4. The endpoint of this experiment shows blue colour which requires special care for identification.

14.5 EXERCISE: 2

14.5.1. To determine the strength of a given solution of ferrous ammonium sulphate by titrating it against $K_2Cr_2O_7$ solution and using N-phenyl anthranilic acid as an internal indicator.

Theory: Same as in exercise-1.

Procedure:

a) Preparation of N/30 ferrous ammonium sulphate solution (Known solution):

To prepare standard FAS solution prepare N/10 solution in 250 mL volumetric flask at your convenience. To prepare N/30 ferrous ammonium sulphate solution in 250 mL weight desired weight of FAS by using the following equation:

$$w = \frac{ENV}{1000}$$

w = weight needed, E = equivalent weight, N = normality, V= desired volume

The equivalent weight of ferrous ammonium sulphate is =392. 12

The weight of ferrous ammonium sulphate is $w = \frac{392.12 \text{ x } 1 \text{x } 250}{30 \text{ x} 1000}$ = 3.267 gm.

Transfer the 3.267 gm. of ferrous ammonium sulphate to a volumetric flask of 250 mL capacity and add half a test tube of dil. H_2SO_4 (avoid hydrolysis) of ferrous ammonium sulphate, shake the flask well till all the particles of ferrous ammonium sulphate are dissolved. Add additional distilled water to make up the volume of 250mL which represents N/30 ferrous ammonium sulphate solution.

b) Standardization of $K_2Cr_2O_7$ solution with known ferrous ammonium sulphate solution: Rinse a clean burette with distilled water and fill with $K_2Cr_2O_7$ solution. Record the initial reading of the burette. Pipette out 25 ml of standard ferrous ammonium sulphate in a conical flask and add equal volume of dil. 2N - H_2SO_4 solution. Put a series of drops of indicator (N- phenyl anthranilic acid) with the help of glass rod on a plate. Add slowly dichromate solution from burette to it until the colour of the titration mixture just turn to violet red. This is end-point of the titration and note it carefully. Repeat the titrations to get at and record all readings in observation table 1. This reading will be $V_{1.}$

c)Titration with given ferrous ammonium sulphate solution:

Use the same standardized $K_2Cr_2O_7$ solution to fill the burette, and then proceed as in step (b) above with 25 mL of the ferrous ammonium sulphate unknown solution in a conical flask. To obtain two readings that agree, repeat the titrations. Make note of every measurement in the observation table 2. This reading will be $V_{1.}$

Observations:

Table: 3. Titration with a known solution of ferrous ammonium sulphate

S.N.	Volume of standard FAS taken in the conical flask (mL)	Burette readings		Volume of $K_2Cr_2O_7$ used (mL)
		Initial(mL)	Final(mL)	
1	25.0	0.0	....	....
2	25.0	0.0	....	....
3	25.0	0.0	....	.... (say V_1 ml)

Table 4 : Titration with unknown solution of ferrous ammonium sulphate

S.N.	The volume of FAS solution taken in the conical flask (mL)	Burette readings		Volume of $K_2Cr_2O_7$used, (mL)
		Initial(mL)	Final(mL)	
1	25.0	0.0	....	....
2	25.0	0.0	....	....
3	25.0	0.0	....	.... (say V_2 ml)

Calculations:

Let, V_1 = Volume of $K_2Cr_2O_7$ used against known solution.

V_2 = Volume of $K_2Cr_2O_7$ used against unknown solution.

N_1 = Normality of $K_2Cr_2O_7$ solution

According to Normality equation

Vol. x normality of known solution = Vol. x normality of $K_2Cr_2O_7$ solution

$$25 \times \frac{4 \times w}{392.12} = V_1 \times N_1$$

$$N_1 = \frac{25}{V1} \times \frac{4 \times w}{392.12}$$

Hence, In titration against given solution.

$$25 \times N = V_2 \times N_1$$

Where, N is the normality of given solution.

$$N = \frac{v2}{25} \times \frac{25}{V1} \times \frac{4 \times w}{392.12}$$

Strength of given solution = $392.12 \times \frac{V2}{V1} \times \frac{4 \times w}{392.12}$

$$= \frac{4 \times w \times V2}{V1} \text{ gm / litre}$$

Result:

The strength of given ferrous ammonium sulphate solution is……….. gm / litre

Precautions:

1. Use clean and dry glassware for titration.

2. Take $K_2Cr_2O_7$ solution in burette and handle carefully as it is corrosive.

3.Add sufficient sulphuric acid in conical flask before titration.

4. The endpoint of this experiment shown blue colour which requires special care for identification.

14.6 SUMMARY

- Titration is an important technique in the field of analytical chemistry and is also referred to as volumetric analysis.

- In exercises 1& 2 learners are able to determine the strength of a given solution of ferrous ammonium sulphate by titrating it against $K_2Cr_2O_7$ solution and using external and internal indicators.
- This unit also explains the properties of indicators and importance of indicators in titration process.

14.7 TERMINAL QUESTIONS

Q.1 Discuss the procedure of titrations, in general.

Q.2 What is the endpoint and equivalence point?

Q. 3 What is an indicator?

Q.4 What is the equivalent weight of ferrous ammonium sulphate?

Q.5 How do you identify the endpoint of titration of FAS solution with $K_2Cr_2O_7$?

Q.6 Define external and internal indicators used in the titration process.

14.8 REFERENCES

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UNIT 15: ORGANIC EXERCISE: CHEMICAL, PHYSICAL AND FUNCTIONAL GROUP TESTS

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15.3 Preliminary and functional group tests
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    15.3.2 Functional group tests
15.4 Detection of functional group for carboxylic acids, ester and nitro compounds (both aliphatic and aromatic).
    15.4.1 Functional Groups Carboxylic acids group (-COOH)
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15.6 Terminal questions
15.7 References

15.1 INTRODUCTION

Qualitative analysis of an organic compound refers to detecting the elements present in a compound. The most common elements present in an organic compound are carbon, hydrogen, oxygen, nitrogen, halogen and sulphur. Sometimes, components such as phosphorus and some metals may also be present. Therefore, qualitative analysis is limited to the detection of only a small number of elements usually present in organic compounds. In this chapter, students learn the following objectives.

15.2 OBJECTIVES

- To detect nitrogen, sulfur, and halogen in a given mixture, aiming to enhance understanding of elemental analysis techniques.
- To identify functional groups of carboxylic acids, esters, and nitro compounds (both aliphatic and aromatic) using known samples, to apply qualitative analysis methods in organic chemistry.

15.3 PRELIMINARY AND FUNCTIONAL GROUP TESTS

15.3.1 Preliminary Examination:

a) Physical State, Colour and Oduor: A careful observation of the physical state, colour and characteristic smell of the compound gives useful regarding the nature of the compound gives useful information regarding the nature of the compound. The physical attributes and chemical nature can be somewhat related with the aid of the following table.

Colourless solids	Carbohydrates, simple acids, some phenols, amides, and anilides
Colourless solids	Nitro compounds, amines, phenols, quinines.
Colourless Liquids	Alcohols, aldehydes, ketones, simple hydrocarbons and simple

	acids.
Coloured Liquids	Nitro compounds, phenols, amines.
Carbolic smell	Phenols.
Smell of bitter almonds	Benzaldehyde and nitrobenzene.
Fruity –pleasant smell	Esters
Spirituous smell	Alcohols
Pungent smell	Formic acid or formalin.

b) Ignition Test:

Take a small portion of the given compound on a metallic spatula ignite it over the non-luminous flame and note the changes.

Observation	Inference
1. Burns with a sooty flame	May be an aromatic compound.
2. Yellow and non- sooty flame	May be an aliphatic compound.
3. Chars	Maybe a carbohydrate, hydroxyl acid / sulphonic acid
4. Smell of ammonia	Nitrogenous compounds like urea.

c) Solubility Behavior:

The compound's nature can be inferred from its behaviour toward several solvents, such as water, dil. HCl, dil. NaOH, con. H_2SO_4, etc. Solubility of substance in solvent is given below:

Observation	**Inference**
1. Soluble in hot water and solution is acidic to litmus.	Salts of aromatic bases. Lower aliphatic acids, hydroxyl acids/polyhydroxy phenols.
2. Soluble in hot water and solution is acidic	Higher acids or some phenols
3. Soluble in cold water and	Carbohydrate or alcohols

solution is neutral	
4. Soluble in hot water and solution is neutral	Starch, quinones
5. Soluble in cold dil $NaHCO_3$ with effervescence	Carboxylic acids
6. Soluble in cold dil NaOH	Carboxylic acids or phenol
7. Soluble in hot NaOH and give off ammonia	Amides, ammonium salts.
8. Soluble in cold con. H_2SO_4	Aromatic hydrocarbons or phenols.
9. Soluble in hot con. H_2SO_4 and charring occurs	Carbohydrates, aldehydes, ketones, or hydroxyl acids.
10. Soluble in dil HCl	Amines

d) Test for Unsaturation:

i) Test with Bromine: A few drops of bromine water should be added to a chemical solution in water and note the changes:

Observation	Inference
1. Decolorization	Unsaturated compounds containing (C=C) bond
2. A precipitate is obtained	Amines and phenols

ii) Test with Alkaline $KMnO_4$ Solution: Dissolve a small amount of the substance in water. Add to it 1 ml of dil Na_2CO_3 and a few drops of $KMnO_4$ Solution and shake well. If the color of the permanganate disappears the compound may be unsaturated.

15.3.2 Functional group tests:

Organic compounds may be regarded as the derivatives of hydrocarbons having different functional groups in place of one or more hydrogen atoms. Their characteristic properties and reactions are largely due to the presence of functional groups present in them. Correct detection of functional groups in the organic compounds leads to a very reasonable and accurate identification of those compounds.

For the sake of convenience, all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds.

Type I: Compounds containing C and H with or without oxygen.

S.N.	Experiment	Observation	Inference
1.(a)	On the treatment of the compound with $NaHCO_3$ solution	Brisk effervescence appears	Acids
(b)	On treating of the compound with blue litmus,	Blue litmus turns red	Acids
2.	On adding ceric ammonium nitrate solution to the compound,	The red colouration is observed	Alcohols
3.(a)	Two drops of $FeCl_3$ are added to an aqueous of alcoholic solution of the compound,	Typical colour changes are observed	Phenols
(b)	Phthalein test is performed,	A positive result is observed	Phenols
4.	The compound is heated with Fehling's solution or Benedict's solution,	Red precipitate is formed	Aldehydes or reducing sugars
5.	The compound is treated with Schiff's solution.	The pink colouration is observed.	Aldehydes
6.	On Shaking the compound with sodium bisulphite solution,	A white precipitate is formed.	Aldehydes or Ketones
7.	The compound is treated with an alkaline sodium nitroprusside solution,	Red colouration appears	Methyl Ketones
8.	Molisch's test is performed,	Result is positive	Sugars

9.	On heating the compound with dil. NaOH solution containing a drop of phenolphthalein	Pink colour is slowly discharged	Esters
10.	On heating the compound with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated hydrocarbons Saturated aliphatic hydrocarbons or ethers

Type II: Compounds containing C, H and halogens with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	On boiling the compound with alcoholic $AgNO_3$,	(i) White ppt. soluble in NH_4OH (ii) Light yellow ppt. Partially soluble in NH_4OH (iii) Deep yellow ppt. insoluble in NH_4OH	Choro compounds Bromo compounds Iodo compounds
2.	If the compound is heated with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated alkyl halides Saturated aliphatic alkyl halides

Type III.: Compounds containing C, H and N with or without oxygen.

S.N.	Experiment	Observation	Inference

1.	The compound is boiled with aq. NaOH,	The smell of ammonia is noticed	Amides
2.	The compound is treated with dil. HCl followed by $NaNO_2$ drowse in cold,	(i) Brisk effervescence occurs (ii) Brown or green ppt. is formed (iii) Blue colouration appears	Amides, amino acids, primary amines or urea
3.	On treating the above contents with an alkaline β - naphthol solution,	Bright orange-red dye informed	Aromatic primary amines
4.	The compound is boiled with water,	Yellow colouration	Nitro phenols or nitro compounds
5.	The compound is boiled with zinc dust and aq. NH_4Cl, filtered and filtrated is treated with Tollen's regent,	The grey precipitate is formed	Nitro compounds

Type IV (A): Compounds containing C, H and S with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	To the aq. solution of the substance is added few drops of $FeCl_3$ solution,	Violet or red colour is observed	Sulphonic acids of phenols or hydrocarbons
2.	Equal quantities of substance and animal charcoal are mixed and filled one-third of the ignition tube with it and heated,	A disagreeable garlic-like odour is noticed	Sulphones

(B): Compounds containing C, H, S and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	2ml. of NaOH solution are	Brown or black colour or	Thioureas

	added to a trace of the substance in a test tube, heated to boiling, cooled, and added 2 drops of aq. lead acetate,	precipitate appears	
2.	A trace of the substance is dissolved in 2ml. of water by boiling in a test tube and a piece of blue litmus paper is introduced in it,	(i) If the color changes to red. (ii) If no change in color	Test (a) given below is performed Test (b) is performed as given below
(a)	A trace of the substance is dissolved in 3ml. of dil. HCl cooled in ice cold water and added 3ml. of 2% sodium nitrite solution and then 4ml. of alkaline β naphthol solution	Red coloration appears	Amino sulphonic acids
(b)	5 drops of conc. H_2SO_4 are added to a trace of substance and heated gently for few minutes, cooled and diluted with 2ml. water. Then added flakes of NaOH and a piece of moistened red litmus paper is brought near the mouth of the test tube,	Colour changes to blue and smell of NH_3 is noticed	Sulphonamide or saccharin

15.4 DETECTION OF FUNCTIONAL GROUP FOR CARBOXYLIC ACIDS, ESTER, AND NITRO COMPOUNDS (BOTH ALIPHATIC AND AROMATIC).

The accurate identification of components is a major factor in determining the functional group. By using the melting or boiling points of organic compounds, one may determine their name after the functional group that makes them up is known. In next step is to study some specific reactions of the compounds and then to confirm their names by preparing suitable derivatives.

15.4.1 Functional Groups of Carboxylic acids group (-COOH):

Organic compounds containing carboxyl functional groups are called carboxylic acids. The term carboxyl derives its name from the combination of words carbonyl and hydroxyl because the carboxylic functional group contains both of these groups (—COOH) These acids turn blue litmus red and react with sodium hydrogen carbonate solution to produce effervescence due to the formation of carbon dioxide. This is a test that distinguishes carboxylic acids from phenols.

$$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2$$

The functional groups are then confirmed by normal and sometimes by performing some special test.

1. **Aliphatic Carboxylic acids group (-COOH):**

(i) Litmus paper test: If the blue litmus paper or solution is added to the aq. solution or suspension of the compound, it turns red.

(ii) Sodium bicarbonate test: If a small amount of the compound is added to about 3ml. of saturated sodium bicarbonate solution, brisk effervescence is noticed.

(iii) Fluorescence test: 0.2gm. of organic compound is heated gently with 0.5gm. of resorcinol and a few drops of conc. H_2SO_4 in a hard test tube for two minutes, cooled, and poured the contents into a beaker containing NaOH diluted largely with water. Intense green fluorescence is formed indicating the presence of 1,2 or ortho dicarboxylic group (i.e. phthalic acid)

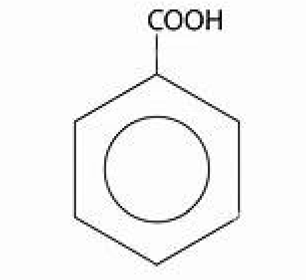
(iv) Ester formation: A small quantity of the substance is heated with ethyl alcohol and a little conc. H_2SO_4 was cooled and poured into a tube containing water. A fruity smell due to the formation of an ester indicates the presence of the carboxylic group.

(v) Ferric chloride test: 0.5gm. of the acid is neutralized with excess ammonia in a boiling test tube, the solution is boiled to remove the excess ammonia, cooled, and added a few drops of neutral $FeCl_3$ solution are: If a reddish-brown precipitate is formed: indicate the presence of aliphatic carboxylic acids.

Note. Phenols and α-naphthylamine also produce color with $FeCl_3$.

2. Aromatic Carboxylic acids group (-COOH):

a) Benzoic acid:



(Melting point:121^{0}C)

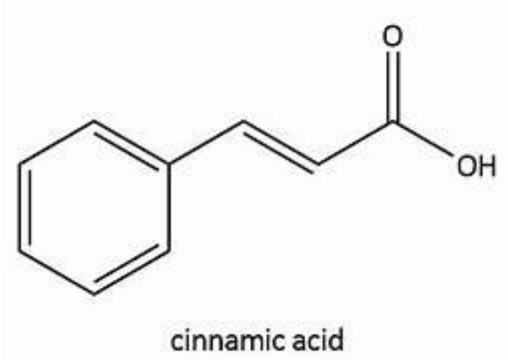
(i) Sodium bicarbonate test: This gives a normal $NaHCO_3$ test of carboxylic acid. Therefore, on adding a saturated solution of $NaHCO_3$ to benzoic acid, CO_2 gas exits with intense bubbling.

(ii)Specific tests are as follows:

Addition of ferric chloride ($FeCl_3$) to a neutral solution of benzoic acid results in a camel hair-like buff precipitate.

The flammable vapor of benzene is obtained when benzoic acid is heated with soda lime.

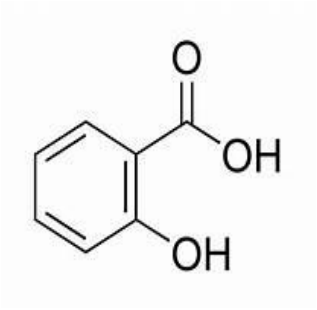
b) Cinnamic acid:



(Melting point:133^{0}C)

- It oxidizes to benzaldehyde upon heating in an acidified KMnO4 solution, which is distinguished by a little bitter almond taste.
- It is decolorised alkaline KMnO4 solution.

c) Salicylic acid:

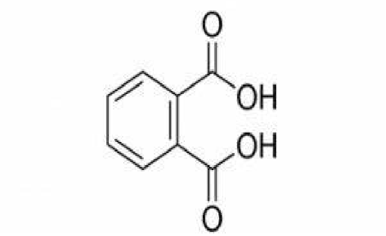


(Melting point:159^{0}C)

Salicylic acid

- Aqueous solution of acid added few drops of $FeCl_3$ – violet / purple color is obtained.
- Given white colour precipitate with Br_2 water.
- Add methyl alcohol and con. H_2SO_4 to a heated mixture of salicylic acid. The smell of oil of wintergreen (iodex type) is detected.

d) Phthalic acid:



(Melting point:195^{0}C)

Phthalic acid

- When it reacts with resorcinol, it produces red solutions, such as those containing green fluorescein.
- Fill a test tube with phenol and con. H_2SO_4 in equal amounts after taking a few crystals of an acid. Apply dil. NaOH solution excess after gently heating, cooling, and diluting with water. One gets a pink color.

15.4.2 Functional Groups of Ester (- RCOOR′):

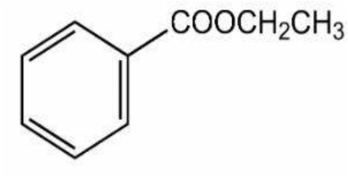
1. Aliphatic Ester group (- RCOOR′): Esters are chemical compounds consisting of a carbonyl adjacent to an ether linkage. They are derived by the reaction of an acid with a hydroxyl compound such as an alcohol or phenol. Esters are usually derived from an inorganic acid or organic acid in which at least one -OH (hydroxyl) group is replaced by an –O-alkyl (alkoxy) group, and most commonly from carboxylic acids and alcohols.

All the esters possess fruity smell.

- Phenolphthalein test: To 3ml. of the compound are added 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heated gently, the pink colour is gradually discharged (due to hydrolysis of ester).

2. Aromatic Ester group (- RCOOR′):

a) Ethyl benzoate:

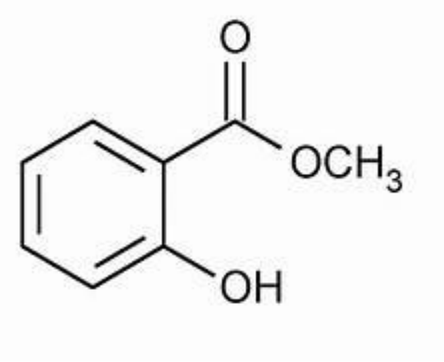


Boiling point: 213^0C

Ethyl benzoate

- Reflux 2 milliliters of ester in 4 to 5 milliliters of alcoholic KOH solution for approximately 20 minutes. With dil HCl, cool and acidify. One gets a benzoic acid precipitate that is white. As a derivative, filter and retain.

b) Methyl Salicylate:



Boiling point: 223^0C

Methyl Salicylate

- Gives violet colour with $FeCl_3$.
- Salicylic acid is produced upon hydrolysis using the process outlined for ethyl benzoate.

• 15.4.3Functional Groups of Nitro (- NO_2)

1. Aliphatic Nitro group (- NO_2): In organic chemistry, nitro compounds are organic compounds that contain one or more nitro functional groups ($-NO_2$). The nitro group is one of the most common exospheres (functional group that makes a compound explosive) used globally. The nitro group is also strongly electron-withdrawing. Because of this property, C−H bonds alpha (adjacent) to the nitro group can be acidic.

Almost all nitro compounds are light yellow or yellow in colour.

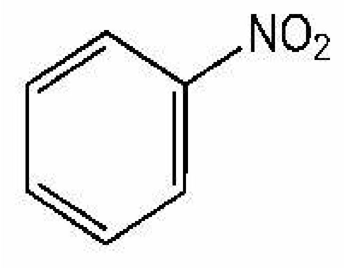
(i) Sodium hydroxide test: A small amount of the compound is shaken with 2ml. of NaOH solution, yellow, intense yellow or orange colour is produced due to nitro group.

(ii) Zinc-ammonium chloride test: A small amount of the substance is boiled with 5ml. of 5% alcohol, 0.2gm. each of NH_4Cl and zinc dust, cooled, filtered and added to the filtrate 2 ml. of Tollen's reagent. On heating, a black grey precipitate is formed due to nitro compounds.

(iii) Azo-dye test: 0.1gm. of the substance is heated with 0.5ml. conc. HCl and 2-3 small pieces of metallic tin for 3-4 minutes, filtered, cooled and added 3ml. of aq. $NaNO_2$ solution. This is poured into a beaker containing alkaline β naphthol solution. An orange red dye is formed.

2. Aromatic Nitro group (- NO_2):

a) Nitrobenzene:

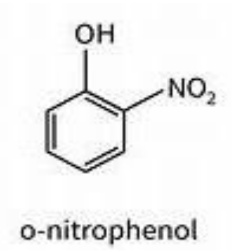


Boiling point: 210.9^{0}C

Nitrobenzene

- Combine 2 milliliters of con HNO3 and 2 milliliters of H2SO4 to make the chemical. Shake in 1 ml of nitrobenzene. Pour the mixture into cold water after heating it for a few minutes. A thick, greasy film forms first and then solidifies. Wash and dry the filter.

b) Ortho -Nitrophenol:

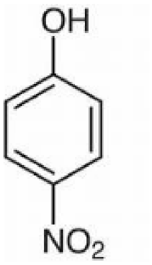


Melting point: 44^{0}C

Ortho -Nitrphenol

- Yellow crystalline solid, soluble in hot water and dissolves in alkali giving orange solution.

c) para -Nitrophenol:

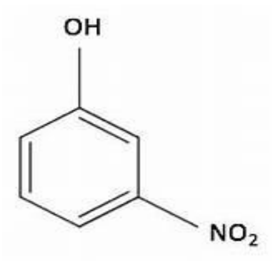


Melting point: 114^{0}C

para -Nitrophenol

- Yields a yellow solution upon dissolution in an alkali.
- When using $FeCl_3$, an aqueous solution turns violet.

d) meta –Nitrophenol:



Melting point: 97^{0}C

meta –Nitrophenol

- Dissolve a few crystals of the compounds in hot water and add a few drops of $FeCl_3$, an aqueous solution turns violet–red.
- The compound dissolves in alkali giving orange- red solution.

15.5 SUMMARY

- Functional groups are specific atoms, ions, or groups of atoms having consistent properties. For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens.
- After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds.
- The functional groups are then confirmed by normal and sometimes by performing some special test.

15.6 TERMINAL QUESTIONS

1. What is the Preliminary test to the detection of functional groups?

2. How to correct the detection of functional groups in the organic compounds, when compounds
containing C and H with or without oxygen?

3. Define the functional group test of the aliphatic Carboxylic acids group.

4. Define the functional group test of the aromatic Carboxylic acids group.

5. Define the functional group test of the aliphatic ester group.

6. Define the functional group test of the aromatic ester group.

7. Define the functional group test of the aliphatic nitro group.

8. Define the functional group test of the aromatic nitro group.

15.7 REFERENCES

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UNIT 16: PHYSICAL EXERCISE: CRITICAL SOLUTION TEMPERATURE AND KINETICS

CONTENTS:

16.1 Introduction
16.2 Objectives
16.3 Study of the effect of NaCl / succinic acid on CST of phenol-water system
    16.3.1 Chemicals and Apparatus Required
    16.3.2 Principle
    16.3.3 Procedure
    16.3.4 Observations
    16.3.5 Result
16.4 To determine the kinetics of acid-catalyzed hydrolysis of methyl acetate
    16.4.1 Chemicals and apparatus required
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16.1 INTRODUCTION

Two liquids can be mixed to form one of the following systems.

(a) The two liquids are completely miscible like alcohol and water.

(b) The two liquids are partially miscible like phenol and water.

(c) The two liquids are practically immiscible like carbon disulphide and water.

These systems are called condensed systems in which the vapour phase is ignored and only solid and/or liquid phases are considered. The pressure is considered to be 1 atm while the temperature and concentration are the only variables which can be changed independently.

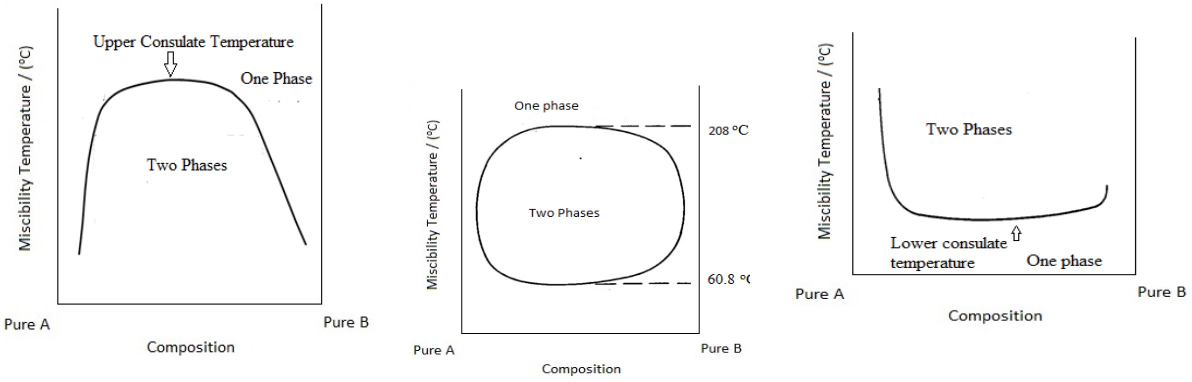


Figure 16.1. Liquid pairs exhibiting upper and lower consulate temperatures.

The condensed phase rule for such a two system is given by P+F=C+1

Where P is the number of phases, F is the number of degrees of freedom and C is the number of components. Two partially miscible liquids may become completely miscible at a higher temperature and the two phases become one homogeneous phase. This miscibility temperature is different for different compositions of the mixture. The highest miscibility temperature is called the upper critical solution temperature. Above this temperature all compositions of this mixture are completely miscible. Lower critical solution temperature is the lowest temperature below which the components are miscible in all proportions. Liquid pairs exhibiting upper and lower consulate temperatures are depicted in Fig. 16.1.

Esters are chemical compounds that are derived from organic or inorganic acids were atleast one hydroxyl group is replaced by an alkoxy group. They are characterized by some water solubility due to their participation in hydrogen bonding. In easy terms, Hydrolysis is a simple reaction with water.

Acid-Catalyzed Hydrolysis of Methyl Esters

Since water is such a poor nucleophile, the method of increasing the rate of nucleophilic addition with an ester is to increase the electrophilicity of the ester. This can be achieved in a number of ways. The most common is to use a Lewis acid or Bronsted acid to form appositively charged intermediate that is far more reactive and even mild nucleophiles such as water will react.

16.2 OBJECTIVES

After reading this unit you should be able to:

- Explain the phase separation of liquid mixtures due to partial miscibility.
- Explain the effect of temperature and composition on the solubility limit of two partially miscible liquids.
- Define critical solution temperature (CST).
- Explain the effect of impurities on Critical Solution Temperature (CST).
- Learn some terms and concepts in chemical kinetics like chemical reaction, mechanism, reactant, product, rate, rate law and rate constant.
- To obtain the order of an acid-catalyzed reaction experimentally by volumetric titrations.

16.3 STUDY OF EFFECT OF NaCl /SUCCINIC ACID ON CST OF PHENOL-WATER SYSTEM

16.3.1 Chemicals and Apparatus Required

Phenol-8 g, succinic acid and distilled water. Test tube, cork stopper carrying a thermometer, an aluminium stirrer and a beaker.

16.3.2 Principle

The presence of impurities in the phenol-water mixture affects the critical solution temperature. If the impurity is soluble in both liquids, the CST is lowered. The impurity keeps distributing itself between the two conjugate solutions and increases the mutual solubility of the liquids. An example is when succinic acid is added to the phenol-water system. If the impurity added is soluble only in one of the liquids, then the CST is raised for eg. the addition of NaCl or KCl raises the CST of the phenol-water system.

16.3.3 Procedure

1. Prepare 250 cm^3 of 0.2 M succinic acid solution.
2. Transfer 10, 20, 30, 40 and 50 cm^3 of this solution into five dry 100 cm^3 volumetric flasks and makeup with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of succinic acid, respectively.
3. Determine the miscibility temperature using 5 g of phenol and 5 cm^3 of 0.02 molar succinic acid solution.
4. Repeat the experiment using 5 g of fresh phenol and 5 cm^3 of each of the other concentrations and also an unknown solution. Record your readings as shown in Table 2 and Table 3.
5. Plot a graph of miscibility temperature against concentration of phenol-water system for each concentration of succinic acid (Fig.3). Determine the CST of phenol-water system for each concentration of succinic acid. Determine the CST of the given solution of unknown concentration also.
6. Plot a graph of CST against concentration of succinic acid (Fig.4). A linear plot is obtained. The concentration of unknown solution of succinic acid is obtained from the above graph by extending a straight line from the CST of unknown solution of succinic acid on Y axis and dropping a perpendicular from the point where this meets the straight line to the X axis.

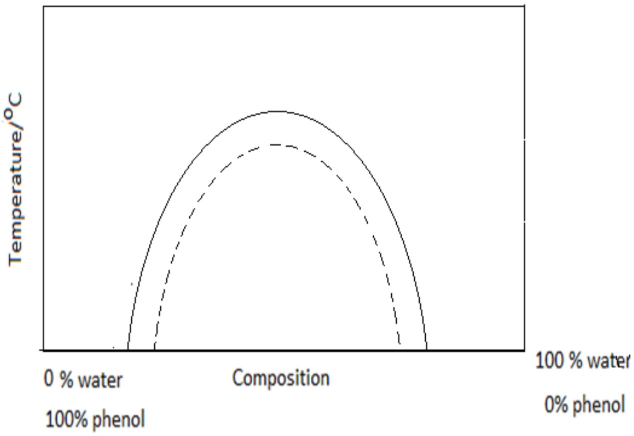


Figure 16.2. Effect of NaCl/succinic acid on CST of phenol-water system

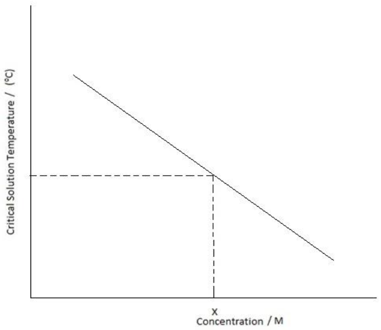


Figure 16.3. Plot of CST of a Phenol-Water system against concentration of succinic acid

16.3.4 Observations

Table 1. Miscibility Temperature of Phenol-Water system for each concentration of succinic acid solution

Concentration(M) of succinic acid solution	Wt % Phenol	Miscibility temperature (^{o}C)
0.02		
0.04		
0.06		
0.08		
0.10		

Table 2. Critical Solution Temperature (^{o}C) of a phenol-water system for each concentration of succinic acid solution

Concentration (M)	0.02	0.04	0.06	0.08	0.10	unknown
Critical Solution Temperature (^{o}C)						

16.3.5 Result

The critical solution temperature of a phenol-water system containing succinic acid is ……….

The concentration of succinic acid in a phenol-water system containing unknown amount of succinic acid is ……….

16.4 TO DETERMINE THE KINETICS OF ACID-CATALYZED HYDROLYSIS OF METHYL ACETATE

16.4.1 Chemicals and apparatus required

0.05 N NaOH, methyl acetate, 0.5 N hydrochloric acid, phenolphthalein indicator and ice., bottles (250 cm^3), pipettes (5 cm^3), burette (50 cm^3), conical flasks (100 $cm^{3)}$, stop watch, and a thermostat.

16.4.2 Principle

Acid-catalyzed hydrolysis of methyl acetate takes place according to the reaction

$$CH_3COOCH_3 + H_2O \xrightarrow{H+} CH_3COOH + CH_3OH$$

The reaction is catalysed by HCl. Water is taken in excess so that the rate of the reaction depends only on the concentration of the ester. Such a reaction is called pseudo uinimolecular reaction. The acetic acid formed during the reaction is titrated against NaOH solution.

The rate constant of a first order reaction is given by the following expression:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

In a volumetric method a and (a-x) are replaced by (V_α -V_o) and (V_α -V_t) respectively. (V_α -V_o) corresponds to the initial concentration of the ester and (V_α -V_t) corresponds to (a-x), the concentration of the ester at time, t.

16.4.3 Procedure

1. Prepare 0.05 N NaOH and 0.5 N hydrochloric acid.
2. Transfer 100 cm^3 of 0.5 N hydrochloric acid in a 250 cm^3 bottle. Keep this bottle in a thermostatically controlled water bath.
3. Standardise sodium hydroxide solution with 0.05 oxalic acid.
4. Pipette out 50 cm^3 of ester (methyl acetate) into a 250 cm^3 bottle and place it in the same thermostatically maintained water bath. Note the temperature of the water bath.
5. Pipette out 10 cm^3 of 0.2 N methyll acetate into the bottle containing 100 cm^3 of 0.5 N hydrochloric acid and shake well. Immediately pipette out 5 cm^3 of this reaction mixture into a conical flask containing a few ice pieces and two drops of phenolphthalein indicator. The ice pauses the reaction. Start a stop watch.

6. Titrate against standard 0.05 N sodium hydroxide solution from burette. The end point is the appearance of pale pink colour. Note the burette reading as given in Table 1. The volume of sodium hydroxide solution consumed is the value, V_o, corresponding to time, t = 0.
7. Pipette out 5 cm^3 of reaction mixture into a conical flask containing ice and phenolphthalein at regular time intervals of 10, 10, 15, 15, and 20 minutes. Titrate each with standard sodium hydroxide as before. Note the volume of sodium hydroxide consumed each time. This gives the values for V_t.
8. Pipette out 15 cm^3 of the reaction mixture and warm the bottle in a water bath at 80°C for 20 minutes. This procedure brings the reaction to completion. Pipette out 5 cm^3 of this solution in a conical flask containing ice pieces and phenolphthalein indicator. Titrate this mixture with sodium hydroxide solution in the burette. The titre values give V_α.
9. A plot of log (V_α -V_t) against t would yield a straight line, Figure 1, with slope equal to -2.303/k from which k can be calculated.

Table 3. Titration of reaction mixture against standardized NaOH solution

S. No.	Time (sec)	Burette reading (cm^3)		Volume of sodium hydroxide (cm^3)	(V_α -V_t)	log [(V_α -V_o)/(V_α - V_t)]	Rate constant, k (s^{-1})
		Initial Reading	Final Reading				

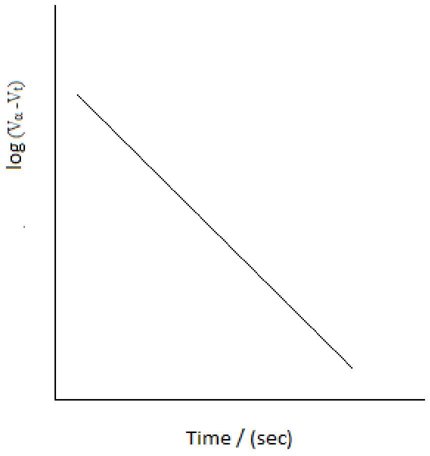


Fig. 16.4 A plot of log (V_α -V_t) against t

16.4.4 Calculations

The reaction is a pseudo-first-order reaction. The rate constant is given by

$$k = \frac{2.303}{t} \log [(V_\alpha - V_o)/(V_\alpha - V_t)]$$

$(V_\alpha - V_o)$ corresponds to the initial concentration of the ester, a.

$(V_\alpha - V_t)$ corresponds to (a-x), the concentration of the ester at time, t.

16.4.5 Result

The rate constant of the acid catalysed hydrolysis of the ester at ….^{o}C

a. By calculation, k = …………………s^{-1}.
b. From graph, k = …………………s^{-1}.

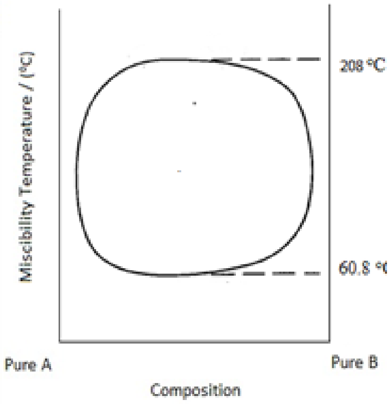
16.5 SUMMARY

- In this unit you have studied that the phase separation in partially miscible liquid pairs depends on the temperature and composition of the liquid mixture. Critical solution temperature is the highest or lowest point on the mutual solubility curve of liquid mixtures.
- The upper critical solution temperature (upper consolute temperature) is the highest temperature at which phase separation occurs. Above this temperature, the two components are fully miscible.
- Some systems show a lower critical solution temperature (lower consolute temperature), below which they mix in all proportions and above which they form two phases. Presence of impurities affects the critical solution temperature eg. presence of succinic acid increases the CST of phenol-water system.
- In this chapter we learned about the kinetics of reaction, mechanism of hydrolysis of ethyl acetate. We get knowledge about order of reaction and its determination by volumetric analysis. The experiments also provided an idea about rate constant and determination of energy of activation.

16.6 TERMINAL QUESTIONS

1. Define critical solution temperature.
2. Can partially miscible liquid pairs have more than one critical temperature? Give an example.

3. How does impurity affect the CST of a pair of two partially miscible liquids?
4. How many phases exist in the region enclosed within the curve in the given diagram?



5. Define rate of a reaction.
6. Define order of a reaction.
7. What is the order of acid-catalyzed hydrolysis of methyl acetate?
8. How to determine alkaline hydrolysis of ethyl acetate by conductometry?

16.7 REFERENCES

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