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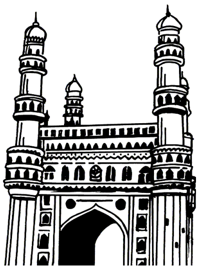

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- **(ii) Accuracy**
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UNIT - I

(Inorganic Chemistry)

S3-I-1: Chemistry of f-block elements

Chemistry of Lanthanides**:** Position in periodic table, Electronic structure, oxidation state, ionic and atomic radii - lanthanide contraction - cause and consequences, anomalous behavior of post lanthanides-complexation - type of donor ligands preferred. Magnetic properties - paramagnetism. Colour and spectra, f-f transitions - occurrence and separation - ion exchange method, solvent extraction.

Chemistry of actinides - general features - electronic configuration, oxidation state, actinide contraction, colour and complex formation. Comparison with lanthanides.

S3-I-2: Coordination Compounds-I

Simple inorganic molecules and coordination complexes. Nomenclature – IUPAC rules, 1. Coordination number, coordination geometries of metal ions, types of ligands. 2. Brief review of Werner's theory, Sidgwick's electronic interpretation and EAN rule and their limitations. (Valence bond theory (VBT) – postulates and application to (a) tetrahedral complexes $[Ni(NH_3)_4]^{2+}$, $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ (b) Square planar complexes $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$ (c) Octahedral complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[FeF_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$. Limitations of VBT. 3. Isomerism in coordination compounds, stereo isomerism – (a) geometrical isomerism in (i) square planar meta l complexes of the type $[MA_2B_2]$, $[MA_2BC]$, $[M(AB)_2]$, $[MABCD]$. (ii) Octahedral metal complexes of the type $[MA_4B_2]$, $[M(AA)_2B_2]$, $[MA_3B_3]$ using suitable examples, (b) Optical isomerism in (i). tetrahedral complexes [MABCD], (ii). Octahedral complexes $[M(AA)_2B_2]$, $[M(AA)_3]$ using suitable examples. Structural isomerism: ionization, linkage, coordination ligand isomerism using suitable examples.

S3-I-3: Metal carbonyls and Organometallic Chemistry

Metal carbonyls: Preparation and properties of $Ni(CO)_4$. Structural features of $Ni(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $Cr(CO)_6$ -18 valence electron rule. Definition, nomenclature and classification of organometallic compounds. Methods of preparation, properties and applications of alkyl and aryl compounds of Li, Mg & Al.

S3-I-1: Chemistry of f-block Elements

1.1 Chemistry of Lanthanides: Position in Periodic table, Electronic Structure, Oxidation State, Ionic and Atomic Radii

Q1. Write the electronic configuration of lanthanides and their position in periodic table.

Ans :

These are elements which in addition to containing incompleted d-orbital of the penultimate shell also have incomplete f-orbital of the antipenultimate (inner to the penultimate, i.e., n – 2) shell. The f-block elements are also known as inner transition elements.

f-block elements is $(n-2)\,f^{1-14}, (n-1)s^2\,(n-1)p^6\,(n-1)d^{0-1}\,ns^2$.

4f-block series, first inner transition series, Lanthanides or Lanthanones. In these elements differentiating electron goes to 4f-orbitals. Since, the number of electrons in the outermost, as well as in the penultimate shell, remains the same, all these fourteen elements are placed in the sixth period of the periodic table. Originally these elements were called rare-earths.

The reason for this is the remarkable similarities among the chemical properties of the lanthanides and also among the various members of actinides. d-block elements in which differentiating d-electrons are involved in chemical interaction.

These elements were placed inside the body of the periodic table.

Electronic configuration of Lanthanides

In lanthanides (Ce_{58} to Lu_{71}), the 5d orbital remains vacant and the differentiating electron enters successively in the 4f orbital except in gadolinium, Gd (Z = 64) it enters the 5d orbital so that the stable $4f^7$ (exactly-half-filled) configuration is retained. At ytterbium, Yb (Z = 70) since all the 4f orbitals are filled, the differentiating electron in the next element lutetium, Lu(Z = 71) enters 5d orbital.

Electronic Configuration of Lanthanides

At. No.	Element	Symbol	One view	Second view
57	Lanthanum	La	$[Xe]\,4f^0\,5d^1\,6s^2$	$[Xe]\,4\,f^0\,5d^1\,6s^2$
				$[Xe]\,4\,f^1\,5d^1\,6s^2$ or
58	Cerium	Ce	$[Xe]\,4\,f^1\,5d^1\,6s^2$	$[Xe]\,4\,f^2\,6s^2$
59	Praseodymium	Pr	$[Xe]\,4f^2\,5d^1\,6s^2$	$[Xe]\,4\,f^3\,6s^2$
60	Neodymium	Nd	$[Xe]\,4f^3\,5d^1\,6s^2$	$[Xe]\,4\,f^4\,6s^2$
61	Promethium	Pm	$[Xe]\,4f^4\,5d^1\,6s^2$	$[Xe]\,4\,f^5\,6s^2$
62	Samarium	Sm	$[Xe]\,4f^5\,5d^1\,6s^2$	$[Xe]\,4\,f^6\,6s^2$
63	Europium	Eu	$[Xe]\,4f^6\,5d^1\,6s^2$	$[Xe]\,4\,f^7\,6s^2$
64	Gadolinium	Gd	$[Xe]\,4f^7\,5d^1\,6s^2$	$[Xe]\,4\,f^8\,6s^2$
65	Terbium	Tb	$[Xe]\,4f^8\,5d^1\,6s^2$	$[Xe]\,4\,f^9\,6s^2$
66	Dysprosium	Dy	$[Xe]\,4f^9\,5d^1\,6s^2$	$[Xe]\,4\,f^{10}\,6s^2$
67	Holmium	Ho	$[Xe]\,4f^{10}\,5d^1\,6s^2$	$[Xe]\,4\,f^{11}\,6s^2$
68	Erbium	Er	$[Xe]\,4f^{11}\,5d^1\,6s^2$	$[Xe]\,4\,f^{12}\,6s^2$

69	Thulium	Tm	[Xe] $4f^{12}\,5d^1\,6s^2$	[Xe] $4\,f^{13}\,6s^2$
70	Ytterbium	Yb	[Xe] $4f^{13}\,5d^1\,6s^2$	[Xe] $4\,f^{14}\,6s^2$
71	Lutetium	Lu	[Xe] $4f^{14}\,5d^1\,6s^2$	[Xe] $4\,f^{14}\,5d^1\,6s^2$

Q2. Discuss the oxidation states of lanthanides.

Ans :

Oxidation States

The lanthanides display variable oxidation states but much less than those displayed by the transition elements. The characteristic and the most stable oxidation state of the lanthanides is +3 (Ln^{3+}).

(i) Lanthanum show only the +3 oxidation state the characteristic most stable oxidation state of all the (Ln^{3+}) configuration of La^{3+} ions is similar to that of Xenon which being highly stable does not lose electrons forming La^{4+} ion.

(ii) Gadolinium (Gd) and Lutetium (Lu) also form only the tripositive M^{3+} ions because the removal of three electrons gives the stable $4f^7$ (half filled) and $4f^{14}$ (completely filled) configuration respectively.

(iii) In addition to the usual +3 oxidation state, few of the lanthanides also show +2 and +4 oxidation states. Then +2 and +4 oxidation states may be explained in terms of extra stability associated with empty, half-filled or completely-filled 4f subshell. For example.

Ce^{4+} has f^0; Eu^{2+} has f^7, Yb^{2+} has f^{14} and Tb^{4+} has f^7 configuration.

(iv) Certain oxidation states e.g., Sm^{2+} having f^6, Tm^{2+} having f^{13}, Pr^{4+} having f^1 configuration, etc., cannot be explained on the basis of extra stability of an empty, half-filled or completely-filled f-subshell. The stabilities of such oxidation states are based on highly complicated thermodynamic and kinetic considerations.

1.2 LANTHANIDE CONTRACTION - CAUSE AND CONSEQUENCES, ANOMALOUS BEHAVIOR OF POST LANTHANIDES - COMPLEXATION - TYPE OF DONOR LIGANDS PREFERRED

Q3. What is Lanthanide contraction? Discuss its consequences?

Ans : **(Imp.)**

Ionic Radii (Lanthanide Contraction)

It consists of a regular decrease in the size of atoms/ions with increase in atomic number as we move across from La to Lu. Thus, among lanthanides, Lanthanum has largest and Luteium has the smallest radius. This show decrease in size is known as the lanthanide contraction.

Cause of Lanthanide Contraction

The configuration of lanthanides show that the additional electron enters the 4f-subshell. The shielding of one 4f electron by another from the increasing nuclear charge is very little (i.e., imperfect), being even smaller than that encountered in case of d-electrons (d-transition series). The imperfect shielding of f-electrons is due to the shape (very much diffused) of f orbitals. Thus as atomic number increases, the nuclear charge increases by unity at each step, while no comparable increase in the mutual shielding effect of 4f-electrons occurs. This causes a contraction in the size of the 4f-subshell. Consequently the atomic and ionic size go on decreasing as we move from La to Lu.

Consequence of Lanthanide Contraction

(i) Occurrence of Ytterbium (a transition element) with heavier lanthanides

Since the size of Y^{3+} ion (~ 0.90 $\overset{\circ}{A}$) is comparable to the heavier lanthanide ions viz. Tb^{3+}, Dy^{3+}, Ho^{3+} and Er^3 the crystal structure, solubility and chemical properties of the ytterbium compounds are so close to the corresponding compounds of the heavier lanthanides that are commonly referred to a ytterbium earths.

(ii) Basicity Differences

The basic strength of the oxides and hydroxides of lanthanides decreases with increase in atomic number. Thus $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic. This is explained on the basic of lanthanide contraction. This successive decrease in size of the lanthanide cations (lanthanide contraction) successively increases the covalent character (i.e., decreases the ionic character) between the lanthanides ion and the hydroxide ion (Fajan's rules), thereby reducing the basic character of the lanthanide hydroxides.

Q4. Explain the anomalous behaviour of postlanthanides?

Ans :

The elements following lanthanides are called post-lanthanide elements. Transition elements of the third series (i.e., the transition elements following the lanthanides) have virtually the same atomic and ionic sizes as the corresponding elements just above them in their respective sub-groups.

1.3 MAGNETIC PROPERTIES - PARAMAGNETISM, COLOUR AND SPECTRA

Q5. Discuss the colour and magnetic properties of lanthanides.

Ans : **(Imp.)**

Colour

Lanthanide	No. of 4f or	Colour	No. of electrons 4f unpaired	4f	Lanthanide ion
La^{3+}	0	Colourless	0	14	Lu^{3+}
Ce^{3+}	1	Colourless	1	13	Yb^{3+}
Pr^{3+}	2	Pale green	2	12	Tm^{3+}
Nd^{3+}	3	Reddish	3	11	Er^{3+}
Pm^{3+}	4	Yellowish	4	10	Ho^{3+}
Sm^{3+}	5	Yellowish	5	9	Dy3+
Eu^{3+}	6	Colourless	6	8	Tb3+
Gd^{3+}	7	Colourless	7	7	Gd^{3+}

the colour of the ions depends on the number of unpaired f electrons.

Lanthanide ions having empty, half-filled or completely filled 4f orbital are colourless, e.g., La^{3+} ($4f^0$), Gd^{3+} ($4f^7$) and Lu^{3+} ($4f^{14}$) and Lu^{3+} ($4f^{14}$) ions are colourless.

Ce^{3+} and Yb^{3+} are colourless although both contain one unpaired electron each.

Dipositive and tetrapositive ions which are isoelectronic with tripositive ions (ions having same number of unpaired electrons) have different colours.

Ln^{3+} ion	Colour	No. of unpaired	Colour	Ln^{2+}/Ln^{4+} ions
La^{3+}	Colourless	0	Orange-red	Ce^{4+}
Eu^{3+}	Pale pink	6	Reddish	Sm^{2+}
Gd^{3+}	Colourless	7	Straw-yellow	Eu^{+2}
Lu^{3+}	Colourless	0	Green	Yb^{+2}

The colour absorption in turn depends on the energy needed by electrons to be excited from one level to another, i.e., f-f transition. This energy in turn depends upon the number of available orbitals to which 4f electrons can be excited in the individual cation.

Magnetic Properties

Diamagnetism (repulsion by a magnet) in an ion arises due to pairing of electrons. In pairing, opposite spins of the two electrons cancel each other with the result a substance made up entirely of paired electrons will have no overall spin and will therefore, be diamagnetic, paramagnetism (attraction by a magnet) arises when an atom, ion or molecule possesses one or more unpaired electrons.

Thus La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$), having no unpaired electron do not show paramagnetism while all other tripositive ions of lanthanides are paramagnetic.

1.4 f-f TRANSITIONS - OCCURRENCE AND SEPARATION - ION EXCHANGE METHOD, SOLVENT EXTRACTION

Q6. Write the separation methods of Lanthanides ion-exchange method and solvent extraction.

Ans :

Separation of The Lanthanides

The separation method based on slight differences in their solubilities, complex formation, based on the slight differences in their solubilities complex formation basic properties and hydration. These differences in properties in turn is due to very slight size differences of their trivalent ions.

Ion Exchange Method

The method is based upon the fact that the steady decrease in size and consequent in basicity causes the statue increase with increasing atomic number in the binding of ligands. This causes increases in the hydrated radii of the lanthanide^{3+} ions with the increase in atomic number and lastly the affinity for the resin decreases with the radius of the hydrated ion. When a mixture of lanthanide^{3+} ions is passed slowly through a column of cation exchange resin the heavier members come through first.

$$Ln^{3+}\,(aq.) + 3HR \longrightarrow 3H^+\,(aq.) + LnR_3$$

This can be verified by the law of mass action.

$$K = \frac{[H^+(aq.)]^3}{[HR]^3} \times \frac{LnR_3}{Ln^{3+}(aq.)}$$

Since the ratio LnR_3/Ln^{3+} (aq.) decreases with the increasing atomic number, the constant K decreases i.e., the absorption of lanthanide$^+$ ions decreases with the increases in atomic number.

The above separation obtained because of difference in the absorption of the hydrated cations by the cation exchange resin, can be enhanced by the use of complexing agents, viz. ethylene diamine tetra-acetate (EDTA), citrates, and other hydroxy or amino carboxylic acids at an appropriate pH.

A synthetic ion-exchange resin with functional groups like – COOH and – SO_3H is packed in a long column fixed in a vertical position. A solution of mixture of lanthanide ions is allowed to flow through the vertical column. The lanthanide ions (M^{3+}) replace H^+ ions of the functional groups.

$$3H-(\text{Resin}) + M^{3+} \longrightarrow M-(\text{Resin})_3 + 3H^+$$

The H^+ ions flow down the column and move out through the tap provided at the bottom. The column now contains the lanthanide ions fixed on to the resin. In order to recover them, the column is eluted (i.e., leached) with a buffered solution of critic acid/ammonium citrate. As the citrate solution moves down, the lanthanide ions in the resin come out and form citrate complex.

$$M-(\text{Resin})_3 + 3H(\text{citrate}) \longrightarrow 3H-\text{Resin} + M-(\text{citrate})_3$$

As the citrate complex travels down, the M^{3+} is recaptured by the resin. As more eluting solution comes down, the M^{3+} ions again come off the resin. This process of getting off and getting recaptured continues through their journey in the vertical column.

The tendency of a lanthanide cation to exchange with the hydrogen of the resin increases with cation size, the tendency to form complex ions with citrate increases much more rapidly with decreasing cation size, i.e., as the solution passes through the exchange column the elements are displaced in the reverse order of the atomic number. This is because of greater hydration of smaller ions in aqueous solution. Thus the heavier most lanthanide (lutetium) comes first and the lightest most lanthanide (lanthanum) comes last. Although the method was first applied on tracer quantities it was used to separate kilogram quantities of the lanthanides in a very pure state nearly 99.99%.

Solvent Extraction Method

This method is based on the slight difference in partition coefficients of the salts of these metals between water and organic solvents. For example, the partition coefficient of $Gd(NO_3)_3$ between water and normal tributyl phosphate (TBP) is 1.06 times greater than that of $La(NO_3)_3$. This means that $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in tributyl phosphate. Thus gadolinium can be obtained from the organic phase by very large number of partitions performed using a counter current appratus.

1.5 Chemistry of Actinides - General Features - Electronic Configuration, Oxidation State, Actinide Contraction, Colour and Complex Formation

Q7. What are actinides. Explain the electronic configuration, oxidation states of actinides.

Ans :

The Actinide Series

The elements with atomic numbers 89 – 103, in which the 5f orbitals are being filled up, constitute the actinide series. In actinides the antipenultimate 5f orbital is filled successively by the addition of one electron at each step. Thus, lanthanides constitute the first inner transition series while actinide constitute the second inner transition series.

General Characteristics of Actinides

Electronic Configuration

There is some uncertainty about the electronic structure of these elements. The uncertainty with respect to the entry of electrons is 5f or 6d orbital is due to the fact that both of these orbitals are of almost equal energy. Thus, there are two views regarding the electronic configuration of these elements. According to one (Seaborg view) the 5f-orbital starts filling at thorium while according to other (Dawson view) the 5f-orbital starts filling at Neptunium. The elements following Uranium, in which the 5f-orbital is definitely being filled, are called uranides.

Thus the general electronic configuration of actinides is

[Rn] $5f^{0-14}\ 6d^{0-2}\ 7s^2$

where [Rn] is the electronic configuration of Radon, i.e.,

[Rn] = $1s^2\ 2s^2\ p^6\ 3s^2\ p^6\ d^{10}\ 4s^2\ p^6\ d^{10}\ f^{14}\ 5s^2\ p^6\ d^{10}\ 6s^2\ p^6$

Element	Symbol	Seaborg View	Dawson View
Actinium	Ac	[Rn] $6d^1\ 7s^2$	[Rn] $6d^1\ 7s^2$
Thorium	Th	[Rn] $5f^1\ 6d^1\ 7s^2$	[Rn] $5f^0\ 6d^2\ 7s^2$
Protactinium	Pa	[Rn] $5f^2\ 6d^1\ 7s^2$	[Rn] $5f^0\ 6d^3\ 7s^2$
Uranium	U	[Rn] $5f^3\ 6d^1\ 7s^2$	[Rn] $5f^0\ 6d^4\ 7s^2$
Neptunium	Np	[Rn] $5f^4\ 6d^1\ 7s^2$	[Rn] $5f^4\ 6d^1\ 7s^2$
Plutonium	Pu	[Rn] $5f^5\ 6d^1\ 7s^2$	[Rn] $5f^5\ 6d^1\ 7s^2$
Americium	Am	[Rn] $5f^7\ 6d^0\ 7s^2$	[Rn] $5f^6\ 6d^1\ 7s^2$
Curium	Cm	[Rn] $5f^7\ 6d^1\ 7s^2$	[Rn] $5f^7\ 6d^1\ 7s^2$
Berkelium	Bk	[Rn] $5f^8\ 6d^1\ 7s^2$	[Rn] $5f^8\ 6d^1\ 7s^2$
Californium	Cf	[Rn] $5f^9\ 6d^1\ 7s^2$	[Rn] $5f^9\ 6d^1\ 7s^2$
Einsteinium	Es	[Rn] $5f^{10}\ 6d^1\ 7s^2$	[Rn] $5f^{10}\ 6d^1\ 7s^2$
Fermium	Fm	[Rn] $5f^{11}\ 6d^1\ 7s^2$	[Rn] $5f^{11}\ 6d^1\ 7s^2$
Mendelevium	Md	[Rn] $5f^{12}\ 6d^1\ 7s^2$	[Rn] $5f^{12}\ 6d^1\ 7s^2$
Nobelium	No	[Rn] $5f^{13}\ 6d^1\ 7s^2$	[Rn] $5f^{13}\ 6d^1\ 7s^2$
Lowrencium	Lr	[Rn] $5f^{14}\ 6d^1\ 7s^2$	[Rn] $5f^{14}\ 6d^1\ 7s^2$

Oxidation States

Actinides show a variety of oxidation states, viz. Uranium show all the oxidation states from +3 to +6, Np and Pu from +3 to +7. The principal oxidation states of actinides are +3 and +4, although in some cases +2, +5 and +6 oxidation states are most important. The +3 oxidation state is the most stable in Ac, Am and all the following elements, +4 oxidation state is the most stable in Th and Pu; +2 in No, +5 in Pa and Np, and +6 in U.

The ionic radius of actinides decreases regularly along the series. The decrease in ionic radii, known as actinide contraction. (if lanthanide contraction), is due to the poor screening of the nuclear charge by the f electrons.

Q8. Discuss the colour and complex formation of actinides.

Ans :

Colour

Actinide ions are usually coloured. The colour depends upon the number of 5f electrons; ions having no $5f^0$ electron of $5f^7$ electrons are colourless. The colour arrises due to f-f transitions between various energy states within the 5f subshell.

Complex Formation

The actinides have large tendency to form complexes than lanthanides because their ions have high charge and smaller ions. The degree of complex formation decreases in the order.

$$M^{4+} > MO_2^{2+} > M^{3+} > MO^{2+}$$

The complexing power of different singly charged and doubly charged anions follows the order.

$$F^- > NO_3^- > Cl^-$$

$$CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$$

Actinides also form complexes with a large number of organic substances.

1.6 Comparison with Lanthanides

Q9. Write the differences between Lanthanides and actinides.

Ans : **(Imp.)**

In both elements f-orbital is being progressively filled, the two series of elements resemble each other. On the other hand, they also differ from each due to lower binding energies of the 5f electrons (in actinides) than those of 4f electrons (in lanthanides). Moreover, since the 5f electrons also provide less effective shielding than the 4f electrons, the actinides have much greater tendency to form complexes than the lanthanides.

Similarities between Lanthanides and Actinides

1. In both series the predominant oxidation state is +3.
2. In both series f-orbitals are being progressively filled.
3. Both show decrease (contraction) in covalent/ionic radii with the increase in atomic number.
4. Element of both series have low electronegativity and are very reactive.
5. The nitrates, perchlorates and sulphates of the trivalent actinides as well as lanthanides are soluble while the hydroxides, fluorides and carbonates are insoluble.
6. Actinides, like lanthanides, show ion-exchange behaviour.

Difference

Lanthanides	Actinides
1. The additional electron enters 4f orbital.	1. The additional electron enters 5f orbital.
2. Due to large energy difference between 4f and 5d sub-levels, their chemistry is fairly similar.	2. Due to very small difference between 5f and 6d sub-levels, there is a considerable variability in the chemistry of these elements.
3. Binding energies of 4f-orbitals are higher.	3. Binding energies of 5f orbitals are lower.
4. 4f-Electrons have greater shielding effect.	4. 5f-Electrons have poor shielding effect.
5. Maximum oxidation state exhibited by lanthanides is + 4 e.g. Ce^{4+}	5. Due to lower binding energies they show higher oxidation states such as +4, +5, +6 and +7.
6. They do not form complexes easily. Their complexes with π bonding ligands are not known.	6. They have much tendency to form complexes. They form complexes even with π-bonding ligands such as thioethers.
7. They do not form oxocations.	7. They form oxocations such $UO_2^{2-}, UO^+, NpO_2^+, PuO_2^+$ etc.
8. Except promethium, they are non radioactive	8. All of them are radioactive
9. Most of their ions are colourless.	9. Most of their ions are coloured
10. They are paramagnetic and their magnetic properties can be explained.	10. They are also paramagnetic but the magnetic properties are very difficult to interpret.
11. Their compounds are less basic	11. Their compounds are more basic.

S3-I-2: COORDINATION COMPOUNDS-I

1.7 SIMPLE INORGANIC MOLECULES AND COORDINATION COMPLEXES

Q10. Define simple salts & double salts?

Ans :

Simple Salts

Simple salts dissolved in water, these salts ionise and produce ions in solution.

Ex NaCl

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

Molecular or Addition Compounds

When solutions containing two or more salts in stoichiometric proportions are allowed to evaporate. We get crystals of compounds known as molecular or addition compounds. These are two types.

1. Those which lose their identity in solution (double salts)
2. Those which retain their identity in solution (complexes)

Double Salts

In aqueous solution they give the test of all their constituent ions.

$KCl.\ MgCl_2.\ 6H_2O \rightarrow K^+ + Mg^{2+} + 3Cl^- + 6H_2O$

Carnallite

$FeSO_4\ (NH_4)_2\ SO_4\ .\ 6H_2O \rightarrow Fe^{2+}\ (aq) + 2NH_4^+\ (aq) + 2SO_4^{2-}\ (aq)$

Mohr's salt

$K_2SO_4.\ Al_2(SO_4)_3.24H_2O \rightarrow 2K^+\ (aq) + 2Al^{3+}\ (eq) + 4SO_4^{2-}\ (aq) + 24H_2O$

Potashalum

Q11. What is coordination complex?

Ans :

Coordination or Complex Compounds

When potassium ferrocyanide is dissolved in water it does not give the usual tests for Fe^{2+} and CN^- ions indicating that these ions which were originally present are not formed when potassium ferrocyanide is dissolved in water. These ions are present in the forms of new ion called ferrocyanide ion which is a complex ion and does not ionise into constituent ions.

$$K_4\ [Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Compounds containing complex ions are called complex compounds. Complex ion may be defined as an electrically charged (cationic or anionic) or even a neutral species and is formed by the combination of a simple cation with more than one neutral molecule or negative ion.

1.8 NOMENCLATURE – IUPAC RULES, COORDINATION NUMBER, COORDINATION GEOMETRIES OF METAL IONS, TYPES OF LIGANDS

Q12. What are the terms used in coordination compounds?

Ans :

Terms Used in Coordination Compounds

Central Ion

The cation to which one or more neutral molecules or anions are attached is called the centre of coordination.

Ligand

Any atom, ion, or molecule which is capable of donating a pair of e^-s to the central atom is called a coordinating group of ligand. Ex. F^-, Cl^-, Br^-, CN^-, I^-

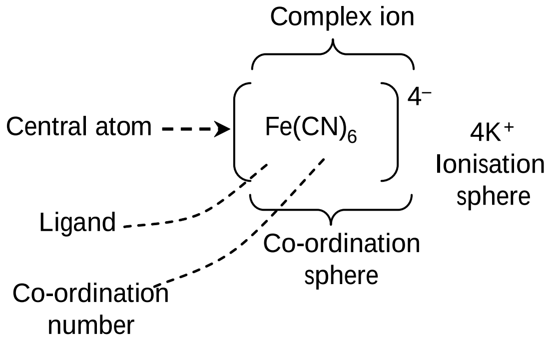
Coordination Number (CN)

The total number of ligands attached to the central ion is known as the coordination number of that ion.

Ex : $[Ag(NH_3)_2]^+$ CN is 2

Coordination Sphere

The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.



Q13. Define oxidation number findout the oxidation number in different complexes.

Ans :

Oxidation Number

It is a number which represents the electric charge on the central metal atom of a complex ion.

Ex : Potassium Ferrocyanide $K_4[Fe(CN)_6]$

The complex has four monovalent cations outside the coordination sphere, the complex must carry four negative charge i.e., $[Fe(CN)_6]^{4-}$. The no. of CN^- ions 6 represents the coordination number of iron ion. Cyanide is unidentate

$[Fe(CN)_6]^{4-}$

$x + (-6) = -4$

$x = -4 + 6 = +2$

$[Co(NH_3)_3(NO_2)_3]$

The complex does not carry any charge i.e., it is neutral. The central atom is attached to $3NH_3$, $3NO^-_2$, radicals both are unidentats. ∴ CN of cobalt is 6

$[Co(NH_3)_3 (NO_2)_3]$

$x + (O)_3 + (-3) = 0$

$x - 3 = 0$

$x = +3$

$[Cr(C_2O_4)_3]^{3-}$

Here the oxalate is bidentate ligand. Three oxalate ligands carry a total charge of – 6. Hence CN of Cr is 6. Cr – Oxidation no + 3

$x + (-2 \times 3) = -3^-$

$x - 6 = -3$

$x = -3 + 6$

$x = +3$

$Ni(CO)_4$

CN of Ni is 4 carbonyl group is unidentate complex as well as the ligand has no charge. Nickel atom must be nutral. ∴ Ni oxidation number is zero.

Q14. Classify the ligands.

Ans :

Classification of Ligands

1. **Classification based on donor and acceptor properties of the ligands.**

   a) Ligands having one or more lone pair of e⁻s. Ligands which contain vacant π-type orbitals that can recent back donate π - e⁻s from the metal ion in low oxidation state.

   Ex : CO, NO, CN, NC

   The complexes formed by these metals & ligands both metal and the ligand function both as donors and acceptors

   $$M \underset{\pi}{\overset{\sigma}{\leftrightarrows}} L$$

   b) Ligands which donot have vacant orbitals to receive back donated e⁻s from the metal.

   Ex : H_2O, NH_3, F.

   c) Ligands having no lonepairs of e^- but have π-bonding e⁻s. e.g: ethylene, benzene, cyclopentadienyl ion.

2. **Classification based on the number of donor atoms present in the ligands**

   The ligands classified into

   (a) Monodentate or Unidentate Ligands

   The ligands which have only one donor and can co ordinate to the central metal ion at one site only are called monodentate ligands. The ligands may be neutral molecules, negatively charged ions (anions) or positively charged ions (cations)

   (b) Neutral Monodentate Ligands

   The names of neutral ligands are not systematic

   Ex : H_2O - Aquo
   NH_3 - Ammine
   CO - Carbonyl
   NO - Nitrosyl
   CS - Thiocarboxyl

   Negative mono dentate ligands

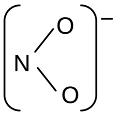
   F^- - Fluoro
   Cl^- - Chloro
   Br^- - Bromo
   I^- - Iodo

   CN^- - Cyano
   OCN^- - Cyanato
   SCN^- - Thiocyanato
   NO_2^- -Nitro
   OH^- - Hydroxo

   H^- - Hydrido
   NH_2^- - Amido
   NO_3^- - Nitrato
   SO_4^{-2} - Sulphato
   CO_3^{-2} - Carbonate

(c) Ambidentate Ligands

These are ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time. Those ligands are called ambidentate ligands.



ion - Nitro (M – NO_2)

Nitrito (M – ON = O)

CN^- ion - Cyano (MCN)

Isocyano (MNC)

NCS^- ion - Thiocyanate (MSCN)

iso thiocyanate [MNCS]

$S_2O_3^{2-}$ ion - Thiosulphato-S [$MOSO_2S$]

4. Positive Monatentate Ligands

NO^+ - Nitrosylium

$H_2N\,NH_3^+$ - Hydrazinium

5. Bridging Ligands

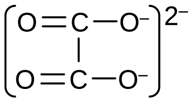
The monodentate ligand may have more than one free e^- pair. Thus may simultaneously coordinate with two or more atoms. The ligand forms two σ-bonds with two metal atoms and acts a bridge between the metal atoms. The ligand is called bridging ligand.

Ex : OH^-, F^-, Cl^-, NH_2^-, CO, O^{2-}, SO_4^{2-}

6. Bidentate, Tridentate .. Polydentate Ligands

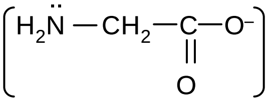
The ligands having two, three, four, five or six donor atoms are called bi, tri tetra, penta and hexa dentate ligands. The bidentate, tridentate etc are called polydentate ligands.

Ex : Ethylene diamine $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ is bidentate ligand with two neutral donor atoms.

Oxalate ion  bidentate with two acidic donors symmetrical bidentate ligands

$$\begin{bmatrix} O=C-O^- \\ | \\ O=C-O^- \end{bmatrix}^{2-}$$

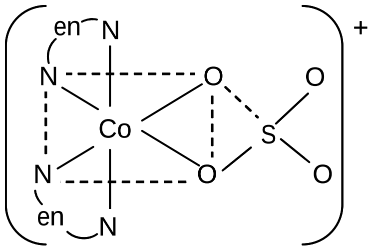
(two donor atoms are the same)

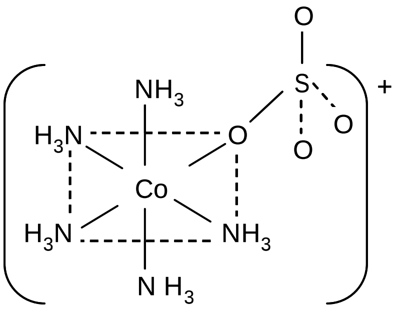
Glycinato ion  two donor atoms are different unsymmetrical bidentate ligand

$$\left[H_2\ddot{N}-CH_2-\underset{\underset{O}{\|}}{C}-O^- \right]$$

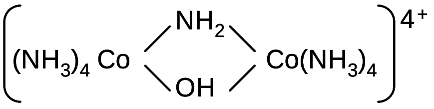
7. Flexidentate Ligands

Polydentate ligands have flexidentate character i.e., polydentate ligand may not necessarily use all its donor atoms to get coordinated to the metal ion. Eg In $[Co^{III}(NH_3)_5SO_4]^+$ and $[Co^{III}(en)_2SO_4]$ sulphate acts as a monodentate and bidentate ligands.



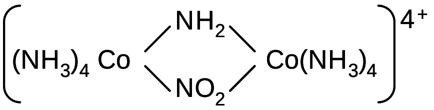


8. Naming of the Bridging ligands of the Bridged Polynuclear Complexes



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ OH\end{matrix}Co(NH_3)_4\right]^{4+}$$

μ-amido μ-hydroxo
octa ammine cobalt(III)
ion



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ NO_2\end{matrix}Co(NH_3)_4\right]^{4+}$$

μ-amido μ-nitro
octa ammine
cobalt (III) ion

IUPAC Names of Complex Compounds

$[Co(NH_3)_6]Cl_3$	-	Hexa ammine Cobalt (III) Chloride
$[CoSO_4(NH_3)_4]NO_3$	-	Tetra ammine sulphato cobalt (III) nitrate
$[Zn(NCS)_4]^{2+}$	-	Tetra thiocyanato - N - Zinc (II)
$Li[AlH_4]$	-	Lithium tetra hydrido Aluminate (III)
$[CoCl(CN)(NO_2)(NH_3)_5]$	-	Tri ammine chloro cyano nitro cabalt(III)
$Na_2[ZnCl_4]$	-	Sodium tetra chloro zincate (II)
$K_4[Fe(CN)_6]$	-	Potassium hexacyano ferrate (II)
$Na_3[Ag(S_2O_3)_2]$	-	Sodium bis (Thiosulphoto) argentate (I)
$[Cr(en)_3]Cl_3$	-	Tris (ethylene diamine) chromium (III) chloride
$[Ni(CO)_4]$	-	Tetracarbonyl Nickel (O)
$[Cr(C_6H_6)_2]$	-	Bis(benzene) chromium (O)
$[PtCl_4(NH_3)_2]$	-	Tetra chloro diamine platinate (II)
$K_3[Fe. C_2O_4)_3].3H_2O$	-	Potassium tris oxalato ferrate (III) water

Q15. Write the IUPAC names for the given coordination complexes.

Ans : **(Imp.)**

1. If the complex compound is ionic in nature, means if it is followed by the name of anionic position.
2. If the complex compound is neutral its name is written as single word.
3. In naming of complex, first the names of the ligand without reference to their charges are written in the order of English alphabets. Then the metal name is to be written.

4. **(i) Naming of ligands**

a) The names of negative ligands shall end with ‘0’.

F^- – Fluoro OH^- – hydroxo

H^- – Hydrido SH^- – Mercapto

b) For neutral ligands, there are no subsidiary names. But some neutral ligands are given special names.

NH_3 – Ammine

H_2O – Aqua

CO – Carbonyl

NO – Nitrosyl

c) The names of positively charged ligands end with “ium” suffix.

$N_2H_4^+$ – Hydrazinium

NO^+ – Nitrosonium

(ii) Numbering of ligands

a) If complex compound possess same type of ligand more than one time then their number is represented by using following prefixes.

2 – di

3 – tri

4 – Tetra

5 – Penta

6 – Hexa

7 – Hepta

8 – Octa

9 – Nona

10 – Deca

b) If a complex ligand of some type is present for more the one time then the number is represented by using following prefix.

2 - bis, 3 - tris, 4 - tetrakis 5 - pentakis

(iii) Naming of Ambidentate Ligands

When ambidentate ligand bonded to the metal then the donor atom which is directly bonded to the metal is represented will brackets after the name of the ligand.

Ex: Cyano (C) CN^- $M \leftarrow CN$ $M \leftarrow NC$ Isocyano (NC)

(iv) Naming of bridged ligand

a) If only one ligand acts as a bridge between two metal at then prefix is used before the name of the ligand.

b) If similar type of ligands more than one acts as a bridge two metal atoms then the number of bridged ligands are given as follows.

Ex : If two ligands acts as a bridge μ - di.

If three ligands acts as a bridge μ - tri.

If four ligands acts as a bridge μ - tetra.

c) If complex process bridged and non-bridged ligands of similar type then first name the bridged ligands with μ prefix followed by non-bridged ligands.

d) If a complex possess different types of bridged and non-bridged ligands first name the non-bridged ligands follow by bridged ligands with prefix μ.

e) In a bridged complex metal atoms number represented by using the prefixes di, tri, tetra etc.

5. Naming of the Metal

a) If coordination sphere is in cationic position (or) if it carries +ve charge (or) if it is neutral then there is no charge to the name of metal.

Ex : Ni – Nickel, Co-Cobalt, Cu-Copper, Zn - Zinc

b) If coordination sphere is in anionic position (or) it carries +ve charge then the name of metal atom ends with ate.

Al - Aluminate	Ti - Titanate
B - Borate	V - Venadate
Be - Berylate	Cr - Chromate

c) If coordination sphere carries +ve or –ve charge after the name of coordination sphere give the word ion.

d) If in cationic position hydrogen is present then the name of metal atom ends with 'ic' acid.

6. The oxidation state number of the metal in the complex is written beside the name of the metal in roman numeral in brackets.

1.9 Brief Review of Werner's Theory, Sidgwick's Electronic Interpretation and EAN Rule and Their Limitations

Q16. Explain the postulates of Werner's theory.

Ans : **(Imp.)**

Postulates of Werner's Theory

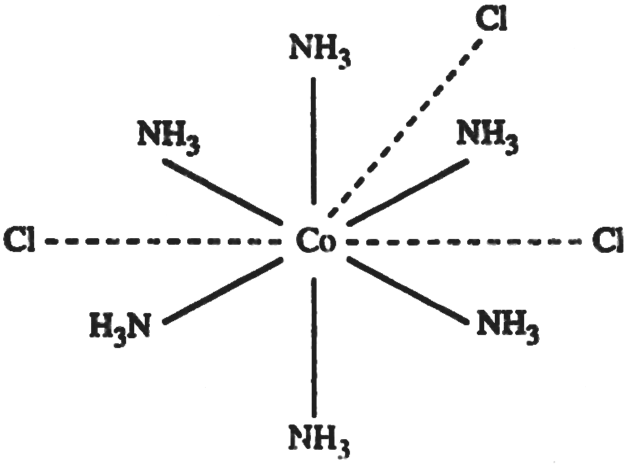
1. Generally, elements exhibit two types of valences, namely primary valence and secondary valence. The primary valence is also known as ionisable valence and secondary valence is known as nonionisable valence. Anions can satisfy primary valence whereas anions or neutral molecules can satisfy secondary valence. In modern terms, the primary valence corresponds to the oxidation number and the secondary valence corresponds to the coordination number.

2. All elements tend to satisfy both primary and secondary valencies. For example, in $CoCl_3.4NH_3$, two of the three chloride ions are attached by secondary valence and hence it is represented as $[Co(NH_3)_4C1_2]C1$.
3. The secondary valencies are directed towards some fixed positions in space. For example, in 4-coordinated complexes the four valencies are arranged in either a planar or a tetrahedral manner and in 6-coordinated complexes the 6 valencies are directed towards the six corners of an octahedron.

Table: Werner's cobalt complexes

Complex	No. of Cl^- ions precipitated as AgCl	Formula	No. of ions in solution	Molar conductivity (Ohm^{-1})
$CoCl_3.6NH_3$ (A)	3	$[Co(NH_3)_6]Cl_3$	4	~404
$CoCl_3.5NH_3$ (B)	2	$[Co(NH_3)_5Cl]Cl_2$	3	~229
$CoCl_3.4NH_3$ (C)	1	$[Co(NH_3)_4Cl_2]Cl$	2	~97
$CoCl_3.3NH_3$ (D)	0	$[Co(NH_3)_3Cl_3]$	0	0

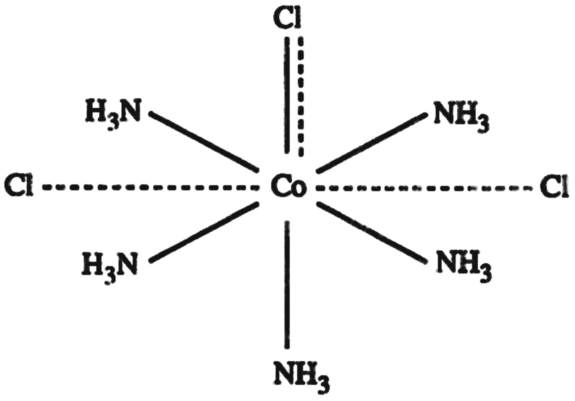
The data in table can be explained by Werner's coordination theory. According to Werner's theory, the first member of the series (A) is formulated as $[Co(NH_3)_6]Cl_3$. In this complex the primary valences (longer dotted lines) are satisfied by the three chloride ions.



Figure

The six secondary valencies (shorter solid lines) are satisfied by the six ammonia molecules. These ammonia molecules are very tightly bound to cobalt and hence they do not dissociate in solution. But the three chloride ions are far away from the central cobalt and hence they are less firmly held by the metal. Therefore, all the three chloride ions dissociate in solution giving $[Co(NH_3)_6]^{3+}$ and $3Cl^-$ ions, with a total of four ions. Thus, Ag^+ precipitates all the three chloride ions as AgCl and the molar conductivity of the complex corresponds to that of a tetra-univalent electrolyte (~ 404 Ohm^{-1}). The bond between the metal and the ligand is called coordinate covalent bond.

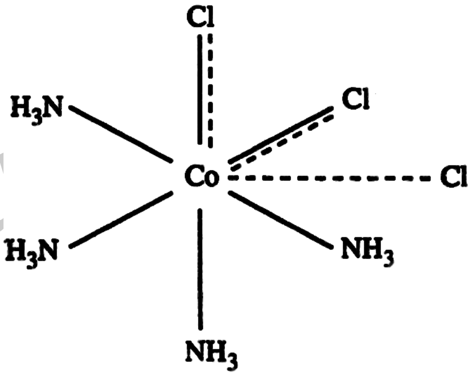
The second member (B) of the series. $CoCl_3.5NH_3$ is formulated as $[Co(NH_3)_5Cl]Cl_2$. Since there are only five ammonia molecules to satisfy the secondary valencies, one chloride ion must play the double role of satisfying both a primary and a secondary valency. This is because the fulfillment of all secondary valences is essential according to one of the postulates of Werner.



Figure

Werner represented the bond between such a ligand and the central metal by a combined solid and dotted line as shown in Figure. The chloride playing the double role is very firmly held by the central metal and hence is not precipitated as AgCl by Ag^+ ions in solution. Two-thirds of its chloride content of the complex is present in the second coordination sphere; therefore, it is formulated as $[Co(NH_3)_5Cl]Cl_2$. In solution it gives a total of 3 ions, $[Co(NH_3)_5Cl]^{2+}$ and 2Cl. Its molar conductivity corresponds to that of bi-univalent electrolyte (~ 229 Ohm^{-1}).

The next member of the series $CoCl_3.4NH_3$, leads to the structure figure with the Werner formulation $[Co(NH_3)_4Cl_2]Cl$.



Figure

The two chloride ions in this complex satisfy both the primary and secondary valencies. Hence, both of them are tightly bound to the central metal. In solution the complex dissociates into two ions, $[Co(NH_3)_4Cl_2]^+$ Cl^-. Only 1/3 of its chloride content gets precipitated as AgCl and its molar conductivity corresponds to that of a uni-univalent electrolyte (~ 97 Ohm^{-1}), (+1, –1).

Werner's theory predicts structure shown in Figure for the next member of the series, $CoCl_3.3NH_3$ and it is formulated as $[Co(NH_3)_3C1_3]$. This theory also predicts that this complex will not yield any chloride ion in solution. Actually, no chloride ion is precipitated as AgCl on treating it with $AgNO_3$ solution. It is a non-electrolyte in solution because no ions are produced its solution.

Defects of Werner's theory

1. Werner's theory describes the structures of many coordination compounds successfully; however, it does not explain the nature of bonding within the coordination sphere.

2. More than 90% of the known complexes at Werner's time were either 4- coordinated or 6-coordinated. Werner's theory is unable to account for the preference for 4-and 6-coordination among complexes.
3. Werner's theory fails to account for the fact that certain 4-coordinated complexes are square-planar whereas some others are tetrahedral.

Q17. Describe sidgwick electronic interpretation a nd EAN rule and their limitations.

Ans : **(Imp.)**

Postulates of Sidgwicks' theory

1. Number of electrons lost by the metal atom to form the metal ion cause its primary valency.
2. Secondary valency is due to the acceptance of the lone pairs of electrons by the metal atom or ion from the groups around the metal atom or ion.
3. An ionic bond is formed between the metal atom and primary valency.
4. Coordinate covalent bond is formed between the metal ion and ligand by accepting the lone pair of electrons by the metal ion of the ligands. The process by which this bond is formed is different from that of the conventional covalent bond. But after the bond formed, bond acquires complete covalent character and is denoted as $M \leftarrow L$.
5. A new concept of effective atomic number was introduced to correlate the coordination number of the metal atom in the complex compounds with atomic number of metal ion.

Effective Atomic Number [EAN] - its Calculation

The number of electrons acquired by the central metal atom in coordination compounds gaining them either from the ligands or otherwise is called effective atomic number.

EAN is generally equal to the atomic number of the inert gas element in the period in the periodic table in which the central metal atom is present.

EAN atomic number of metal atom – Number of e^- lost by metal atom to form positive ion + electrons gained from the ligand.

EAN = Atomic number of metal atom – O.S of metal ion + 2 × coordination number.

Ex : $[Co(CO)_6]$

EAN = Atomic number of metal atom – Number of e^- lost by metal + e^- gained from the ligand.

= 24 – 0 + 12 = 36 – Kr $e^{\ominus}$ configuration

$[Fe(CN)_6]^{-4}$

= 26 – 2 + 12 = 36 = Kr $e^{\ominus}$ configuration

EAN of central metal atom in coordination compounds is equal to the atomic number of nearest inert gas element, it is believed that in the formation of the coordination compounds the metal atom acquires nearest inert gas element configuration and the complex compound attains stability.

If the EAN is different from the atomic number of the nearest inert gas element, the difference is equal to the number of unpaired electrons in the central metal atom.

$[Fe(CN)_6]^{-3}$ EAN of iron = 35 Fe^{3+} = 26 – 3 + 2 × 6 = 35

$[Cu(NH_3)_4]^{+2}$ EAN of copper = 35 Cu^{2+} = 29 – 2 + 2 × 4 = 35

This means that the metal ions Fe^{+3}, Cu^{+2} in these complexes contain each one unpaired electron.

1.10 (VALENCE BOND THEORY (VBT) – POSTULATES AND APPLICATION TO (A) TETRAHEDRAL COMPLEXES $[Ni(NH_3)_4]^{2+}$, $[NiCl_4]^{2-}$ AND $[Ni(CO)_4]$ (B) SQUARE PLANAR COMPLEXES $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$ (C) OCTAHEDRAL COMPLEXES $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[FeF_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$. LIMITATIONS OF VBT

Q18. Write about valence bond theory (VBT) and its postulates.

Ans : **(Imp.)**

Valence Bond Theory

This theory was given by Linus Pauling.

The ground state electronic configuration of central metal atom, electron configuration of central metal atom in the excited state and hybridization of atomic orbitals of the central metal atom play an important role in this theory.

Salient features of the theory

(i) Central metal ion has a number of empty orbitals for accommodating electrons denoted by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.

(ii) Metal orbitals overlap with ligand orbitals to form strong bond thus greater the extent of overlapping, stronger will be the bond and hence more stable will be the complex.

(iii) Atomic orbitals of the metal ion hybridize to form a new set of equivalent hybridized orbitals which are arranged in particular manner which gives a particular geometry to the metal complex.

sp – Linear

sp^2 – Trigonal planar

sp^3 – Tetrahedral

dsp^2 – Square planar

sp^3d – Trigonal bipyamidal

dsp^3 – square pyramidal

sp^3d^2 – Octahedral outer orbital

d^2sp^3 – Octahedral inner orbital

(iv) The d-orbitals involved in hybridization may be either inner d-orbitals or outer nd-orbitals. The complexes formed by penultimate d-orbitals (inner d-orbitals) known as inner orbital complex. The complexes formed by using outer d-orbitals are known as outer orbital complex.

(v) A covalent bond is formed by the overlap of vacant hybridized metal orbital and filled orbital of the ligand.

(vi) If the complex contains unpaired $e^{\ominus}$, it is paramagnetic in nature while if it does not contain unpaired $e^{\ominus}$, it is diamagnetic in nature.

(vii) Under the influence of strong field, the electrons can be forced to pair up against Hund's rule of maximum multiplicity.

Q19. Explain the structure of $[Ni(NH_3)_4]^{2+}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ by using VBT theory.

Ans :

Complexes with Coordination number 4

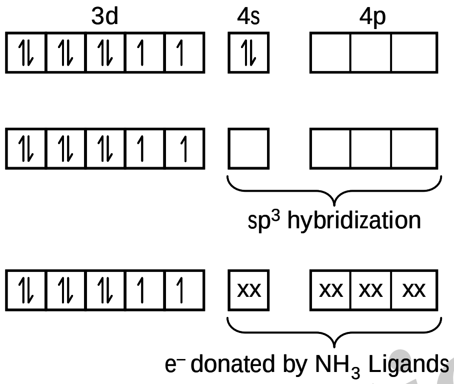
Complex compound with coordination number 4 for central metal atom may posses either tetrahedral geometry (or) square planar geometry.

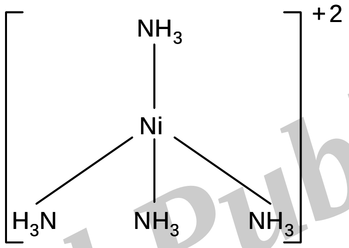
1. $[Ni(NH_3)_4]^{+2}$

Ni = $[Ar]3d^8\,4s^2\,4p^0$
(Ground state of atom)

Ni^{+2} = $[Ar]3d^8\,4s^0\,4p^0$
(Excited state of ion)

$[Ni(NH_3)_4]^{+2}$





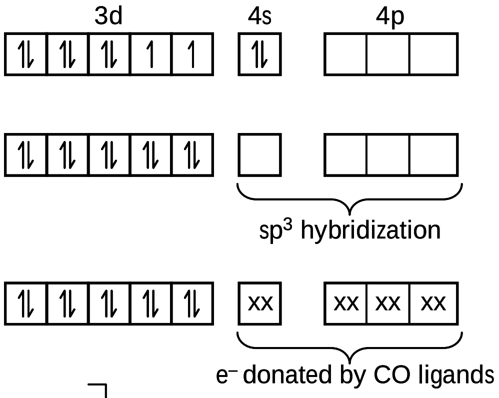
Geometry : Tetrahedral shape

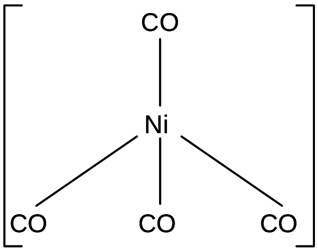
2. $[Ni(CO)_4]$

Ni = $[Ar]3d^8\,4s^2\,4p^0$
Ground state of atom

Ni = $[Ar]3d^{10}\,4s^0\,4p^0$
Excited state of atom

$[Ni(CO)_4]$





Geometry : Tetrahedral

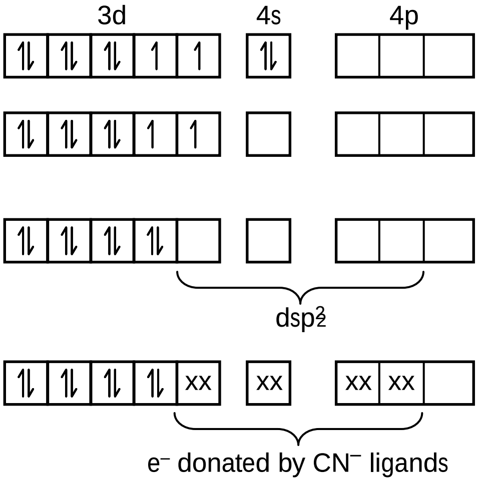
3. $[Ni(CN)_4]^{-2}$

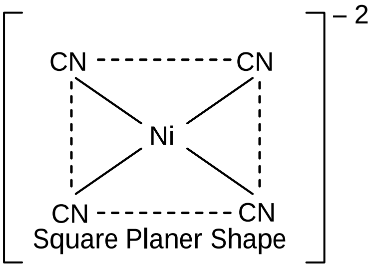
Ni = $[Ar]3d^8\ 4s^2\ 4p^0$

Ni^{+2} = $[Ar]3d^8\ 4s^0\ 4p^0$
Ground state

Ni^{+2} = $[Ar]3d^8\ 4s^0\ 4p^0$
Excited state

$[Ni(CN)_4]^{-2}$





Geometry: Square planar

Q20. Explain the drawbacks of Valence Bond Theory.

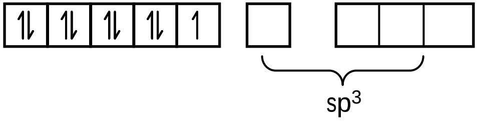
Ans :

Drawbacks of Valence Bond Theory

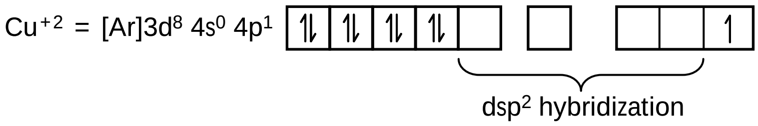
1. It fails to explain the colour property of complexes.
2. Some metals form complex compounds of distorted geometries. Ex. Cu(II) ion forms distorted octahedral complexes. This theory could not give satisfactory explanation for this fact.
3. Different kinds of ligands form with same metal complex compounds of different stabilities. This theory could not explain.
4. According to this theory paramagnetic moment of paramagnetic complex compound is related to number of unpaired electrons in the complex. But in some complexes, the magnetic moment theoretically calculated on the basis of unpaired electrons in it are not same as those value of the moment determined experimentally.
5. Some octahedral complexes are inner orbital complexes and some are outer orbital complexes. This theory could not explain what are the conditions that favour outer orbital and inner orbital complex formation.
6. This theory cannot predict whether the coordination complex formed by a metal with coordination number 4 is either tetrahedral or square planar in shape.

   E.x: According to this theory in $[Cu(NH_3)_4]^{+2}$ complex, the hybridization of the central metal atom is sp^3 and the complex is tetrahedral in shape.

   Cu^{+2} = $[Ar]3d^9\ 4s^0\ 4p^0$



   But X-ray diffraction studies revealed that this complex is having square planar shape. In this case hybridization of Cu in the complex must be dsp^2. For this pauling proposed that the unpaired electron in 3d is promoted to 4p orbital.



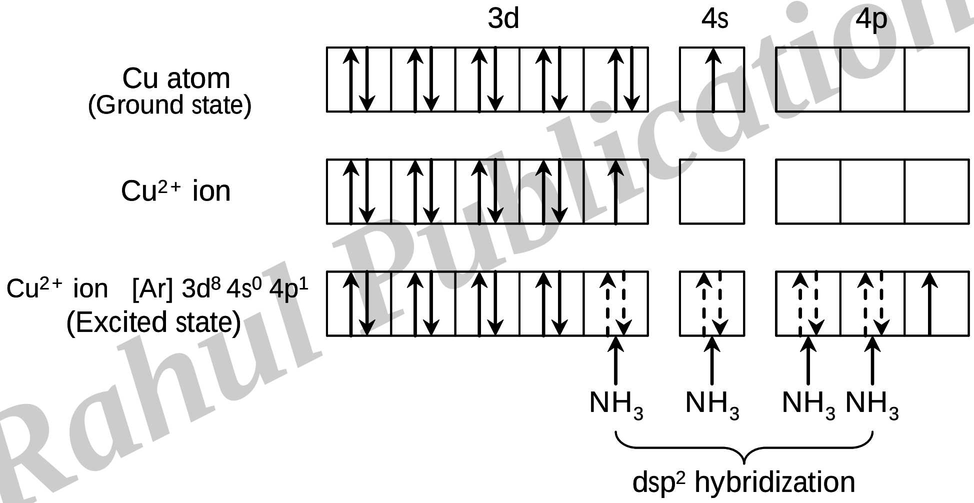
But this promotion requires high energy. From where this high energy is obtained was not explained by pauling.

Q21. Explain the structure and bonding in $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ complexes by valance bond theory.

Ans :

1. $[Cu(NH_3)_4]^{2+}$

The complex $[Cu(NH_3)_4]^{2+}$ represents square planar complex. It uses dsp^2 hybridization for the formation of complex as shown in figure.



Figure

There is one unpaired electron, the complex is paramagnetic in nature.

The square planar shape of $[Cu(NH_3)_4]^{2+}$ ion is as shown in figure.

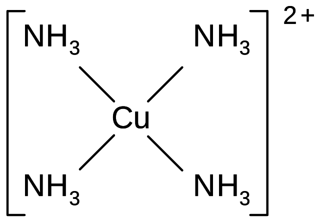
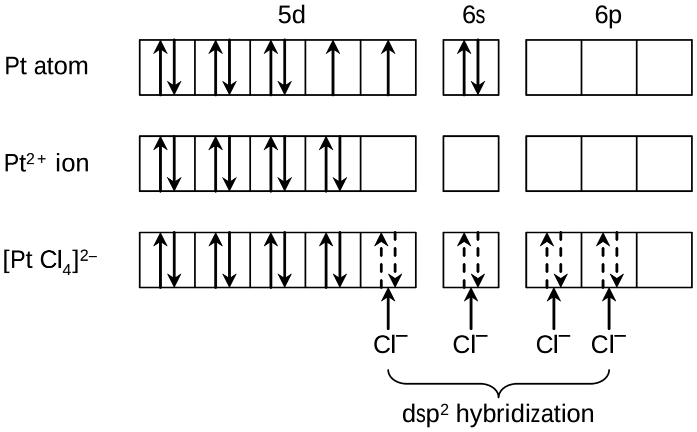


Figure: Structure of $[Cu(NH_3)_4]^{2+}$ ion

2. $[Pt\,Cl_4]^{2-}$

The electronic configuration of Pt atom and $[Pt\,Cl_4]^{2-}$ complex is shown in figure.



Figure

From the above figure it can be observed that the complex have no unpaired electrons. Thus, the complex is diamagnetic in nature.

The square planar shape of $[PtCl_4]^{2-}$ ion is as shown in figure as

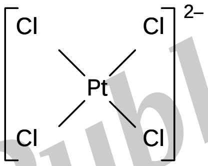


Figure : Structure of $[PtCl_4]^{2-}$ ion

Q22. Explain the structure and bonding of given octahedral complexes according to Valence Bond Theory.

(a) $[Fe(CN)_6]^{3-}$ (b) $[FeF_6]^{4-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[CoF_6]^{3-}$

Ans :

(a) $[Fe(CN)_6]^{3-}$

This ion represents an octahedral complex. It uses d^2sp^3 hybridization for the formation of complex. As central metal ion of complex is bounded with six ligands, its coordination number is 6. The electronic configuration of Fe atom, Fe^{2+} ion and $[Fe(CN)_6]^{3-}$ ion is as shown in figure as,

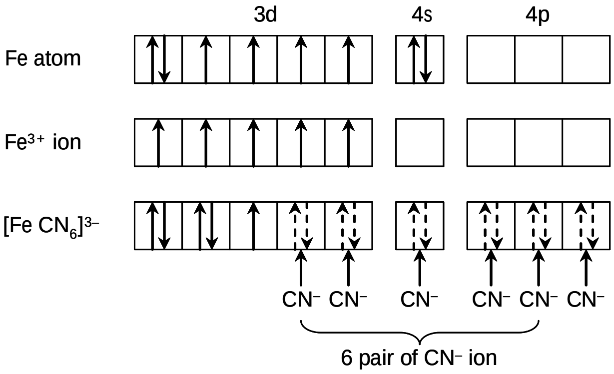


Figure: Formation of $[Fe(CN)_6]^{3-}$ ion using d^2sp^3 hybridization

The six cyanide ions occupy the six hybridized Fe orbitals and form a complex $[Fe(CN)_6]^{3-}$ by using d^2sp^3 hybridization. As there are one unpaired electron, it is paramagnetic in nature. The octahedral structure of $[Fe(CN)_6]^{3-}$ ion is as shown in figure below.

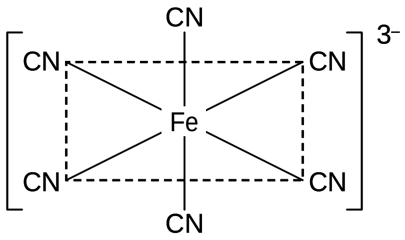


Figure : Structure of $[Fe(CN)_6]^{3-}$ ion

(b) $[FeF_6]^{4-}$

The complex $[FeF_6]^{4-}$ uses sp^3d^2 hybridization for the formation of complex. As central metal ion of complex is bounded with six ligands, its coordination number is 6. The electronic configuration of Fe atom, Fe^{2+} ion and $[FeF_6]^{4-}$ ion is shown in figure (3) as

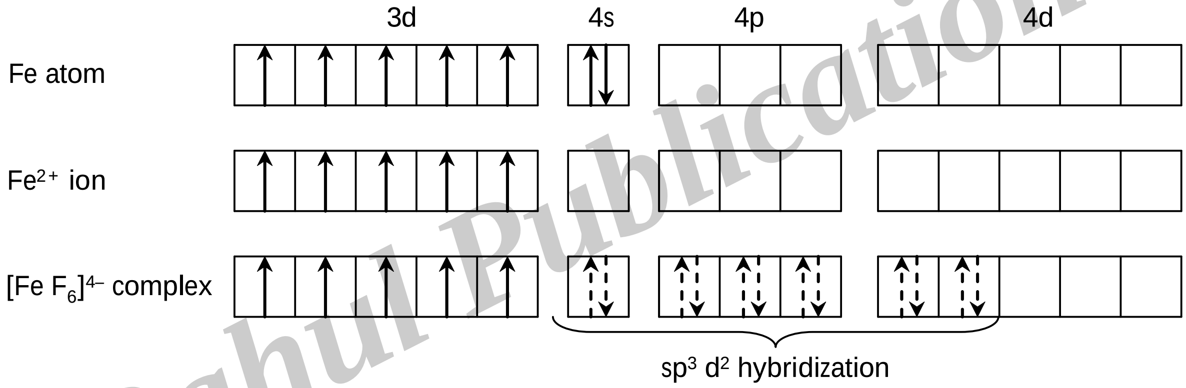


Fig. (3): Formation of $[FeF_6]^{3-}$ ion using sp^3d^2 Hybridization

The six fluoride ions occupies six hybridized orbitals and form a complex $[FeF_6]^{4-}$. As there are four unpaired electrons, it is paramagnetic in nature. The octahedral structure of $[FeF_6]^{4-}$ ion is as shown in figure.

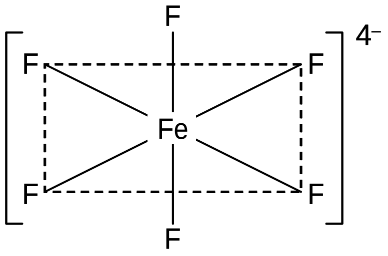


Figure: Structure of $[FeF_6]^{4-}$ ion

(c) $[Co(NH_3)_6]^{3+}$

The complex $[Co(NH_3)_6]^{3+}$ represents an octahedral complex. It uses d^2sp^3 hybridisation for the formation of complex as shown in figure.

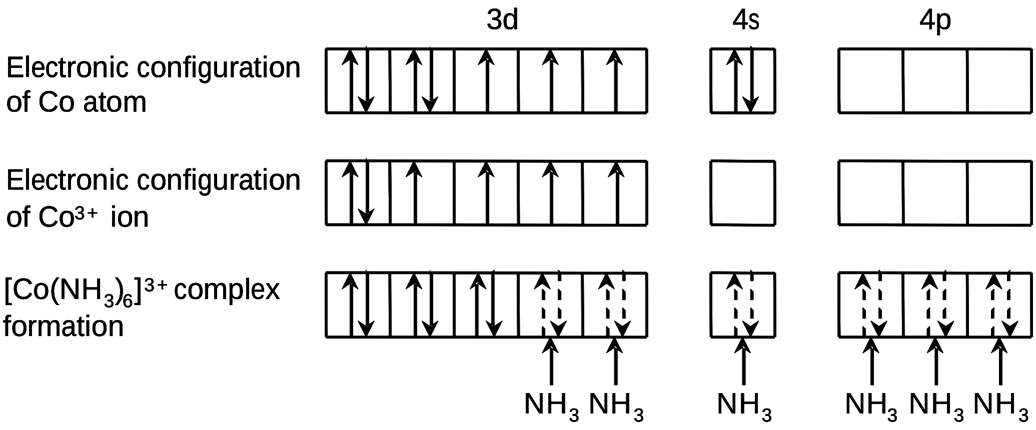


Figure : Formation of $[Co(NH_3)_6]^{3+}$ Complex by using d^2sp^3 hybridisation

As the complex does not contain any unpaired electrons it is diamagnetic in nature.

(d) $[CoF_6]^{3-}$

The complex $[CoF_6]^{3-}$ represents an octahedral complex. This complex uses sp^3d^2 hybridization for the formation of complex and its coordination number is 6. The electronic configuration of Co atom, Co^{3+} ion and $[CoF_6]^{3-}$ ion is as shown in figure as

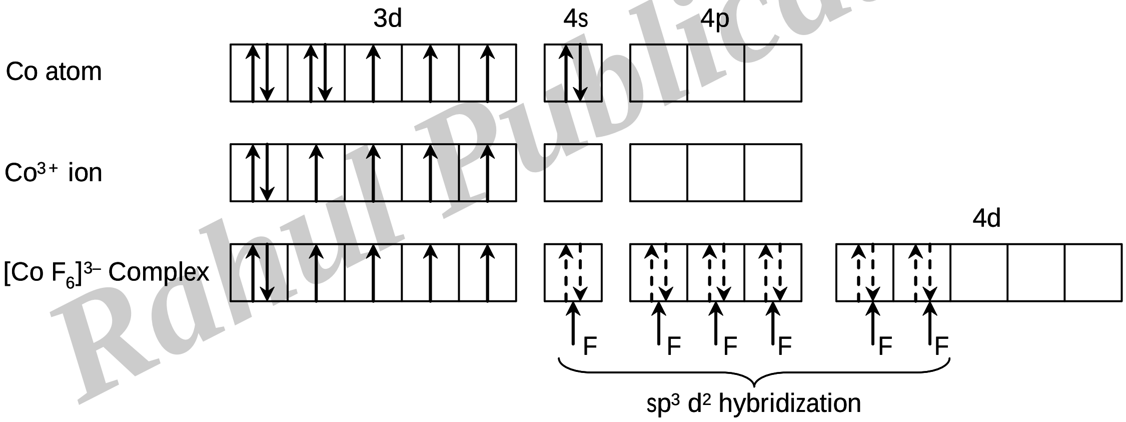


Figure : Formation of $[CoF_6]^{3-}$ ion using sp^3d^2 Hybridization

From the above figure, it is observed that there are four unpaired electrons, it is paramagnetic in nature.

Hence, the structure of $[CoF_6]^{3-}$ is as shown in figure.

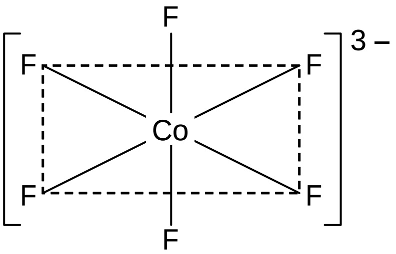


Figure: Structure of $[CoF_6]^{3-}$

1.11 ISOMERISM IN COORDINATION COMPOUNDS, STEREO ISOMERISM – (A) GEOMETRICAL ISOMERISM IN (I) SQUARE PLANAR METAL COMPLEXES OF THE TYPE $[MA_2B_2]$, $[MA_2BC]$, $[M(AB)_2]$, $[MABCD]$

Q23. Explain the geometrical isomerism in square planar metal complexes.

Ans : **(Imp.)**

Stereo Isomerism

Stereo isomers are those which differ in the three dimensional configurations of the coordination compounds though they have same chemical composition and the phenomenon is called stereoisomerism.

Stereoisomerism is of two types,

(i) Geometrical isomerism

(ii) Optical isomerism.

Geometrical Isomerism

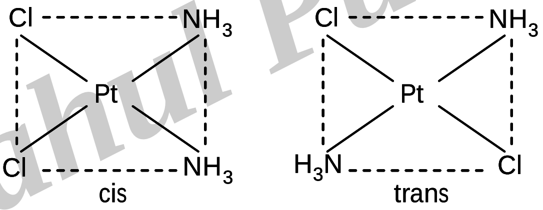
The coordination compounds showing different physical and chemical properties because of the difference in three - dimension arrangements of the groups surrounding the central metal ion, even though their chemical formulas are identical is called geometrical isomerism.

Geometrical isomerism is called cis-trans isomerism and geometrical isomers are called cis and trans isomers.

In cis isomer, identical groups occupy same sides.

In trans isomer, identical groups occupy opposite sides.

Ex:



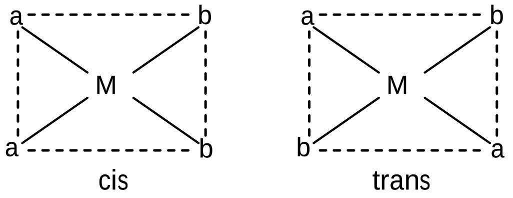
Geometrical Isomerism in complex having coordination number

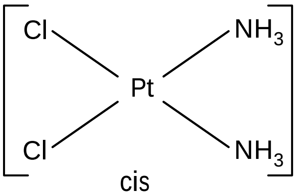
Tetrahedral complex does not exhibit geometrical isomerism. But square planar complexes show geometrical isomerism.

Square Planar Complexes

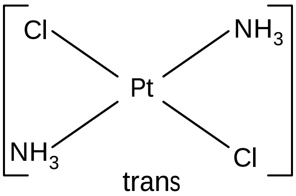
Complexes of the type Ma_4, Ma_3b or Mab_3 (where a, b are different unidentate ligands) do not exhibit geometrical isomerism-square complex of type Ma_2b_2, Ma_2bc and Mabcd may exhibit cis-trans forms.

(a) Complex of type $[Ma_2b_2]^{\pm n}$



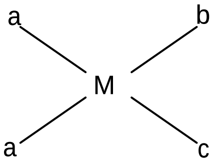


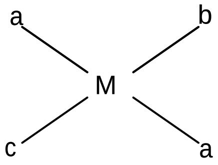
cis

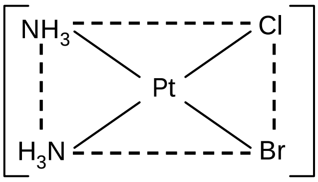


trans

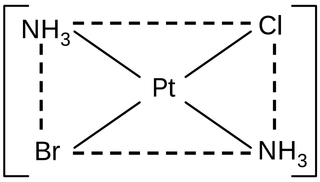
Complexes of type $[Ma_2bc]^{\pm n}$





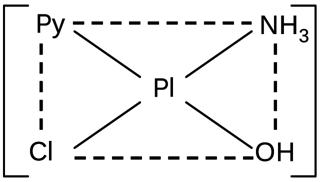


cis



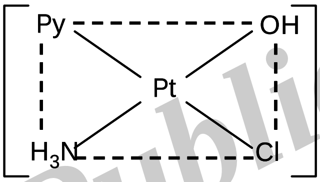
trans

$[Mabcd]^{\pm n}$



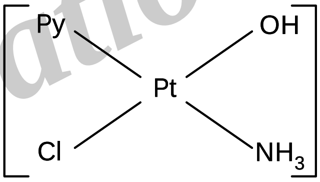
Cis

cis



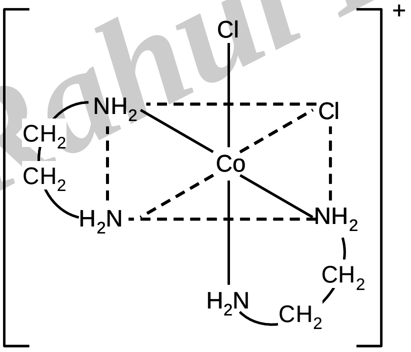
Cis

cis

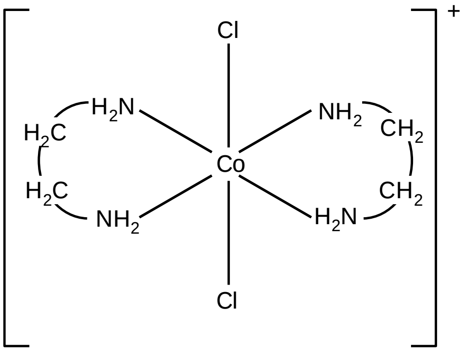


trans

trans

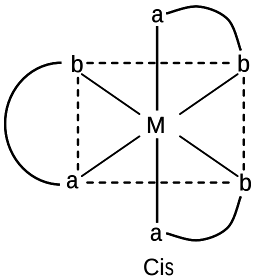


cis

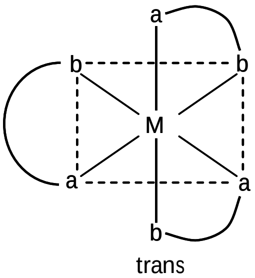


trans

(v) Octahedral complex having three unsymmetrical ligands also exhibit cis-trans isomers.



Cis



trans

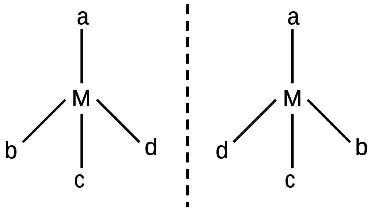
Optical Isomerism

A molecule is said to be optically active it cannot be super imposed on its mirror image and such isomers are called optical isomers.

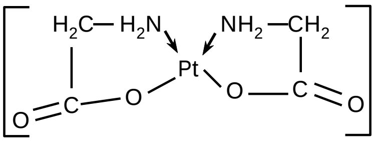
If a complex does not contain a plane of symmetry it exhibits optical activity. Optically active compound has the ability of rotating the plane of polarized light either to left or right. Thus compounds which have same physical and chemical properties but differ in their action on plane polarized light are known as optical isomers.

Square planar complex are not going to exhibit optical isomerism.

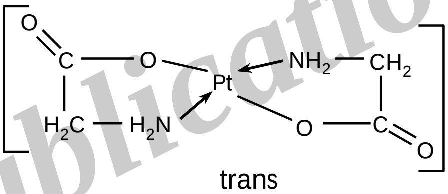
Tetrahedral complex of $[Mabcd]^{\pm n}$ shows optical activity.



$[M(ab)_2]^{\pm n}$ bidentate ligand (unsymmetrical)



cis



trans

1.12 OCTAHEDRAL METAL COMPLEXES OF THE TYPE $[MA_4B_2]$, $[M(AA)_2B_2]$, $[MA_3B_3]$ USING SUITABLE EXAMPLES, (B) OPTICAL ISOMERISM IN (I) TETRAHEDRAL COMPLEXES [MABCD],(II). OCTAHEDRAL COMPLEXES $[M(AA)_2B_2]$, $[M(AA)_3]$ USING SUITABLE EXAMPLES

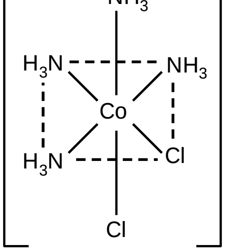
Q24. Describe the optical and geometrical isomerism in octahedral complexes.

Ans : **(Imp.)**

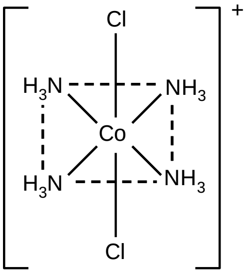
Geometrical isomerism in coordination complex with coordination no – 6 :

(i) Compounds of the type $[Ma_6]$ $[Ma_5b]$ and $[Mba_5]$ do not exhibit stereo isomerism.

(ii) Compounds of the type $[Ma_2b_4]$ exist is two geometrical isomers **Ex:** $[Co(NH_3)_4Cl_2]^+$



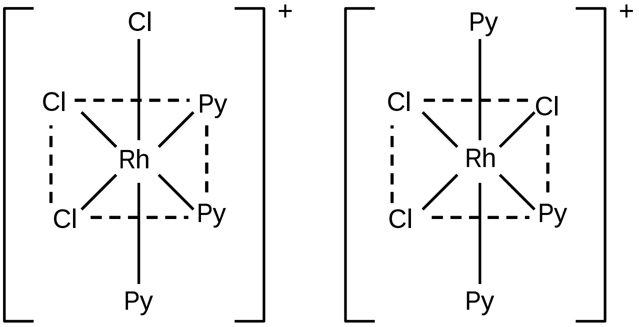
cis



trans

(iii) Complexes of type $[Ma_3b_3]$ exist in two geometrical isomeric forms.

Ex : $[Rh(Py)_3 Cl_3]$



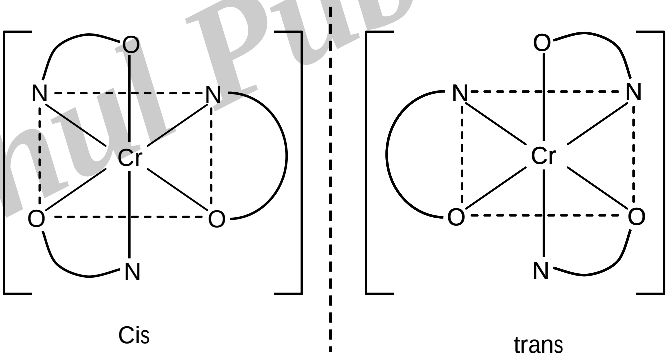
cis trans

(iv) Complexes having two bidentate ligands $[M(aa)_2 b_2]$ also exist in Cis - trans form.

Ex : $[CoCl_2(en)_2]^+$

en – ethylenediamine

Ex : $M(ab)_3 = [Cr(gly)_3]$



Cis trans

Octahedral complexes exhibit optical isomerism extensively. The general formulas of the complexes exhibiting this isomerism are:

$[M(aa)b_2c_2]^{\pm n}$

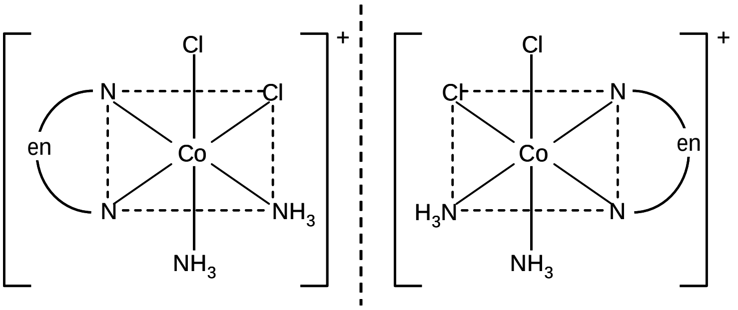
$[M(aa)_2 b_2]^{\pm n}$ aa = symmetrical bidentate ligand

$[M(aa)_3]^{\pm n}$ ab = unsymmetrical bidentate ligand

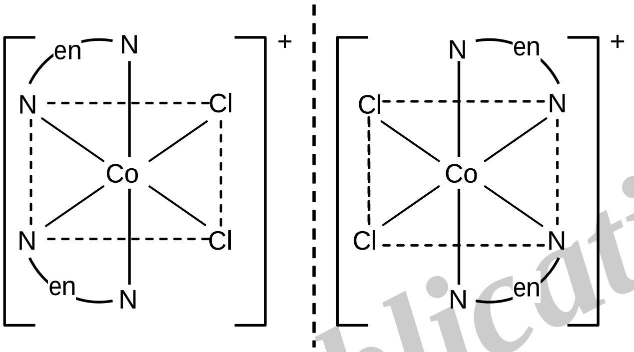
$[M(ab)_3]^{\pm n}$

Ex: For $[M(aa)b_2c_2]^{\pm n} = [Co(en)(NH_3)_2Cl_2]^+$

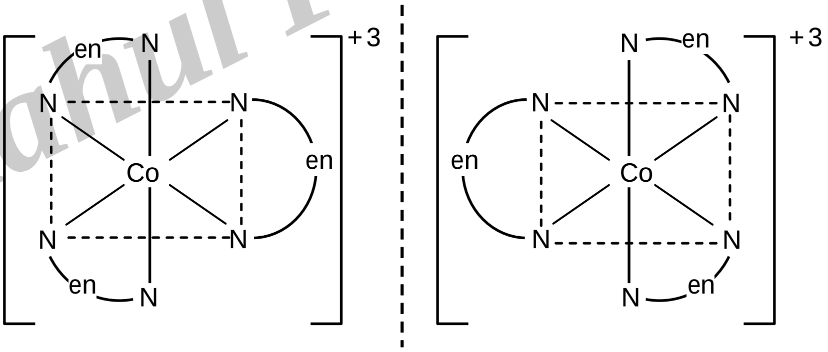
en(Ethylenediamine) $H_2N - CH_2 - CH_2 - NH_2$



Ex: for $[M(aa)_2b_2]^{\pm n}$ = $[Co(en)_2Cl_2]^{+}$



Ex: for $[M(aa)_3]^{\pm n}$ = $[Co(en)_3]^{+3}$



1.13 STRUCTURAL ISOMERISM: IONIZATION, LINKAGE, COORDINATION LIGAND ISOMERISM USING SUITABLE EXAMPLES

Q25. Explain the different types of isomerisms with suitable examples.

Ans :

Isomerism in Complex Compounds

The ions (or) molecules with same chemical composition but with different molecular structures are called “isomerism”.

Structural Isomerism

(i) Ionization Isomerism

In coordination complexes, the ions present outside the coordination sphere, when enter into the coordination sphere, they lose their ionic character.

The complex compounds having same molecular formula but in solution give different ions are called ionization isomers. The phenomenon is called ionization isomerism.

$$\textbf{Ex:}\quad \begin{array}{cc} [Co(NH_3)_5\,Br]\,SO_4 & [Co(NH_3)_5\,SO_4]\,Br \\ \downarrow & \downarrow \\ [Co(NH_3)_5\,Br]^{+2} + SO_4^{-2} & [Co(NH_3)_5\,SO_4]^{+} + Br^{-} \end{array}$$

(ii) Hydration Isomerism

This is similar to ionization isomerism. In this ionization isomerization sphere and those outside the coordination sphere. In hydration isomerism neutral water molecules, exchange with negative ions.

$[Cr\,(H_2O)_6]\,Cl_3$	$[Cr\,(H_2\,O)_5\,Cl]\,Cl_2 \bullet H_2\,O$	$[Cr\,(H_2\,O)_4\,Cl_2]\,Cl.2H_2O$
Violet	green	Dark green

(iii) Linkage isomerism

Some ligands possess more than one donor atom. Hence they posses alternative coordinating ability. The isomerism arising from such ligands are called linkage isomerism.

$[Co(NH_3)_5\,ONO]Cl_2$; $[Co(NH_3)_5\,NO_2]Cl_2$

$[Cr(H_2O)_5\,SCN]^{+2}$; $[Cr(H_2O)_5\,NCS]^{+2}$

(iv) Coordination Isomerism

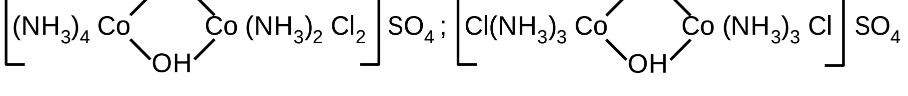
If a complex compound contains one complex cation and one Co complexation, there will be a possibility of exchange of ligands between.

This results in coordination isomerism.

$[Co(NH_3)_6]^{+3}\,[Cr(CN)_6]^{-3}$, $[Cr(NH_3)_6]^{+3}\,[Co(CN)_6]^{-3}$

(v) Coordination Position Isomerism

In multi centre complexes if ligands get exchanged between the central metal ions, this type of isomerism is exhibited.



S3-I-3: METAL CARBONYLS AND ORGANOMETALLIC CHEMISTRY

1.14 METAL CARBONYLS: PREPARATION AND PROPERTIES OF Ni(CO)$_4$

Q26. Explain the preparation and properties of Ni(CO)$_4$.

Ans :

Nickel tetra carbonyl, Ni(CO)$_4$. Preparation

It is prepared by,

(i) Passing CO over finely-divided nickel at 60°C.

(ii) By reducing potassium tetra cyano nickelate (II), $K_2[Ni(CN)_4]$ with H-Hg amalgam. When $K_2[Ni(CN)_4]$ is reduced (I), $K_2[Ni(CN)_3]$ is obtained. This compound absorbs CO at 90°C, probably forming $K_2[Ni(CN)_3(CO)]$. On treating the solution of this compound with HCl, $Ni(CO)_4$ is obtained.

$$K_2[Ni(CN)_3] + CO \xrightarrow{90^\circ C} K_2[Ni(CN)_3(CO)]$$

$$4K_2[Ni(CN)_3(CO)] + 2HCl \longrightarrow \underset{(Ni=0)}{Ni(CO)_4} + 3K_2\underset{(Ni=+2)}{[Ni(CN)_4]} + 2KCl + H_2$$

(iii) By the action of CO on nickel (II) phenyl dithiocarbamate, $Ni(S.SC.NH.C_6H_5)_2$. (Laboratory preparation).

$$\underset{\substack{\text{Nickel(II)phenyldithic}\\ \text{carbamate(Ni=+2)}}}{2Ni(S.SC.NHC_6H_5)_2} + 4CO \longrightarrow \underset{(Ni=0)}{Ni(CO)_4} + \underset{\substack{\text{Nickel(IV)phenyl}\\ \text{dithiocarbamate(Ni=+4)}}}{Ni(S.SC.NH.C_6H_5)_4}$$

(iv) By passing CO through an alkaline suspension of $Ni(CN)_2$ or NiS.

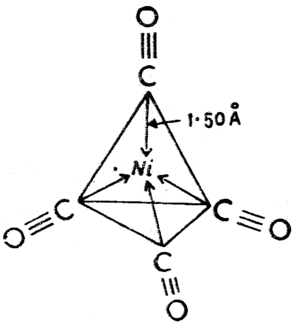
$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$

$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$

Structure

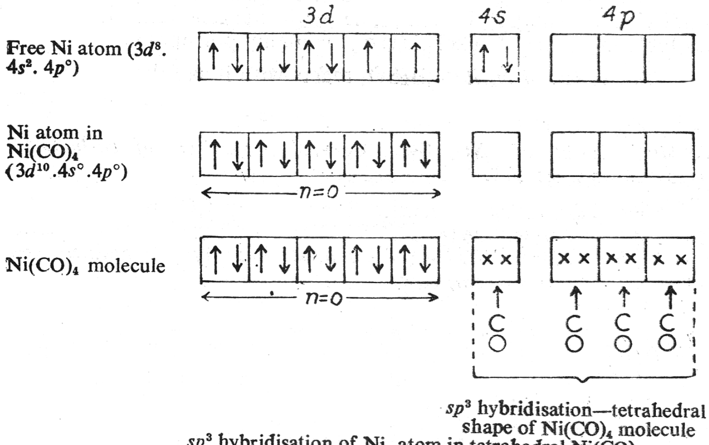
The vapour density of nickel tetra carbonyl and the freezing point of its solution in benzene has shown that the molecular formula of this compound is $Ni(CO)_4$.

Electron diffraction studies made on this compound in the vapour state and X-ray diffraction studies made on this compound in the solid state have shown that $Ni(CO)_4$ molecule has tetrahedral shape with Ni – C – O linear units. The Ni – C bond length in this molecule has been found to be equal to 1.50 A° which is shorter by 0.32 A° in comparison to Ni – C single bond length (= 1.82 A°) found in carbonyls. The C – O bound length in this carbonyl has been found to be equal to 1.15 A° which is larger than the C – O bond length in CO molecule (= 1.128 A°).



Tetrahedral structure of $Ni(CO)_4$ molecule

Tetrahedral shape of $Ni(CO)_4$ results from sp^3 hybridisation of Ni-atom. Since $Ni(CO)_4$ molecule is diamagnetic, all the ten electrons present in the valence shell of Ni-atom (Ni = $3d^s$ $4s^2$) get paired in 3d orbitals. Thus the valence-shell configuration of Ni-atom in $Ni(CO)_4$ molecule becomes $3d^{10}.4S^0$ OC → Ni-bond results by the overlap between the empty sp^3 hybrid orbital on Ni-atom and doubly-filled sp hybrid orbital on C atom in CO molecule figure.



sp^3 hybridisation of Ni atom in tetrahedral $Ni(CO)_4$. × × indicate the electron pair donated by CO molecules. These electrons are in opposite spin.

1.15 Structural Features of $Ni(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $Cr(CO)_6$ -18 Valence Electron Rule

Q27. Classify the metal carbonyls and write and explain the structure.

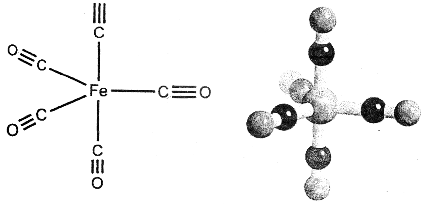
Ans :

Classification of Metal Carbonyls

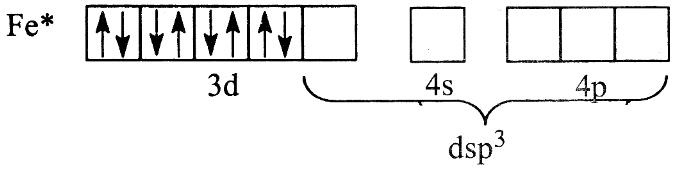
Metal carbonyls are broadly classified into two types, namely, mononuclear and polynuclear metal carbonyls. Mononuclear metal carbonyls are those which contain only one central metal atom. Example for mononuclear metal carbonyls are $[V(CO)_6]$, $[Cr(CO)_6]$, $[Fe(CO)_5]$, $[Ni(CO)_4]$ etc. Polynuclear metal carbonyls are central metal atoms polynuclear carbonyls are called binuclear, trinuclear, tetranuclear metal carbonyls. These polynuclear metal carbonyls are further classified into homopolynuclear and heteropolynuclear metal carbonyls. Homopolynuclear metal carbonyls are those which contain the same central metal atoms. For example, $[Mn_2(CO)_{10}]$, $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[CO_2(CO)_8]$, $[CO_4(CO)_{12}]$, $[CO_6(CO)_{16}]$ etc. Heteropolynuclear metal carbonyls are those which contain more than one kind of central metal atom. For example, $[Mn_2Fe(CO)_{14}]$, $[CoMn(CO)_9]$, $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$ etc.

$Fe(CO)_5$

Structure of $Fe(CO)_5$ is trigonal bipyramidal. In this Fe is surrounded by three equatorial CO groups and two axial CO groups, as shown below.

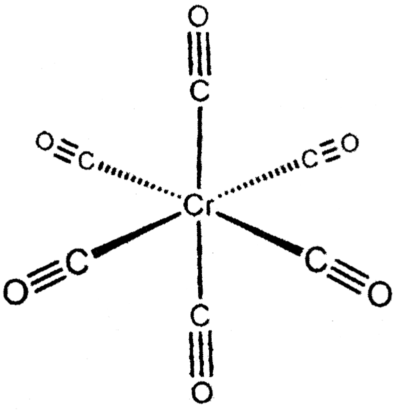


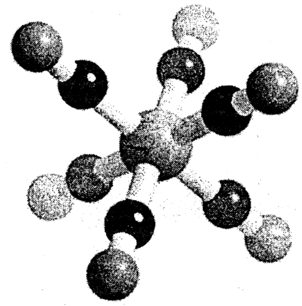
Electronic configuration of Fe is $3d^6$ $4s^2$. In exited state, the two electrons in 4s along with the six electrons in 3d rearrange to give four pairs four d orbitals leaving one d orbital for dsp^3 hybridisation.



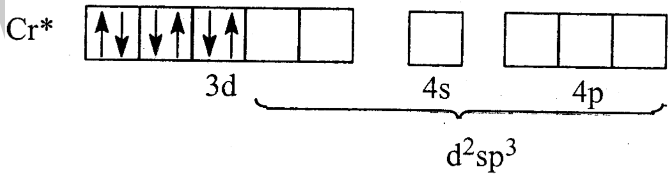
Cr(CO)$_6$

Structure of $Cr(CO)_6$ is octahedral. In this Cr is surrounded by six CO groups lying at the corners of a regular octahedron, as shown below.



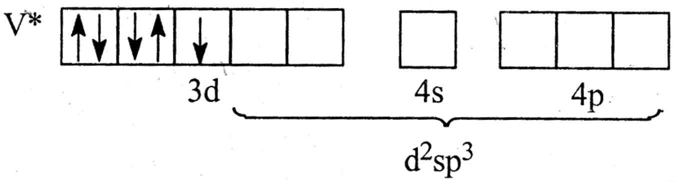


Electronic configuration of Cr is $3d^5$ $4s^1$. In the excited state the 4s electron rearranges in 3d to give three pairs of electrons in three d orbitals, thus leaving two 3d orbitals for d^2sp^3 hybridisation.



V(CO)$_6$

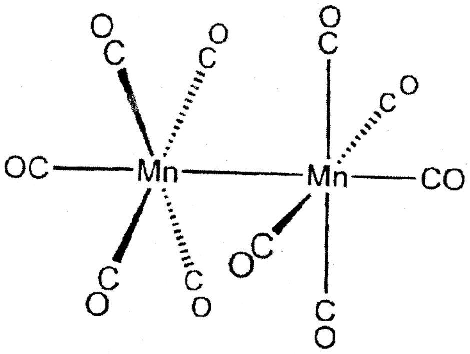
Structure of $V(CO)_6$ is octahedral. Electronic configuration of V is $3d^3 4s^2$. In the excited state, the two 4s electrons rearrange themselves in 3d level as follows.

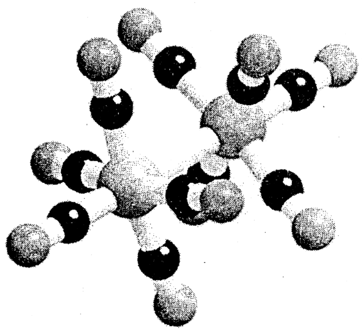


The unpaired electron in 3d accounts for the observed paramagnetism of $V(CO)_6$.

$Mn_2(CO)_{10}$

Structure of $Mn_2(CO)_{10}$ consists of two $Mn(CO)_5$ units held together by metal-metal bond between the two Mn atoms as shown below.

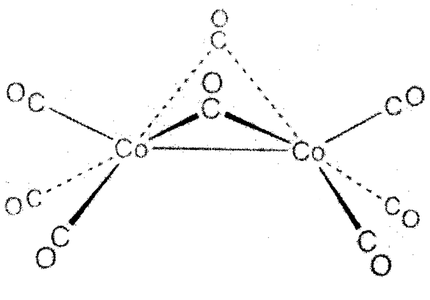


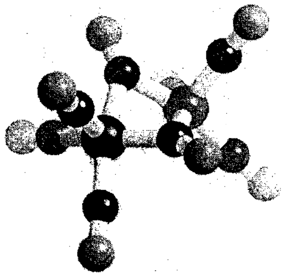


The two $Mn(CO)_5$ groups are in staggered configuration. Though the empirical stoichiometry of $Mn(CO)_5$ would imply that it is a paramagnetic molecule with 17 valence electrons, $Mn_2(CO)_{10}$ is diamagnetic which indicates that it is a dimeric structure. There is no IR evidence for any bridging CO groups.

$Co_2(CO)_8$

Structure of $Co_2(CO)_8$ in the solid state consists of two CO atoms each bonded to three terminal CO groups and joined together by two bridging carbonyl groups as well as a Co-Co bond as shown below.





For this structure, the total number of electrons for each metal atom.

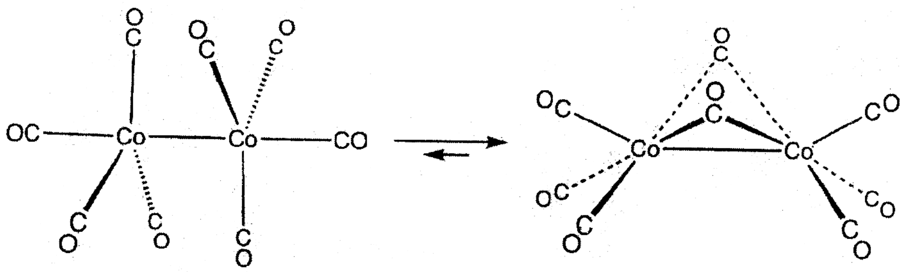
$$= 27 + 6 + 2 + 1$$

(due to metal-metal bond)

(due to two bridging CO groups)

(due to three terminal CO bonds)

However in solution, this structure is in equilibrium with a second form as shown below which has no bridging carbonyls and the two $Co(CO)_4$ units are held together by a Co-Co bond.



For this structure, the total number of electrons for each metal atom.

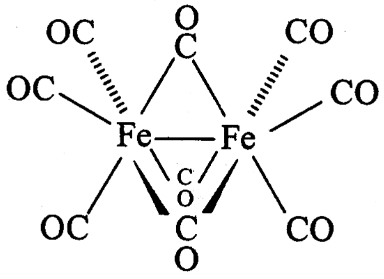
$$= 27 + 8 + 1$$

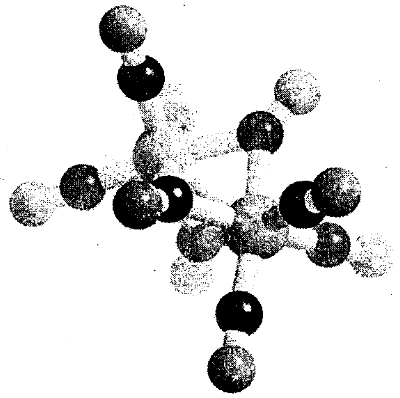
(due to metal-metal bond)

(due to four terminal CO bonds)

$Fe_2(CO)_9$

Structure of $Fe_2(CO)_9$ is confacial bioctahedron, in which two octahedra share one face. This is shown below.





At each Fe, the total number of electrons

$$= 26 + 6 + 3 + 1$$

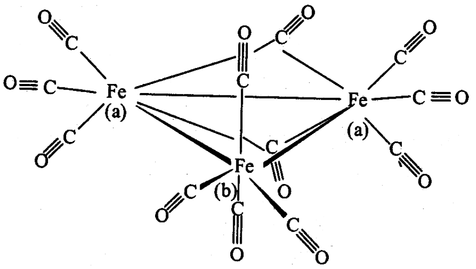
(due to metal-metal bond)

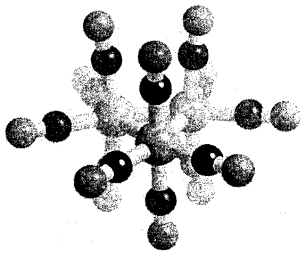
(due to three bridging CO bonds)

(due to three terminal CO bonds)

$Fe_3(CO)_{12}$

Structure of $Fe_3(CO)_{12}$ consists of three metal-metal bonds among the three Fe atoms. There are two kinds of iron atoms. In one case two Fe(a) atoms are each bonded to three terminal CO groups and two bridged CO groups. In the other case, the Fe(b) atom is bonded only to four terminal CO groups. The structure of $Fe_3(CO)_{12}$ is given below.





At Fe(b), the total number of electrons

$$= 26 + \underset{\text{(due to 4 terminal CO bonds)}}{8} + \underset{\text{(due to two metal-metal bonds)}}{2} = 36$$

At Fe(a), the total number of electrons.

$$= 26 + \underset{\text{(due to three terminal CO bonds)}}{6} + \underset{\text{(due to two bridging CO bonds)}}{2} + \underset{\text{(due to two metal-metal bonds)}}{2} = 36$$

Q28. What is 18 Valence electron rule.

Ans :

The sum of the electrons on the metal plus the electrons donated by the ligands is called the effective atomic number (Z) and when this equals 36 (Kr) or 54 (Xe) or 86 (Rn) the effective atomic number (EAN) rule is said to be obeyed. In these cases the outer electronic configuration corresponds to $ns^2(n-1)\,d^{10}np^6$ with 18 electrons in the valence shell. It is therefore referred to as 18 electron rule. In the case of mononuclear carbonyls with the exception of $V(CO)_6$ all others obey 18 electron rule.

In molecular orbital terminology, the 18 electron rule is a generalization relating to the usage of five (n – 1)d orbitals, one ns orbital and three np orbitals. A complex species is stable whenever the σ bonding and σ non bonding orbitals are completely occupied and the σ^* anti bonding orbitals are empty. The rule is therefore restrictive to strong field ligands such as CO. The 18 electron is suggestive that all electrons in the valence shell should participate in bonding.

Metals with odd atomic numbers cannot satisfy the 18 electron rule by the simple addition of CO ligands. There are several options for such metal ions to attain the 18 electrons by (a) the formation of anion(b) formation of a carbonyl halide or hydroxide and (c) formation of dimers.

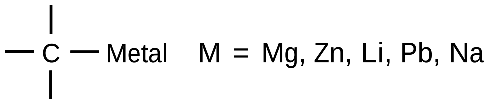
1.16 DEFINITION, NOMENCLATURE AND CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS

Q29. Define organometallic chemistry.

Ans :

Definition

Organometallic compounds are those in which a metal atom (including non-metallic elements like B, Si, P, as etc which are less electronegative then carbon) is bonded directly to a carbon atom of a hydrocarbon radical or molecule.



$-\overset{|}{\underset{|}{C}}-\text{Metal} \quad M = Mg, Zn, Li, Pb, Na$

Q30. Write the classification of organometallic compounds.

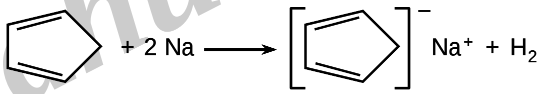
Ans :

Organometallic compounds are classified into 4 types depending upon the nature of the metal carbon bond.

1. **Ionic Organometallic Compounds**

   The organometallic compounds of highly electropositive metals are usually ionic in nature. In these compounds the metal cation forms an ionic bond with the anion of the organic compound. This type of bond is referred as electrostatic chemical bond. Highly electropositive elements like alkali and alkaline earth metals form ionic organometallic compounds. Represented by R_2M M = (Ca, Ba).

   Ex.: $(C_6\,H_5)_3\,C^-\,Na$, $(C_5H_5)_2^-\,Na^+ + H_2$



   Ionic organo metallic compounds insoluble in non-polar solvents and hydrolysed by water.

2. **σ-bonded covalent Organometallic Compounds**

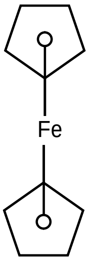
   In this type of compounds a covalent bond is present between the metal atom and the carbon atom of an organic group. This kind of bond is formed by metals with low electropositive nature.

   Ex.: $(CH_3)_3\,SnCl$, $(CH_3)_2\,SiCl_2$, $(C_2\,H_5)_4\,Pb$, $(CH_3)_2\,Zn$.

   The polarity of the bond depends not only on the differnce in electronegativity between metal and carbon but also on the available metal orbitals, steric requirements and polarisability of the $e^{\ominus}$ cloud. The strength of the M-C bond depends on the nature of the R group & also on the nature of other ligands on metals, those having π acceptor ligands given more stable M-C bonds.

3. **π-Bonded Organometallic Compounds**

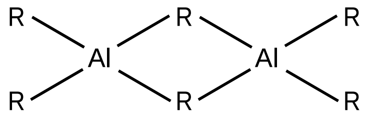
   Transition metals form π-bonded compounds the first π-bonded compounds. The first π-bonded organometallic compound prepared was bicyclic pentdineyl iron or Ferrocene $(C_5\,H_5)_2$ Fe. It is a sandwich structure in which the iron atom lies between two planar C_5H_5 rings. The bonding involves overlap of $\pi e^{\ominus}$ of the cyclopentadienyl rings with unfilled d-orbitals of the metal and form π-bonds.



4. Alkyl Bridged Organometallic Compounds

In these compounds two metal atoms are bridged by alkyl groups.

Ex: Dimeric trialkyl aluminium ($Al_2 R_6$), Polymeric dimethyl beryllium ($(BeMe_2)n$).



The bonding is explained on the basis of molecular orbital theory in which M–C–M bond is formed by the use of sp^3 hybrid orbitals of carbon atom and of each one of the metal atoms.

1.17 Methods of Preparation, Properties and Applications of Alkyl and Aryl Compounds of Li, Mg & Al

Q31. Write the preparation and properties of Lithium organometalic compounds.

Ans :

Preparation of Organo lithium Compounds

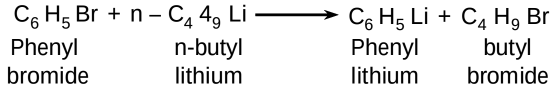
1. By the interaction of alkyl halides with metals

Lithium reacts directly with alkyl halides to form organo lithium compounds.

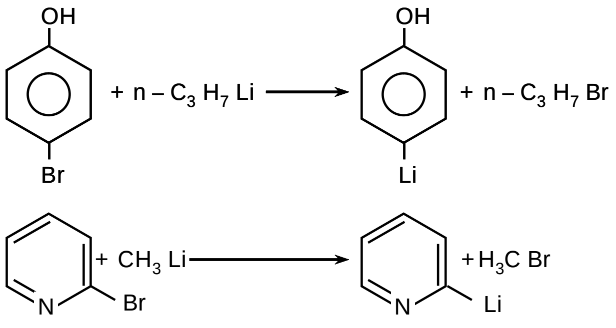
$$RX + 2Li \xrightarrow[\text{ether}]{-10°C} RLi + LiX$$

2. Metal - Halogen Exchange

Generally aryl, vinyl halides do not directly react with lithium. The reaction carried out by halogen - metal exchange.

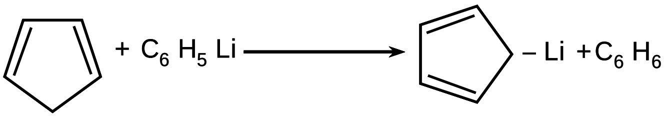


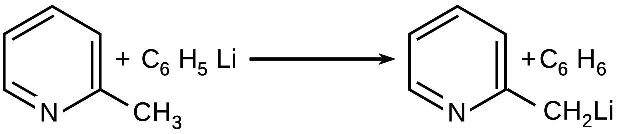
$$\underset{\substack{\text{Phenyl}\\\text{bromide}}}{C_6H_5Br} + \underset{\substack{\text{n-butyl}\\\text{lithium}}}{n-C_4 4_9 Li} \longrightarrow \underset{\substack{\text{Phenyl}\\\text{lithium}}}{C_6H_5Li} + \underset{\substack{\text{butyl}\\\text{bromide}}}{C_4H_9Br}$$



3. Metalation by Phenyl Lithium

In these reactions hydrogen and metal exchange in their places.





4. Metal Exchange Reaction

This is a reaction between a metal which is higher in the electrochemical series and on organometallic compound of a metal which is lower in the series.

$$R_2Hg + 2Li \rightarrow 2\,R\,Li + Hg$$

Properties

Lithium compounds are liquids or low melting solids.

Lithium compounds are readily attacked by water.

Preparation of Hydrocarbons

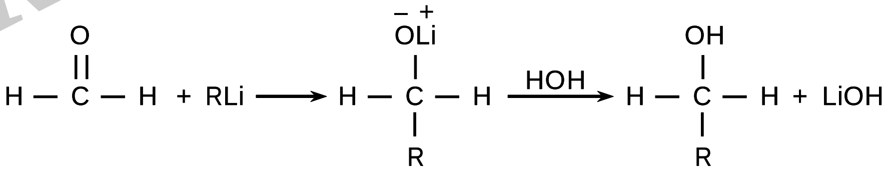
These organometallic compounds react with compounds like water, alcohol form hydrocarbons.

$$H_3C-Li + HOH \rightarrow H_3C-H + LiOH$$

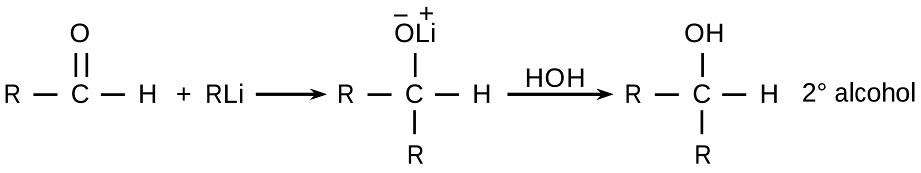
$$H_3C-CH=CHLi + R-OH \rightarrow H_3C-CH=CH_2 + LiOR$$

Preparation of Alcohols

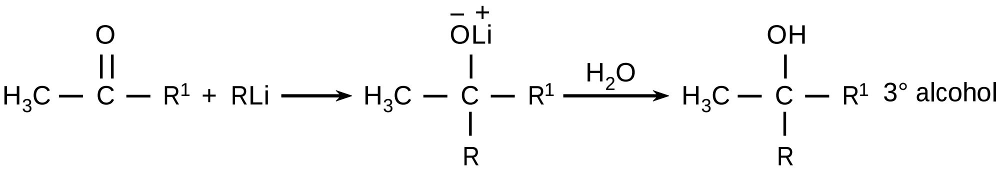
Organo lithium compounds produce primary alcohols with formaldehyde, secondary alcohols with other aldehydes and tertiary alcohols with ketones.



$$H-\overset{\overset{O}{\|}}{C}-H + RLi \longrightarrow H-\underset{\underset{R}{|}}{\overset{\overset{\overset{-\ +}{OLi}}{|}}{C}}-H \xrightarrow{HOH} H-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-H + LiOH$$



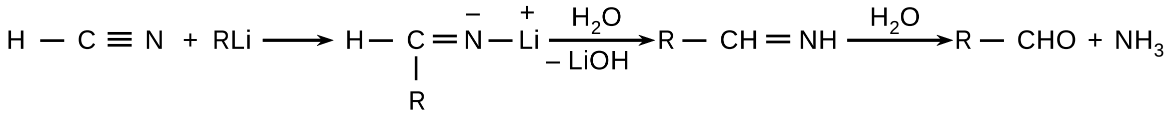
$$R-\overset{\overset{O}{\|}}{C}-H + RLi \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{\overset{-\ +}{OLi}}{|}}{C}}-H \xrightarrow{HOH} R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-H \quad 2° \text{ alcohol}$$



$$H_3C-\overset{\overset{O}{\|}}{C}-R^1 + RLi \longrightarrow H_3C-\underset{\underset{R}{|}}{\overset{\overset{\overset{-\ +}{OLi}}{|}}{C}}-R^1 \xrightarrow{H_2O} H_3C-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R^1 \quad 3° \text{ alcohol}$$

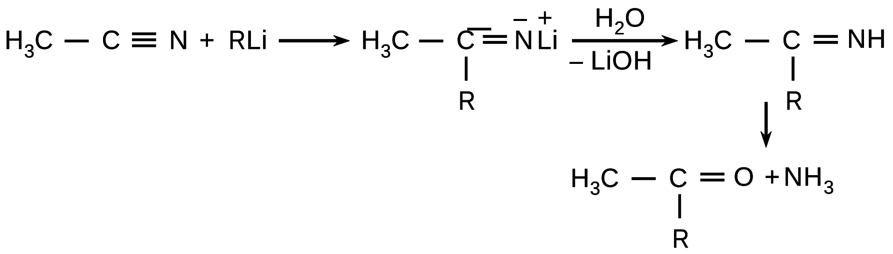
Preparation of Aldehydes

Aldehydes are prepared by the reaction between organo lithium compounds with hydrogen cyanide.



$$H - C \equiv N + RLi \longrightarrow H - \underset{\displaystyle R}{\underset{|}{C}} = \overset{-}{N} - \overset{+}{Li} \xrightarrow[-\,LiOH]{H_2O} R - CH = NH \xrightarrow{H_2O} R - CHO + NH_3$$

Preparation of Ketones



$$H_3C - C \equiv N + RLi \longrightarrow H_3C - \underset{\displaystyle R}{\underset{|}{C}} = \overset{-\,+}{NLi} \xrightarrow[-\,LiOH]{H_2O} H_3C - \underset{\displaystyle R}{\underset{|}{C}} = NH \longrightarrow H_3C - \underset{\displaystyle R}{\underset{|}{C}} = O + NH_3$$

Q32. Write the preparation of Mg organometallic compounds and explain its properties.

Ans :

Organo Magnesium Compounds Preparation

1. Direct Reaction with the Metal

Alkyl halide is reacted with magnesium metal in the presence of anhydrous ether.

$$C_2H_5Br + Mg \xrightarrow{\text{dry ether}} C_2H_5MgBr \text{ (Griganard reagent)}$$

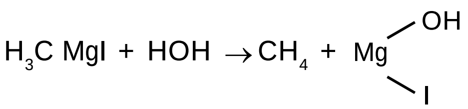
2. Metal Exchange Reaction

$$R_2Hg + \underset{\text{excess}}{Mg} \rightarrow R_2Mg + Hg$$

Properties

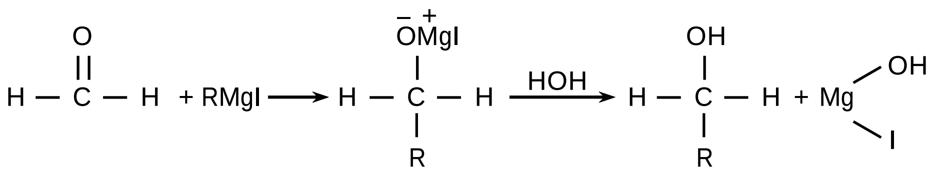
Preparation of Hydrocarbons

These organometallic compounds react with compounds like water, alcohol and form hydrocarbons.



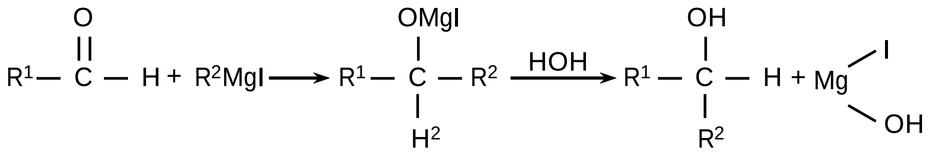
$$H_3C\,MgI + HOH \rightarrow CH_4 + Mg\begin{matrix} \diagup OH \\ \diagdown I \end{matrix}$$

Primary Alcohols



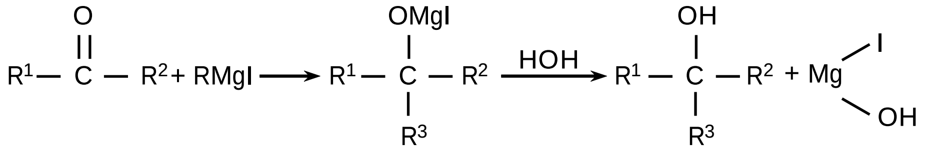
$$H - \overset{\displaystyle O}{\overset{||}{C}} - H + RMgI \longrightarrow H - \underset{\displaystyle R}{\underset{|}{\overset{\overset{-\,+}{OMgI}}{\overset{|}{C}}}} - H \xrightarrow{HOH} H - \underset{\displaystyle R}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - H + Mg\begin{matrix} \diagup OH \\ \diagdown I \end{matrix}$$

Secondary Alcohols



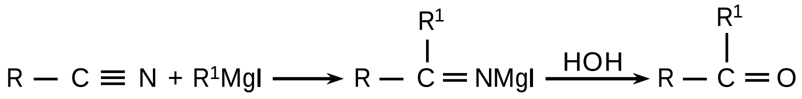
$$R^1-\overset{\overset{O}{||}}{C}-H + R^2MgI \longrightarrow R^1-\underset{\underset{H^2}{|}}{\overset{\overset{OMgI}{|}}{C}}-R^2 \xrightarrow{HOH} R^1-\underset{\underset{R^2}{|}}{\overset{\overset{OH}{|}}{C}}-H + Mg\begin{matrix} I \\ OH \end{matrix}$$

Tertiary Alcohols



$$R^1-\overset{\overset{O}{||}}{C}-R^2 + RMgI \longrightarrow R^1-\underset{\underset{R^3}{|}}{\overset{\overset{OMgI}{|}}{C}}-R^2 \xrightarrow{HOH} R^1-\underset{\underset{R^3}{|}}{\overset{\overset{OH}{|}}{C}}-R^2 + Mg\begin{matrix} I \\ OH \end{matrix}$$

Preparation of Ketones



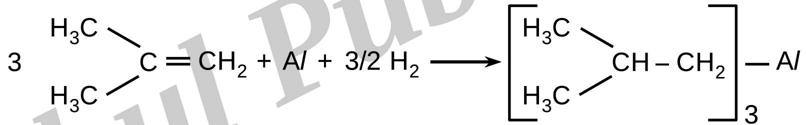
$$R-C\equiv N + R^1MgI \longrightarrow R-\overset{\overset{R^1}{|}}{C}=NMgI \xrightarrow{HOH} R-\overset{\overset{R^1}{|}}{C}=O$$

Q33. What are aluminium organometallic compounds write its preparation and properties.

Ans :

Organo aluminium Compounds

Organo aluminium compounds are prepared commercially by heating aluminium powder, hydrogen and alkene.



Isobutene

Tri-isobutyl aluminium

Mono, di and trialkyl aluminium compounds prepared by treating aluminium chloride with the appropriate amount of grignard reagent.

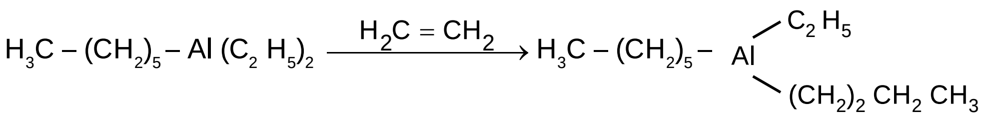
$H_3C\ MgCl + AlCl_3 \rightarrow H_3C\ AlCl_2 + MgCl_2$

$2H_3C\ MgCl + AlCl_3 \rightarrow (H_3C)_2\ AlCl + 2MgCl_2$

$3H_3C\ MgCl + AlCl_3 \rightarrow (H_3C)_3\ Al + 3MgCl_2$

The most important use of trialkyl aliminium is as a catalyst Ziegler - Natto type.

$$H_3C-CH_2-Al\,(C_2H_5)_2 \xrightarrow{H_2C=CH_2} H_3C-CH_2-CH_2-CH_2\,Al\,C_2H_5 \xrightarrow{H_2C=CH_2}$$



Application of Organometallic Compounds

- Aluminium triethyl is a catalyst in the polymerisation of ethylene.
- Alkyl lithium compounds are used in the rubber manufacture.

Short Question & Answers

1. What is Lanthanide contraction?

Ans :

It consists of a regular decrease in the size of atoms/ions with increase in atomic number as we move across from La to Lu. Thus, among lanthanides, Lanthanum has largest and Luteium has the smallest radius. This show decrease in size is known as the lanthanide contraction.

2. Explain the anomalous behaviour of postlanthanides?

Ans :

The elements following lanthanides are called post-lanthanide elements. Transition elements of the third series (i.e., the transition elements following the lanthanides) have virtually the same atomic and ionic sizes as the corresponding elements just above them in their respective sub-groups.

3. What is coordination complex?

Ans :

When potassium ferrocyanide is dissolved in water it does not give the usual tests for Fe^{2+} and CN^- ions indicating that these ions which were originally present are not formed when potassium ferrocyanide is dissolved in water. These ions are present in the forms of new ion called ferrocyanide ion which is a complex ion and does not ionise into constituent ions.

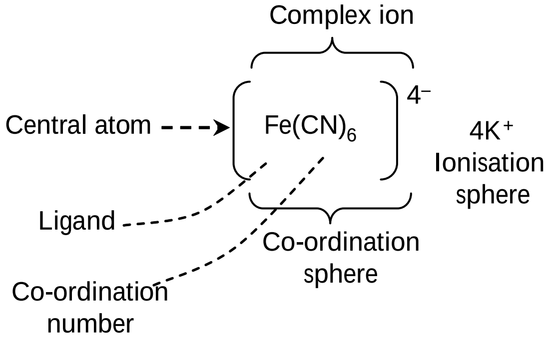
$$K_4\,[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Compounds containing complex ions are called complex compounds. Complex ion may be defined as an electrically charged (cationic or anionic) or even a neutral species and is formed by the combination of a simple cation with more than one neutral molecule or negative ion.

4. What is Coordination Sphere?

Ans :

The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.



5. Find the oxidation number of $[Cr(C_2O_4)_3]^{3-}$.

Ans :

Here the oxalate is bidentate ligand. Three oxalate ligands carry a total charge of – 6. Hence CN of Cr is 6. Cr – Oxidation no + 3

$x + (-2 \times 3) = -3^{-}$

$x - 6 = -3$

$x = -3 + 6$

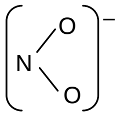
$x = +3.$

---

6. What are Ambidentate Ligands?

Ans :

These are ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time. Those ligands are called ambidentate ligands.



ion - Nitro ($M - NO_2$)

Nitrito ($M - ON = O$)

CN^- ion - Cyano (MCN)

Isocyano (MNC)

NCS^- ion - Thiocyanate (MSCN)

iso thiocyanate [MNCS]

$S_2O_3^{2-}$ ion - Thiosulphato-S [$MOSO_2S$]

7. What are Flexidentate Ligands?

Ans :

Polydentate ligands have flexidentate character i.e., polydentate ligand may not necessarily use all its donor atoms to get coordinated to the metal ion. Eg In $[Co^{III}(NH_3)_5SO_4]^+$ and $[Co^{III}(en)_2SO_4]$ sulphate acts as a monodentate and bidentate ligands.

8. What is Effective Atomic Number [EAN] ?

Ans :

The number of electrons acquired by the central metal atom in coordination compounds gaining them either from the ligands or otherwise is called effective atomic number.

EAN is generally equal to the atomic number of the inert gas element in the period in the periodic table in which the central metal atom is present.

EAN atomic number of metal atom – Number of e^- lost by metal atom to form positive ion + electrons gained from the ligand.

EAN = Atomic number of metal atom – O.S of metal ion + 2 × coordination number.

Ex : $[Co(CO)_6]$

EAN = Atomic number of metal atom – Number of e^- lost by metal + e^- gained from the ligand.

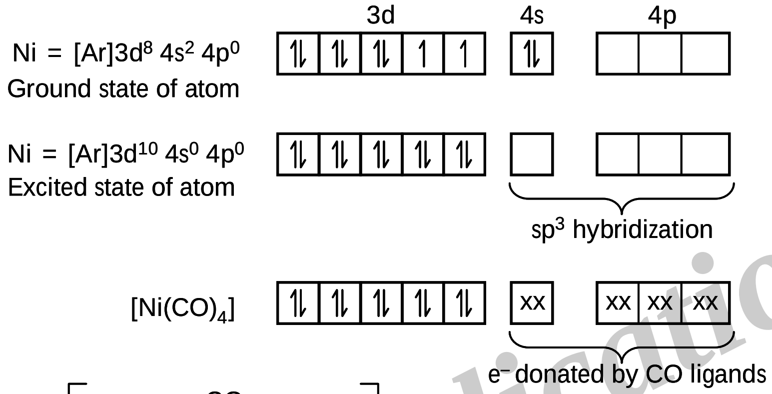
= 24 – 0 + 12 = 36 – Kr $e^{\ominus}$configuration

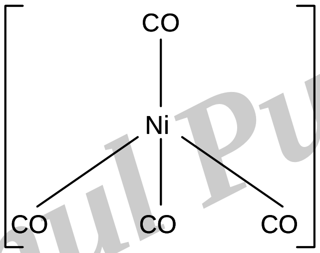
$[Fe(CN)_6]^{-4}$

= 26 – 2 + 12 = 36 = Kr $e^{\ominus}$configuration

9. Explain the structure of $[Ni(CO)_4]$ by VBT Theory.

Ans :





Geometry : Tetrahedral

10. What is Geometrical Isomerism give one example?

Ans :

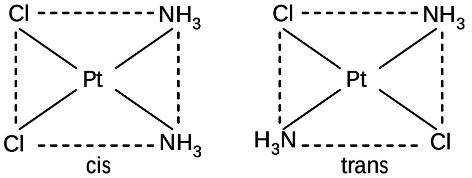
The coordination compounds showing different physical and chemical properties because of the difference in three - dimension arrangements of the groups surrounding the central metal ion, even though their chemical formulas are identical is called geometrical isomerism.

Geometrical isomerism is called cis-trans isomerism and geometrical isomers are called cis and trans isomers.

In cis isomer, identical groups occupy same sides.

In trans isomer, identical groups occupy opposite sides.

Ex:



cis trans

11. What is Linkage isomerism, Give Examples.

Ans :

Some ligands possess more than one donor atom. Hence they posses alternative coordinating ability. The isomerism arising from such ligands are called linkage isomerism.

$[Co(NH_3)_5\ ONO]Cl_2$; $[Co(NH_3)_5\ NO_2]Cl_2$

$[Cr(H_2O)_5\ SCN]^{+2}$; $[Cr(H_2O)_5\ NCS]^{+2}$

12. What is 18 Valence electron rule?

Ans :

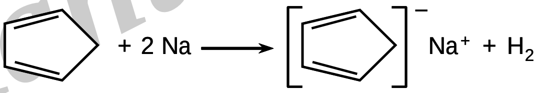
The sum of the electrons on the metal plus the electrons donated by the ligands is called the effective atomic number (Z) and when this equals 36 (Kr) or 54 (Xe) or 86 (Rn) the effective atomic number (EAN) rule is said to be obeyed. In these cases the outer electronic configuration corresponds to $ns^2(n-1)\ d^{10}np^6$ with 18 electrons in the valence shell. It is therefore referred to as 18 electron rule. In the case of mononuclear carbonyls with the exception of $V(CO)_6$ all others obey 18 electron rule.

13. What are Ionic Organometallic Compounds?

Ans :

The organometallic compounds of highly electropositive metals are usually ionic in nature. In these compounds the metal cation forms an ionic bond with the anion of the organic compound. This type of bond is referred as electrostatic chemical bond. Highly electropositive elements like alkali and alkaline earth metals form ionic organometallic compounds. Represented by R_2M M = (Ca, Ba).

Ex.: $(C_6\ H_5)_3\ C^-\ Na$, $(C_5H_5)_2^-\ Na^+ + H_2$



Ionic organo metallic compounds insoluble in non-polar solvents and hydrolysed by water.

Choose the Correct Answer

1. The total number of elements present in f-block of the periodic table are [b]

   (a) 14
   (b) 28
   (c) 42
   (d) None of these

2. In f-block elements, the extra electron enters [c]

   (a) n f orbital
   (b) (n – 1) f orbital
   (c) (n – 2) f orbital
   (d) (n – 1) d orbital

3. As the atomic number increases from 57 to 71, in tripositive lanthanon inons the number of unpaired electrons. [b]

   (a) Increases regularly from 0 to 14
   (b) First increases from 0 to 7 and then falls to 0.
   (c) Increases from 0 to 5 and then falls to 0.
   (d) Does not show any regularity.

4. Properties of ziroconium and hafnium are similar because [d]

   (a) Both are d-block elements
   (b) Both are f-block elements
   (c) Both belong to the same group
   (d) Both have similar radii

5. All the lanthanides exhibit a valency of [a]

   (a) 3
   (b) 4
   (c) 2
   (d) 6

6. In lanthanide contraction [a]

   (a) Size of M^{3+} ions decreaes
   (b) Size of M^{4+} ions decreases
   (c) Atomic radii increase
   (d) None

7. In actinides the differentiating electron enters successively to [d]

   (a) 3d
   (b) 4d
   (c) 4f
   (d) 5f

8. $[CoF_6]^{4-}$ is [d]

   (a) Outer orbital and diamagnetic
   (b) Inner orbital and paramagnetic
   (c) Inner orbital and diamagnetic
   (d) Outer orbital and paramagnetic

9. An octahedral complex of a metal ion has a magnetic moment of 5.92 BM and another octahedral complex of the some metal ion in the same oxidation state has a magnetic moment of 1.75 BM. Which one of the following ions could it be? [c]

   (a) Fe^{2+}
   (b) Co^{2+}
   (c) Fe^{3+}
   (d) Co^{3+}

10. A dipositive metal ion of first transition series forms an octahedral complex with magnetic moment of 4.9 BM and another octahedral complex which is diamagnetic. The metal ion is [a]

(a) Fe^{2+} (b) Co^{2+}

(c) Mn^{2+} (d) Ni^{2+}

11. A metal ion from the first transition series forms a tetrahedral complex which has a magnetic moment of 2.83 BM and a square planar complex which is diamagnetic. The metal ion is [b]

(a) Co^{2+} (b) Ni^{2+}

(c) Fe^{2+} (d) None of the above

12. $Ni(CO)_4$ is [b]

(a) square planar and paramagnetic (b) tetrahedral and diamagnetic

(c) square planar and diamagnetic (d) tetrahedral and paramagnetic

13. $[NiCl_4]^{2-}$ is paramagnetic. Hence its geometry is [b]

(a) square planar (b) tetrahedral

(c) tetragonal (d) None of the above

14. Pickout the complex whose aqueous solution (equal concentrations) is expected to have the highest molar conductivity. [a]

(a) $Cr(NH_3)_6Br_3$ (b) $Cr(NH_3)_3Br_3$

(c) $Cr(NH_3)_5Br_3$ (d) $Cr(NH_3)_4Br_3$

15. The d-orbital used for dsp^2 hybridization in $[Ni(CN)_4]^{2-}$ ion is [b]

(a) d_{z^2} (b) $d_{x^2-y^2}$

(c) d_{xz} (d) d_{yz}

16. Paramagnetic moment is expressed in [c]

(a) Debye unit (b) k Joules

(c) BM (d) ergs

17. The instrument used to measure the magnitude of magnetic moment is [a]

(a) Gouy balance (b) Metier balance

(c) UV spectrometer (d) None of the above

18. Which of the following is not diamagnetic? [d]

(a) Sc^{3+} (b) Cu^{+}

(c) Zn^{2+} (d) Fe^{3+}

19. Which of the following is not paramagnetic? [c]

(a) Cr^{2+} (b) Ti^{3+}

(c) Ti^{4+} (d) Mn^{3+}

20. Which of the following compounds is paramagnetic? [b]

(a) $Cr(CO)_6$ (b) $V(CO)_6$

(c) $Ni(CO)_4$ (d) $Fe(CO)_5$

21. Which of the following is diamagnetic? [d]

(a) $[Fe(CN)_6]^{4-}$
(b) $[Co(NH_3)_6]^{3+}$
(c) $Fe(CO)_5$
(d) All the above

22. Assuming that this complex obeys EAN rule, what is the fomula for a carbonyl complex of Mn, $(CO)_xMn - Mn(CO)_x$ where there is a single covalent bond between the two Mn atoms. [a]

(a) $Mn_2(CO)_{10}$
(b) $Mn_2(CO)_8$
(c) $Mn_2(CO)_{12}$
(d) None of the above

23. The molecular formula for mononuclear molybdenum carbonyl is [a]

(a) $[Mo(CO)_6]$
(b) $[Mo(CO)_7]$
(c) $[Mo(CO)_5]$
(d) None of the above

24. The EAN for iron in $Fe(CO)_5$ is [c]

(a) 35
(b) 37
(c) 36
(d) 34

25. The metal carbonyl that does not obey the EAN rule is [b]

(a) $Ni(CO)_4$
(b) $V(CO)_6$
(c) $Cr(CO)_6$
(d) All the above

26. The simplest cobalt carbonyl is [d]

(a) $Co(CO)_4$
(b) $Co_3(CO)_9$
(c) $Co_4(CO)$
(d) $Co_2(CO)_8$

27. In $Mn_2(CO)_y$ the Mn-Mn bond is a normal two-electron covalent bond; there is no bridging CO group. The value of –y is [a]

(a) 10
(b) 8
(c) 9
(d) 12

28. $2\,NiCN + 4\,CO \rightarrow Ni(CO)_4 + Ni(CN)_2$. This type of reaction is a/an [a]

(a) Disproportionation reaction
(b) Oxidation reaction
(c) Reduction reaction
(d) Chelation

29. Which one of the following is paramagnetic? [d]

(a) $Fe(CO)_5$
(b) $Cr(CO)_6$
(c) $Ni(CO)_4$
(d) $V(CO)_6$

30. Which one of the following metal carbonyls is not paramagnetic? [d]

(a) $Ni(CO)_4$
(b) $Co_2(CO)_8$
(c) $W(CO)_6$
(d) All the above

31. The formula for cobalt carbonylnitrosyl is, [b]

(a) $Co(CO)_2(NO)_2$
(b) $Co(CO)_3NO$
(c) $Co(CO)(NO)_2$
(d) $Co(CO)_2(NO)_3$

32. $Fe(CO)_5$ on treatment with NaOH gives, [c]

(a) $Na_2[Fe(CO)_4]$ (b) $Na_2[Fe(CO)_4]H$

(c) $Na[Fe\ (CO)_4]$ (d) $Na_2[FeH(CO)_4]$

33. Mond's process makes use of the formation of [a]

(a) $Ni(CO)_4$ (b) $Ni(CO)_5$

(c) $Cr(CO)_6$ (d) None of the above

34. The species that is isoelectronic with $Ni(CO)_4$ is [b]

(a) $[Fe(CO)_4]^+$ (b) $[Co(CO)_4]^-$

(c) $[Fe(CO)_4]^-$ (d) All the above

35. The C-O stretching frequency in free CO is about [d]

(a) 1700 cm^{-1} (b) 1900 cm^{-1}

(c) 1850 cm^{-1} (d) 2150 cm^{-1}

36. The formula for the tetranuclear cobalt carbonyl is [a]

(a) $Co_4(CO)_{12}$ (b) $Co_4(CO)_{16}$

(c) $Co_4(CO)_{10}$ (d) None of the above

37. A poly nuclear metal carbonyl which does not contain bridging carbonyl groups is [c]

(a) $Fe_2(CO)_9$ (b) $Co_4(CO)_{12}$

(c) $Tc_2(CO)_{10}$ (d) All the above

Fill in the blanks

1. The electronegativity values of lanthanides are comparable to those of s-block elements, therefore lanthanides are expected to form ________ compounds.
2. Except ________ all lanthanides are non-radioactive.
3. Lanthanide ions having empty, half-filled or completely filled 4f orbitals are ________.
4. With the increase in atomic number, the ionic radius of lanthanides ________ .
5. The most important oxidation state of lanthanides and actinides is ________ .
6. In a coordination complex the negative groups or neutral molecules attached to the central atom are called ________.
7. The number of ligands attached to the central atom is termed the ________ of the central atom.
8. Example for hexadentate ligand ________.
9. In Werner's theory primary valancies are satisfied by ________.
10. EAN = ________.
11. $d^2 sp^3$ hybridation of the central metalatom give ________ orbital complexes.
12. Tetrahedral complexes do not exhibit ________ isomerism.
13. $[Fe(CN)_6]$ EAN = ________.
14. If the complex contains unpaired electrons ________ in nature.
15. $Na_3[Fe(CN)_5 NO]$ IUPAC Name is ________ .

ANSWERS

1. Ionic
2. Pm
3. Colourless
4. Decreaes
5. + 3
6. Ligands
7. Cordination Number
8. Ethylenediammine tetraacetate
9. Negative ions
10. Atomic no. of metalatom – oxidation no. + 2 × coordination number
11. Inner
12. Geometrical
13. 36
14. Paramagnetic
15. Sodium pentacyano nitrosyl ferrate (II)

UNIT - II

(Organic Chemistry)

S3-O-1: Carboxylic Acids and Derivatives

Preparation: a) Hydrolysis of Nitriles, amides and esters. b) Carbonation of Grignard reagents. Special methods of preparation of Aromatic Acids - Oxidation of Arenes. Physical properties hydrogen bonding, dimeric association. Chemical properties – Reactions involving H, OH and COOH groups - salt formation, anhydride formation, Acid halide formation, Esterification (mechanism) & Amide formation. Reduction of acid to the corresponding primary alcohol - via ester or acid chloride. Degradation of carboxylic acids by Huns Diecker reaction, Schmidt reaction (Decarboxylation). Arndt – Eistert synthesis, Halogenation by Hell – Volhard - Zelensky reaction. Carboxylic acid Derivatives – Hydrolysis and Ammonolysis of acid halides, Acid anhydrides and esters (mechanism of ester hydrolysis by base and acid). Hydrolysis and dehydration of amides.

S3-O-2: Nitrohydrocarbons

Preparation of Nitroalkanes. Reactivity - halogenation, reaction with HNO_2 (Nitrous acid), Nef reaction, reduction. Aromatic Nitrohydrocarbons: Preparation of Nitrobenzene by Nitration, Physical properties, chemical reactivity – Reduction of Nitrobenzenes in different media.

S3-O-3: Amines, Cyanides and Isocyanides

Amines: classification into 1^o, 2^o, 3^o Amines and Quarternary ammonium compounds. Preparative methods – Ammonolysis of alkyl halides, Gabriel synthesis, Hoffman’s bromamide reaction (mechanism). Reduction of Amides and Schmidt reaction. Physical properties. Use of amine salts as phase transfer catalysts. Chemical Properties: a) Alkylation b) Acylation c) Carbylamine reaction d) Hinsberg separation. Reaction with Nitrous acid of 1^0, 2^0, 3^0 (Aliphatic and aromatic amines). Electophilic substitutions of Aromatic amines – Bromination and Nitration, oxidation of aryl and 3^0 Amines, diazotisation. Diazonium salts: Preparation with mechanism. Synthetic importance – a) Replacement of diazonium group by – OH, X (Cl)- Sandmeyer and Gatterman reaction, by fluorine (Schiemann’s reaction), by iodine, CN, NO_2, H and aryl groups. Coupling Reaction of diazonium salts. i) with phenols ii) with anilines. Reduction to phenyl hydrazines.

Cyanides and isocyanides: Structure. Preparation of cyanides from a) Alkyl halides b) from amides c) from aldoximes. Preparation of isocyanides from Alkyl halides and Amines. Properties of cyanides and isocyanides, a) hydrolysis b) addition of Grignard reagent iii) reduction iv) oxidation.

S3-O-1: CARBOXYLIC ACIDS AND DERIVATIVES

2.1 PREPARATION: A) HYDROLYSIS OF NITRILES, AMIDES AND ESTERS B) CARBONATION OF GRIGNARD REAGENTS

Q1. Write the preparation methods of carboxylic acids.

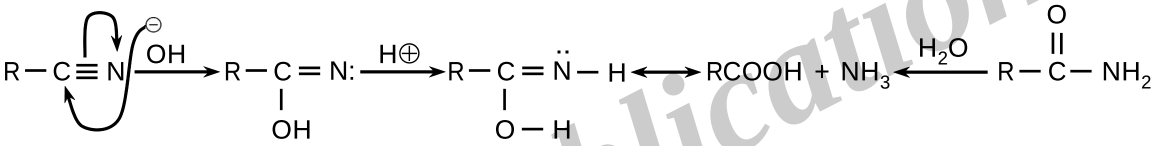
Ans :

A) Preparation of Carboxylic Acids by Hydrolysis of Nitriles, Amides and esters

1. Hydrolysis of Nitriles

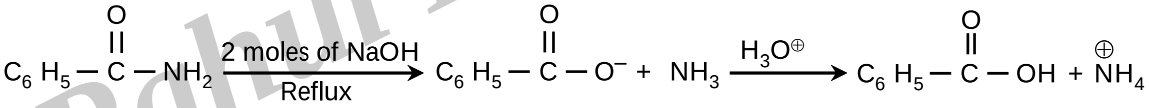
$$R-X \xrightarrow[-\,NaX]{NaCN} R-C\equiv N \xrightarrow{H_2O} R-COOH + NH_3$$

$$H_3C-CN \xrightarrow{\text{aq NaOH}} H_3C-COONa + NH_3 \xrightarrow{H_3O^{\oplus}} H_3C-COOH$$



2. Hydrolysis of Amides

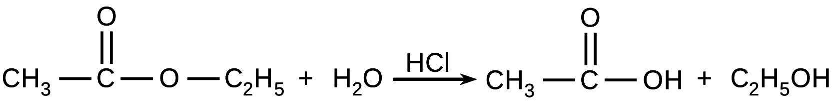
Amides can be hydrolysed with alkalies.



$$C_6H_5-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow[\text{Reflux}]{\text{2 moles of NaOH}} C_6H_5-\overset{\overset{O}{||}}{C}-O^- + NH_3 \xrightarrow{H_3O^{\oplus}} C_6H_5-\overset{\overset{O}{||}}{C}-OH + NH_4^{\oplus}$$

3. Hydrolysis of Esters

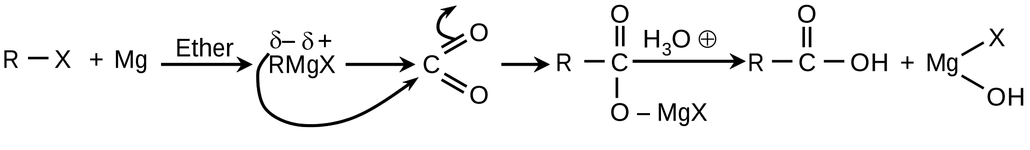
Esters can be hydrolysed with mineral acids or alkalies.



$$CH_3-\overset{\overset{O}{||}}{C}-O-C_2H_5 + H_2O \xrightarrow{HCl} CH_3-\overset{\overset{O}{||}}{C}-OH + C_2H_5OH$$

B) Carbonation of Grignard Reagent

Addition of carbon dioxide is called carbonation Grignard reagents form addition product with CO_2 and on Hydrolysis produces carboxylic acids.

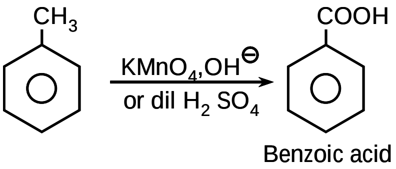


2.2 SPECIAL METHODS OF PREPARATION OF AROMATIC ACIDS - OXIDATION OF ARENES

Q2. Write about preparation methods of Aromatic acids.

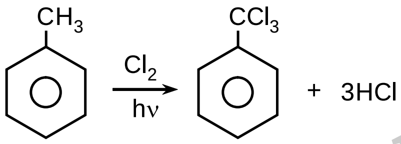
Ans : **(Imp.)**

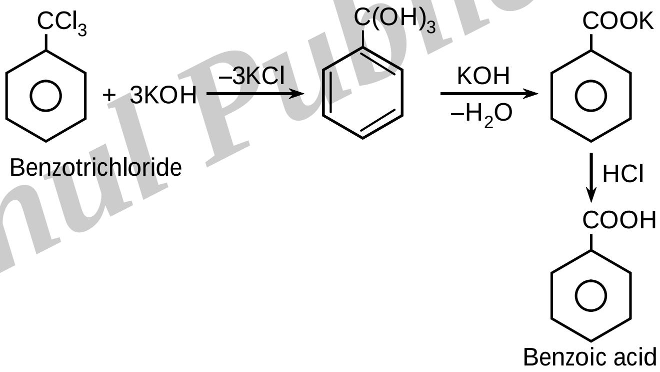
Alkyl benzene on oxidation with acidified $K_2Cr_2O_7$ or alkaline $KMnO_4$ or dil HNO_3 alkyl group oxidized to – COOH group.



Hydrolysis of Benzotrichloride

Benzotrichloride is hydrolysed with aq - potassium hydroxide. Potassium benzoate on acidification in cold yields benzoic acid.





2.3 PHYSICAL PROPERTIES HYDROGEN BONDING, DIMERIC ASSOCIATION

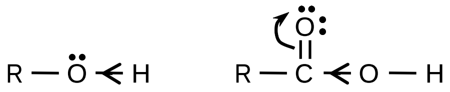
Q3. Explain the physical properties of carboxylic acids.

Ans :

Physical Properties

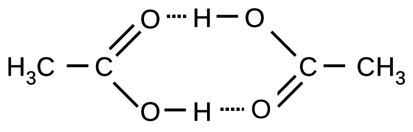
Physical State: The first three members $C_1 - C_3$ are colourless, pungent smelling liquids, $C_4 - C_9$ are oily liquids.

Boiling Points of Carboxylic Acids: Like alcohols carboxylic acids also form intermolecular hydrogen bonding and exist as associate molecules. The strength of hydrogen bonding between the carboxylic acid molecules is stronger than alcohols. The –OH bonding of carboxylic acids more polar than of alcohols due to the presence of $e^{\ominus}$ withdrawing carboxyl group in adjacent position.



$R-\ddot{O}\leftarrow H \qquad R-\overset{\overset{\ddot{O}:}{\|}}{C}\leftarrow O-H$

In addition to –OH grouping carbonyl group also involves in hydrogen bonding between two molecules two hydrogen bonds leading to formation of ring structure between them. These carboxylic acids exist as cyclic dimers.



Solubility

First few acids are soluble in water the solubility is due to the hydrogen bonding between carboxylic acid and water.

2.4 Chemical Properties – Reactions Involving H, OH and COOH Groups - Salt Formation, Anhydride Formation, Acid Halide Formation, Esterification (Mechanism) & Amide Formation. Reduction of Acid to the Corresponding Primary Alcohol - via Ester or Acid Chloride. Degradation of Carboxylic Acids by Huns Diecker Reaction, Schmidt Reaction (Decarboxylation). Arndt – Eistert Synthesis, Halogenation by Hell – Volhard - Zelensky Reaction

Q4. Write the reactions involving H-atom, OH group and –COOH group.

Ans :

Reactions Involving H-atom of Carboxyl Group

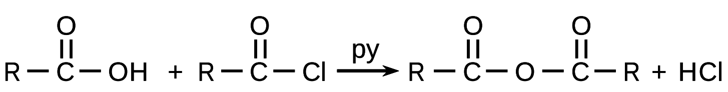
Carboxylicacids react with metal hydroxides form salts.

$$H_3CCOOH + NaOH \rightarrow H_3C-COONa + H_2O$$

Sodium acetate

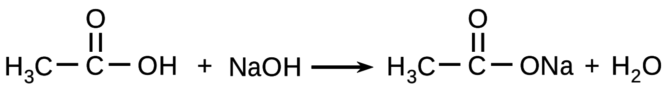
Reactions Involving –OH Part of Carboxylic Group Formation of Anhydride

Carboxylic acids can be converted into acid anhydrides by their reaction with acid halides in presence of pyridine.

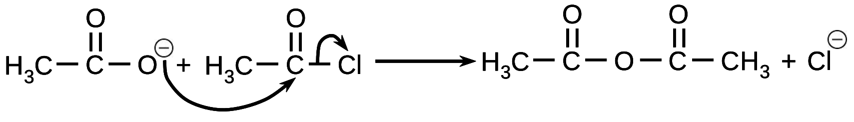


$$R-\overset{\overset{O}{\|}}{C}-OH + R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{py} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + HCl$$

Acid anhydride



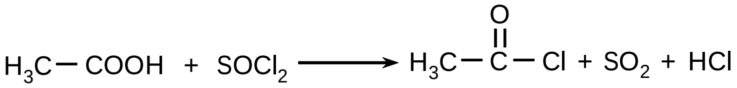
$$H_3C-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-ONa + H_2O$$



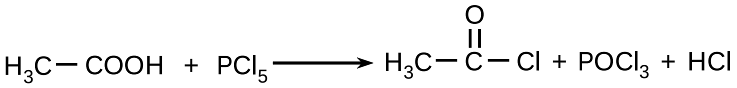
$$H_3C-\overset{\overset{O}{\|}}{C}-O^{\ominus} + H_3C-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + Cl^{\ominus}$$

Formation of Acid Chlorides

Acids on treatment with phosphorus pentachloride or phosphorus trichloride or thionyl chloride get converted into acid chlorides.



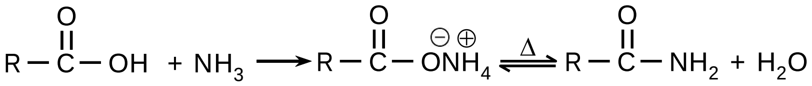
$$H_3C-COOH + SOCl_2 \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + SO_2 + HCl$$



$$H_3C-COOH + PCl_5 \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + HCl$$

$$3H_3C-COOH + PCl_3 \longrightarrow 3C_6H_5COCl + H_3PO_3$$

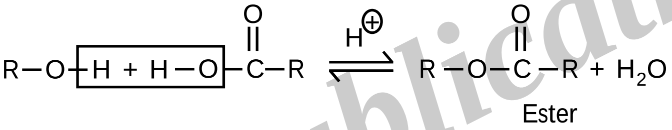
Formation of Amides



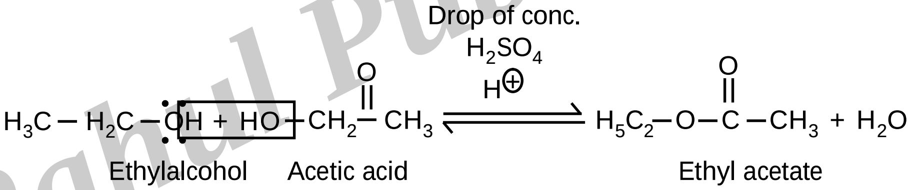
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus\oplus}{ONH_4} \overset{\Delta}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2O$$

Esterification

Esterification involves the replacing hydrogen atom of the alcohol and – OH group of acid.



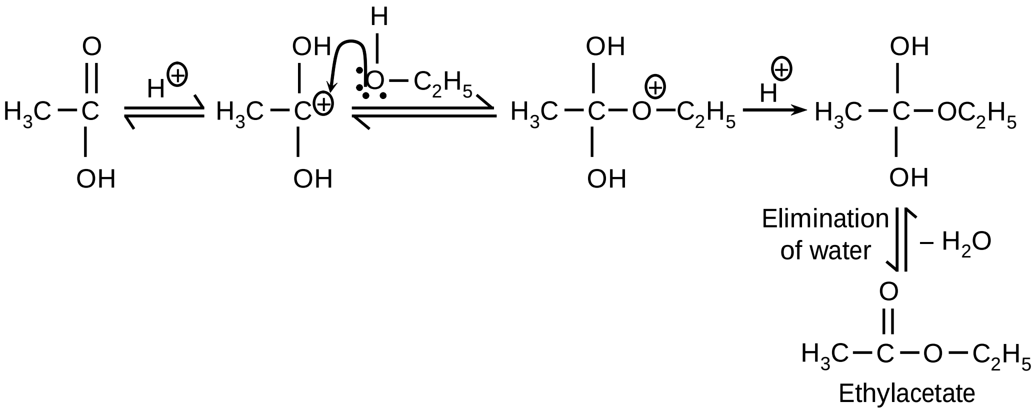
$$R-O-\boxed{H + H-O}-\overset{\overset{\displaystyle O}{\|}}{C}-R \overset{H^{\oplus}}{\rightleftharpoons} \underset{\text{Ester}}{R-O-\overset{\overset{\displaystyle O}{\|}}{C}-R} + H_2O$$



$$\underset{\text{Ethylalcohol}}{H_3C-H_2C-\ddot{O}}\boxed{H + HO}-\underset{\text{Acetic acid}}{\overset{\overset{\displaystyle O}{\|}}{C}H_2-CH_3} \xrightleftharpoons[]{\substack{\text{Drop of conc.}\\ H_2SO_4\\ H^{\oplus}}} \underset{\text{Ethyl acetate}}{H_5C_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + H_2O$$

Mechanism

1. Protonation of carboxylic acid
2. Nacleophilic attack of C_2H_5OH
3. Elimination of water molecule.



$$H_3C-\underset{OH}{\overset{O}{\overset{\|}{C}}} \overset{H^{\oplus}}{\rightleftharpoons} H_3C-\underset{OH}{\overset{OH}{\overset{|}{C}^{\oplus}}} \overset{H-\ddot{O}-C_2H_5}{\rightleftharpoons} H_3C-\underset{OH}{\overset{OH}{\overset{|}{C}}}-\overset{\oplus}{O}-C_2H_5 \xrightarrow{-H} H_3C-\underset{OH}{\overset{OH}{\overset{|}{C}}}-OC_2H_5 \xrightleftharpoons[\text{of water}]{\text{Elimination}\ -H_2O} \underset{\text{Ethylacetate}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5}$$

Q5. Write about acid-anhydrides and its reactions.

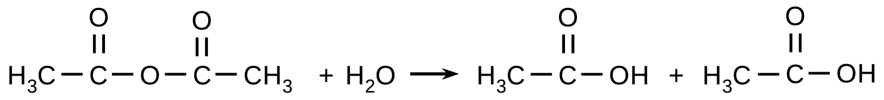
Ans :

Acid Anhydride Properties

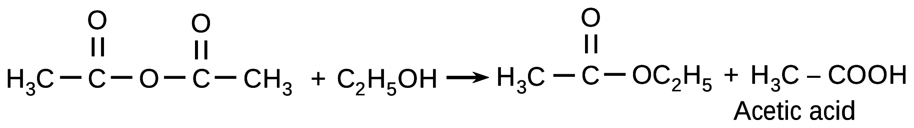
Acetic anhydride closely resembles acetyl chloride in chemical reactions but slowly reacts with nucleophilic agents. The carboxyl carbon atom of the anhydride is not so electron deficient as the carboxyl carbon atom of acetyl chloride because oxygen atom has the tendency to donate the lone pair of electrons to the carboxyl carbon.

1. **Hydrolysis**

Acetice anlydride reacts with water to give acetic acid and with alcohol to produce esters.



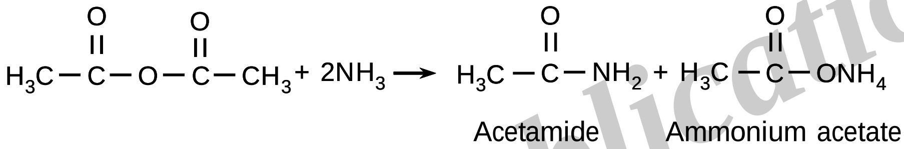
$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-OH + H_3C-\overset{O}{\overset{\|}{C}}-OH$$



$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + C_2H_5OH \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_3C-COOH$$

Acetic acid

2. **Ammonolysis**

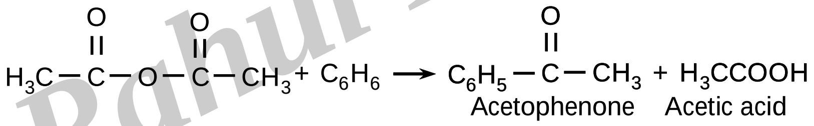


$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + 2NH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + H_3C-\overset{O}{\overset{\|}{C}}-ONH_4$$

Acetamide Ammonium acetate

3. **Synthesis of Ketones (Friedel - Crafts reaction)**

Acetic anhydride reacts with benzene in the presence of anhydrous $AlCl_3$ to form methyl phenyl ketone.



$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + C_6H_6 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + H_3CCOOH$$

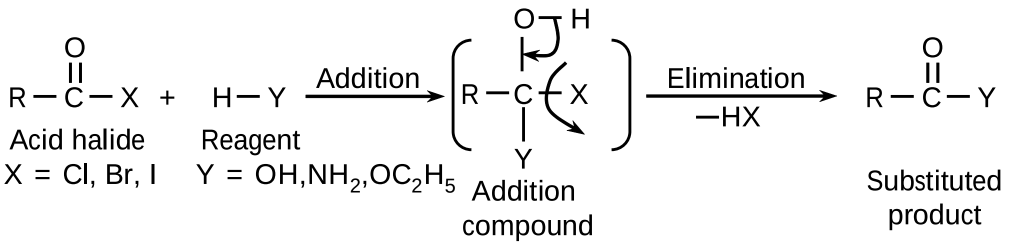
Acetophenone Acetic acid

Q6. Give the reactions of acid halides.

Ans :

Acid chlorides Properties

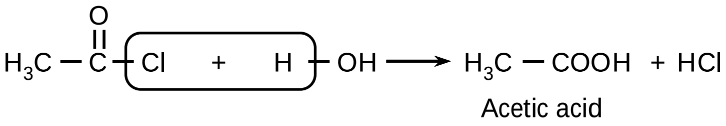
Acid chlorides undergoes acylation reaction. Acylation reaction takes place by an addition elimination process. In which a nucleophilic reactant bonds to the electrophotic carboxyl carbon atom to create a tetrahedral intermediate. This tetrahedral intermediate then undergoes an elimination reaction to yield the product.



$$R-\overset{O}{\overset{\|}{C}}-X + H-Y \xrightarrow{\text{Addition}} \left[R-\underset{Y}{\underset{|}{\overset{O-H}{\overset{|}{C}}}}-X\right] \xrightarrow[-HX]{\text{Elimination}} R-\overset{O}{\overset{\|}{C}}-Y$$

1. Hydrolysis

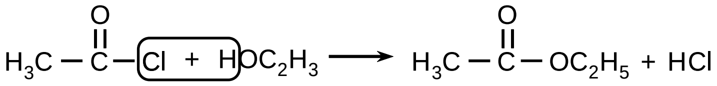
Acetyl chloride reacts vigorously with water and is hydrolysed to acetic acid.



$$H_3C-\overset{O}{\overset{\|}{C}}-\boxed{Cl\quad+\quad H}-OH \longrightarrow \underset{\text{Acetic acid}}{H_3C-COOH} + HCl$$

2. Reaction with Alchol (Alcoholysis)

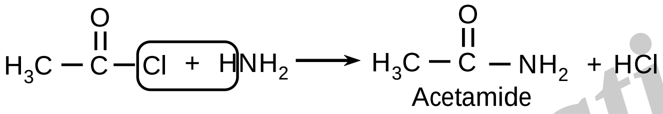
Acetyl chloride reacts with ethyl alochol at ordinary temperature to form ethylacetate (ester)



$$H_3C-\overset{O}{\overset{\|}{C}}-\boxed{Cl + H}OC_2H_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-OC_2H_5 + HCl$$

3. Reaction with Nitrogenous Compounds (Ammonolysis)

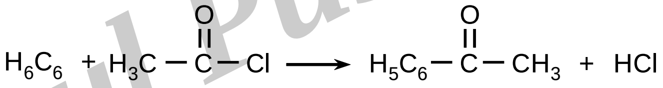
Acetyl chloride reacts with conc. ammonia and forms acetamide



$$H_3C-\overset{O}{\overset{\|}{C}}-\boxed{Cl + H}NH_2 \longrightarrow \underset{\text{Acetamide}}{H_3C-\overset{O}{\overset{\|}{C}}-NH_2} + HCl$$

4. Synthesis of Ketones

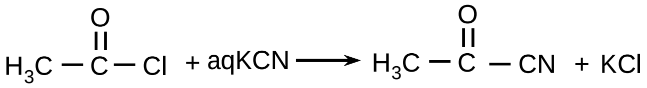
Acetyl chloride reacts with benzene in the presence of anhydrous $AlCl_3$ to form methyl phenyl ketone or acetophenone



$$H_6C_6 + H_3C-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow H_5C_6-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

5. Formation of Acetyl Cyanide

Acetyl chloride reacts with aqueous solution of potassium cyanide to form acetyl cyandide.



$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + aqKCN \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-CN + KCl$$

Q7. What is Huns Diecker reaction. Explain the mechanism.

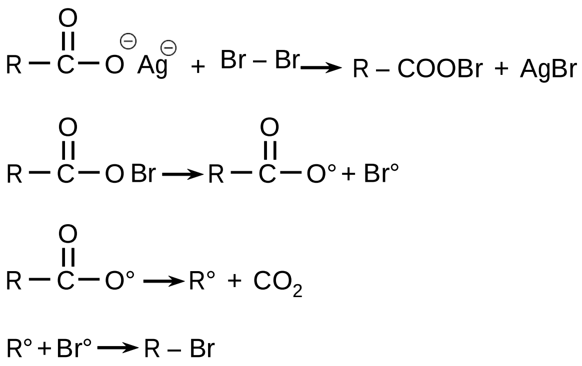
Ans : **(Imp.)**

It is a decarboxylative halogenation. Heavy metal salts (Ag, Hg, Pb) of carboxylic acid in CCl_4 when heated with bromine or iodine gives an alkyl halide with one carbon less than the starting carboxylic acid. The reaction is called Huns diecker reaction. The reaction involves the loss of carbon dioxide hence it is a decarboxylation reaction.

$$R-COO^-Ag^+ + Br_2 \xrightarrow[\Delta]{CCl_4} RBr + AgBr\downarrow + CO_2\uparrow$$

$$R-COO^-Ag^+ + I_2 \xrightarrow[\Delta]{CCl_4} RI + CO_2\uparrow + Ag\downarrow$$

Mech



$$R-\overset{\overset{O}{\|}}{C}-O^{\ominus}Ag^{\ominus} + Br-Br \longrightarrow R-COOBr + AgBr$$

$$R-\overset{\overset{O}{\|}}{C}-O\,Br \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^{\circ} + Br^{\circ}$$

$$R-\overset{\overset{O}{\|}}{C}-O^{\circ} \longrightarrow R^{\circ} + CO_2$$

$$R^{\circ} + Br^{\circ} \longrightarrow R-Br$$

Q8. Explain Schmidt reaction with mechanism.

Ans : **(Imp.)**

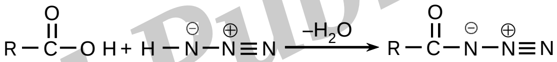
It is a decarboxylative animation. The reaction is useful for the conversion of carboxylic acids to amines directly.

Carboxylic acids on treatment with hydrazoic acid (N_3H) produce acyl azides as intermediate products, which on rearrangement in acidic medium produce primary amines.

$$R-COOH + N_3H \xrightarrow{H_2SO_4} R-NH_2 + N_2 + CO_2$$

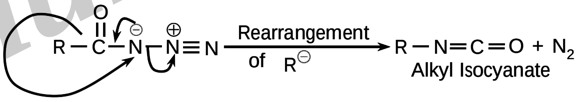
Mech

1. Formation of Acid Azides.



$$R-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \xrightarrow{-H_2O} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N$$

2. Rearrangement of $R^{\ominus}$to form alkyl or aryl isocyanate.



$$R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \xrightarrow[\text{of } R^{\ominus}]{\text{Rearrangement}} \underset{\text{Alkyl Isocyanate}}{R-N=C=O} + N_2$$

3. Hydrolysis of isocyanate to form primary amines.

$$R-N=C=O + HOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2 + CO_2}$$

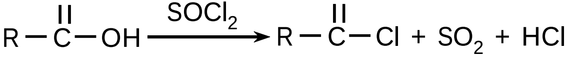
Q9. Discuss the mechanism of Arndt-Eistert synthesis.

Ans : **(Imp.)**

Arndt – Eistert Synthesis

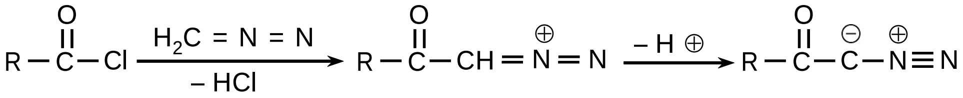
It involves the conversion of an acid into its next higher homologues acid ($R-CH_2-COOH$) i.e., chain length increases by one carbon atom. It is also called as Arndt-Eistert homologation.

1. Conversion of carboxylic acid to its chloride.



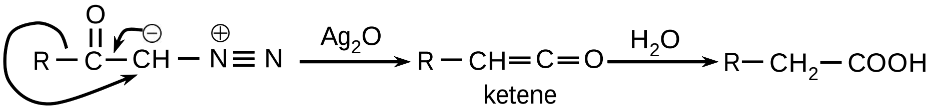
$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{SOCl_2} R-\overset{\overset{O}{\|}}{C}-Cl + SO_2 + HCl$$

2. Acid chloride to diazoketone by treating with excess of diazomethane $H_2C\ N_2$.



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-\ HCl]{H_2C\ =\ N\ =\ N} R-\overset{O}{\overset{\|}{C}}-CH=\overset{\oplus}{N}=N \xrightarrow{-\ H\ \oplus} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N$$

3. α-Diazoketone when heated with silver oxide rearranges to ketene which is in presence of water gives the homologous acid.



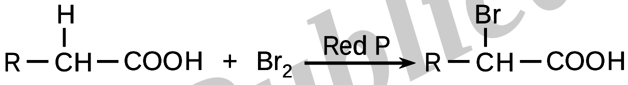
$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-\overset{\oplus}{N}\equiv N \xrightarrow{Ag_2O} \underset{\text{ketene}}{R-CH=C=O} \xrightarrow{H_2O} R-CH_2-COOH$$

Q10. Write the halogenation of carboxylic acids by Hell-Volhard - Zelinsky reaction.

Ans :

Reactions involving Alkyl Group of the acid Halogenation. Hell-Volhard-Zelinsky reaction (HVZ)

Aliphatic carboxylic acids containing α-hydrogens undergo halogenation with Cl_2 or Br_2 in presence of catalyst red phosphorus in sunlight or on boiling to form alkyl substituted products. The reaction is known as Hell - Volhard - Zelinsky (HVZ) reaction. During the reaction electrophilic substitution takes place on alkyl group. The carboxyl group is electron an with-drawing group that makes α-hydrogens acidic in nature.



$$R-\overset{H}{\overset{|}{C}H}-COOH + Br_2 \xrightarrow{\text{Red P}} R-\overset{Br}{\overset{|}{C}H}-COOH$$

α-Bromo acid

$$H_3C-COOH \xrightarrow[(-HCl)]{Cl_2/P} H_2Cl-COOH$$

Monochloro acetic acid

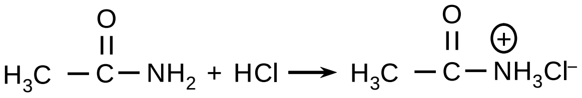
2.5 Carboxylic acid Derivatives – Hydrolysis and Ammonolysis of Acid Halides, Acid Anhydrides and Esters (Mechanism of Ester Hydrolysis by Base and Acid). Hydrolysis and Dehydration of Amides

Q11. Discuss the reactions of acid amides and esters.

Ans :

In amides presence of nitrogen group donates its lone pair of $e^{\ominus}$s diminishes the electron deficiency of carboxyl atom. It can not accept the electrons from ROH or $R-NH_2$

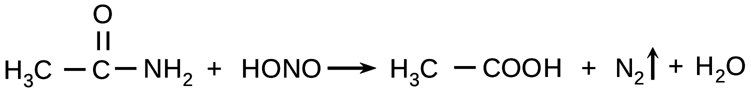
1.



$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + HCl \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{N}H_3Cl^-$$

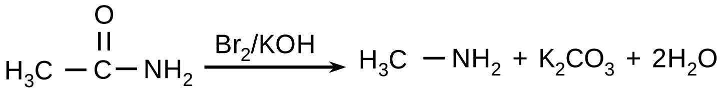
Acetamide behaves as weak base towards strong base

2. Treating with Nitrous acid



$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + HONO \longrightarrow H_3C-COOH + N_2\uparrow + H_2O$$

3. Haffmann degradation reaction.



$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/KOH} H_3C-NH_2 + K_2CO_3 + 2H_2O$$

S3-O-2: NITROHYDROCARBONS

2.6 PREPARATION OF NITROALKANES

Q12. Give the preparation methods of nitroalkanes.

Ans :

1. By heating alkyl halide with aq alcoholic silver nitrite.

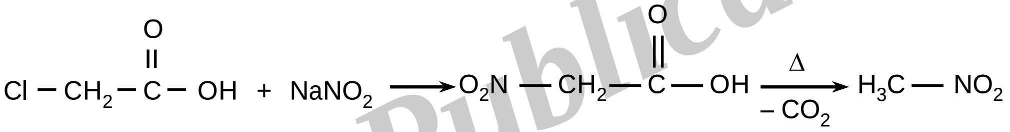
   $C_2H_5Br + AgNO_2 \rightarrow C_2H_5-NO_2 + AgBr$

   the mixture of nitro alkanes and alkyl nitrites separated by fractional distillation.

2. By the direct nitration of paraffins.

   $$H_2C=CH_2 + HONO_2 \xrightarrow{400^o} H_3C-CH_2-NO_2 + H_2O$$

3. By the action of sodium nitrite on α-halo carboxylic acids.



$$Cl-CH_2-\overset{\overset{O}{\|}}{C}-OH + NaNO_2 \longrightarrow O_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} H_3C-NO_2$$

4. 3°– Nitro alkanes are obtained by the oxidation of 3° – Amine with $KMnO_4$.

   $$R_3C-NH_2 \xrightarrow{KMnO_4} R_3C.NO_2 + H_2O$$

2.7 REACTIVITY - HALOGENATION, REACTION WITH HNO_2 (NITROUS ACID) NEF REACTION, REDUCTION

Q13. Write the reactions of halogenation of Nitro compounds.

Ans :

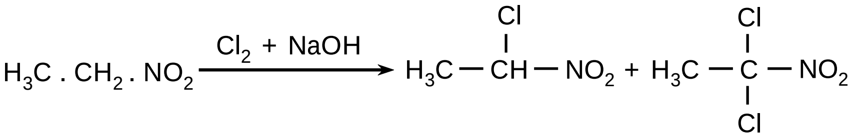
Halogenation

1°, 2° nitro paraffins are readily halogenated in alkali solution (X_2 + NaOH). The halogen atom enters the α-position.

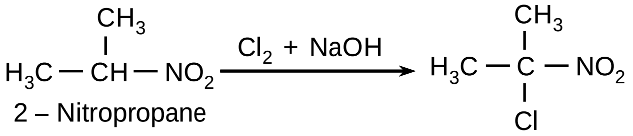
$$H_3CNO_2 \xrightarrow{Cl_2+NaOH} CCl_3.NO_2$$

Nitormethane (chloropicrin)

Chloropicrin is a lachrymatory substance and also used as soil sterilizing agent.



$$H_3C.CH_2.NO_2 \xrightarrow{Cl_2 + NaOH} H_3C-\overset{\overset{Cl}{|}}{CH}-NO_2 + H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-NO_2$$



$$H_3C-\overset{\overset{CH_3}{|}}{CH}-NO_2 \xrightarrow{Cl_2\ +\ NaOH} H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-NO_2$$

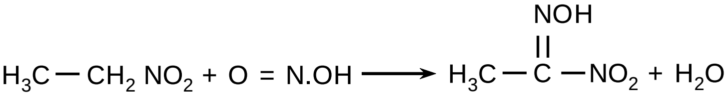
2 – Nitropropane

Q14. Discuss the reactions of Nitro compounds with HNO_2.

Ans :

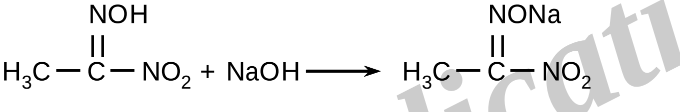
Action of Nitrous Acid

(a) 1° – Nitro alkanes react with nitrous acid to form nitrolic acid which dissolve in sodium hydroxide giving red solution.



$$H_3C-CH_2\,NO_2 + O = N.OH \longrightarrow H_3C-\overset{\overset{NOH}{||}}{C}-NO_2 + H_2O$$

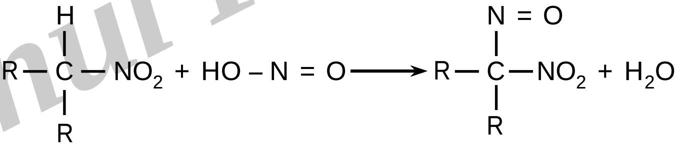
Nirolic acid



$$H_3C-\overset{\overset{NOH}{||}}{C}-NO_2 + NaOH \longrightarrow H_3C-\overset{\overset{NONa}{||}}{C}-NO_2$$

Sodium Nitrolate (red)

(b) 2° – Nitroalkanes reacts with nitrous acid to give colourless crystalline pseudonitrole which gives blue colour in solution.



$$R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-NO_2 + HO-N=O \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{N=O}{|}}{C}}-NO_2 + H_2O$$

Pseudonitrol (blue)

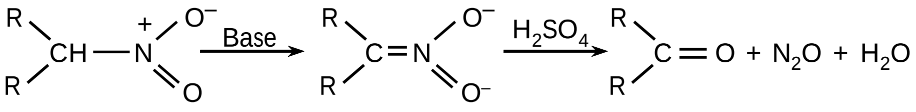
(c) 3° – Nitro alkanes do not react with nitrous acid because they do not contain α - hydrogens. The distinction between 1°, 2°, 3° alcohols is called **victor - meyer** test.

Q15. Explain the Nef reaction with mechanism.

Ans : **(Imp.)**

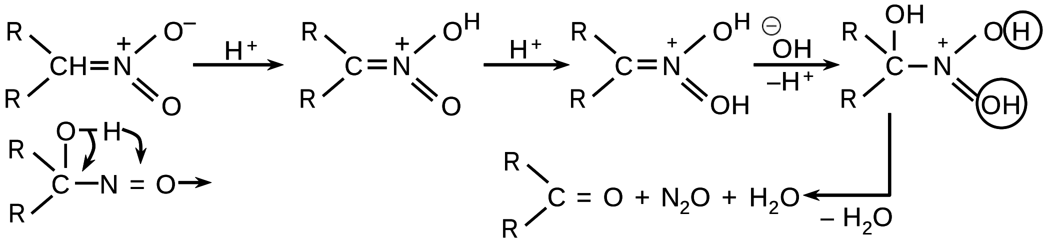
Nef Reaction

1°/2° aliphatic nitro compounds hydrolysed to aldehydes or ketones by treatment of their conjugate bases with H_2SO_4. This reaction is called Nef reaction.



$$R_2CH-\overset{+}{N}(=O)O^- \xrightarrow{Base} R_2C=N(O^-)O^- \xrightarrow{H_2SO_4} R_2C=O + N_2O + H_2O$$

Mechanism



2.8 Aromatic Nitrohydrocarbons: Preparation of Nitrobenzene by Nitration, Physical Properties, Chemical Reactivity – Reduction of Nitrobenzenes in Different Media

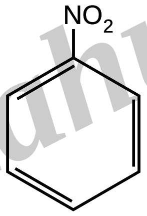
Q16. What are aromatic nitro compounds.

Ans :

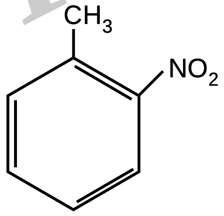
Aromatic Nitro Compounds

Aromatic nitro compounds are the derivatives of aromatic hydro carbons in which one or more hydrogen atoms of the benzene nucleus has been replaced by nitro – NO_2 – group.

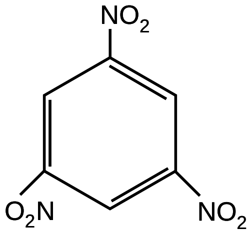
Compounds in which $-NO_2$ group is attached to the side chain $C_2H_5 - CH_2 - NO_2$ are more correctly known as aryl - substituted nitro alkanes and the aromatic nitro compounds are those in which $-NO_2$ group is directly present on the aromatic nucleus.



Nitro benzene



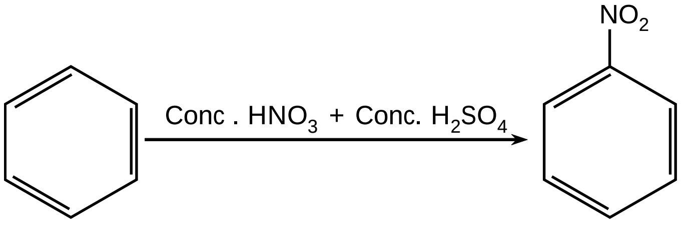
O – Nitro Toluene



1, 3, 5 – Trinitro Benzene

Q17. Explain the preparation of nitrobenzene by nitration.

Ans :



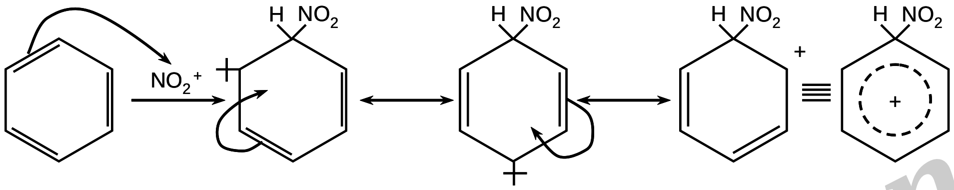
Mechanism

1. Formation of Electrophile

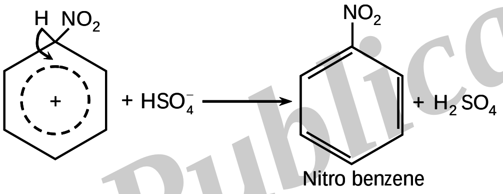
Generation of electrophile in nitration nitronium ion NO_2^+.

$$\begin{aligned} HO-NO_2 + H_2SO_4 &\longleftrightarrow H_2O^+-NO_2 + HSO_4^{\ominus} \\ H_2O^+-NO_2 &\longleftrightarrow H_2O + NO_2^+ \\ H_2O^+ + H_2SO_4 &\longleftrightarrow H_3O^+ + HSO_4^{\ominus} \\ \hline HONO_2 + 2H_2SO_4 &\longleftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^{\ominus} \end{aligned}$$

ii) Formation of 'σ' complex



iii) Removal of H^+



Q18. Write the reduction reactions of Nitro benzenes in different media.

Ans : **(Imp.)**

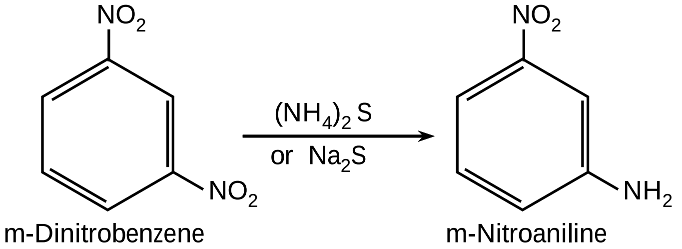
Reduction

i) In acidic medium

Nitrobenzene is reduced with a metal and acid (Sn + HCl), Zn + HCl, $SnCl_2$ + HCl, Fe + H_2O + HCl. Aniline is the main product.

$$\underset{}{C_6H_5NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

Selective Reduction: Reduction of dinitrobenzene with ammonium sulphide reduces only one $-NO_2$ group.



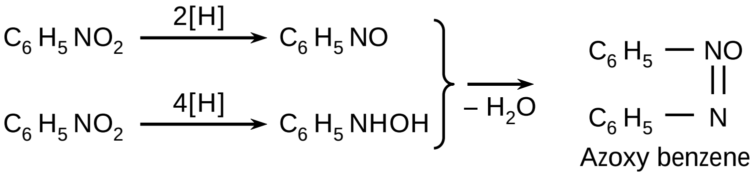
ii) In Neutral Medium

Zn dust + NH_4Cl, Al – Hg couple and water phenyl hydroxyl amine is formed.

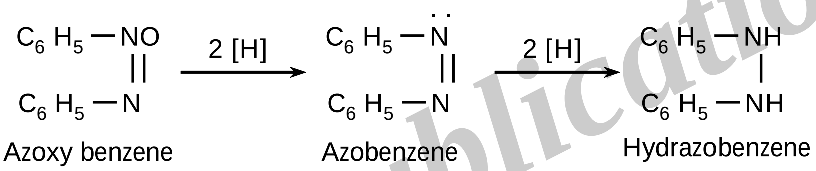
$$C_6H_5NO_2 + 2[H] \xrightarrow[-H_2O]{Zn\ dust\ +\ NH_4Cl} \underset{\text{Nitroso benzene}}{C_6H_5NO} \xrightarrow{2[H]} \underset{\text{Phenyl hydroxyl amine}}{C_6H_5NOH}$$

iii) In Alkaline Medium

Nitrobenzene is reduced with an alkaline reducing agent the intermediate reduction products nitrobenzene and phenyl hydroxyl amine interact to form dinuclear product like azoxy benzene, azobenzene and hydrazo benzene.



Azoxy benzene on further reduction yields azo benzene and hydrazo benzene



S3-O-3: AMINES, CYANIDES AND ISOCYANIDES

2.9 AMINES: CLASSIFICATION INTO 1°, 2°, 3° AMINES AND QUARTERNARY AMMONIUM COMPOUNDS. PREPARATIVE METHODS – AMMONOLYSIS OF ALKYL HALIDES, GABRIEL SYNTHESIS, HOFFMAN'S BROMAMIDE REACTION (MECHANISM). REDUCTION OF AMIDES AND SCHMIDT REACTION

Q19. Write the classification of Amines with examples.

Ans : **(Imp.)**

Amines are broadly classified into

(a) Aliphatic amines

(b) Aromatic amines

The amines which directly attached to aromatic ring are called aromatic amines, all other amines are called aliphatic amines.

These amines are again classified into three types.

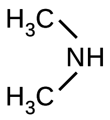
1. 1° amines – the NH_2 group attached to one 'C' atom.

Example:

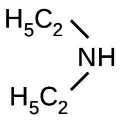
H_3C-NH_2	$C_2H_5NH_2$	$(H_3C)_2CHNH_2$
Methyl amine	Ethyl amine	Isopropyl amine

2. 2^o amines – the NH group attached to two 'C' atoms.

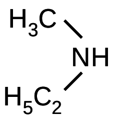
Example:



Dimethyl amine



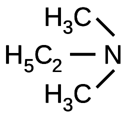
Diethyl amine



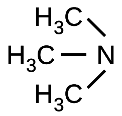
Ethyl methyl amine

3. 3^o amines – the N group attached to three 'C' atoms.

Example:



Ethyl dimethyl amine



Trimethyl amine

Q20. Write any three preparation methods of amines.

Ans :

Preparation Methods

1. **Ammonolysis of Alkyl halide**

Aqueous or alcoholic solution of ammonia is heated in a sealed tube at 100°C.

$$C_2H_5I + HNH_2 \longrightarrow C_2H_5NH_2 + HI$$

Ethylamine

$$C_2H_5I + H_2NC_2H_5 \longrightarrow C_2H_5NHC_2H_5 + HI$$

$$C_2H_5I + H_2NC_2H_5 \longrightarrow (C_2H_5)_4^+NI^-$$ Tetraethyl ammonium iodide

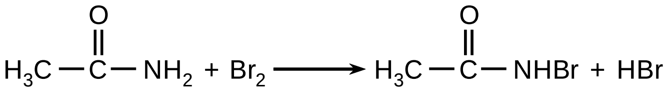
2. **Hofman Degradation of Amides (Hoffman's Bromide reaction)**

This is one of the most convenient methods for the preparation of primary amines. It involves action of halogen and alkali NaOH (or) KOH on amide to form amines with one carbon atom less.

$$H_3C.CONH_2 + Br_2 + 4KOH \longrightarrow H_3CNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

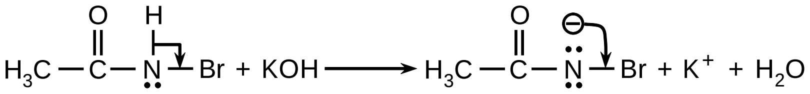
Mechanism

(a) The first step involves the halogenation of the amide to give an N-haloamide.



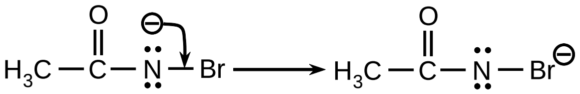
$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-NHBr + HBr$$

(b) The second step involves the reaction with potassium hydroxide which removes hydrogen of – NHBr as water.



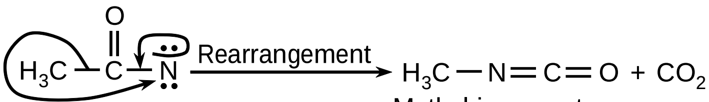
$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\ddot{N}}-Br + KOH \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{\ddot{N}}-Br + K^+ + H_2O$$

(c) The third step involves the separation of halide ion to form a species having e̅ deficient nitrogen atom.



$$H_3C-\overset{\overset{O}{\|}}{C}-\ddot{N}^{\ominus}-Br \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-\ddot{N}-Br^{\ominus}$$

(d) Alkyl group migrates from carbon to nitrogen to form alkyl isocyanate.



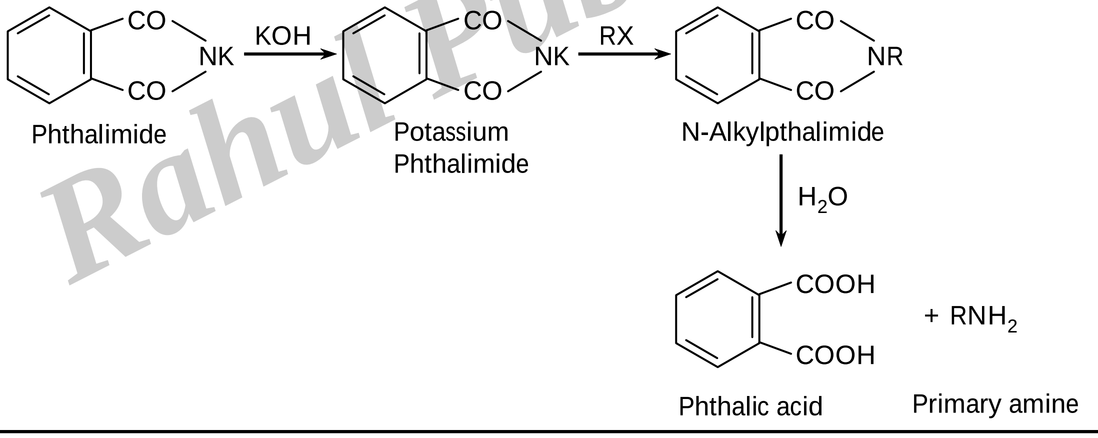
$$H_3C-\overset{\overset{O}{\|}}{C}-\ddot{N} \xrightarrow{\text{Rearrangement}} \underset{\text{Methyl isocyanate}}{H_3C-N=C=O} + CO_2$$

(e) Alkyl isocyanate is hydrolysed to form the primary amine.

$$H_3C-N=C=O + H_2O \xrightarrow{\text{Alkali}} \underset{\text{Methyl amine}}{H_3CNH_2} + CO_2$$

3. Gabriel Phthalimide (Gabriel synthesis)

Phthalimide is treated with KOH to form potassium pthalimide which on heating with 20% hydrochloric acid under pressure to give primary amine.



Q21. What is a carbyl amine reaction.

Ans : **(Imp.)**

Carbylamine Reaction

Primary amines when heated with chloroform and alcoholic caustic potash give Isocyanides (carbylamine) having very unpleasant smell which can be easily detected.

$$C_2H_5NH_2 + CHCl_3 + KOH \rightarrow \underset{\text{Ethyl Isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$

Q22. How can primary, secondary, and tertiary amines be distinguished by using nitrous acid.

Ans : **(Imp.)**

Reactions of Aliphatic and Aromatic Amines with Nitrous Acid

Aliphatic Amines React with Nitrous Acid

1. Primary amines except methyl amine form primary alcohols with nitrous acid.

$$C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$$

Ethyl amine Ethyl alcohol

Methylamine react with Nitrous acid to form methyl Nitrile and dimethyl ether

$$H_3C - NH_2 + 2HNO_2 \longrightarrow H_3C - O - N = O + N_2 + H_2O$$

Methyl Nitrite

$$2H_3CNH_2 + 2HNO_2 \longrightarrow H_3C - O - CH_3 + 2N_2 + 3H_2O$$

2. Secondary Amines react with nitrous acid to form N-Nitroso amines.

$$(CH_3)_2\ NH + HONO \longrightarrow (H_3C)_2\ N - N = 0 + H_2O$$

N - Nitroso dimethyl amine

Nitroso amines are water insoluble yellow oils and when warmed with a crystal of phenol and a few drops of conc.H_2SO_4 produce a green solution which turns blue on adding alkali. This reaction is known as **libermann's nitroso reaction** may be used as a test for secondary amines.

Nitroso amines when heated with conc HCl regenerate to secondary amines.

$$(H_3C)_2\ N - N = O + H_2O \xrightarrow{\text{Conc.HCl}} (CH_3)_2\ NH + HONO$$

3. Tertiary Amines Dissolve in Cold Nitrous acid to form unstable nitrites which decompose on warming to give nitrosoamine.

$$(CH_3)_3\ N + HNO_2 \longrightarrow (CH_3)_3\ NH.NO_2 \xrightarrow{\text{Heat}} (CH_3)_2\ N.NO + HNO_3$$

Nitroso amine

Aromatic Amines Reacting with Nitrous Acid

Diazotization

An ice cold solution of a primary aromatic amine in hydrochloric acid is treated with an ice-cold aq. solution of sodium nitrite. Water soluble compounds known as diazonium salts are formed.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$C_6H_5NH_2.HCl + HONO \longrightarrow C_6H_5N_2Cl + 2H_2O$$

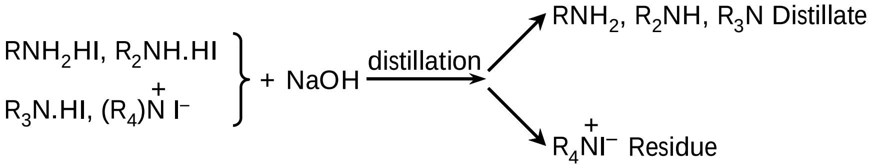
Aniline hydrochloride Benzene diazonium chloride

Q23. How do you separate primary, secondary, tertiary amines from a mixture, by hinsberg separation method.

Ans : **(Imp.)**

Separation of Mixture of Amines

When an alkyl halide (or) alcohol is treated with ammonia a mixture of 1°, 2° and 3° amines along with quaternany ammonium salt is obtained. For obtaining different amines from the mixture, it is distilled with KOH (or) NaOH solution when the 1°, 2° and 3° amines distilled over leaving behind the non-volatile quaternary ammonium salt.



Hinsberg Method

The mixture of amines is treated with benzene sulphonyl chloride (Hinsberg's reagent) and shaken with alkali solution when the three amines behave in different ways.

1. Primary amine forms alkylbenzene sulphonamide which dissolves in alkali to form sodium or potassium salt of monoalkyl sulphonamide.
2. Secondary amine forms dialkyl sulphonamide which does not form salt with alkali and remains insoluble in alkali solution.
3. Tertiary amine doesnot react with the Hinsberg reagent.

$$C_6H_5SO_2Cl + HNHR \longrightarrow C_6H_5SO_2NHR \xrightarrow{KOH} C_6H_5SO_2NKR$$

Benzene sulphonyl chloride — Monoalkyl benzene sulphonamide — Pot. salt of Mono sulphonamide

$$C_6H_5SO_2Cl + NHR_2 \longrightarrow C_6H_5SO_2\ NR_2 \xrightarrow{KOH} \text{No action (insoluble in water)}$$

(Soluble in ether)

$$C_6H_5SO_2Cl + 2NR_3 \longrightarrow \text{NO reaction (soluble in ether).}$$

The above alkaline solution of the amines is extracted with ether when tertiary amine and dialkyl benzene sulphonamide remains in the water layer. The two layer are then separated.

(a) Recovery of Primary Amine : The aqueous layer containing potassium monoalkyl benzene sulphonamide is acidified with dil. HCl Monoalkyl benzene sulphonamide is formed. The latter is heated with conc. HCl to form primary amine hydrochloride which is distilled with caustic soda to regenerate primary amine as distillate.

$$C_6H_5SO_2NKR + HCl\ (dil) \longrightarrow C_6H_5SO_2NHR + KCl$$

(Potassium monoalkyl benzene sulphnonamide) — Monoalkyl benzene sulphonamide

$$C_6H_5SO_2NHR + H_2O \xrightarrow{\text{Conc.HCl}} \underset{\text{Benzene Sulphonic acid}}{C_6H_5SO_2OH} + RNH_2.HCl$$

$$RNH_2.\ HCl + NaOH \xrightarrow{\text{distill}} R-NH_2 + NaCl + H_2O$$

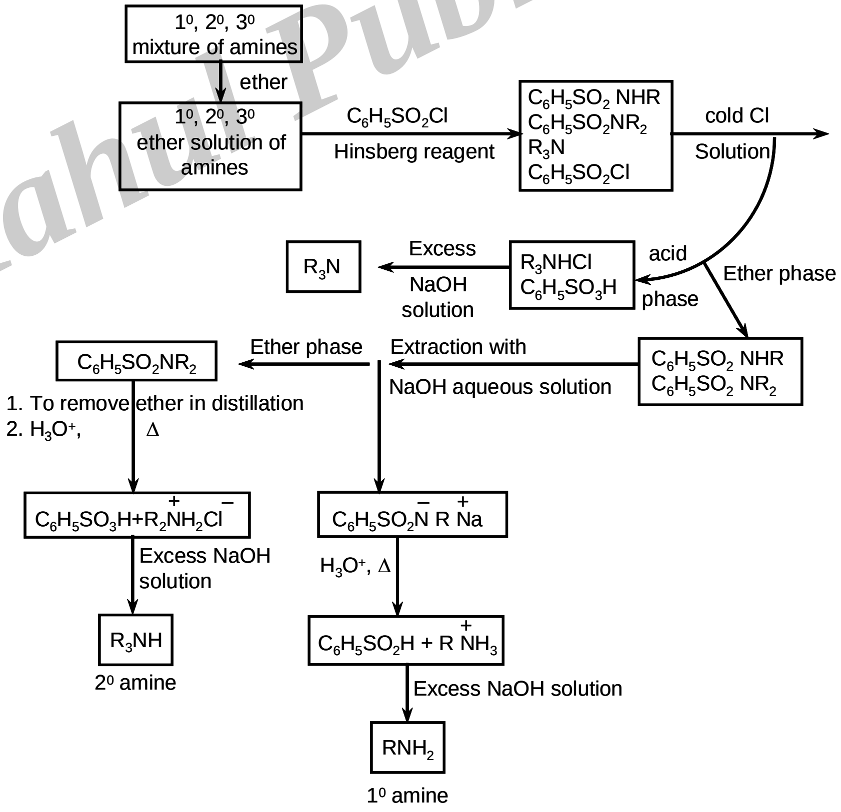
(b) Recovery of Secondary and Tertiary Amines: The etheral layer is fractionally distilled when ether and tertiary amine distilled over in quick succession leaving behind solid dialkylbenzene sulphonamide as residue. The latter is hydrolysed by boiling with conc. HCl to form 2° amine hydrochloride which is then distilled with caustic soda to get free amine.

$$\begin{array}{c}\text{Dialkyl benzene Sulphonamide}\\ +\\ \text{Free tertiary amine}\end{array} \xrightarrow[\text{Distillation}]{\text{Fractional}} \begin{array}{c}\text{Ether + tertiary amine}\\ \text{(distillate)}\end{array}$$

$$\text{Ethernal layer} \qquad \begin{array}{c}C_6H_5SO_2NR_2\\ \text{(Residue)}\end{array}$$

$$C_6H_5SO_2NR_2 + H_2O \xrightarrow{\text{Conc.Hcl}} C_6H_5SO_2OH + \underset{\text{2° Amine hydrochloride}}{R_2NH.HCl}$$

$$R_2NH\ .\ HCl + NaOH \xrightarrow{\text{distillation}} \underset{\text{2° amine}}{R_2NH} + NaCl + H_2O$$



2.10 Physical Properties. Use of Amine Salts as Phase Transfer Catalysts. Chemical Properties: a) Alkylation b) Acylation c) Carbylamine Reaction d) Hinsberg Separation. Reaction with Nitrous Acid of 1^0, 2^0, 3^0 (Aliphatic and Aromatic Amines). Electophilic Substitutions of Aromatic Amines – Bromination and Nitration, Oxidation of Aryl and 3^0 Amines

Q24. Write any two chemical properties of amines.

OR

Write a note on alkylation and Acylation of amines.

Ans :

Alkylation

Like aliphatic amines, the primary aryl amines can be alkylated (replacement of hydrogen atom by alkyl group) to give successively secondary, tertiary and quarternary ammonium salts.

$$\underset{\substack{\text{Aniline}\\\text{(1° amine)}}}{C_6H_5NH_2} \xrightarrow{CH_3I} \underset{\substack{\text{N-Methyl aniline}\\\text{(2° amine)}}}{C_6H_5NHCH_3} \xrightarrow{CH_3I} \underset{\substack{\text{N,N-Dimethyl aniline}\\\text{(3° amine)}}}{C_6H_5N(CH_3)_2} \xrightarrow{CH_3I} \underset{\substack{\text{N,N,N-trimethyl aniline}\\\text{(4° salt)}}}{C_6H_5\overset{+}{N}(CH_3)_3I^-}$$

All of these are nucleophilic substitution reactions.

Acylation

Like alkyl amines, aryl amines react with acid chlorides or acid anhydrides to form aryl substituted amides commonly called **anilides**. The reaction is best carried out in presence of a base like pyridine.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CH_3COCl \xrightarrow{\text{Pyridine}} \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + HCl$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow{\text{NaOH}} \underset{\text{Benzanilide}}{C_6H_5NHCOC_6H_5} + HCl$$

Q25. Give electrophilic substitution reactions of aromatic amines:

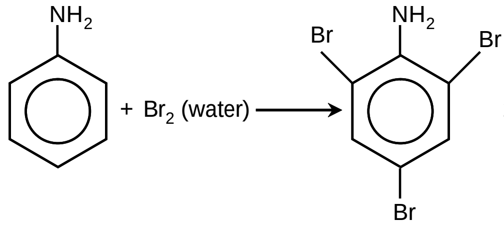
(a) Bromination

(b) Nitration

Ans :

Halogenation (or) Bromination

Chlorination or Bromination of aniline directly gives 2, 4, 6 Trihalo - aniline.



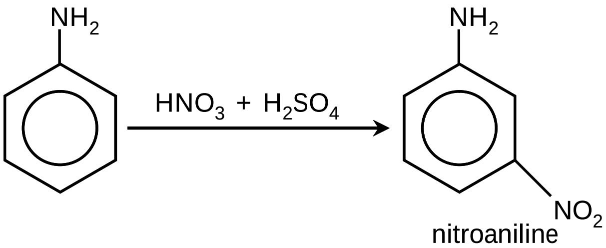
2, 4, 6 Tribromo aniline

Nitration

Direct nitration of aniline very susceptible to oxidation leads to the formation of oxidation production in addition to nitrated products.

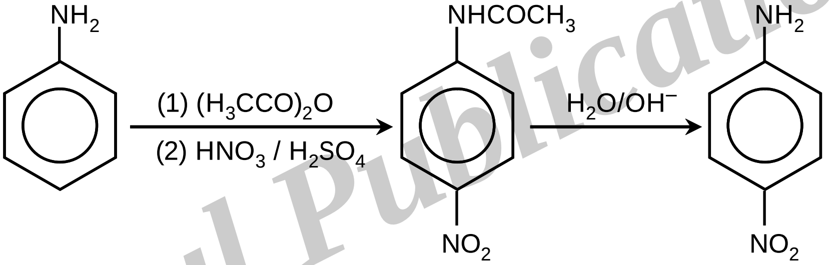
Nitration Involves Acidic Medium

Protonation of aniline takes place forming anilinium ion which being m-directing forms mainly m-nitro aniline. Direct nitration of aniline forms the following products in addition to 'o' and 'p' nitro anilines.



nitroaniline

In order to prevent the above two reactions the amino group is protected by acetylation to give acetanilide which is nitated and finally hydrolysed to 'o' and 'p' nitroanilines.



p-nitro accetanilide p-nitroaniline

2.11 Diazotisation Diazonium Salts: Preparation With Mechanism. Synthetic Importance – a) Replacement of Diazonium Group by – OH, X (Cl)- Sandmeyer and Gatterman Reaction, by Fluorine (Schiemann's Reaction), by iodine, CN, NO_2, H and Aryl Groups. Coupling Reaction of Diazonium Salts. i) With Phenols ii) With Anilines. Reduction to Phenyl Hydrazines

Q26. What is diozotisation. Describe the laboratory method for the preparation of benzene diazorouum chloride.

Ans : **(Imp.)**

Diazotization

An ice cold solution of a primary aromatic amine in hydrochloric acid is treated with an ice-cold aq. Solution of sodium nitrite. Water soluble compounds known as diazonium salts are formed.

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

$C_6H_5NH_2.HCl + HONO \longrightarrow C_6H_5N_2Cl + 2H_2O$

Aniline hydrochloride Benzene diazonium chloride

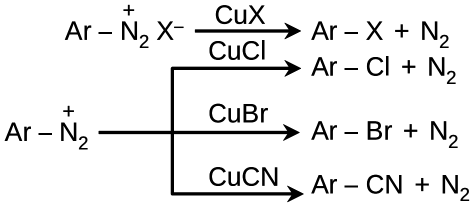
Q27. Write a note on Sandmeyer reaction.

Ans :

Reactions of Diazonium Salts

1. Sandmeyer Reaction

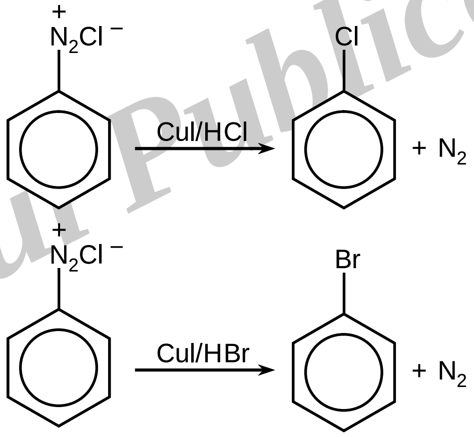
Replacement of the diazonium group by Cl or Br is carried out by mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide is called sandmeyer reaction.



Q28. Give the mechanism of Gattermann reaction.

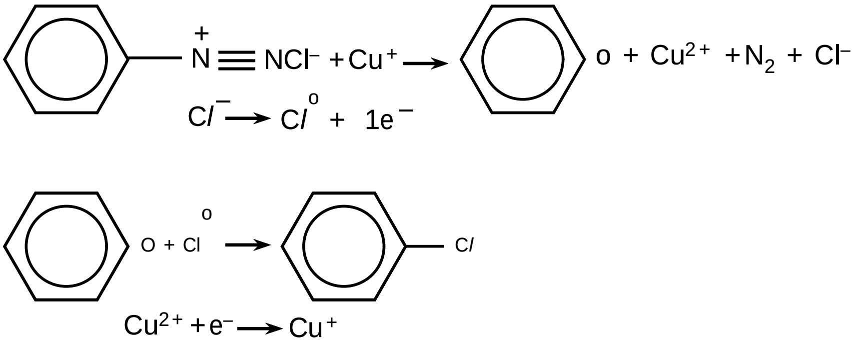
Ans :

A modified form of sandmeyer's reaction is gattermann's reaction in which the cuprous halide is replaced by copper powder and the halogen acid.



Mechanism

This reaction undergoes electrophilic free radical substitution mechanism.

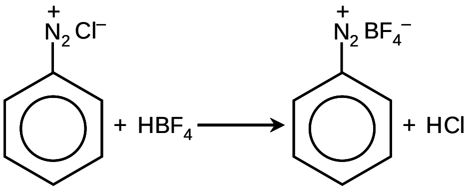


Q29. Describe the mechanism of Schiemann's reaction.

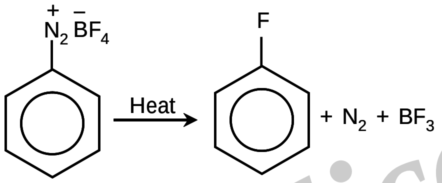
Ans : **(Imp.)**

Schiemann's Reaction (Replacement by fluorine)

The diazonium group is replaced by fluorine by treating diazonium salt with fluoroboric acid (HBF_4). The diazonium fluroborate which is precipitated is isolated. It is dried and heated to get aryl halide. The reaction is known as schiemann reaction.



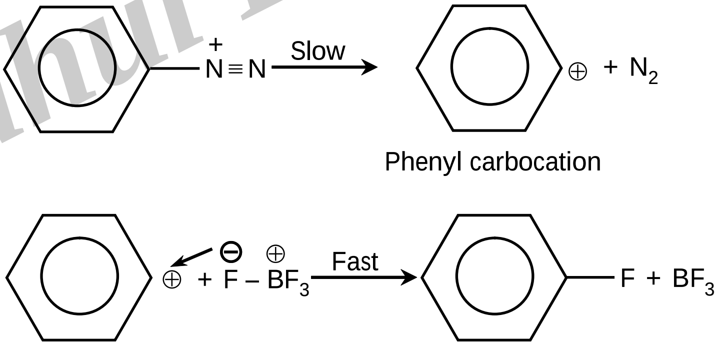
Benzene diazonium flouroborate



Flurobenzene

Mechanism

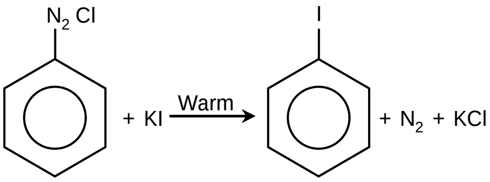
The reaction follows SN^1 mechanism which is completed in two steps.



Phenyl carbocation

Flurobenzene

Replacement of Iodine



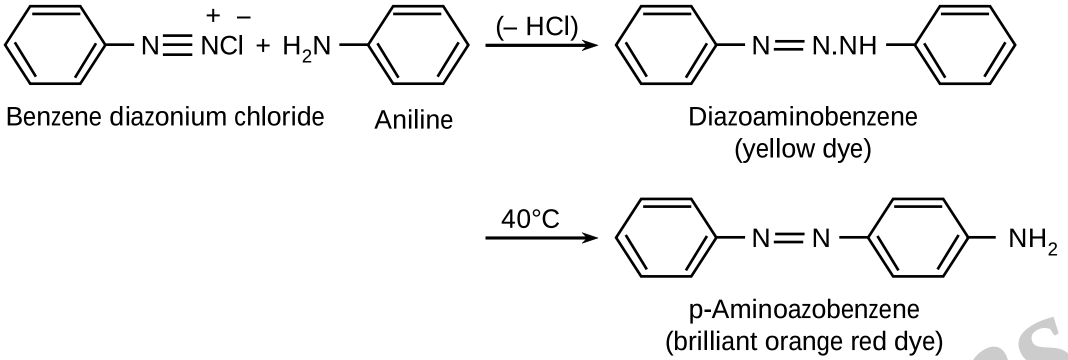
Iodobenzene

Q30. What is coupling reaction? Give the mechanism for coupling reaction of diazonium salts with phenols and amines.

Ans : **(Imp.)**

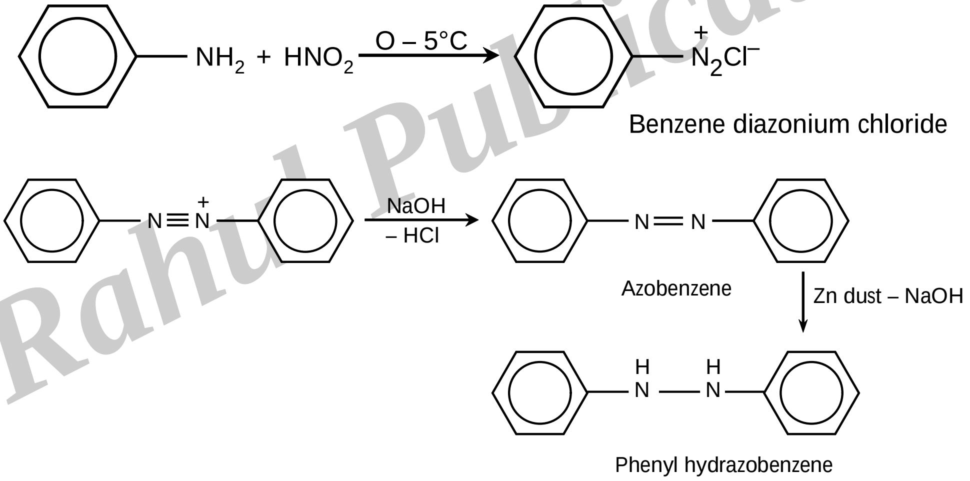
Coupling Reaction

Aniline couples with diazonium salts in the para position to give azo dyes.



Q31. How is diazonium salts are reduced to phenyl hydrazine?

Ans :



2.12 CYANIDES AND ISOCYANIDES: STRUCTURE. PREPARATION OF CYANIDES FROM A) ALKYL HALIDES B) FROM AMIDES C) FROM ALDOXIMES. PREPARATION OF ISOCYANIDES FROM ALKYL HALIDES AND AMINES. PROPERTIES OF CYANIDES AND ISOCYANIDES, A) HYDROLYSIS B) ADDITION OF GRIGNARD REAGENT III) REDUCTION IV) OXIDATION

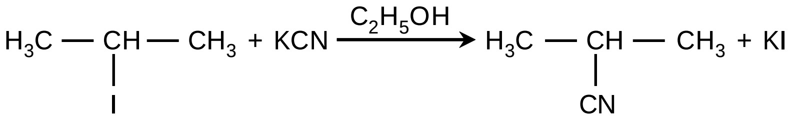
Q32. Discuss the preparation methods of cyanides and Isocyanides.

Ans :

1. Preparation from Alkyl Halides

Alkyl cyanides may be prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that it yields a mixture of nitrile and Isonitirile. Isonitrile can be removed by partial hydrolysis because it is hydolysed more rapidly than nitile.

$$RX + KCN \longrightarrow RCN + RNC + KX$$



$$H_3C-\underset{\displaystyle I}{\underset{|}{CH}}-CH_3 + KCN \xrightarrow{C_2H_5OH} H_3C-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_3 + KI$$

Alkyl halides on reaction with AgCN gives isocyanides

$$R-X + AgCN \longrightarrow R-NC + AgX$$

2. From Acid Amides

Pure nitriles may be prepared by dehydration of acid amides with phosphorous pentoxide.

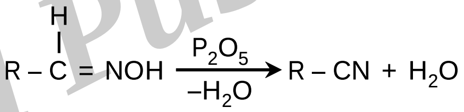
$$RCONH_2 \xrightarrow[-H_2O]{P_2O_5} RCN + KX$$

$$H_3CCONH_2 \xrightarrow{P_2O_5} H_3CCN + H_2O$$

$$\text{Acetamide} \xrightarrow{P_2O_5} H_3CCN + H_2O$$

3. From Aldoximes

Aldoximes are converted into alkyl cyanides when distilled with phosphorous pentoxide (or) acetic anhydride are converted into alkyl cyanides.



$$R-\overset{\displaystyle H}{\overset{|}{C}}=NOH \xrightarrow[-H_2O]{P_2O_5} R-CN + H_2O$$

4. Carbylamine Reaction

amines are reacting with chloroform in presence of alc.KOH gives isocyanids.

$$R-NH_2 \xrightarrow[\text{alc.KOH}]{CHCl_3} R-NC$$

Q33. Write the chemical properties of cyanides and isocyanides.

Ans :

Chemical Properties of Cyanides and Isocyanides

Hydrolysis

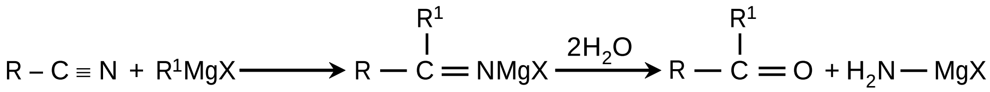
Alkyl cyanides get on hydrolysis amides are formed. On complete hydrolysis acids are obtained.

$$R-CN \xrightarrow{H_2O} RCONH_2 \xrightarrow{H_2O} RCOOH + NH_3$$

$$R-N\equiv C + 2H_2O \xrightarrow{H^+} H_3C-NH_2 + HCOOH$$

Reaction with Grignard Reagent

Alkyl cyanide yields a ketones which further reacts to yield a tertiary alcohol.



$$R - C \equiv N + R^1MgX \longrightarrow R - \overset{R^1}{\overset{|}{C}} = NMgX \xrightarrow{2H_2O} R - \overset{R^1}{\overset{|}{C}} = O + H_2N - MgX$$

Oxidation

Cyanides are not oxidised. The oxidation of Isocyanides with HgO.

$$H_3C - N \equiv C + HgO \longrightarrow H_3C - N = C = O$$

Reduction

Cyanides on reduction gives amines, Isocyanides on reduction gives 2^o amines.

$$R - CN \xrightarrow[H^+ \text{ (or) } OH^-]{Na - C_2H_5OH} R - CH_2 - NH_2$$

$$R - CN \xrightarrow{LiAlH_4} R - CH_2 - NH_2$$

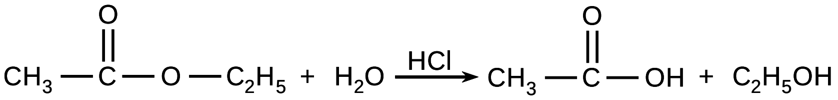
$$R - NC \xrightarrow{LiAlH_4} R - NH - CH_3$$

Short Question & Answers

1. Give the esterfication reaction.

Ans :

Esters can be hydrolysed with mineral acids or alkalies.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5 + H_2O \xrightarrow{HCl} CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH$$

2. What is Huns Diecker reaction.

Ans :

It is a decarboxylative halogenation. Heavy metal salts (Ag, Hg, Pb) of carboxylic acid in CCl_4 when heated with bromine or iodine gives an alkyl halide with one carbon less than the starting carboxylic acid. The reaction is called Huns diecker reaction. The reaction involves the loss of carbon dioxide hence it is a decarboxylation reaction.

$$R-COO^-Ag^+ + Br_2 \xrightarrow[\Delta]{CCl_4} RBr + AgBr\downarrow + CO_2\uparrow$$

$$R-COO^-Ag^+ + I_2 \xrightarrow[\Delta]{CCl_4} RI + CO_2\uparrow + Ag\downarrow$$

3. Give Schmidt reaction.

Ans :

It is a decarboxylative animation. The reaction is useful for the conversion of carboxylic acids to amines directly.

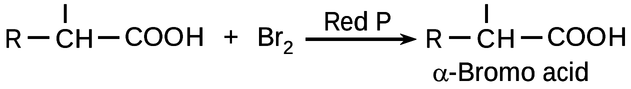
Carboxylic acids on treatment with hydrazoic acid (N_3H) produce acyl azides as intermediate products, which on rearrangement in acidic medium produce primary amines.

$$R-COOH + N_3H \xrightarrow{H_2SO_4} R-NH_2 + N_2 + CO_2$$

4. Write the HVZ reaction.

Ans :

Aliphatic carboxylic acids containing α-hydrogens undergo halogenation with Cl_2 or Br_2 in presence of catalyst red phosphorus in sunlight or on boiling to form alkyl substituted products. The reaction is known as Hell - Volhard - Zelinsky (HVZ) reaction.



$$R-\overset{\overset{H}{|}}{C}H-COOH + Br_2 \xrightarrow{\text{Red P}} R-\overset{\overset{Br}{|}}{C}H-COOH$$

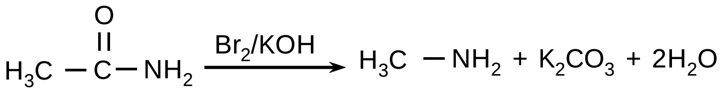
α-Bromo acid

$$H_3C-COOH \xrightarrow[(-HCl)]{Cl_2/P} H_2Cl-COOH$$

Monochloro acetic acid

5. Give Haffmann degradation reaction.

Ans :

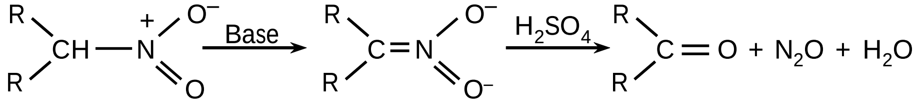


$$H_3C-\overset{\overset{O}{\parallel}}{C}-NH_2 \xrightarrow{Br_2/KOH} H_3C-NH_2 + K_2CO_3 + 2H_2O$$

6. Write the Nef Reaction.

Ans :

1°/2° aliphatic nitro compounds hydrolysed to aldehydes or ketones by treatment of their conjugate bases with H_2SO_4. This reaction is called Nef reaction.



7. Give Hofman Degradation of Amides (Hoffman's Bromide reaction)

Ans :

This is one of the most convenient methods for the preparation of primary amines. It involves action of halogen and alkali NaOH (or) KOH on amide to form amines with one carbon atom less.

$$H_3C.CONH_2 + Br_2 + 4KOH \longrightarrow H_3CNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

8. What is a carbyl amine reaction.

Ans :

Primary amines when heated with chloroform and alcoholic caustic potash give Isocyanides (carbylamine) having very unpleasant smell which can be easily detected.

$$C_2H_5NH_2 + CHCl_3 + KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$$

Ethyl Isocyanide

9. What is diozotisation.

Ans :

An ice cold solution of a primary aromatic amine in hydrochloric acid is treated with an ice-cold aq. Solution of sodium nitrite. Water soluble compounds known as diazonium salts are formed.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

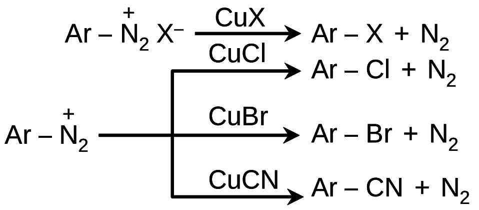
$$C_6H_5NH_2.HCl + HONO \longrightarrow C_6H_5N_2Cl + 2H_2O$$

Aniline hydrochloride Benzene diazonium chloride

10. Write the Sandmeyer Reaction.

Ans :

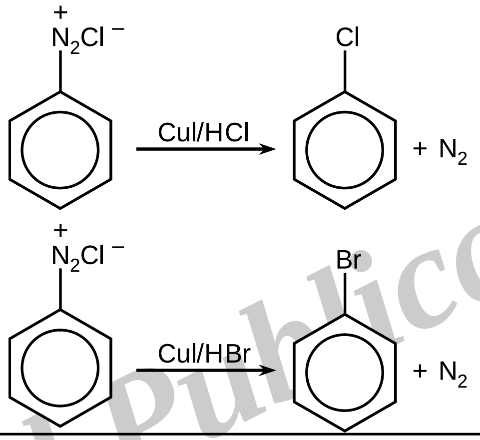
Replacement of the diazonium group by Cl or Br is carried out by mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide is called sandmeyer reaction.



11. Give the Gattermann reaction.

Ans :

A modified form of sandmeyer's reaction is gattermann's reaction in which the cuprous halide is replaced by copper powder and the halogen acid.



12. Write the Carbylamine Reaction.

Ans :

amines are reacting with chloroform in presence of alc.KOH gives isocyanids.

$$R - NH_2 \xrightarrow[\text{alc.KOH}]{CHCl_3} R - NC$$

Choose the Correct Answer

1. What is obtained when acetic acid is heated with chlorine in presence of red phosphorus. [b]

(a) Acetyl chloride (b) α - chloroacetic acid

(c) Trichloro acetic acid (d) Chloral

2. Carboxylic acid undergoes ionization due to [d]

(a) Hydrogen bonding (b) Absence of α-Hydrogen

(c) High reactivity of α Hydrogen (d) Resonance stabilization of carboxylate ion.

3. Which of the following compounds is the strongest acid [c]

(a) HCOOH (b) $H_3C - COOH$

(c) $Cl_2 - CHCOOH$ (d) Resonance stabilization of carboxylate ion.

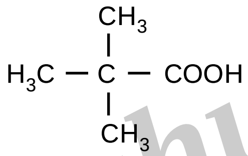
4. Monocarboxylic acids react with alcohols in presence of an acid catalyst to form. [c]

(a) HCOOH (b) $H_3C - COOH$

(c) $Cl_2 - CHCOOH$ (d) Resonance stabilization of carboxylate ion.

5. The correct order of acidic strength of carboxylic acids. [d]

(a) $H_3C - COOH$ (b) ClC_2HCOOH

(c) 

$H_3C - \overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}} - COOH$

(d) $C_3lC - COOH$

6. Compare the acidity of Alcohols, acids lphenols which is having more acidity. [b]

(a) Alcohol (b) Acids

(c) Phenols (d) All the above

7. The reaction $RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + Ag\,Br + CO_2$ is called [b]

(a) HVZ reaction (b) Hundiecker reaction

(c) Hufmann's reaction (d) Carbylamine reaction

8. $RCOOH + N_3H \xrightarrow{H_2SO_4\,(con\,c)} R - NH_2 + CO_2 + N_2$ the above reaction is called [c]

(a) HVZ reaction (b) Hunsdiecker reaction

(c) Schmidt reaction (d) Decarboxylation reaction

9. Acetone reacts with grignard reagent to form [c]

(a) Primary alcohal (b) Secondary alcohal

(c) Tertiary alcohal (d) None of the above

10. When acetic acid is treated with p_2O_5 the product is [d]

(a) ester (b) ether

(c) alcohal (d) anhydride

11. Which of the following statement is incorrect about nitrobenzene. [c]

(a) It is formed by nitration of benzene at temperatures below 60°C.

(b) Can be further nitrated to give m-dinitrobenzene

(c) Can be oxidized with $KMNO_4$ to give benzoic acid

(d) Can be reduced with SnlHCl to give aniline

12. Which of the following compounds reacts least rapidly in electrophilic substitution reaction. [a]

(a) Nitrobenzene (b) Phenol

(c) Bromobenzene (d) Toluene

13. Nitrobenzene reacts with Br_2 in the presence of $FeCl_3$ to give [d]

(a) O - Chloronitrobenzene (b) O - Bromonitor benezene

(c) m - Chloronitrobenzene (d) m - bromonitro benzene

14. Nitration of nitrobenzene with HNO_3/H_2SO_4 gives [c]

(a) O - Chloronitrobenzene (b) O - Bromonitro benezene

(c) m - dinitrobenzene (d) m - bromonitro benzene

15. Nitrobenzene undergoes reduction with zinc and KOH to give [b]

(a) Anibne (b) Hydrozobenzene

(c) Azobenzene (d) None of these.

16. Reduction of p-nitrotoluene with sn + HCl gives. [a]

(a) p - methylaniline (b) Toluene

(c) m - methylaniline (d) N-Methylaniline

17. Benzamide is treated separately with the following reagents. Which one of these would give aniline? [b]

(a) PCl_5 (b) NaOH + Br_2

(c) Soda lime (d) Hot conc. H_2SO_4

18. A primary amine gives : [b]

(a) Luca's test (b) Carbylamine test

(c) Iodoform test (d) Victor Meyer test

19. Which one is the most basic? [a]

(a) $(CH_3)_2NH$ (b) $(C_6H_5)_2NH$

(c) $(CH_3)_3N$ (d) CH_3NH_2

20. The compound X when treated with aqueous nitrous acid at low temperature produces on oily substance, X is [c]

(a) Aniline
(b) Benzyl amine
(c) N-methylaniline
(d) N, N-dimethylaniline

21. A diazonium salt is formed by the action of $NaNO_2$ and HCl upon [c]

(a) Ethyl amine
(b) Benzyl amine
(c) Phenyl amine
(d) All the above

22. When benzene diazonium chloride is treated with cuprous chloride in HCl, monochlorobenzene is formed. This is called [c]

(a) Cannizzaro reaction
(b) Perkin's reaction
(c) Sandmeyer reaction
(d) Diazo reaction

23. When aniline is treated with bromine water, the product formed is [d]

(a) o-bromoaniline
(b) p-bromoaniline
(c) both A and B
(d) 2, 4, 6-tribromoaniline

24. Acetanilide is formed by the reaction of : [b]

(a) Aniline and benzoic acid
(b) Aniline and acetyl chloride
(c) Aniline and benzoyl chloride
(d) All the above

25. Aniline is treated with chloroform and alcoholic caustic potash, the product formed is : [b]

(a) Phenyl cyanide
(b) Phenyl isocyanide
(c) Phenyl isocyanate
(d) All the above

26. Nitrobenzene, on reduction with zinc dust and ammonium chloride gives [b]

(a) Aniline
(b) Phenylhydroxylamine
(c) Azobenzene
(d) Hydrazobenzene

27. Reaction of nitrobenzene with fused potassium hydroxide to form p-nitrophenol is an example of [b]

(a) Electrophilic substitution
(b) Nucleophilic substitution
(c) Free radical substitution
(d) All the above

28. Reaction of aniline with benzenediazonium chloride in presence of acid is known as : [c]

(a) Diazotisation
(b) Amination
(c) Coupling
(d) All the above

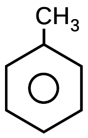
29. Reaction of aliphatic primary amine with nitrous acid in cold leads to the formation of : [d]

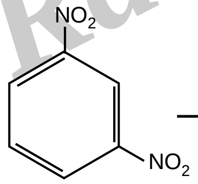
(a) A diazonium salt
(b) A nitrite
(c) A nitro compound
(d) An alcohol

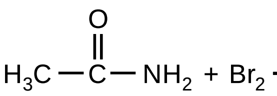
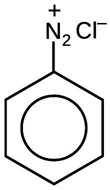
30. Which of the following compounds gives a primary amine upon hydrolysis? [b]

(a) An alkyl cyanide
(b) An alkyl isocyanide
(c) A nitroparaffin
(d) Hydrazobenzene

Fill in the blanks

1. Hinsberg reagent is ________.
2. Identification of 1° amines by ________.
3. In Haff mann bromide degradation reaction amides are converted to amines.
4. Diazonum salts react with aromatic amines ephenols to give azo compounds is known as ________.
5. Reaction of anibre with sodium nitrite & hydrochloric acid at low temperature to form benzene diazonium chlorid is known as ________.
6. $H_3C - NC + HgO \longrightarrow$ ________.
7. $R - CONH_2 \xrightarrow{P_2O_5}$ ________.
8. $Ph - NH_2 + HNO_2 \xrightarrow{O-5^\circ C}$ ________.
9. $Ph - \overset{+}{N}_2 X^- + CuBr \longrightarrow$ ________.
10. $Ph - NH_2 \xrightarrow{HNO_3 + H_2SO_4}$ ________.
11. 

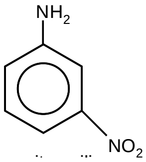
$\xrightarrow[\text{or dil } H_2 SO_4]{KMnO_4, OH^\ominus}$ ________.
12. $H_3C - COOH + SOCl_2 \longrightarrow$ ________.
13. 

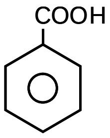
m-Dinitrobenzene
$\xrightarrow[\text{or } Na_2S]{(NH_4)_2 S}$ ________.
14. 
$H_3C - \overset{\overset{\displaystyle O}{||}}{C} - NH_2 + Br_2 \longrightarrow$ ________.
15. 

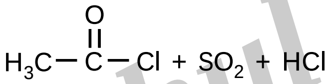
$+ HBF_4 \longrightarrow$ ________.

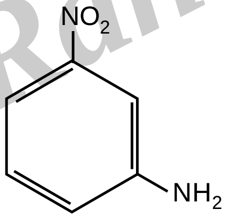
ANSWERS

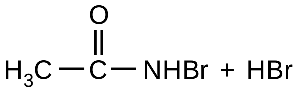
1. Benzene sulphoxyl chloride
2. Carbyl amine
3. Amines
4. Coupling reaction
5. Diazotisation
6. CH_3 NCO
7. RCN
8. Ph – $\overset{+}{N}_2$
9. Ph – Br

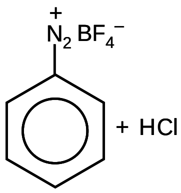
10. 

11. 

12. 
$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + SO_2 + HCl$

13. 

14. 
$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NHBr + HBr$

15. 

UNIT - III

(Physical Chemistry)

S3-P-1: Thermodynamics - I

A brief review of - Energy, work and heat units, mechanical equivalent of heat, definition of system, surroundings. First law of thermodynamics statement - various forms mathematical expression. Thermodynamic quantities - extensive properties and intensive properties, state function and path functions. Energy as a state function and exact differential. Work of expansion and heat absorbed as path function.

Expression for work of expansion, sign convention problems on first law. Heat changes at constant pressure and heat changes at constant volume. Enthalpy. Heat capacities at constant pressure and constant volume. Derivation of Cp - Cv = R. Isothermal adiabatic processes. Reversible and irreversible processes. Reversible change and maximum work. Derivation of expression for maximum work for isothermal reversible process. Problems. Internal energy of an ideal gas. Joules experiment. Joule - Thompson coefficient. Adiabatic changes in ideal gas, derivation of equation, PV^{γ} = constant. P - V curves for isothermal and adiabatic processes. Heat of a reaction at constant volume and at constant pressure, relation between ΔH and ΔV. Variation of heat of reaction with temperature. Kirchhoff's equation and problems. Limitations of first law and need for second law. Statement of second law of thermodynamics. Cyclic process. Heat engine, Carnot's theorem, Carnot's cycle. Derivation of efficiency of heat engine. Problems. Thermodynamic scale of temperature.

S3-P-2: Thermodynamics-II

Entropy: Definition from Carnot's cycle. Entropy as a state function. Entropy as a measure of disorder. Sign of entropy change for spontaneous and non- spontaneous processes & equilibrium processes. Entropy changes in i) Reversible isothermal process, ii) Reversible adiabatic process, iii) Phase change, iv) Reversible change of state of an ideal gas. Problems. Entropy of mixing of ideal gases. Free energy Gibb's function (G) and Helmholtz'sfunction (A) as thermodynamic quantities. Concept of maximum work and network ΔG as Criteria for spontaneity. Derivation of equation $\Delta G = \Delta H - T\Delta S$. Significance of the equation. Gibbs equations and Maxwell relations. Variation of G with P, V and T.

S3-P-1: THERMODYNAMICS - I

3.1 A BRIEF REVIEW OF - ENERGY, WORK AND HEAT UNITS, MECHANICAL EQUIVALENT OF HEAT, DEFINITION OF SYSTEM, SURROUNDINGS

Q1. Give in brief energy, work, and heat and their units.

Ans :

Work (mechanical work) is defined as the displacement of system with the application of a force.

$$W = F \times l$$

The performance of the work need not necessarily be always achieved by muscular effort as in mechanical work.

Work done = A generalized force (intensity factor) × A generalized displacement (capacity factor)

(i) Electrical work: Here intensity factor is the E.M.F. and capacity factor is the quantity of electricity flowing through the current. Thus,

Electrical work = E.M.F. × Quantity of electricity.

(ii) Gravitational work: When an object is moved against the force of gravity, the work done is called the gravitational work. In such cases, the force is the weight (mg) and the displacement is the height (h) through which it is moved.

$$\text{Work done} = mg \times h$$

Energy may be defined as the capacity to do work. It may appear as kinetic or potential energy. Chemical nature of the substance as well as upon its temperature, pressure and volume. This energy associated with every substance is known as intrinsic or internal energy and is designated by the letter 'E'.

Thus if E_1 and E_2 are the internal energies of a system in the initial and final states respectively, then the change in internal energy (Δ E) is given by

$$\Delta E = E_2 - E_1$$

At constant pressure, the heat absorbed (δQ) is used in increasing the internal energy, dE and in doing the pressure-volume work, PdV. The two factors (Internal energy and pressure-volume work) when combined together gives rise to a new function called enthalpy or heat content of the system. It is denoted by H and mathematically defined by the equation.

$$H = E + PV$$

The enthalpy or heat content (H) of a substance or a system is the total amount of energy stored in that substance or the system.

Q2. Define system and surroundings.

Ans :

System and Surroundings

Any specified portion of matter under study is known as system. It may be as simple as water in a beaker or as complex as the water of a polluted lake.

The remaining portion of the universe excluding the system is called surroundings. A chemical reaction taking place between two aqueous solutions in a beaker. The contents of the beaker constitute the system; the beaker itself, the air surrounding the beaker and other objects in the vicinity constitute the surrounding of the system, while the walls of the beaker constitute the boundary.

3.2 FIRST LAW OF THERMODYNAMICS STATEMENT - VARIOUS FORMS MATHEMATICAL EXPRESSION

Q3. State the first law of thermodynamics in its various forms write the mathematical statement of the law.

Ans : **(Imp.)**

The first law of thermodynamics is simply the law of conservation of energy which states that “energy can neither be created nor destroyed although it can be converted from one form to another”. The law may also be stated in the following ways:

(i) The total energy of an isolated system* remains constant although it can undergo a change from one form to another.

(ii) Whenever a quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy must be produced.

(iii) It is impossible to construct a perpetual motion machine, i.e., a machine which would produce work continuously without consuming energy.

(iv) For a system in constant with its surroundings, the sum of the energies of the system and the surroundings at a particular time remains constantly.

Mathematical formulation of the first law of thermodynamics (Relation between internal energy, work and heat)

Suppose the system while undergoing change from initial state A (having internal energy E_A) to final state B (having internal energy E_B) absorbs heat Q from the surroundings and also performs some work, W. The absorption of heat by system tends of raise the energy of the system. The performance of work by the system tends to lower the energy of the system since performance of work requires expenditure' of energy. Hence the change of internal energy, ΔE {i.e., $E_B - E_A$) accompanying the above process will be given by

$$\Delta E = Q - W$$

This equation is the mathematical formulation of the first law of thermodynamics.

If the changes are very small, equation may be written as

$$dE = \delta Q - \delta W$$

If the work done is the work of the expansion only and the volume increases by a small amount dV against the external pressure P, then we know that

$$\delta W = P.dV$$

Substituting the value of δ W in equation,

$$dE = \delta Q - PdV.$$

3.3 THERMODYNAMIC QUANTITIES - EXTENSIVE PROPERTIES AND INTENSIVE PROPERTIES, STATE FUNCTION AND PATH FUNCTIONS. ENERGY AS A STATE FUNCTION AND EXACT DIFFERENTIAL WORK OF EXPANSION AND HEAT ABSORBED AS PATH FUNCTION

Q4. What are intensive and extensive properties of a system?

Ans :

Extensive and intensive variables (Properties)

A property that depends upon the quantity of the substance or substances present in the system is called the capacity or extensive property. The common examples of these properties are mass, volume, energy, heat capacity, etc. The extensive properties are additive, i.e., the total value of an extensive property is equal to the sum of the values for the separate parts into which the system may be divided.

A property which depends only upon the nature of the substance and not on the amount (s) of the substance (s) present in the system is known as intensity or intensive property. The common examples of these proprieties are temperature, pressure, concentration, refractive index, viscosity, density, surface tension, specific heat etc.

The ideal gas equation, PV = nRT has two extensive variables (n and V) and two intensive variables (P and T). However, if the two extensive variables n and V of the ideal gas equation are fused into each other, the resulting expression has three intensive variables c, P and T.

$$P = \frac{n}{V}RT \quad \text{or} \quad P = cRT. \quad \left(\frac{n}{V} = C\right)$$

Q5. Give various state functions and path functions.

Ans :

Variables which are determined by the initial and final states of the system only and not be the path followed, i.e., not on the manner by which initial state is changed to final state, are called state functions. For example, if we heat a sample of water from 0°C to 25°C, the change in temperature is equal to difference between the initial and final temperatures, i.e.,

$$\Delta T = T_{final} - T_{initinal} = 25°C$$

The way in which the temperature change is brought above has no effect on the result. Mass, pressure, volume, internal energy, entropy, free energy, enthalpy and work function are other examples of state functions.

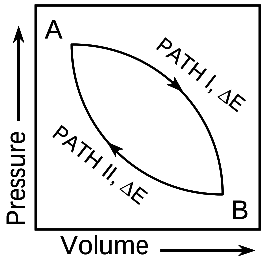
On the other hand, a thermodynamic variable, the change in the value of which during a process depends upon the path followed is called a path function. Heat and work the important examples of path functions. Internal energy is a definite property and is exact differential whereas work and heat are not.

Q6. Show the internal energy of a system is a state function.

Ans :

Internal energy is a state function

The internal energy is a state function, i.e. when a process occurs the change in its value depends only upon its values in the initial and final states and is independent of the path.



Consider a system having a particular pressure, volume and temperature represented by the point A (initial state) in Figure. Suppose the pressure, volume and temperature are changed in such a way that the system is brought to the point B (final state) by path I. Let the change in internal energy of the system during the conversion of A to B is ΔE. Further suppose B is converted back to A but through another path, path II. The change in internal energy during this process (say ΔE') must be equal in -magnitude to that involved in path I. If the energy changes involved in paths I and II are not same in magnitude, then suppose by path I is greater than the decrease in internal energy along path II, i.e., ΔE>ΔE'.

Then by a coupling of these two processes,

$$A \xrightarrow{\text{Path I}} B \xrightarrow{\text{Path II}} A$$

the system would return to its initial state with the creation of a certain amount of energy which is equal to ΔE – ΔE'. By repeating the same cycle over and over again, energy would be generated continuously and a perpetual motion machine would be possible which is contrary to the first law of thermodynamics. Hence ΔE = ΔE'.

Thus we can say that energy change accompanying a process depends upon the initial and the final states of the system and is independent of the path by which this change is brought about.

Two more important points about the internal energy are :

(i) The internal energy depends upon the quantity of the substance present in the system. Hence, it is an expensive property.

(ii) The internal energy of ideal gases is a function of temperature only Hence in isothermal processes (processes carried out at constant temperature), there is no change in internal energy, i.e., ΔE = 0.

Q7. Discuss work and heat are path functions.

Ans :

Work and Heat are Path Functions

Let a system changes from state A to state B. This may be done by following different paths as shown in the following figures :

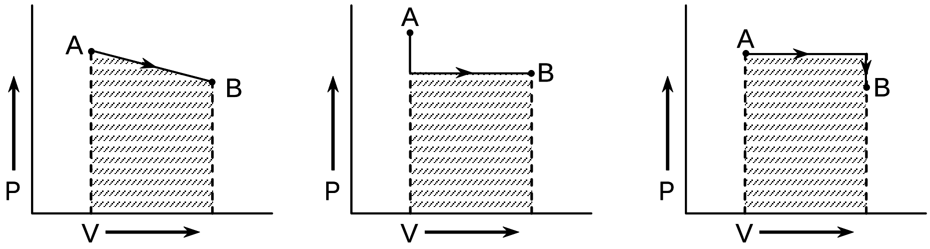


Figure: Different paths followed for the conversion of a system from state A to state B

Work done for a small change in volume dV is P dV where P is the external pressure. Thus the total work done is the sum of P dV terms which is equivalent to the area under the curve in the P – V diagrams. Now since the areas (or the P dV terms) under the curves in the above three figures are different, work done in the three paths will be different. Hence, we can say that work is a path function, i.e., its value does not depend upon the initial and final states of the system but depends upon the path by which this change is brought about.

Heat is also a path function and not state function. It can directly be realized from the mathematical formulation of the first law of thermodynamics, *viz*.

$$\Delta E = Q - W$$

Now since ΔE is a definite quantity, therefore, if W is not a definite quantity, Q also cannot be a definite quantity. It is interesting to note that neither Q nor W is a state function, yet the quantity Q – W (i.e., ΔE) is a state function.

3.4 EXPRESSION FOR WORK OF EXPANSION, SIGN CONVENTION PROBLEMS ON FIRST LAW

Q8. Give the expression for work of expansion.

Ans : **(Imp.)**

Pressure - Volume Work or PV work or Expansion Work

This is the most important form of work used in the study of thermodynamics. It is the work done when the gas expands or contracts against the external pressure (generally atmospheric pressure). It is the work done when the gas expands or contracts against the external pressure (generally atmospheric pressure). It is a type of mechanical work.

Consider an ideal gas contained in a cylinder fitted with frictionless piston. If P_{ext} is the pressure (of surrounding atmosphere) acting on the piston of cross-sectional area. Further suppose the gas in the cylinder expands by an infinitesimally small amount and as a result the piston is pushed out through an infinitesimally small distance *dl* cm.

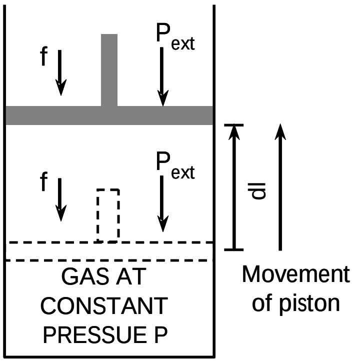


Figure: P – V work in the expansion of an ideal gas

Now since pressure is force per unit area, i.e.,

$$P_{ext} = \frac{f}{A}$$

$\therefore \quad f = P_{ext} \times A$

$\therefore$ Work done (W) by the gas (i.e., the system),

$$W = \text{Force} \times \text{Distance}$$

$$= f \times dl$$

$$= P_{ext} \times A \times dl$$

But A × d = dV, a small increase in the volume of the gas. Hence, the small amount of work (δw) done by the gas (system) can be represented as

$$\delta W = P_{ext} \times dV$$

If this expansion of gas is brought about infinitesimally slowly in a reversible manner in a number of stages from an initial volume V_1 to the final volume V_2 then total work (W) done by the gas will be given by

$$W = \int_{V_1}^{V_2} P_{ext}\, dV$$

If the external pressure, P_{ext}, against which the gas expands remains constant throughout the process, the total work done may be written as,

$$W = P_{ext} \int_{V_1}^{V_2} dV$$

$$= P_{ext} (V_2 - V_1)$$

$$= P_{ext}\, \Delta V$$

where ΔV, i.e., $V_2 - V_1$, is the total change in volume of the gas. In case ΔV is positive, i.e., when $V_2 > V_1$; as in the expansion of the gas, the work will be done by the system (gas) on the surroundings and will have a positive sign.

If ΔV is negative as in the contraction of the gas, i.e, when $V_2 < V_1$ (this happens when external pressure, P_{ext} is slightly more than the pressure of the gas, i.e., $P_{ext} > P$), the work will be done by the surrounding on the system and will have a negative sign.

To sum up

(i) In the case of expansion of a gas, $V_2 > V_1$, the work is done by the system on the surroundings and has a positive value.

(ii) In the case of compression (contraction) of a gas, $V_2 < V_1$, the work is done by the surroundings on the system and has negative value.

Units of Work

In CGS system, the unit of work is erg, which is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 cm. In SI units, work is expressed in Joule (J). The two units are related to each other as below:

$$1 \text{ joule} = 10^7 \text{ erg}$$

or $$1 \text{ erg} = 10^{-7} \text{ joule.}$$

3.5 HEAT CHANGES AT CONSTANT PRESSURE AND HEAT CHANGES AT CONSTANT VOLUME ENTHALPY

Q9. Define enthalpy and write its units?

Ans :

The enthalpy or heat content (H) of a substance or a system is the total amount of energy stored in that substance or the system.

The process where $H_2 > H_1$, i.e., in exothermic process, ΔH is negative; while the process where $H_2 < H_1$, i.e., in which heat is absorbed (endothermic process), ΔH is positive. The units of ΔH are kilocalories (kcal) or kilojoules (kJ).

Q10. Write the relation between heat of reaction at constant volume and at constant pressure.

OR

The relation between Q_V and Q_P.

Ans :

From the earlier discussion we know that

$$\Delta H = \Delta E + P\Delta V$$

$$Q_v = \Delta E \quad \text{and} \quad Q_p = \Delta H$$

Substituting the values of Q_v and Q_p in the top most equation

$$Q_p = Q_v + P\,\Delta\,V \qquad \text{... (i)}$$

For an ideal gas, $PV = nRT$

where V is the volume occupied by n moles of the gas.

If n_1 and n_2 are the number of moles of the gaseous reactants and gaseous products, respectively, then

Difference in number of moles of products and reactants,

$$\Delta n = n_2 - n_1$$

Hence the change in volume,

$$\Delta V = \frac{V}{n}\Delta n$$

Work done at constant pressure,

$$W = P\Delta V$$

$$= P\,\frac{V}{n}\Delta n$$

$$= \frac{nRT}{n}\times\Delta n \qquad (\because PV = nRT)$$

$$W = RT \times \Delta n$$

$$\therefore \quad P\Delta V = RT \times \Delta n$$

Substituting the values of PΔV in equation (i), we get

$$Q_p = Q_v + \Delta nRT$$

or $$\Delta H = \Delta E + \Delta nRT$$

The above equation holds good only for gases. In reactions involving only solids or liquids since change in volume (ΔV) is negligible, i.e., $\Delta V = 0$, equation (i) becomes.

$$Q_p = Q_v$$

Thus in reactions involving only solids or liquids, heat of reaction at constant pressure and a at constant volume is almost equal.

3.6 HEAT CAPACITIES AT CONSTANT PRESSURE AND CONSTANT VOLUME DERIVATION OF C_p - C_v = R

Q11. Establish the relation between heat of reaction at constant volume and constant pressure.

Ans : **(Imp.)**

Heat capacity of a system means the capacity to absorb heat and store energy. If Q calories is the heat absorbed by a system and the temperature rises from T_1 to T_2, then the heat capacity (C) of the system is given by the expression.

$$C = \frac{Q}{(T_2 - T_1)} = \frac{Q}{\Delta T} \quad \text{... (i)}$$

Thus heat capacity of a system may be defined as the amount of heat absorbed by it in raising its temperature by one degree (K or °C).

Heat capacities for 1 gm of a substance are known as specific heat while heat capacities for 1 mole of gas are known as molar heat capacities and designated by C. In the foregoing discussion, the word ‘heat capacity’ is used for molar heat capacity.

Since, the heat capacity varies with temperature, it value must be considered over a very narrow range of temperature. This if δQ is the small amount of heat absorbed by a system and temperature of the system increases by a small amount dT (say from T to T + dt), then the heat capacity of the system will be given by

$$C = \frac{\delta Q}{dT} \quad \text{... (ii)}$$

Thus heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.

Heat capacity is expressed in calories per degree per mole (cal K^{-1} mol^{-1}) or joules per degree per mole (J K^{-1} mol^{-1}).

(i) Heat capacity measured at constant volume, C_v.

(ii) Heat capacity measured at constant pressure, C_p.

Heat Capacity at Constant Volume (C_v)

According to the first law of thermodynamics

$$Q = \Delta E + W$$

or $$Q = \Delta E + P\Delta V \qquad (\because W = P\Delta V)$$

At constant volume, $\Delta V = 0$

$\therefore \quad Q_v = \Delta E$ (At constant volume)

According to definition, heat capacity at constant volume is given by

$$C_v = \left(\frac{Q_v}{T_2 - T_1}\right)$$

Substituting the values of Q,

$$C_v = \left(\frac{\Delta E}{T_2 - T_1}\right)$$

or $$C_v = \left(\frac{\Delta E}{T_2 - T_1}\right) \quad \text{... (iii)}$$

in general, $$C_v = \frac{dE}{dT} \quad \text{... (iv)}$$

Thus heat capacity of a system at constant volume is defined as the increase in internal energy of the system per degree rise of temperature at constant volume. In other words, it may be defined as the rate of change of internal energy with temperature at constant volume.

Heat Capacity at Constant Pressure

Again according to the first law of thermodynamics,

$$Q_p = \Delta E + P\Delta V$$

Also, according to definition, heat capacity at constant pressure is given by

$$C_p = \left(\frac{Q_p}{T_2 - T_1}\right)$$

Substituting the value of Q

$$C_p = \left(\frac{\Delta E + P\Delta V}{T_2 - T_1}\right)$$

$\therefore$ $$C_p = \left(\frac{\Delta H}{T_2 - T_1}\right) \quad (\because \Delta H = \Delta E + P\Delta V)$$

or $$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{... (v)}$$

In general, $$C_p = \frac{dH}{dT} \quad \text{... (vi)}$$

Thus, heat capacity of a system at constant pressure is equal to the increase in enthalpy (heat content) of the system per degree rise of temperature at constant pressure. In other words, it may be defined as the rate of change of enthalpy with temperature at constant pressure.

From equations (iii) and (v), heat changes at constant volume and at constant pressure are related with C_v and C_p as below.

$$C_v = \frac{\delta Q_V}{dT} \qquad \text{(at constant volume)}$$

$$C_p = \frac{\delta Q_P}{dT} \qquad \text{(at constant pressure)}$$

For large changes in temperatures (say T_1 to T_2) the above expressions take the following shapes.

$$Q_v = \int_{T_2}^{T_1} C_V dT \qquad \text{(at constant volume)}$$

$$Q_p = \int_{T_2}^{T_1} C_P dT \qquad \text{(at constant pressure)}$$

These on integration give

$$Q_v = C_v (T_2 - T_1)$$

$$Q_P = C_P (T_2 - T_1)$$

Q12. Derive an Ideal gas equation $C_p - C_v = R$.

Ans : **(Imp.)**

Relation Between C_p and C_v

Whenever a gas is heated at constant volume, no work is done by the gas and thus the heat absorbed by the system is used completely to increase the internal energy of the gas. However, when a gas is heated at constant pressure, some increase in volume of the gas will take place and the gas will expand and do some external work. Thus at constant pressure, if the temperature of the system is to be raised through the same value (or internal energy is to be increased to the same extent) as at constant volume, then some extra heat is required for doing the work of expansion. Hence, $C_p > C_v$. The difference between C_p and C_v gives the work done by 1 mole of the gas in expansion when heated through 1°C, i.e., W.

Thus,

$$C_p - C_v = W \qquad \text{... (i)}$$

Now we know that

$$W = P\Delta V$$

and for 1 mole of an ideal gas

$$PV = RT \qquad \text{... (ii)}$$

When the temperature is raised from T to T + 1, the volume changes from V to V + ΔV, then

$$P(V + \Delta V) = R(T + 1) \qquad \text{... (iii)}$$

Substracting (ii) from (iii), we have

$$P \Delta V = R$$

or

$$W = R \qquad \text{... (iv)} \ (\because P\Delta V = W)$$

From (i) and (iv), we get

$$\boxed{C_p - C_v = R}$$

Thus the difference between the molar heat capacity of a gas at constant pressure (C_p) and at constant volume (C_v) is equal to the gas constant R, *viz*., 1.987 cal or 8.314 J.

Alternatively, relationship between C_p and C_v can be obtained on the basis of differential calculus.

We know that

$$C_v = \frac{dE}{dT} \qquad \text{... (i)}$$

and $$C_p = \frac{dH}{dT} \qquad \text{... (ii)}$$

Subtracting (i) from (ii),

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT} \qquad \text{... (iii)}$$

But H = E + PV (by definition)

For 1 mole of an ideal gas

$$PV = RT$$

$$\therefore \quad H = E + RT$$

Differentiating this equation with respect to temperature, we get

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

or $$\frac{dH}{dT} = \frac{dE}{dT} + R \qquad \text{... (iv)}$$

From equations (iii) and (iv), we get

$$C_p - C_v = R \qquad \text{(for 1 mole of an ideal gas)}$$

or $$C_p = C_v + R$$

3.7 ISOTHERMAL ADIABATIC PROCESSES. REVERSIBLE AND IRREVERSIBLE PROCESSES REVERSIBLE CHANGE AND MAXIMUM WORK

Q13. Explain the types of thermodynamic processes.

Ans :

Thermodynamic Processes

The operation by which a thermodynamic system changes from one state to another is called a thermodynamic process. A thermodynamic process is always accompanied by change in energy although in case of open system change of matter may also occur. Depending upon the condition of change, five different types of thermodynamic systems have been recognized.

(i) **Isothermal process :** A process in which although heat enters or leaves the system yet the temperature of the system remains constant throughout the process is called as isothermal process. Suppose a chemical reaction is taking place in a closed but not insulated vessel of the type shown in Figure. In case the process is exothermic, the evolved gas is given out by the system to the surroundings instantaneously and thus the temperature of the system does not rise at all at any stage of the process. If on the other hand, the reaction is endothermic, the required amount of heat is absorbed instantaneously by the system from the surroundings and thus, again the temperature of the system does not fall at any stage of the process.

Isothermal processes are often carried out by placing the system in a thermostat (a constant temperature bath). For an isothermal process, change in temperature (dT) = 0.

(ii) **Adiabatic process:** A process during which no heat enters or leaves the system during any step of the process is known as **adiabatic process.** In this process since, no heat enters or leaves the system, the temperature will decrease or increase when the reaction is endothermic and exothermic respectively. Such reactions (processes) are often carried out in closed insulated containers such as thermos bottle.

For an adiabatic process, change in heat (δq) = 0.

(iii) **Isobaric process:** A process during which pressure of the system remains constant throughout the reaction is known as **isobaric process.** For example, heating of water to its boiling point, and its vaporization takes place at the same atmospheric pressure.

For an isobaric process. $dP = 0$.

(iv) **Isochoric process:** A process during which volume of the system remains constant throughout the reaction is known as **isochoric process.** The heating of substance in a non-expanding chamber is an example of isochoric process.

For an isochoric process, $dV = 0$.

(v) **Cyclic process:** A process during which the system comes to its initial state through a number of different processes is called a **cycle or cyclic process.**

For a cyclic process. $dE = 0$. $dH = 0$.

Q14. What are reversible and irreversible process.

Ans :

When a thermodynamic process occurs in such a way that the properties of the system at any instant remain practically uniform, the process is called a reversible process. A reversible process can be conceived to proceed very slowly through a succession of infinitesimal steps and its direction can be reversed at any point by making a small change in a variable like temperature, pressure etc.

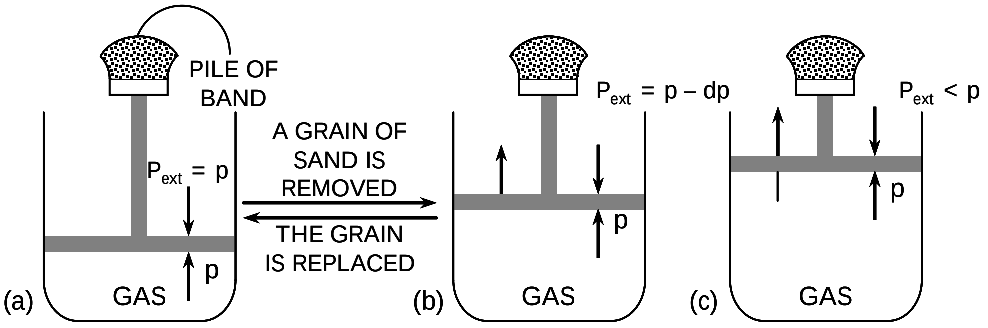


Fig.: (a) and (b) Illustration of the concept of reversible process
(c) Illustration of the concept of irreversible process.

A reversible process is that which is carried out infinitesimally slowly to that all changes occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium at all times. Alternatively, a reversible process may be defined as that which is carried out in stages and the driving force at every stage is only infinitesimally greater than the opposing force and which can be reversed by increasing the opposing force by an infinitesimal amount.

An irreversible process is that which is not carried out in infinitesimally slowly steps (instead it is carried out in a single step) and cannot be carried in the reverse order. All the spontaneous processes occurring around us, like expansion of gases, flow of heat from hot bodies to colder ones, etc. are irreversible.

3.8 DERIVATION OF EXPRESSION FOR MAXIMUM WORK FOR ISOTHERMAL REVERSIBLE PROCESS. PROBLEMS. INTERNAL ENERGY OF AN IDEAL GAS

Q15. The work done in an isothermal reversible expansion of an ideal gas is greater than the work done in reversible adiabatic expansion explain.

Ans : **(Imp.)**

Consider an ideal gas enclosed in a non-insulated cylinder fitted with a weightless and frictionless piston. It is supposed to be in thermal equilibrium with the surroundings so that the temperature of the gas remains constant throughout the experiment. Suppose P is the pressure of the gas contained in the cylinder.

We know that the reversible expansion of the gas takes place in a finite number of infinitesimally small steps. To start with, the external pressure on the piston is arranged equal to the internal pressure of the gas and the piston remains stationary. Now the external pressure on the piston is lowered by the infinitesimal amount dP, i.e., it falls from P to P – dP with the result the piston will move up through a small distance and the gas will expand by an infinitestimal volume dV, i.e., the volume increases from V to V + dV. As a result of expansion the pressure of the gas within the cylinder also falls from P to P–dP, i.e., it becomes equal to the new external pressure and thus the piston again becomes stationary. The external pressure is lowered further by the same infinitesimal amount, i.e., dP; and the same type of changes take place again leading to an increase of an infinitesimal amount of volume, i.e., dV.

The small amount of work (δW) done by the gas in each step of expansion is given by the product of the external pressure and the increase in volume, i.e.,

$$\delta W = (P - dP)\, dV \qquad \text{... (i)}$$

$$= P\, dV - dP\, dV$$

Ignoring the product dP dV as both the quantities are infinitesimal,

$$\delta W = P\, dV \qquad \text{... (ii)}$$

The total work W done by the gas in expansion from original volume V_1 to final volume V_2 will be the sum of series of the terms P dV in which the value of P goes on decreasing while volume of he gas goes on increasing gradually. Mathematically this may be expressed as below.

$$W = -\int_{V_2}^{V_1} P\, dV \qquad \text{... (iii)}$$

For *n* moles of an ideal gas,

$$PV = nRT$$

or $$P = \frac{nRT}{V} \qquad \text{... (iv)}$$

Substituting the value of P in equation (iii), we get

$$W = \int_{V_2}^{V_1} \frac{nRT}{V} dV \qquad \text{... (v)}$$

For an isothermal process, T is constant. Also n and R are constant quantities. Hence equation (v) may be written as

$$W = nRT \int_{V_2}^{V_1} \frac{dV}{V}$$

$$= nRT \ln \frac{V_2}{V_1} \qquad \text{... (vi)}$$

$$= nRT\ 2.303 \log \frac{V_2}{V_1} \qquad \text{... (vii)}$$

Further, since the process is isothermal, i.e., the temperature remains constant, therefore Boyle's law can be applied.

$$P_1V_1 = P_2V_2 \qquad \text{(Boyle's law)}$$

or $$\frac{P_1}{P_2} = \frac{V_2}{V_1} \qquad \text{... (viii)}$$

where P_1 and V_1 are the initial pressure and volume while P_2 and V_2 are the final pressure and volume of the system.

Substituting the value of $\frac{V_2}{V_1}$ in equation (vii), we get

$$W = nRT\ 2.303 \log \frac{P_1}{P_2}$$

3.9 JOULES EXPERIMENT. JOULE - THOMPSON COEFFICIENT. ADIABATIC CHANGES IN IDEAL GAS, DERIVATION OF EQUATION

Q16. Explain joule - Thompson effect what is Thompson coefficient.

Ans : **(Imp.)**

Joule and Thompson observed that when a compressed gas is forced through a porous plug into vacuum or a region of low pressure, under a adiabatic conditions, it gets appreciably cooled. Hydrogen and Helium are exceptions as they get warmed up under similar conditions. However, at very low temperature (below – 80°C for H_2 and below – 240°C for He), these gases also show the above behaviour. The temperature below which a gas becomes cooler on expansion (e.g., – 80°C for H_2) is known as the Inversion temperature.

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the Joule-Thompson effect.

Joule-Thompson Experiment

The apparatus used by Joule and Thompson to measure the temperature change on expansion of a given volume of a gas is illustrated schematically in Figure.

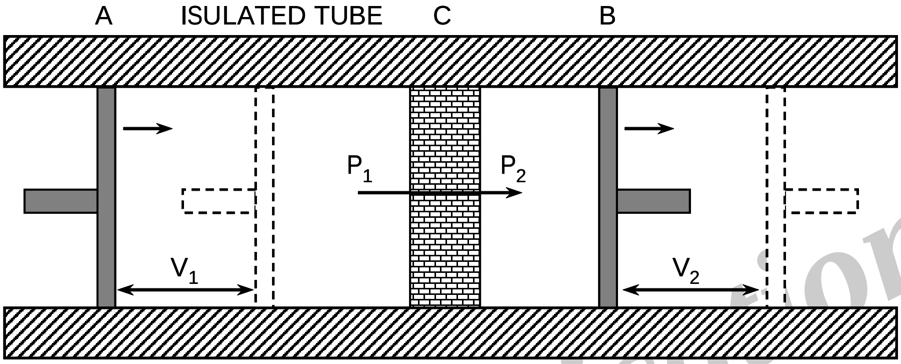


Figure : Joule-Thompson experiment (expansion of a real gas through a porous plug).

A tube thoroughly insulated (to ensure adiabatic conditions) is fitted with a porous plug C in the middle and two pistons A and B on the sides. The pressures on the left and right sides of the plug are kept at P_1 and P_2 respectively where $P_1 > P_2$.

A volume V_1 of the gas enclosed between piston A and porous plug C at a higher pressure P_1 is forced very slowly (so as not to change the pressure P_1) through the porous plug by moving the piston A inwards and is allowed to expand to volume V_2 at a lower pressure P_2 by moving the piston B outward. The change in temperature is found by taking readings on the two thermometers and it was observed that when the experiment is done at room temperature, all gases (except H_2 and He) show a fall in temperature on expansion.

Joule-Thompson effect and change in enthalpy

Since the process is carried out adiabatically,

$$Q = 0.$$

According to first law of thermodynamics,

$$\Delta E = Q - W$$

$$\therefore \quad \Delta E = Q - W \qquad \text{... (i)}$$

$$\text{or} \quad W = -\Delta E$$

Thus the work done during the expansion of the gas under adiabatic conditions is at the expense of the internal energy. In other words, when the work of expansion is done adiabatically, the internal energy and hence temperature of the gas decreases.

Further on the left side of the plug, the work is done on the system whereas on the right side of the plug, work is done by the system.

Work done on the system on the left side $= -P_1V_1$

Work done by the system on the right side $= P_2V_2$

(The -ve sign indicates the nature of work only)

$\therefore$ Net work done by the system, $W = P_2V_2 - P_1V_1$ ... (ii)

Substituting the value of W in equation (i), we get

$$\Delta E = -(P_2V_2 - P_1V_1)$$

$$= P_1V_1 - P_2V_2$$

Further we know that $\Delta E = E_2 - E_1$

$$\therefore \quad E_2 - E_1 = P_1V_1 - P_2V_2$$

or $$E_2 + P_2V_2 = E_1 + P_1V_1$$

or $$H_2 = H_1 \quad (\therefore H = E + PV)$$

$$\Delta H = 0$$

We can say that when a gas expands adiabatically through porous plug, the enthalpy of the system remains constant while internal energy changes. In other words. adiabatic expansion of a gas takes place at constant enthalpy such expansion is known as isoenthalpic.

Joule-Thompson coefficient

From the above experiment (Joule-Thompson effect), it is obvious that whenever a real gas expands under adiabatic conditions, temperature decreases, except in case of H_2 and He which under these conditions get warmed. Joule and Thompson further showed that the actual change in the temperature of the gas, under these conditions, depends upon the initial temperature and pressure of the gas. They introduced the term Joule-Thompson coefficient, represented by p, for expressing the change in temperature produced by change in pressure during adiabatic expansion of a real gas. They defined p by the expression.

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H$$

Thus Joule-Thompson coefficient may be defined as the change in the number of degrees of temperature produced by a drop of one atmospheric pressure when the gas expands under conditions of constant enthalpy. From the above expression, it is obvious that.

(i) If μ is positive (i.e., when dT and dP both are negative), the gas cools on adiabatic expansion. Most gases have positive μ and hence they cool on expansion at room temperature.

(ii) If μ is negative, (i.e., when dT is positive and dP is negative), the gas warms up on adiabatic expansion at room temperature. Hydrogen and helium have negative μ and hence, they warm up on expansion at room temperature.

(iii) If μ = zero (i.e., when dT = 0 for any value of dP) the gas neither cooled nor warms up on adiabatic expansion.

It has been found that at a particular pressure, every gas has a definite temperature at which $\mu = 0$. below this, temperature μ is positive and above this temperature μ is negative. This temperature (at a particular pressure) at which $\mu = 0$ and below which p is positive (i.e., the gas undergoes cooling on adiabatic expansion) and above which μ negative (i.e., the gas undergoes heating on adiabatic expansion) is cooled the inversion temperature. In short the temperature (at a particular pressure) at which the sign of μ changes is called the inversion temperature.

The inversion temperature of H and He are very low (being must below 0°C) and hence, these gases undergo heating on adiabatic expansion at room temperature. However, if these gases are first cooled to temperatures below their inversion temperatures and then allowed to expand adiabatically, these gases also undergo cooling.

$$\text{For Ideal gas } \mu = \left(\frac{\delta T}{\delta p}\right)_H = 0$$

3.10 PV$^\gamma$ = CONSTANT. P - V CURVES FOR ISOTHERMAL AND ADIABATIC PROCESSES

Q17. Give derivation of equation PV$^\gamma$ = constant. Derive the expression for adiabatic changes in ideal gas.

Ans : **(Imp.)**

As described earlier an adiabatic process is that in which no heat enters or leaves the system at any stage.

Thus for every infinitesimal change of the process,

$$\delta Q = 0$$

Putting this value in the first law of thermodynamics, i.e.,

$$dE = \delta Q - dW$$

We get $$dE = -\delta W \qquad \text{... (i)}$$

Now we know that the small work of expansion δ W is given by P dV where dV is the small increase in volume and P is the pressure of the gas, i.e.,

$$\delta W = PdV \qquad \text{... (ii)}$$

Substituting the value of δ dE in equation (i),

$$dE = -PdV \qquad \text{... (iii)}$$

We know that the molar heat capacity of an ideal gas at constant volume, C_v is given by the expression

$$C_v = \frac{dE}{dT}$$

or $$dE = C_v\, dT \qquad \text{... (iv)}$$

From equations (iii) and (iv),

$$C_v dT = -P\, dV \qquad \text{... (v)}$$

From equation (i), we observe that dE and δW have opposite sign. Thus if δW is negative, i.e., work is done on the system, dE will be positive, i.e., internal energy of the system increases and hence, temperature would rise. If dE is positive, i.e., work is done by the system, dE will be negative, i.e., internal energy of the system decreases and hence temperature of the system would fall.

Alternatively, from equation (v), it is obvious that dT and dV have opposite sign. Thus in adiabatic process, if the volume of the gas increases as in expansion, the temperature will fall. On the other hand, if the volume of the gas decreases as in compression, the temperature will rise.

The exact relation between (i) temperature and volume and (ii) pressure and volume in a reversible adiabatic expansion or compression of an ideal gas may be derived in the following manner.

Relationship between temperature and volume

Consider 1 mole of an ideal gas at pressure P and volume V. Then according to gas equation,

$$PV = RT$$

or $$P = \frac{RT}{V}$$

Substituting the value of P in equation (v), we get

$$C_v dT = -\frac{RT}{V} dV$$

or $$C_v \frac{dT}{T} = -R\frac{dV}{V}$$

Integrating equation (vi) between the limits T_1 and T_2; and V_1 and V_2 and considering C_v to be constant, we get

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R\int_{V_1}^{V_2} \frac{dV}{V}$$

Thus $$C_v \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

or $$C_v \ln\frac{T_2}{T_1} = R\ln\frac{V_1}{V_2} \quad \text{... (vii)}$$

or $$C_v \ln\frac{T_2}{T_1} = (C_p - C_v)\ln\frac{V_1}{V_2} \qquad (\because R = C_p - C_v)$$

or $$\ln\frac{T_2}{T_1} = \frac{C_p - C_v}{C_v}\ln\frac{V_1}{V_2}$$

or $$\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2} \qquad \left(\because \frac{C_p}{C_v} = \gamma\right)$$

or $$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Taking antilogarithm of both sides, we get

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \text{... (viii)}$$

or $$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

or $$TV^{\gamma-1} = \text{constant} \quad \text{... (ix)}$$

Relationship between Pressure and Volume

According to ideal gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or $$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} \qquad \text{... (x)}$$

On equating equations (viii) and (x), we get

$$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

or $$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

or $$(P_1 V_1)^{\gamma} = (P_2 V_2)^{\gamma}$$

$$PV^{\gamma} = \text{constant}$$

Q18. Draw the PV curves for isothermal and adiabatic process.

Ans :

Comparison Between Isothermal and Adiabatic Expansion of an Ideal Gas

In an isothermal process temperature of a system remains constant, while in an adiabatic process temperature change is must.

The pressure - volume relation for a reversible isothermal process (i.e., when temperature remains constant) is given by Boyle's law, viz.

$PV = \text{Constant}$

On the other hand, pressure - volume relation for a reversible adiabatic process is given by,

$PV^{\gamma} = \text{Constant}$

From our previous discussion we know that C_p is always greater than C_v, hence the ratio of $C_p / C_v = \gamma$ is greater than unity. Thus the increase of volume for a given decrease of pressure will be less in an adiabatic expansion than in an isothermal expansion. Thus the P – V curve will be steeper for an adiabatic than for an isothermal process, starting at the same point figure.

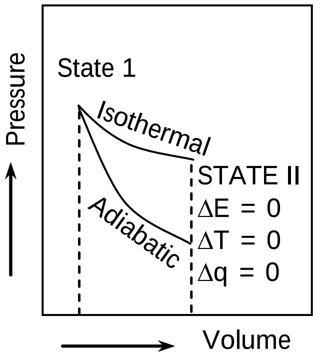


Figure: Curves for Isothermal and Adiabatic Expansions

The smaller change in volume in adiabatic process than in isothermal process can also be explained by the fact that in adiabatic process, expansion takes place at the expense of internal energy which thus becomes less leading to fall in temperature. This cooling effect leads to the shrinkage in volume. On the other hand, in isothermal expansion, heat is absorbed to make up for the expansion work done by the gas and thus the temperature remains constant.

Since the work of expansion is equal to the area under the curve, it is evident from the figure that the work done by an ideal gas is greater in isothermal expansion than in adiabatic expansion.

3.11 HEAT OF A REACTION AT CONSTANT VOLUME AND AT CONSTANT PRESSURE, RELATION BETWEEN ΔH AND ΔV. VARIATION OF HEAT OF REACTION WITH TEMPERATURE. KIRCHHOFF'S EQUATION AND PROBLEMS

Q19. Derive Kirchoff's reaction.

Ans : **(Imp.)**

Variation of Heat of Reaction with Temperature (Kirchoff's Equation)

The amount of heat evolved or absorbed in a process, (physical or chemical) varies with temperature. The exact relationship showing the variation of the heat of reaction with temperature was given by Kirchoff (1858) which is now popularly known as Kirchoff's equation. It can be derived easily with the help of the first law of thermodynamics.

A) When the reaction is carried out at constant pressure

Consider the following simple process

$$A_{(reactants)} \longrightarrow B_{(products)}$$

Now, suppose H_A and H_B are the heat contents (enthalpies) of the reactants and products respectively. Then the heat of reaction (change in enthalpy) accompanying the process will be given by the relation.

$$\Delta H = H_B - H_A$$

Differentiating the equation with respect to temperature at constant pressure, we get

$$\left(\frac{\delta(\Delta H)}{\delta T}\right)_p = \left(\frac{\delta H_B}{\delta T}\right)_p - \left(\frac{\delta H_A}{\delta T}\right)_p \quad \text{... (i)}$$

But according to the definition of heat capacity at constant pressure (C_p), we know that,

$$C_p = \left(\frac{\delta H}{\delta T}\right)_p \quad \text{... (ii)}$$

From equations (i) and (ii), we get,

$$\left(\frac{\delta(\Delta H)}{\delta T}\right)_p = (C_p)_B - (C_p)_A$$

Where $(C_p)_B$ and $(C_p)_A$ are the mean molar heat capacities of the product and reactants respectively at the given pressure.

or $$\left(\frac{\delta(\Delta H)}{\delta T}\right)_p = \Delta C_p \qquad [\therefore (C_p)_B - (C_p)_A = \Delta C_p]$$

Further, since the term ΔH is used for the heats of reaction at constant pressure, the above equation may simply be written as

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p.dT$$

or $$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1) \quad \text{... (iv)}$$

where ΔC_p has been assumed to be constant in the temperature range $T_1 \rightarrow T_2$.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta Cp \quad \text{... (v)}$$

Relations (iii) and (v) are known as Kirchoff's equations at constant pressure and may be defined as below :

The change in the heat of reaction at constant pressure for every degree change of temperature is equal to the change in the heat capacity at constant pressure.

3.12 LIMITATIONS OF FIRST LAW AND NEED FOR SECOND LAW STATEMENT OF SECOND LAW OF THERMODYNAMICS

Q20. State second law of thermodynamics.

Ans :

Spontaneous, Natural or Irreversible Process

A process which proceeds of its own accord, without the help of any external agency, is called a spontaneous process. All natural processes are spontaneous, hence the term natural is also used, for the. spontaneous processes. Further since the spontaneous process cannot be reversed without the help of an external agency, these are also said to be irreversible. The term non-spontaneous is applied to the reverse of a spontaneous or un-natural process.

It is important to note that the term spontaneous does not give any idea of the rate of the process, i.e., whether the process takes place fast or slowly. All that it implies is that the process can occur easily without the help of an external energy.

Few examples of spontaneous processes are given below :

1. Water flows down-hill spontaneously and the direction cannot be reversed unless some external work is done on it.
2. Heat flows spontaneously from the hot end of a metallic bar to its cold end but never from cold to hot end.
3. Heat flows spontaneously from a hot reservoir to a cold reservoir. However, transference of heat from a cold reservoir to a hot reservoir, as in a refrigerator, needs energy from outside the system.
4. Diffusion of a solute from a concentrated solution to a less concentrated solution, when these are in contact with each other, occurs spontaneously'till the equilibrium is achieved.
5. Electricity flows spontaneously from a point of higher potential to a point of lower potential. The direction of flow can be reversed only when an external field is applied in the opposite direction.
6. A gas expands spontaneously from a region of high pressure to region of low pressure. The reverse process cannot occur unless work is done on it.

7. A piece, of zinc dissolves spontaneously in copper sulphate solution, precipitating copper and employing some heat.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4\ (aq) + Cu(s)$$

The above reaction is not reversible under ordinary conditions and it can be reversed only by passing electric current between copper rod and aqueous zinc sulphate, of course the electrical energy required to do so will be more than the heat energy evolved in the direct reaction.

Q21. Discuss the limitations of I law of thermodynamics.

Ans :

Limitations of the First Law of Thermodynamics Need for the Second Law of Thermodynamics

The first law of thermodynamics, has following important limitations:

(i) The first law of thermodynamics states that during a process one form of energy can change into another form but the total amount of energy remains the same.

However, it does not predict whether the process in question can occur spontaneously or not (i.e., whether it is feasible or not) and if so, in which direction. For example, the first law does not indicate whether heat can flow from a colder end to a hotter end or not. All that the first law tells is that if this process occurs, the heat energy gained by one end would be exactly equal to that lost by the other end. Similarly, the first law does not tell whether a gas can diffuse from low pressure to high pressure or not, whether water can itself run uphill or not, etc.

(ii) The first law states that energy of one form can be converted into an equivalent amount of energy of another form. However, by experience it has been observed that although various forms of energy can be completely transformed into other, heat energy cannot be completely converted into equivalent amount of work without producing some change elsewhere.

The second law of thermodynamics covers the above limitations. It can be defined in several ways, the most common are given below :

"All spontaneous processes are thermodynamically irreversible".

It is impossible to convert heat completely into equivalent amount of work without producing changes.

"Without the use of an external agency, heat cannot itself pass from a colder to a hotter body".

3.13 CYCLIC PROCESS HEAT ENGINE, CARNOT'S THEOREM, CARNOT'S CYCLE DERIVATION OF EFFICIENCY OF HEAT ENGINE, PROBLEMS, THERMODYNAMIC SCALE OF TEMPERATURE

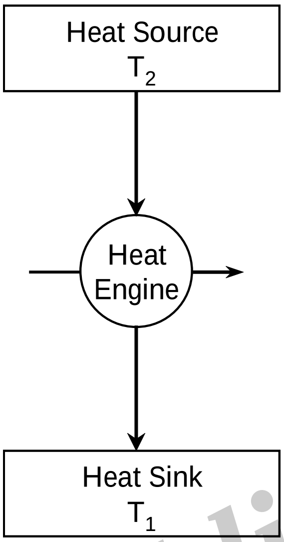
Q22. Derive carnot's cycle. Derive an expression for the efficiency of reversible heat engines working between the temperatures between T_2 and T_1.

Ans : **(Imp.)**

The fraction of the heat absorbed by a machine that it can transform into work is called the efficiency of the machine. Thus if Q is the heat absorbed and W is the work done, then the efficiency (η) of the machine is given by

$$\eta = \frac{W}{Q}$$

The machine used for the conversion of heat into work is called heat engine. In order to bring about the conversion of heat into work, the heat engine absorbs heat from a high-temperature reservoir (called the source), converts some of it into work and returns the remaining heat to a low temperature reservoir (called the sink). A basic heat engine is illustrated in the figure. Steam engine is a typical example of heat engine, here the source is boiler and sink is surroundings.



A heat engine running on a periodic cyclic process can yield work continuously. Cyclic process is a process in which a system returns to its original state after completing a series of change. In case the series of changes in a cycle are conducted constant temperature, the cycle is termed as isothermal cycle. Further, if the changes are carried out reversibly, the process is called reversible cyclic process.

Carnot cycle

Carnot proposed a hypothetical heat engine (called Carnot engine) to show that the efficiency of a heat engine is based upon the temperature between which it operates. Carnot engine has following features :

(i) It consists of a cylinder containing one mole of an ideal gas as the working substance and fitted with a weightless, frictionless piston so that all the operations in the cycle are carried out reversibly, hence the Camot engine is also called reversible heat engine.

(ii) The cylinder is assumed to be insulated on all sides except at the bottom so that heat can flow from or to the system only through the bottom.

(iii) The engine has two heat reservoirs one at a higher temperature T_2 (called the source) and the other at a lower temperature T_1 (called the sink).

(iv) Operations are carried out in two ways.

  (a) If some operation is carried out by placing the cylinder in the source or the sink, it can exchange heat with it and hence the temperature remains constant (isothermal process).

  (b) On the other hand, if some operation is carried out by placing the cylinder on an insulating material, no heat exchange can take place between the system and the surroundings and hence the process is adiabatic.

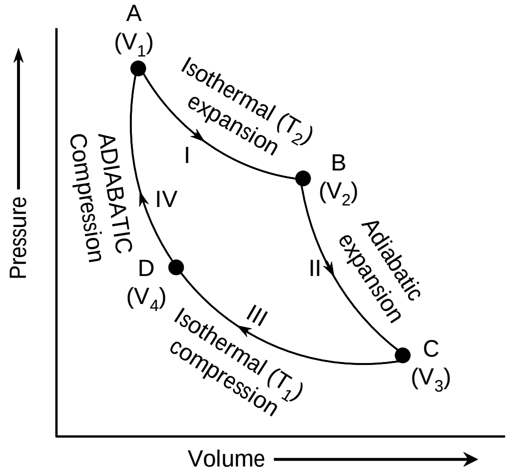


Figure: Carnot cycle

The complete camot cycle consists of four operations or strokes.

1. Isothermal reversible expansion.
2. Adiabatic reversible expansion.
3. Isothermal reversible compression.
4. Adiabatic reversible compression.

The four strokes are carried out as shown in Figure and represented on a pressure-volume diagram (also called indicator diagram). These are described below.

1. Stroke I, Isothermal reversible expansion

The cylinder containing one mole of the ideal gas, occupying a volume V_1, is placed in contact with the heat reservoir at a temperature T_2 (source). The gas absorbs heat (say Q_2) from the source and expands isothermally and reversibly to, volume V_2. In the P – V diagram, the path of the process is represented by the isothermal curve AB.

Work done in stroke I. The stroke I is isothermal, dE = 0. Hence, according to the first law of thermodynamics (viz. $\Delta E = Q - W$), heat absorbed (Q_2) is equal to the work done (say W_1) by the system on the surroundings, i.e.,

$$Q_2 = W_1$$

But
$$W_1 = RT_2 \ln \frac{V_2}{V_1}$$

$$\therefore \qquad Q_2 = RT_2 \ln \frac{V_2}{V_1} \qquad \text{... (i)}$$

2. Stroke II, Adiabatic reversible expansion

The cylinder is removed from the source and placed in contact with the perfectly insulating material. Thus the gas now expands adiabatically and reversibly from volume V_2 to V_3. Work is done in the expansion but since no heat enters or leaves the system, the temperature must fall and suppose it drops to temperature (temperature of sink). In the P – V diagram, this change (path) is shown by the adiabatic curve BC.

Work done in stroke II.

Let the work done by the system $= W_2$

Since this stroke is adiabatic, heat absorbed, i.e., $Q = 0$

Now according to the first law equation,

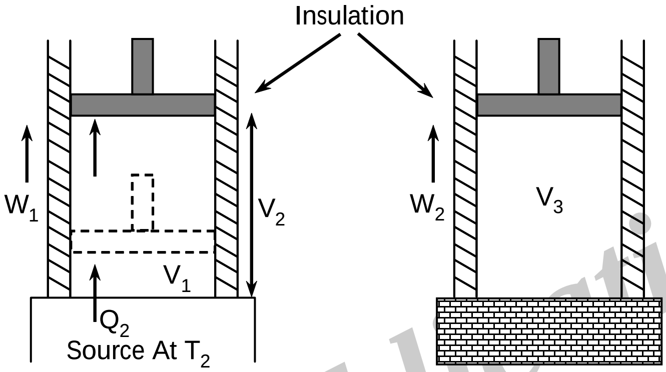
$$\Delta E = Q - W$$

$\therefore$ Here, $\Delta E = -W_2$

But $\Delta E = C_v (T_2 - T_1)$

$\therefore$ $W_2 = C_v (T_2 - T_1)$ ... (ii)

Where, C_v is the heat capacity of the ideal gas.

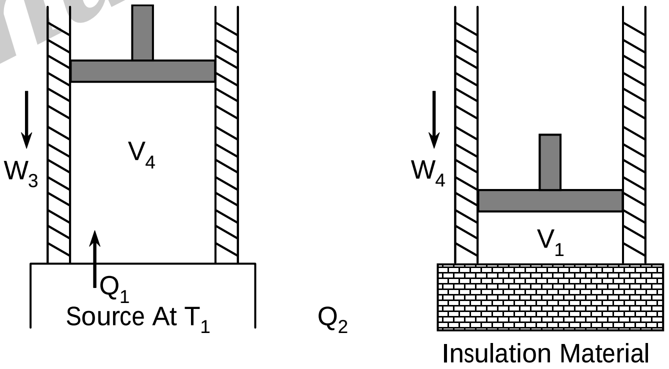


Stroke 1

Isothermal reversible expansion of gas at temperature T_2 from volume V_1 to V_2.

Stroke 2

Adiabatic reversible expansion of gas from volume V_2 to V_3. Temperature falls from T2 to T_1.



Stroke 3

Isothermal reversible compression at temperature T_1 from volume V_3 to V_4.

Stroke 4

Adiabatic reversible compression of gas from volume V_4 to original volume V_1. Temperature rises from T_1, to T_2.

Fig.: Illustration of the four Strokes of the Carnot Cycle

3. Stroke III, Isothermal reversible Compression

The cylinder is now removed from the insulating material and placed in contact with the second heat reservoir at a lower temperature T_1 (sink). The gas is compressed isothermally and reversibly till the volume decreases from V_3 to V_4 (represented by the curve CD in the P - V diagram).

Work done in stroke III. During compression, work is done on the system and hence the gas produces heat which is transferred to the sink. Since compression takes place isothermally, dE = 0. Thus if Q is the heat given to the sink at temperature T_1 and W_3 is the work done on the system, then using the proper signs (i.e., negative) for Q_1 and W_3, we have

$$-Q_1 = -W_3 = RT_1 \ln \frac{V_4}{V_3} \qquad \text{... (iii)}$$

4. Stroke IV, Adiabatic reversible Compression

The cylinder is now removed from the sink and placed again on the insulating material. The gas is compressed adiabatically and reversibly from volume V_4 to the original volume V_3 while the temperature rises from T_1 to the original temperature T_2. In the P – V diagram, this path is shown by the curve DA.

Work done in stroke IV. In this step work (say W_4) is done on the system and hence bears negative (–) sign. The first law equation is therefore written as

$$\Delta = Q - (-W_4)$$

$$= Q + W_4$$

In adiabatic process, $Q = 0$

Hence, $\Delta E = W_4 = C_v (T_2 - T_1)$

or $-W_4 = -C_V (T_2 - T_1)$ ... (iv)

Note that the work done in strokes II and IV (adiabatic operations) is equal but opposite in directions.

Since the system is restored to its initial state, cycle is thus completed.

Net Work Done in One Cycle

The net work (W) done in one cycle is obtained by adding the work done in the four strokes, i.e., equations (i) to (iv).

$$W = W_1 + W_2 + (-W_3) + (-W_4)$$

$$= +RT_2 \ln \frac{V_2}{V_1} - C_v (T_2 - T_1) - RT_1 \ln \frac{V_4}{V_3} + C_v (T_2 - T_1)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \qquad \text{... (v)}$$

Net heat absorbed in one cycle

The net heat **(**Q**)** absorbed in the whole cycle **may** also be given by the sum of heat of all the four strokes. Thus,

$$Q = Q_2 + 0 + (-Q_1) + Q + Q_2 + (-Q_1)$$

$$= Q_2 - Q_1 \qquad \text{... (vi)}$$

where Q_2 and $-Q_1$ are the heats absorbed by the system in strokes I and III respectively.

Substituting the values of Q_2 and Q_1 from equations (i) and (iii) in equation (vi),

$$Q = RT_2 \ln \frac{V_2}{V_1} + \left(-RT_1 \ln \frac{V_4}{V_3}\right)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \qquad \text{... (vii)}$$

From equations (v) and (vii), it is evident that the

Net work done = Net heat absorbed

Since V_1 and V_4 lie on the same adiabatic curve AD and for an adiabatic change, $TV^{\gamma-1} =$ constant

$$\therefore \qquad \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad \text{... (viii)}$$

Similarly, for V_2 and V_3 lying on the same adiabatic curve BC, it follows that

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad \text{... (ix)}$$

Comparing equations (viii) and (ix),

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

or $\dfrac{V_4}{V_1} = \dfrac{V_3}{V_2}$

or $\dfrac{V_4}{V_1} = \dfrac{V_3}{V_2}$

Substituting the value of $\dfrac{V_4}{V_3}$ in equation (v),

$$W = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_1}{V_2}$$

$$= RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \ln \frac{V_2}{V_1} \qquad \text{... (x)}$$

Efficiency of a Heat Engine

Since efficiency, $\eta = \frac{W}{Q}$, it may be obtained by dividing equation (x) by equation (i).

$$\eta = \frac{W}{Q} = \frac{T_2 - T_1}{T_2}$$

S3-P-2: THERMODYNAMICS - II

3.14 ENTROPY: DEFINITION FROM CARNOT'S CYCLE. ENTROPY AS A STATE FUNCTION. ENTROPY AS A MEASURE OF DISORDER. SIGN OF ENTROPY CHANGE FOR SPONTANEOUS AND NON-SPONTANEOUS PROCESSES & EQUILIBRIUM PROCESSES

Q23. Derive the entropy definition from carnot's cycle.

Ans :

When the isothermal and adiabatic processes in a carnot cycle are carried out infinitesimally slowly (i.e., reversibly), the summation of q/T terms is equal to zero.

Any cyclic process, if carried out reversibly, can be shown to consist of a series of carnot cycles. Consider a cyclic process in which the change from the state A to state B and back to the state A (Figure) is carried out reversibly. The path ABA may be considered to comprise of a number of small carnot cycles, i.e., of a series of isothermals and adiabatics, as shown in the figure.

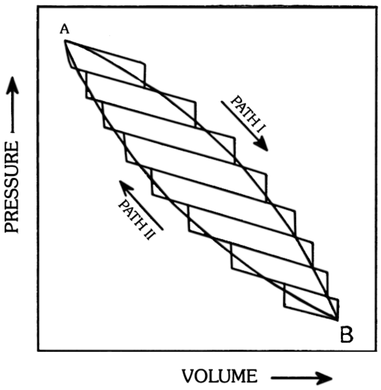


Fig. : Entropy change in a reversible cyclic process

The lines slanting horizontally stand for adiabatics and those slanting vertically stand for isothermals of the small Carnot cycles. If each isothermal and adiabatic change is made extremely minute, i.e., each Carnot cycle is made extremely small by increasing their number, the paths inside the loop cancel one another and the cycle corresponds to the continuous curve ABA. Thus, any reversible cycle can be regarded as being made up of an infinite number of small Carnot cycles.

Knowing that for each Carnot cycle

$$q_1/T_1 + q_2/T_2 = 0, \qquad \text{(ef. Eq. 19)}$$

if follows that in the case of the reversible cycle ABA, comprising of a series of Carnot cycles, the above expression takes the form

$$\Sigma q/T = 0 \qquad \text{... (20)}$$

i.e., the sum of all the q/T terms of the Carnot cycles involved is zero when the changes are infinitesimal, the above equation may be put as

$$\Sigma \frac{dq}{T} = 0 \qquad \text{... (21)}$$

Since the cycle is performed in two steps, viz., from A to B and back from B to A, it follows that

$$\Sigma \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \qquad \text{... (22)}$$

The integral $\int_A^B \frac{dq}{T}$ is the summation of all the $\frac{dq}{T}$ terms when the system changes from A to B along path I and $\int_B^A \frac{dq}{T}$ is the similar summation when the system returns from state B to the original state A along path II.

From equation 22,

$$\int_A^B \frac{dq}{T} \text{(path I)} = -\int_B^A \frac{dq}{T} \text{(path II)}$$

or

$$\int_A^B \frac{dq}{T} \text{(path I)} = \int_A^B \frac{dq}{T} \text{(path II)} \qquad \text{... (23)}$$

It follows from above that $\int_A^B \frac{dq}{T}$ is a definite quantity independent of the path followed for the change and depends only upon the initial and final states of the system. This quantity, therefore, like ΔU and ΔH, should rep-resent the change in some single-valued function of the states A and B of the system. This function is called entropy and is denoted by the symbol, S. If S_A is the entropy in the initial state A and S_B is the entropy in the final state B, then the change in entropy, ΔS, is given by the equation.

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \qquad \text{... (24)}$$

For each infinitesimally small change,

$$dS = dq/T \qquad \text{... (25)}$$

At constant temperature, for a finite change, ds becomes ΔS and dq becomes Δs and dq becomes q.

$$\therefore \quad \Delta S = q/T \qquad \text{... (26)}$$

Entropy is a function of the state only, the change of entropy (ΔS) for the change of state from A and B will invariably be the same whether the change is reversible or not.

Mathematically, it will be given by the equation,

$$\Delta S = \int_A^B \frac{dq}{T} \qquad \text{... (27)}$$

only when the change has been brought about reversibly. This is because the above equation has been derived from carnot cycle in which all the changes are brought about reversibly.

Change of entropy of a system may be defined as the summation of all the terms each involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly.

Thus, the entropy change for a finite change of state of a system at constant temperature is given by.

$$\Delta S = \frac{q_{rev}}{T}$$

Units of entropy. Since entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of calories per degree, i.e., cal deg^{-1}. This is known as entropy unit, e.u.

In SI units, the entropy is expressed in terms of joules per degree Kelvin ($J K^{-1}$).

Q24. Explain how entropy as a measure of disorder.

Ans : **(Imp.)**

Entropy as a Measure of the Disorder of the System

All spontaneous processes, (flow of heat from a hot end to a cold end of a conductor, flow of electricity from a point at a higher potential to a point at a lower potential, expansion of a gas in vacuum, diffusion of a solute from a concentrated to a dilute solution, are accompanied by increase in the 'disorder' of the system. Consider, for example, the flow of heat from a hot end to a cold end of a conductor. Before the transfer of heat takes place, there is a certain amount of order since hot molecules are present at one end and cold molecules are at the other end. But as soon as heat starts flowing from the hot end to the cold end, there is movement of electrons and there is an approach towards uniform distribution of energy in the system. The state of order existing at the two ends is disturbed and gives place to greater disorder. Similarly, consider the transfer of molecules of a solute from a more concentrated to a less concentrated solution. Before the two solutions are brought into contact with each other, there is a certain amount of order as the concentration in one part of the system has one particular value and that in the other part of the system has another particular value. But, the moment the two solutions are brought into contact, spontaneous process of diffusion starts and disorder ensues as there are continuous variations in concentrations in all parts of the system until equilibrium is attained. The, spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system.

It has also been shown that melting of a solid or evaporation of a liquid is accompanied by increase of entropy. At the same time, it is known that a solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in a liquid and least in a gas. Thus, increase of entropy implies increase in disorder.

Thus, entropy is regarded as a measure of the disorder of a system.

Q25. Write the sign of entropy change for spontaneous and non-spontaneous processes Equilibrium processes.

Ans :

1. Any change in a system which is accompanied by an increase in entropy tends to be spontaneous.

$$\Delta S = +ve$$

2. In a reversible process, the net entropy change for the combined system and the surroundings is zero.

$$\Delta S = 0 \quad \text{(equilibrium process)}$$

3. Any change in a system which is accompanied by decrease in entropy tend to be nonspontaneous

$$\Delta S = -ve$$

3.15 ENTROPY CHANGES IN I) REVERSIBLE ISOTHERMAL PROCESS, II) REVERSIBLE ADIABATIC PROCESS, III) PHASE CHANGE, IV) REVERSIBLE CHANGE OF STATE OF AN IDEAL GAS PROBLEMS ENTROPY OF MIXING OF IDEAL GASES

Q14. Write the entropy changes in reversible isothermal process.

Ans :

Entropy change in isothermal expansion of an ideal gas

In isothermal expansion of an ideal gas carried out reversibly, there will be no change in internal energy, i.e., $\Delta U = 0$ and hence from the First law equation (viz., $\Delta U = q+w$),

$$q_{rev} = -w \qquad \text{... (1)}$$

In such a case, the work done in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T, is given by

$$-w = nRT \ln (V_2/V_1) \qquad \text{... (Eq. 1)}$$

$$q_{rev} = -w = nRT \ln (V_2/V_1) \qquad \text{... (2)}$$

Hence, $$\Delta S = \frac{q_{rev}}{T} = \frac{1}{T} \times nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln (V_2/V_1).$$

Q26. Give the entropy changed takes place in adiabatic process.

Ans :

Entropy Changes in Reversible and Irreversible (Spontaneous) Processes: Consider isothermal expansion of an ideal gas at constant temperature into vacuum. This will, evidently, proceed spontaneously, i.e., irreversibly. There is no opposing force, the work done (w) by the system will be Zero, /further, there is no change in temperature during the process, (Here will be no change in the internal energy of the system, i.e., $\Delta U = 0$. Hence, from the First law equation, $q = 0$, i.e., no heat is absorbed or evolved in the process. In other words, no heat is supplied or removed from the surroundings. The entropy of the surroundings, therefore, remains unchanged.

Entropy of a system is a function only of the state of the system, i.e., its temperature and pressure (or volume) and is independent of the previous history of the system. In the process, the volume of the gas increases, from V_1 to V_2 temperature T. Hence, entropy increase of the system, considering that one mole of the gas is involved, would be given by

$$\Delta S = R \ln (V_2/V_1) \qquad \text{... (Equation 1)}$$

The total increase in entropy of the system and its surroundings during the spontaneous process of expansion considered above is, thus, R In (V_2/V_1). Since $V_2 > V_1$, it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surroundings considered together.

Isothermal expansion of the ideal gas from volume V_1 to V_2 carried out reversibly at the same temperature T. The expansion is now carried out infinitesimally slowly, i.e., the pressure on the frictionless piston is so adjusted that it remains always less than that of the gas by an infinitesimally small amount. In this case, the gas does some external work given by $w = -P\Delta V$. An equivalent amount of heat (q_{rev}) is absorbed reversibly by the system from the surroundings at temperature T. Hence, increase in the entropy of the system is q_{rev}/T.

The heat lost reversibly at temperature T by the surroundings also is q_{rev}. Hence, decrease in the entropy of the surroundings is q_{rev}/T.

Giving appropriate sign, positive for increase and negative for decrease of entropy, the net entropy change of the system and its surroundings is

$$q_{rev}/T - q_{rev}/T = 0 \qquad \text{...(32)}$$

In the reversible isothermal expansion of a gas, the total entropy change of the system and its surroundings considered together is zero.

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together while in a thermodynamically reversible process, the entropy of the system and its surroundings taken together remains unaltered.

This generalization constitutes a criterion for distinguishing between an irreversible and a reversible process.

The above statement in the form of the following mathe-matical expressions:

$$(\Delta S_{sys} + \Delta S_{sur}) = 0 \text{ (for reversible process)}$$

$$(\Delta S_{sys} + \Delta S_{sur}) > 0 \text{ (for irreversible process)}$$

Combining the two, we have

$$\Delta S_{SYS} + \Delta S_{SUR} \geq 0 \qquad \text{...(33)}$$

where ‘equal to’ sign refers to a reversible process while the ‘greater than’ sign refers to an irreversible process.

In a reversible process, the entropy of the system and the surroundings taken together remains constant while in an irreversible process, the entropy of the system and the surroundings taken together increases.

All processes in nature occur spontaneously, i.e., irreversibly, it follows that the entropy of the universe is increasing continuously. This is another statement of the Second law.

The essentials of the First law and the Second law of thermodynamics were thus summed up by Clausus as follows :

The energy of the universe remains constant; the entropy of the universe tends towards a maximum.

Q27. Write the entropy changes in phase change.

Ans :

Entropy Change Accompanying Change of Phase

a) From Solid Phase to Liquid Phase

Consider when a solid changes into liquid state at its fusion point. The process requires absorption of heat (heat of fusion).

Consider melting of one mole of a substance reversibly at the fusion point T_f, at constant pressure. Let ΔH_f be the molar heat of fusion. The entropy change of the process, ΔS_f, will then be given by

$$\Delta S_f = \Delta H_f / T_f \quad \text{... (34)}$$

b) From Liquid Phase to Vapour Phase

Suppose one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b, under a constant pressure. If ΔH_v is the molar heat of vaporisation, then the entropy change accompanying the process will be given by

$$\Delta S_V = \frac{\Delta H_v}{T_b} \quad \text{... (35)}$$

Since ΔH_f and ΔH_v are both positive, the processes of fusion and vaporisation are both accompanied by increase of entropy.

If we consider the change of state from vapour to liquid or from liquid to solid, then ΔH_v and ΔH_f will both be negative and hence the process of condensation of vapour or freezing of a liquid would be accompanied by decrease of entropy.

c) From One Crystalline form to Another

The change in entropy when one mole of a solid substance undergoes change of state from one crystalline form (say, rhombic form) to another crystalline form at the transition temperature T, is given by

$$\Delta S_t = \Delta H_t / T \quad \text{...(36)}$$

where ΔH_t is the molar heat of transition of the substance. Molar heat of transition is the amount of heat absorbed or evolved by one mole of a substance when it undergoes change of state from one crytalline form to another at the transition temperature T.

Q28. Write the changes occur during reversible change of state of an Ideal gas.

Ans :

Entropy of a system varies with the state of the system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. Since T is taken generally as one of the variables, the second variable to be considered may be V or P. Thus, the two variables to be considered are either T and V or T and P.

When T and V are the two variables

The increase in entropy of the gas for an infinitesimally small change is given by the expression

$$dS = dq_{rev}/T$$

where dq_{rev} is the small amount of heat absorbed by the gas (system) reversibly from the surroundings at temperature T.

According to the equation of the first law of thermodynamics, viz., $\Delta U = q - w$, we have

$$dq_{rev} = dU + dw \qquad \text{... (37)}$$

If the work involved is due to expansion of the gas, then, for an infinitesimal increase in volume dV against a pressure P,

$$-dw = PdV \qquad \text{... (38)}$$

Substituting the value of dU from $C_v = (\partial U/dT)_v$ and – dw from equation 38, we have

$$dq_{rev} = C_v dT + PdV \qquad \text{... (39)}$$

For one mole of an ideal gas,

$$\therefore \quad dq_{rev} = C_v dT + RTdV/V$$

$$dq_{req}/T = dS = C_v\, dT/T + RdV/V \qquad \text{... (40)}$$

For a finite change of state of a system, the entropy change (ΔS) is obtained by integrating the above equation between the limits of the initial state 1 and the final state 2. Assuming C_v to be constant within the temperature range T_1 and T_2, for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} \qquad \text{...(41)}$$

Thus, $$\Delta S = C_v \, ln\, T_2/T_1 + R \ln V_2/V_1 \qquad \text{...(42)}$$

For n moles of the ideal gas, the above equation may be written as

$$\Delta S = nC_v \ln (T_2/T_1) + nR \ln (V_2/V_1) \qquad \text{...(43)}$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperatures.

When T and P are the two variables: If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$P_1V_1 = RT_1$ for one mole of the gas in the initial state

$P_2V_2 = RT_2$ for one mole of the gas in the final state

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1} \qquad \text{...(44)}$$

Substituting in Eq. 42, for one mole of the gas, we have

$$\Delta S = C_v \ln T_2/T_1 + R \ln T_2/T_1 - R \ln P_2/P_1 \qquad \text{...(45)}$$

Remembering that $C_p - C_v = R$

$$\Delta S = C_P \ln T_2/T_1 - nR\, ln\, (P_2/P_1) \qquad \text{...(46)}$$

For n moles of the ideal gas,

$$\Delta S = nC_p \ln (T_2/T_1) - nR \ln (P_2/P_1) \qquad \text{...(47)}$$

It is evident from the above equations that the entropy change for the change of state of an ideal gas depends on the initial and final pressures as well as on the initial and final temperatures.

Q29. Write the equation of entropy of mixing inert perfect gases.

Ans :

Entropy of Mixing

Entropy of mixing is defined as the difference between the entropy of the mixture of gases and the sum of the entropies of the separate gases, each at a pressure P. Thus,

$$\Delta S_{mix} = \Sigma n(C_p \ln T - R \ln P - R \ln x + S'_0) - \Sigma n(C_p \ln T - R \ln P + S'_0)$$

$$= -R\,\Sigma n \ln x$$

$$= -R\,(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3 + ...)$$

$$= -R\Sigma n_i \ln x_i$$

Where n_i and x_i represent the number of moles and the mole fraction, respectively, of each constituent of the mixture.

If n is the total number of moles, then, evidently,

$$n = n_1 + n_2 + n_3 + ...$$

Dividing both sides by n, we have

$$1 = n_1/n + n_2/n + n_3/n + ...$$

$$= x_1 + x_2 + x_3 + ... = \Sigma x_i$$

Thus, for a total of 1 mole of the gaseous mixture, the entropy of mixing is given by.

$$\Delta S_{mix} = -R\,\Sigma x_i \ln x_i$$

Since x_i is a fraction, the entropy of mixing is always positive.

3.16 FREE ENERGY GIBB'S FUNCTION (G) AND HELMHOLTZ'S FUNCTION (A) AS THERMODYNAMIC QUANTITIES

Q30. What are free energy Gibb's function (G) and Helmholtz's function.

Ans :

Work function and the free energy function represented by A and G, respectively. These are defined by the equations.

$$A = U - TS \quad ... (1)$$

$$G = H - TS \quad ... (2)$$

Since U, H and S depend only upon the state of a system (the temperature is included in the state), it is evident that the functions A and G also depend upon the state of the system only. The exact nature of the functions will be clear from the following.

Let the three functions in Equation (1), in a given state of the system at constant temperature T, be A_1, U_1 and S_1 so that

$$A_1 = U_1 - TS_1 \quad ... (3)$$

Let an appreciable change take place at the same temperature T so that the three functions in another sate of the system become A_2, U_2 and S_2. Then

$$A_2 = U_2 - TS_2 \quad ... (4)$$

Subtracting Equation (3) from (4), we have

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1) \quad \text{... (5)}$$

or $$\Delta A = \Delta U - T\Delta S \quad \text{... (6)}$$

where ΔA is the change in the function A, ΔU is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat absorbed is equal to q_{rev}.

Since from equation, $\Delta S = q_{rev}/T$, hence, substituting in equation 6, we have

$$\Delta A = \Delta U - q_{rev} \quad \text{... (7)}$$

From the equation of the first law of thermodynamics, *viz*., $\Delta U = q + w$, it follows that

$$w_{rev} = \Delta U - q_{rev} \quad \text{... (8)}$$

If during the change under consideration, work is done by the system, it would carry a negative sign so that

$$-w_{rev} = \Delta U - q_{rev} \quad \text{... (9)}$$

Comparing equation 7 with equation 9

$$-\Delta A = w_{rev}. \quad \text{... (10)}$$

The process is carried out reversibly, w represents the maximum work. the decrease in the function A (i.e., $-\Delta A$) gives the maximum work that can be done by the system during the given change. The function A is, therefore, termed as the work function. This is also referred to as Helmholtz free energy or the Helmholtz function.

If G_1, H_1 and S_1 represent the thermodynamic functions for the system in the initial sate and G_2, H_2 and S_2 in the final state, the temperature remaining constant at T all along, we have.

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $$\Delta G = \Delta H - T\Delta S \quad \text{... (11)}$$

But, at constant pressure

$$\Delta H = \Delta U + P\Delta V$$

$$\therefore \quad \Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{... (12)}$$

Comparing with equation

$$\Delta G = \Delta A + P\Delta V \quad \text{... (13)}$$

Since ΔA is equal to $-$ w(cf. Equation 10), hence

$$\Delta G = -w + P\Delta V \quad \text{... (14)}$$

or $$-\Delta G = -w - P\Delta V \quad \text{... (15)}$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P. Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the net work. Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \quad \text{... (16)}$$

Hence, – ΔG is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the Gibbs function or gibbs free energy or merely as free energy. thus, – ΔG is a measure of the decrease in free energy.

3.17 CONCEPT OF MAXIMUM WORK AND NETWORK ΔG AS CRITERIA FOR SPONTANEITY DERIVATION OF EQUATION ΔG = ΔH – TΔS. SIGNIFICANCE OF THE EQUATION

Q31. Write the concept of maximum work and net work ΔG as criteria for spontaneity ?

Ans : **(Imp.)**

The sum total of the entropy change of the system and the surroundings (*viz*., $\Delta S_{sys} + \Delta S_{sur}$) serves as a criterion of spontaneity or feasibility of a process. If the total entropy change is positive, the process is feasible. If it is zero, the system remains in a state of equilibrium.

The process is carried out reversibly, w represents the maximum work. It is thus clear that decrease in the function a (i.e., – ΔA) gives the maximum work that can be done by the system during the given change. The function A is, therefore, termed as the work function. This is also referred to as Helmholtz free energy or the Helmholtz function.

If G_1, H_1 and S_1 represent the thermodynamic functions for the system in the initial sate and G_2, H_2 and S_2 in the final state, the temperature remaining constant at T all along, we have.

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $$\Delta G = \Delta H - T\Delta S \quad \text{... (1)}$$

$$\Delta H = \Delta U + P\Delta V$$

$\therefore$ $$\Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{... (2)}$$

Comparing with equation

$$\Delta G = \Delta A + P\Delta V \quad \text{... (3)}$$

Since ΔA is equal to – w

$$\Delta G = -w + P\Delta V \quad \text{... (4)}$$

or $$-\Delta G = -w - P\Delta V \quad \text{... (5)}$$

The quantity PΔV is the work done by the gas on expansion against the constant external pressure P. Therefore, –ΔG gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the net work. Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \quad \text{... (6)}$$

Hence, – ΔG is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the Gibbs function or gibbs free energy or merely as free energy. thus, – ΔG is a measure of the decrease in free energy.

Q32. Derive the equation $\Delta G = \Delta H - T\Delta S$ and write its significance.

Ans : **(Imp.)**

The Gibbs - Helmhotz Equation

Let G_1, represent the free energy of a system in its initial state at temperature T. Suppose the temperature rises to T + dT where dT is infinitesimally small. Let the free energy at the new temperature be $G_1 + dG_1$.

When the system is in its final state, its free energy is given by G_2 at the temperature T and by $G_2 + dG_2$ at the temperature T + dT. If the pressure remains constant all along, equation is applicable, i.e.,

$$dG_1 = -S_1 dT$$

and

$$dG_2 = -S_2 dT$$

where S_1 and S_2 are the entropies of the system in the initial and final states of the system, respectively

Subtracting Equation, from Equation, we have

$$d(G_2 - G_1) = -(S_2 - S_1)\,dT$$

$$d(\Delta G) = -\Delta S dT$$

As the pressure is constant, therefore,

$$\left(\frac{\partial(\Delta G)}{\partial T}\right) = -\Delta S$$

Also, since from equation

$$-\Delta S = \frac{\Delta G - \Delta H}{T}$$

Hence, equation becomes

$$\frac{\Delta G - \Delta H}{T} = \left(\frac{\partial(\Delta G)}{\partial T}\right)$$

or

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

This equation is known as the Gibbs-Helmholtz equation. It is applicable to all processes occurring at constant pressure. It has been used for calculating the heat change ΔH for a process or a reaction taking place at constant pressure, provided the values of free energy change at two different temperatures are known.

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta U + T\left(\frac{\partial(\Delta A)}{\partial T}\right)_V$$

3.18 GIBBS EQUATIONS AND MAXWELL RELATIONS, VARIATION OF G WITH P, V AND T

Q33. Write the maxwell relations with Gibbs equation.

Ans : **(Imp.)**

Maxwell's Relationships

The various expressions connecting internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G), with relevant parameters such as entropy, pressure, temperature and volume, may be put as

(i) $dU = TdS - PdV$

(ii) $dH = TdS + VdP$

(iii) $dA = -SdT - PdV$

(iv) $dG = -SdT + VdP$

$H = U + PV$ $\qquad$ $A = U - TS$

$\therefore \quad dH = dU + PdV + VdP$ $\qquad$ $\therefore \; dA = dU - TdS - SdT$

From Ist law of thermodynamics $\qquad$ $= dU - dq - SdT$

$= dU + PdV = dq$ $\qquad$ $= -PdV - SdT$

$= dq + VdP$

$= TdS + VdP$

If V is constant so that dV is zero, then, Equation (i) yields the result

$$(\partial U/\partial S)_V = T$$

If S is constant so that dS is zero, then equation (i) yields the result

$$(\partial U/\partial V)_S = -P$$

Differentiating equation with respect to V keeping S constant, and differentiating equation with respect to S keeping V constant, we get

$$\frac{\partial^2 U}{(\partial S)(\partial V)} = \left(\frac{\partial T}{\partial V}\right)$$

and $$\frac{\partial^2 U}{(\partial V)(\partial S)} = -\left(\frac{\partial P}{\partial S}\right)_V$$

It follows from equation and that

$$(\partial T/\partial V)_S = -(\partial P/\partial S)_V$$

Following the same mathematical procedure as above, the following expressions can be easily derived:

$(\partial T/\partial P)_S = (\partial V/\partial S)_P$ from (ii)

$(\partial S/\partial V)_T = (\partial P/\partial T)_V$ from (iii)

$(\partial S/\partial P)_S = -(\partial V/\partial T)_P$ from (iv)

Equation 10 to 11 are known as Maxwell's relationships.

Another set of Maxwell's relationships, which can also be derived from equations (i) to (iv), are as follows:

$(\partial U/\partial S)_V = (\partial H/\partial S)_P$ from (i) and (ii)

$(\partial U/\partial V)_S = (\partial A/\partial V)_T$ from (i) and (iii)

$(\partial H/\partial P)_S = (\partial G/\partial P)_T$ from (ii) and (iv)

$(\partial A/\partial T)_V = (\partial G/\partial P)_P$ from (ii) and (iv)

OR

According to Euler's reciprocity rule dZ = Mdx + Ndy

$$\left(\frac{\partial M}{\partial x}\right)_y = \left(\frac{\partial N}{\partial y}\right)_x$$

(i) dU = TdS – PdV

M = T; x = S, N = –P, y = V

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(ii) dH = TdS + VdP

M = T; x = S, N = V, y = P

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(iii) dA = –SdT – PdV

M = –S ; x = T, N = –P, y = V

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(iv) dG = –SdT + VdP

M = –S ; x = T, N = V, y = P

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Q34. Explain the variation of G with P, V and T.

Ans :

Variation of Free Energy Change with Temperature and Pressure

The variation of free energy change with variation of temperature and pressure may now be considered. According to Equation

$$G = H - TS$$

Since $H = U + PV$

$\therefore \quad G = U + PV - TS$

Upon differentiation,

$$dG = dU + PdV + VdP - TdS - SdT$$

The first law equation for an infinitesimal change may be written as

$$dq = dU - dw$$

If the work done is only due to expansion, then, $-dw = PdV$

$\therefore \quad dq = dU + PdV$

For a reversible process,

$$dS = dq/T$$

or $\quad TdS = dq = dU + PdV$

Combining Equation and, we have

$$dG = VdP - SdT$$

This equation gives change of free energy when a system undergoes, reversibly, a change of pressure as well as change of temperature.

If pressure remains constant, i.e., $dP = 0$, then, from equation

$$dG = -SdT$$

or $\quad (\partial G/\partial T)_T = -S$

On the other hand, if temperature remains constant, i.e., $dT = 0$, then, from equation.

$$dG = VdP$$

or $\quad (\partial G/\partial P)_T = V$

Let the free energy of a system be G_1 in the initial state and G_2 in the final state when an appreciable change in pressure has taken place, at constant temperature. Then, integrating equation, the free energy change, ΔG, is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP$$

where P_1 and P_2 ar the initial and final pressures, respectively.

If one mole of an ideal gas is under consideration, then $PV = RT$.

$$\therefore \quad \Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2}$$

Where V_1 and V_2 are the initial and final volumes, respectively.

For n moles of the gas,

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln (V_1 / V_2)$$

Short Question & Answers

1. Define system and surroundings.

Ans :

Any specified portion of matter under study is known as system. It may be as simple as water in a beaker or as complex as the water of a polluted lake.

The remaining portion of the universe excluding the system is called surroundings.

2. State the first law of thermodynamics.

Ans :

The first law of thermodynamics is simply the law of conservation of energy which states that “energy can neither be created nor destroyed although it can be converted from one form to another”.

3. What are intensive and extensive properties of a system?

Ans :

A property that depends upon the quantity of the substance or substances present in the system is called the capacity or extensive property. The common examples of these properties are mass, volume, energy, heat capacity, etc. The extensive properties are additive, i.e., the total value of an extensive property is equal to the sum of the values for the separate parts into which the system may be divided.

A property which depends only upon the nature of the substance and not on the amount (s) of the substance (s) present in the system is known as intensity or intensive property. The common examples of these proprieties are temperature, pressure, concentration, refractive index, viscosity, density, surface tension, specific heat etc.

4. Define enthalpy and write its units?

Ans :

The enthalpy or heat content (H) of a substance or a system is the total amount of energy stored in that substance or the system.

The process where $H_2 > H_1$, i.e., in exothermic process, ΔH is negative; while the process where $H_2 < H_1$, i.e., in which heat is absorbed (endothermic process), ΔH is positive. The units of ΔH are kilocalories (kcal) or kilojoules (kJ).

5. What is heat capacity.

Ans :

Heat capacity of a system means the capacity to absorb heat and store energy. If Q calories is the heat absorbed by a system and the temperature rises from T_1 to T_2, then the heat capacity (C) of the system is given by the expression.

$$C = \frac{Q}{(T_2 - T_1)} = \frac{Q}{\Delta T}$$

6. What is Adiabatic process

Ans :

A process during which no heat enters or leaves the system during any step of the process is known as **adiabatic process.** In this process since, no heat enters or leaves the system, the temperature will decrease or increase when the reaction is endothermic and exothermic respectively. Such reactions (processes) are often carried out in closed insulated containers such as thermos bottle.

For an adiabatic process, change in heat (δq) = 0.

7. What joule - Thompson effect.

Ans :

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the Joule-Thompson effect.

8. What is Joule-Thompson coefficient

Ans :

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H$$

Thus Joule-Thompson coefficient may be defined as the change in the number of degrees of temperature produced by a drop of one atmospheric pressure when the gas expands under conditions of constant enthalpy.

9. Give Kirchoff's reaction.

Ans :

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p . dT$$

or $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

where ΔC_p has been assumed to be constant in the temperature range $T_1 \rightarrow T_2$.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta Cp$$

10. Give the expression for the efficiency of reversible heat engines working between the temperatures between T_2 and T_1.

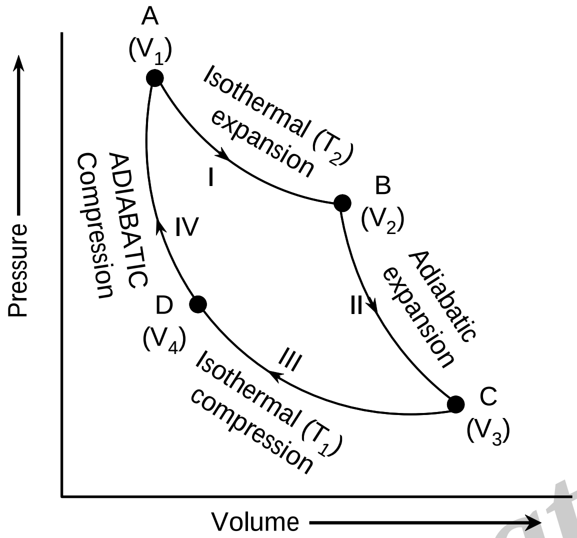
Ans :

The fraction of the heat absorbed by a machine that it can transform into work is called the efficiency of the machine. Thus if Q is the heat absorbed and W is the work done, then the efficiency (η) of the machine is given by

$$\eta = \frac{W}{Q}$$

11. Draw the carnot cycle.

Ans :



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12. Write the Maxwell's Relationships.

Ans :

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V$$

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P$$

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V$$

$$(\partial S / \partial P)_S = -(\partial V / \partial T)_P$$

Choose the Correct Answer

1. The process in which heat is neither allowed to enter nor allowed to leave the system but in which temperature changes is known as [c]

   (a) isothermal (b) isochoric

   (c) adiabatic (d) isobaric

2. In isothermal change the factor that is constant is [b]

   (a) volume (b) temperature

   (c) pressure (d) weight

3. A system which can change neither mass nor energy with the surroundings is called [c]

   (a) open system (b) closed system

   (c) isolated system (d) isothermal system

4. The Joule-Thomson expansion of an ideal gas is an [b]

   (a) isothermal process (b) isochoric process

   (c) isoenthalpic process (d) isobaric process

5. Two moles of an ideal gas expand spontaneously into a vacuum. The work done is [d]

   (a) 2 J (b) 4 J

   (c) infinity (d) zero

6. For an ideal gas at consant temperature. C_v is [c]

   (a) dependent of P (b) dependent on V

   (c) independent on P (d) none of the three

7. For an ideas gas at constant temperature. C_p is [c]

   (a) dependent on V (b) dependent on P

   (c) independent on P (d) none of the three

8. Which of the following is (are) correct ? [b, c]

   (a) $C_p = \left(\frac{\delta E}{\delta T}\right)_p$

   (b) $dE = \delta Q - P\,dV$

   (c) $PV^{\gamma} =$ constant for a reversible adiabatic expansion of an ideal gas

   (d) $W_{max} = 2.303\, nRT \log \frac{V_1}{V_2}$ for a reversible isothermal expansion of an ideal gas

9. When a gas at high pressure expands into a region of low pressure, its temperature [c]
   - (a) increases
   - (b) decreases
   - (c) increases in some cases and decreases in others
   - (d) remains constant

10. In an exothermic reaction, heat is [c]
    - (a) absorbed
    - (b) converted into electricity
    - (c) evolved
    - (d) converted into mechanical work

11. In exothermic reaction [b]
    - (a) $H_R = H_P$
    - (b) $H_R > H_P$
    - (c) $H_R < H_P$
    - (b) $H_R = H_P$

12. Entropy in universe [a]
    - (a) Increases to maximum
    - (b) Decreases to lowest
    - (c) No change

13. When the entropy is maximum the work done by the system is [b]
    - (a) maximum
    - (b) least
    - (c) intermediate

14. The measures of unavailable energy and the extent of disorder is given by [b]
    - (a) enthalpy
    - (b) entropy
    - (c) energy of the system
    - (d) pressure of the system

15. The heat content of a system is called [b]
    - (a) enthalpy
    - (b) free energy
    - (c) internal energy
    - (d) work function

16. In which of the following, $\Delta H = \Delta E$ [a]
    - (a) $N_2 + O_2 \longrightarrow 2NO$
    - (b) $N_2 + 3H_2 \longrightarrow 2NH_3$
    - (c) $PCl_5 \longrightarrow PCl_3 + Cl_2$

17. In isothermal expansion for the ideal gas [a]
    - (a) ΔH and ΔE are positive
    - (b) ΔH and ΔE are negative
    - (c) ΔH are positive and ΔE are positive
    - (d) ΔH are ΔE are zero

Fill in the blanks

1. Work done in isothermal reversible expansion is ________.
2. Maxwell relationship for $dH = TdS + VdP$ is ________.
3. Gibbs Helmholtz equation is ________.
4. Entropy change of mixing of ideal gases is ________.
5. Joule thompsom coefficient μ_{JT} ________.
6. Work obtained in isothermal reversible expansion of an ideal gas is ________ than that in adiabatic expansion.
7. Work of expansion is given by the expression ________.
8. The value of C_p is ________ than C_v.
9. In Joules-Thomson effect gas is allowed to expand ________ from a high pressure to a low pressure.
10. The mathematical formulation of the first law of thermodynamics involving very small changes is written as ________.
11. In an endothermic reaction, enthalpy of the product(s) is ________ than that of reactants and hence ΔH is ________.
12. Gibbs HelmhoHz equation ________.
13. Entropy $\Delta S =$ ________.
14. $\Delta S_{8ys} + \Delta S_{ys} > 0$ is a ________.
15. For equilibrium process $\Delta S =$ ________.
16. Entropy is a ________.

ANSWERS

1. $-2.303\ nRT \log V_2/V_1$
2. $(\partial T / \partial P)_S = (\partial V / \partial S)_P$
3. $\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$
4. $\Delta S_{mix} = -R\ \Sigma x_i \ln x_i$
5. $\mu = \left(\frac{\delta T}{\delta P}\right)_H$
6. greater
7. $P\ \Delta V$
8. greater
9. adiabatically
10. $dE = \delta Q - \delta W$
11. greater, positive
12. $\Delta S = \Delta H - T\Delta S$
13. $\frac{\Delta qre\gamma}{T}$
14. Irrerersible process
15. Zero
16. Measure of disorder

UNIT - IV

(General Chemistry)

S3-G-1 Evaluation of analytical data

Significant figures, accuracy and precision. Errors-classification of errors- determinate and indeterminate errors, absolute and relative errors. Problems based on mean, median, range, standard deviation

S3-G-2: Carbanions-I

Introduction, acidic nature of a-hydrogens and tautomerism in carbonyl compounds, nitro hydrocarbons, ethyl acetoacetate, diethyl malonate. Terminal alkynes. Stabilty of carbanions Reactions : Aldol reaction, Perkin reaction, Benzoin condensation, haloform reaction, conversion of smaller alkynes to higher alkynes.

S3-G-3: Phase Rule

Statement and meaning of the terms – Phase, Component and Degrees of freedom, Gibb's Phase rule, phase equilibria of one component system – water system. Phase equilibria of two-component system – Solid-Liquid equilibria, simple eutectic – Pb-Ag system, desilverisation of lead. Solid solutions – compound with congruent melting point – (Mg-Zn) system and incongruent melting point – (NaCl-H_2O) system.

S3-G-1: EVALUATION OF ANALYTICAL DATA

4.1 SIGNIFICANT FIGURES, ACCURACY AND PRECISION

Q1. Define the following terms

(i) Significant figures

(ii) Accuracy

(iii) Precision

Ans : **(Imp.)**

(i) Significant Figures

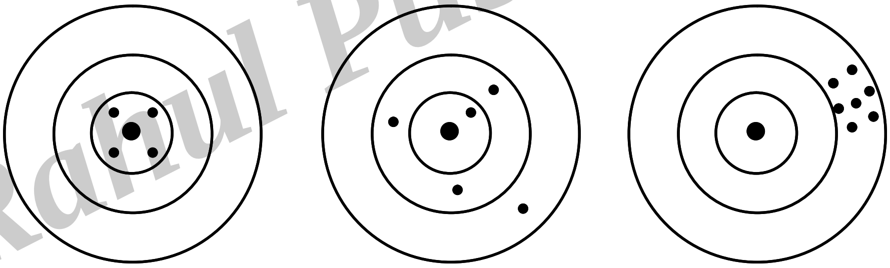
Significant figures are the total number of digits in a number including the last digit whose value is uncertain. **Example:** 876 m has 3 significant figures.

(ii) Accuracy

The closeness to true value is called accuracy. If the average value of different measurements is close to true value, the measurements is said to be accurate.

(iii) Precision

It refers to the closeness of various measurements for the same quantity. If the values of different measurements are close to each other and hence close to their average value, the measurement is said to be precise the precision depends upon the measuring device as well as the skill of the operator.



I
More accuracy
More precision

II
Not accurate
Not Precision

III
More precision
Less accurate

Q2. Write the rule for determining the number of significant figures.

Ans :

(a) All non-zero digits and zeros between non-zero digits are significant.

Example: 876 m has 3 significant figures.

4006 g has 4 significant figures.

(b) Zeros to the left of the first non-zero digit in a number are not significant.

Example: 0.04 m has one significant figure

0.0063 kg has 2 significant figure.

(c) If a number ends in zeros but these zeros are to the right of decimal point, then these zeros are significant.

Example: 6.0 m has 2 significant figure

5.400 g has 4 significant figure.

(d) Zeros at the end or right of a number are significant provided they are on the right side of decimal point, otherwise the zeros are not significant.

Example: 0.400 g has 3 significant figure

200 g has 1 significant figure.

4.2 Errors-classification of Errors - Determinate and Indeterminate Errors, Absolute and Relative Errors

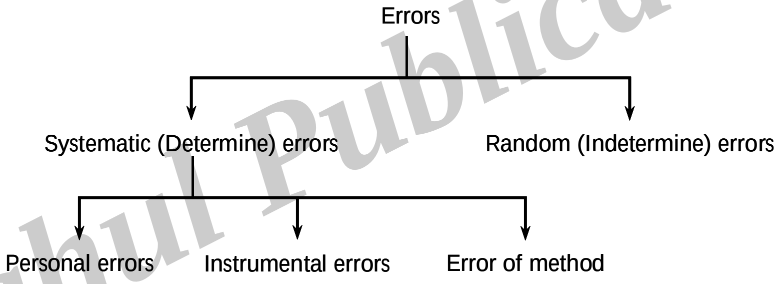
Q3. What are errors? Give the classification of errors.

Ans : **(Imp.)**

Errors

Every scientific measurement will have some uncertainty. This uncertainty is called errors:

Classifications



Figure

(i) **Systematic Errors:** It causes the mean of a set or data to differ from the accepted value. These errors can be avoided. These errors are further classified into 3 types.

- **(a)** **Personal Errors:** These are due to factors for which the individual analyst is responsible and are not connected with the method or procedure. (Error due to negligence of analyst).
- **(b)** **Instrumental errors:** The errors arises due to defect in instrument.
- **(c)** **Error of Method:** The errors arises due to defect in experimental procedure (or) method.

(ii) **Random Errors:** These errors are uncorrectable errors. These are irregular and small. These can be reproduced and accompany every determination. These type of errors are caused by many uncontrollable variables.

Q4. What are absolute and relative errors.

Ans :

Absolute Errors

The absolute error of a measurement is the difference between the measured value and the true value.

$E = x_i - x_t$ E = Absolute error

x_i = Measured value

x_t = True value

Relative Errors

The relative error of a measurement is the absolute error divided by the true value.

$$E_R = \frac{x_i - x_t}{x_i}$$

4.3 PROBLEMS BASED ON MEAN, MEDIAN, RANGE, STANDARD DEVIATION

Q5. Explain the following terms.

(a) Mean

(b) Median

(c) Standard deviation

Ans :

(a) Mean

It is the numerical value obtained by dividing the sum of a set of measurements by the number of individual results in the set.

$$\bar{x} = \frac{x_1 + x_2 + x_3 + ...}{N}$$

N = total number of measurements

(or)

$$\bar{x} = \sum_{i=1}^{N} \frac{x_i}{N}$$

(b) Median

The median is a value about which all the other values are equally distributed. Scientific measurements even, average of middle two numbers (If data in ascending or decsending order is median). If scientific measurement is odd, middle number is median.

(c) Standard Deviation (SD) : ($\bar{d}$)

Measure of precision is standard deviation.

$$\bar{d} = \frac{\Sigma|x_i - x_t|}{N}$$

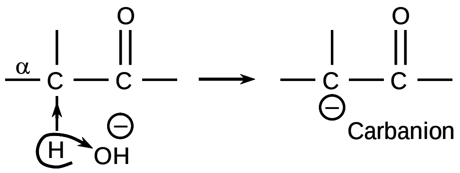
S3-G-2: CARBANIONS-I

4.4 INTRODUCTION, ACIDIC NATURE OF α-HYDROGENS AND TAUTOMERISM IN CARBONYL COMPOUNDS, NITRO HYDROCARBONS, ETHYL ACETOACETATE, DIETHYL MALONATE. TERMINAL ALKYNES

Q6. Explain the acidity of α-hydrogen atoms in carbonyl compounds.

Ans : **(Imp.)**

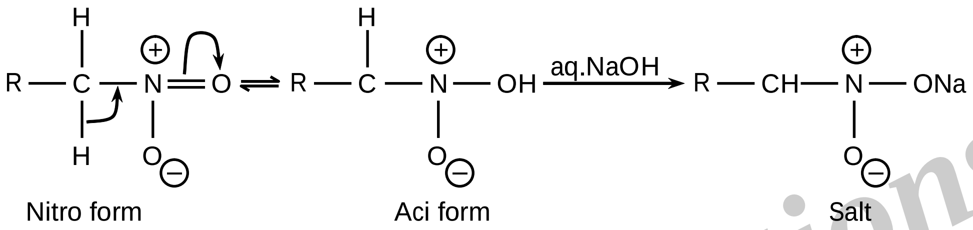
The carboxyl carbon is positive and therefore attracts the electrons in the single bond shared with α - carbon. The α-carbon in turn pulls the electrons towards it the electrons in the next single bond joining hydrogen. Hence carbon - hydrogen bond weakness and α - hydrogen atom splits as proton in the presence of strong base reagents.



The removal of proton gives carbanion which is stabilized by resonance. The carbanion they produced is a good nucleophile and can attack carbonyl group of another molecule.

Q7. Explain the acidic nature of nitro hydrocarbons.

Ans :

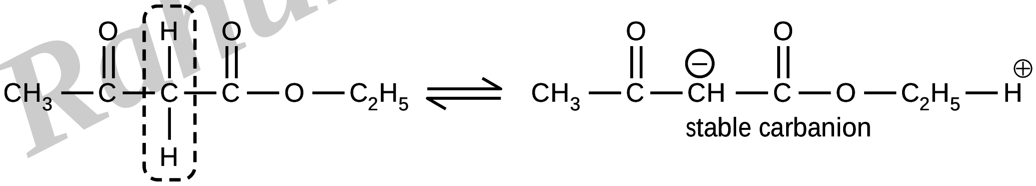


In this nitro from more acidic in nature, Aci form is less acidic. Therefore these are called pseudo acids.

Q8. Discuss in detail the acidic nature of α-hydrogens in ethylaceto acetate and diethyl malonate.

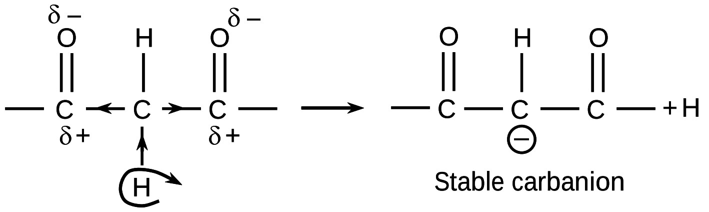
Ans :

Ethyl aceto acetate contains methylene (– CH_2–) group attached by two carbonyl groups the C – H bond in CH_2 group is readily ionisbale because the proton removal forms a very stable carbanion.

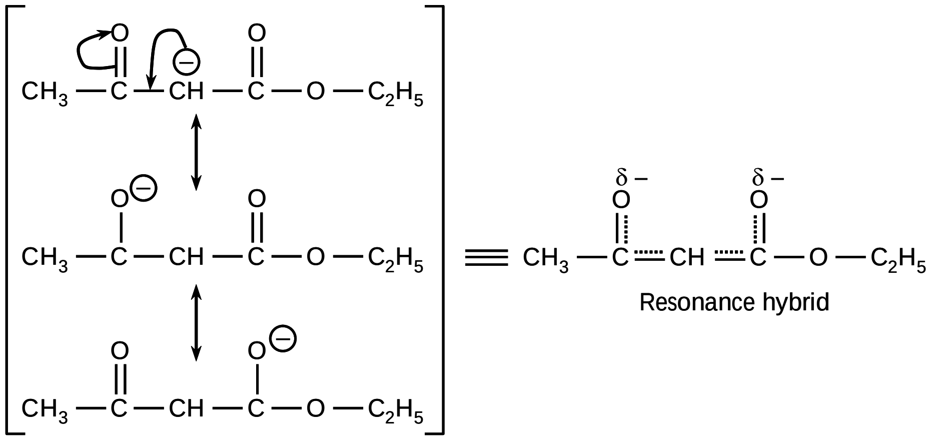


The acidity of the C – H bond of methylene group is explained by two factors.

(i) Inductive effect: Electronegativity of oxygen in the carbonyl group is high. The inductive effect caused by the electron attracting power of the electronegative oxygen atoms if the two carbonyls weakens the C – H bonds. Thus the hydrogen atom can dissocaite to give a stable anion.

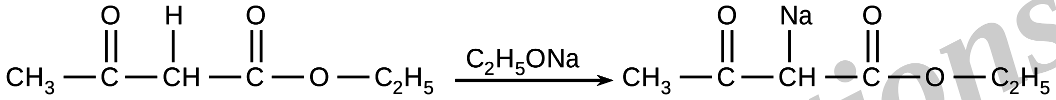


(ii) Resonance Stabilization of Carbanion: The acidity of the C – H bond is enhanced because the negative charge in the carbanion is delocalized into the two carbonyls by resonance. The highly resonance stabilitised carbanion may be represented as,



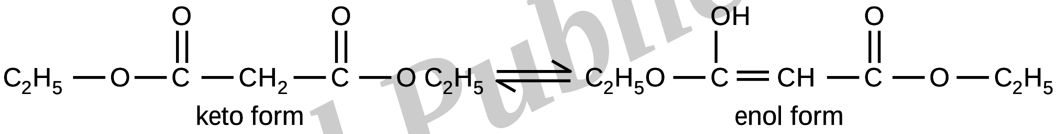
Resonance hybrid

Ethyl aceto acetate is fairly acidic. When it is treated with strong base like sodium ethoxide, its sodium salt is formed.



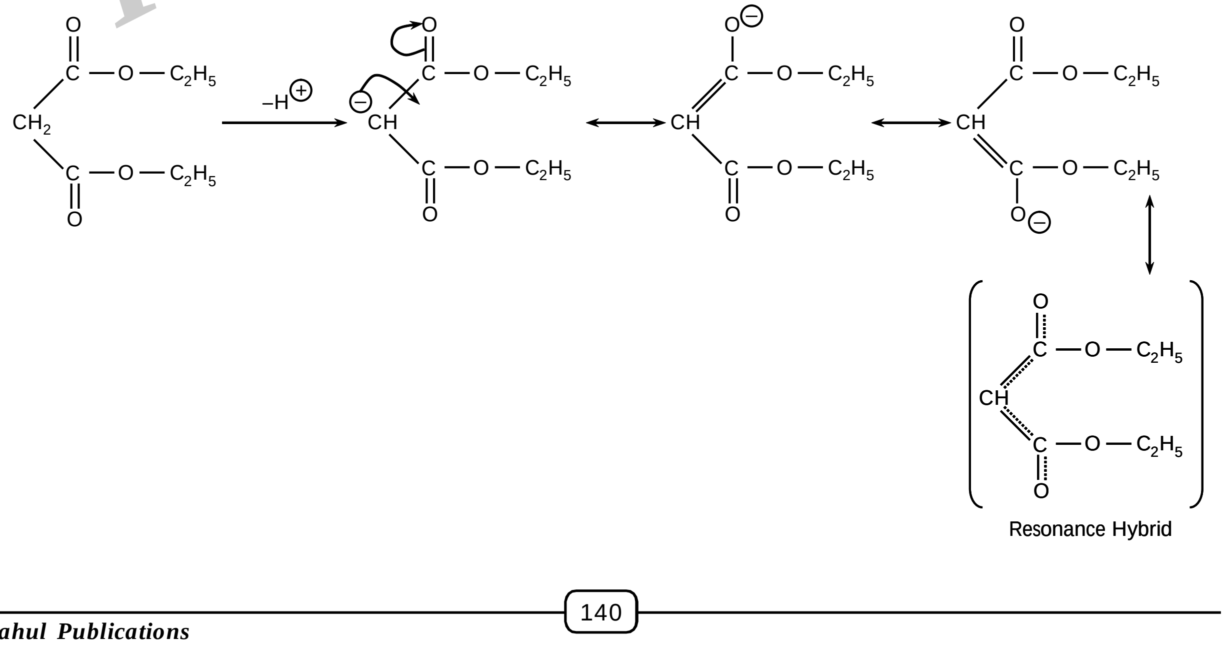
$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-\overset{Na}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

Just like ethyl aceto acetate, diethyl malonate is also having active methylene group. Hence it exist as tautomeric mixture of keto and enol forms.



$$C_2H_5-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons C_2H_5O-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

The ‘α’ – hydrogens in active methylene group are having acidity. Hence these hydrogens can be substituted by active metals like Na, K and alkyl groups. When the hydrogens between two $-\overset{O}{\overset{\|}{C}}-$ groups is dissociated as proton the carbanion formed gets stability due to resonance.



Resonance Hybrid

Q9. Explain the acidic nature of terminal alkynes.

Ans :

When terminal alkynes containing $\equiv CH$ group are passed into liquid ammonia the amide ions accepts hydrogens in 1 – alkyne as proton. Hence terminal alkynes are housing acidity. The hybridisation of carbon in alkynes is sp : s - nature of sp hybrid carbon is greater. Therefore it attracts C – H bond pair electrons. Then hydrogen dissociates as proton that is why those hydrogens can be substituted by metals.

Examples

1. Terminal alkynes react with Na in liquid ammonia as solvent sodium alkynide is formed.

$$2R-C\equiv CH + 2\,Na \xrightarrow{liq\ NH_3} 2R-C\equiv CNa + H_2$$

2. Terminal alkynes react with NaOBr to form the corresponding mono bromo derivatives.

$$R-C\equiv CH + NaOBr \longrightarrow R-C\equiv C-Br + NaOH$$

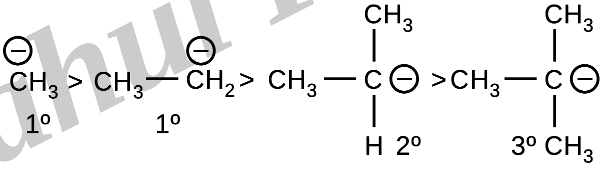
4.5 STABILTY OF CARBANIONS

Q10. Explain the stability of carbanions.

Ans :

Carbanions are classified into 1°, 2° and 3° depending upon the nature of carbon bearing the negative charge. Electron releasing groups render carbanion less stable, because they increase the negative charge on carbon. Electron withdrawing groups make the carbanion more stable due to partial neutralization of the charge. Primary (1°) Carbanion is more stable than secondary (2°) which in turn is more stable than tertiary (3°) one.

Example:



$$\underset{1^o}{\overset{\ominus}{C}H_3} > \underset{1^o}{CH_3-\overset{\ominus}{C}H_2} > \underset{2^o}{CH_3-\overset{CH_3}{\underset{H}{|}}{C}^{\ominus}} > \underset{3^o}{CH_3-\overset{CH_3}{\underset{CH_3}{|}}{C}^{\ominus}}$$

1°>2°>3°

Electron with drawing groups (– I groups – $C\equiv N$, $-NO_2$. Br etc) increase the stability of carbanions.

4.6 REACTIONS : ALDOL REACTION, PERKIN REACTION, BENZOIN CONDENSATION, HALOFORM REACTION

Q11. Explain the mechanism of following reactions.

(i) Aldol condensation

(ii) Benzoin condensation

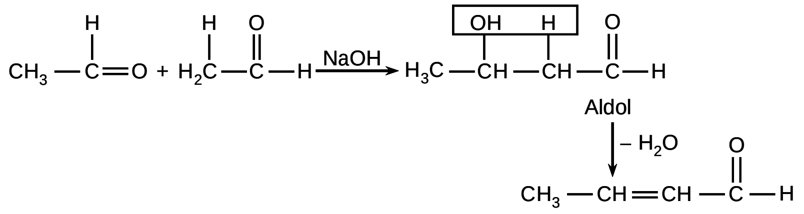
Ans : **(Imp.)**

(i) Aldol Condensation

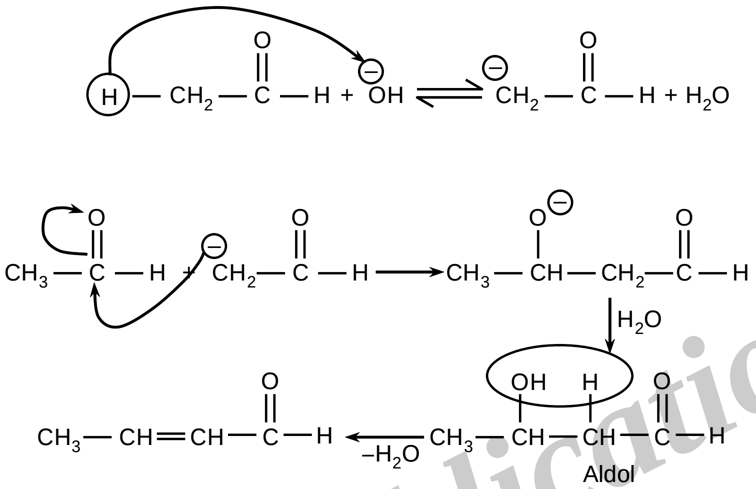
Two moles of carbonyl compound having atleast one 'α' hydrogen on reaction with alkali converted to 'aldol' which is a β-hydroxy carbonyl compound.

Aldol on dehydration converted to α, β unsaturated carbonyl compound.

Example:

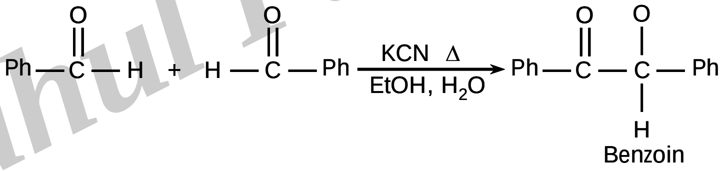


Mechanism

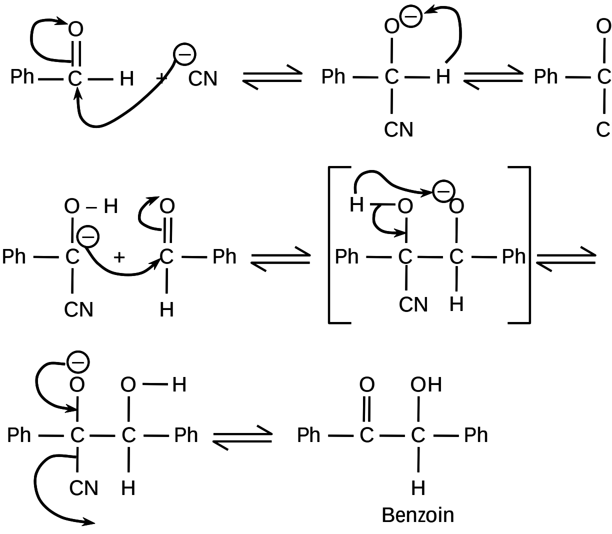


ii) Benzoin Condensation

Two moles of aromatic aldehyde on reaction with KCN gives benzoin, which is an α-hydroxy ketone.



Mechanism



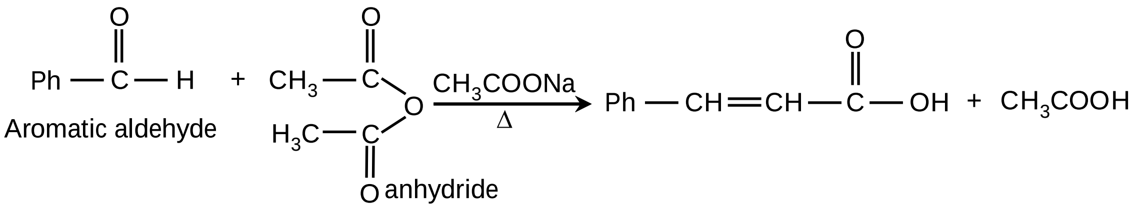
Q12. Explain the mechanism or (i) Perkin reaction (ii) Haloform reaction.

Ans : **(Imp.)**

(i) Perkin Reaction

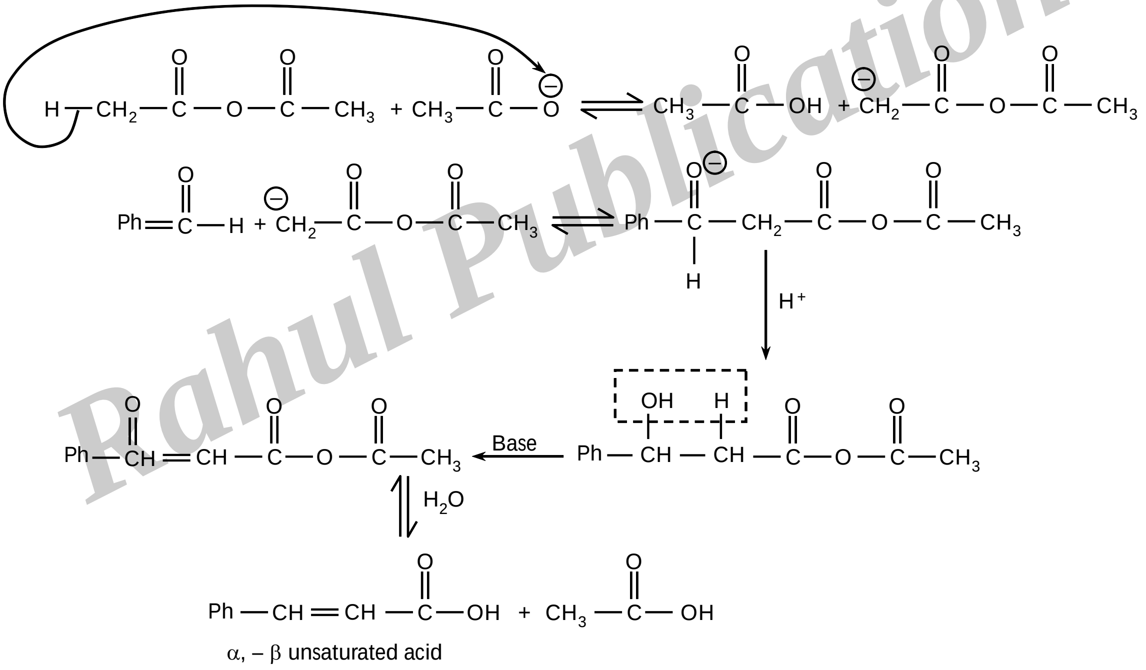
The reaction of an aromatic aldehyde with an aliphatic acid anhydride in presence of sodium or potassium salt of the acid corresponding to anhydride to give an α, β – unsaturated acid is known as perkin reaction.

Example:

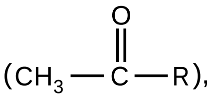
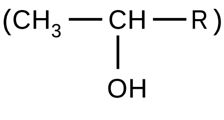


$$Ph-\overset{O}{\overset{\|}{C}}-H + (CH_3CO)_2O \xrightarrow[\Delta]{CH_3COONa} Ph-CH=CH-\overset{O}{\overset{\|}{C}}-OH + CH_3COOH$$

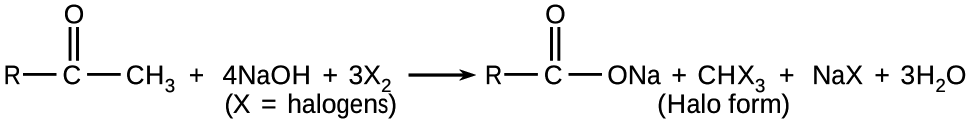
Mechanism



(ii) Haloform Reaction

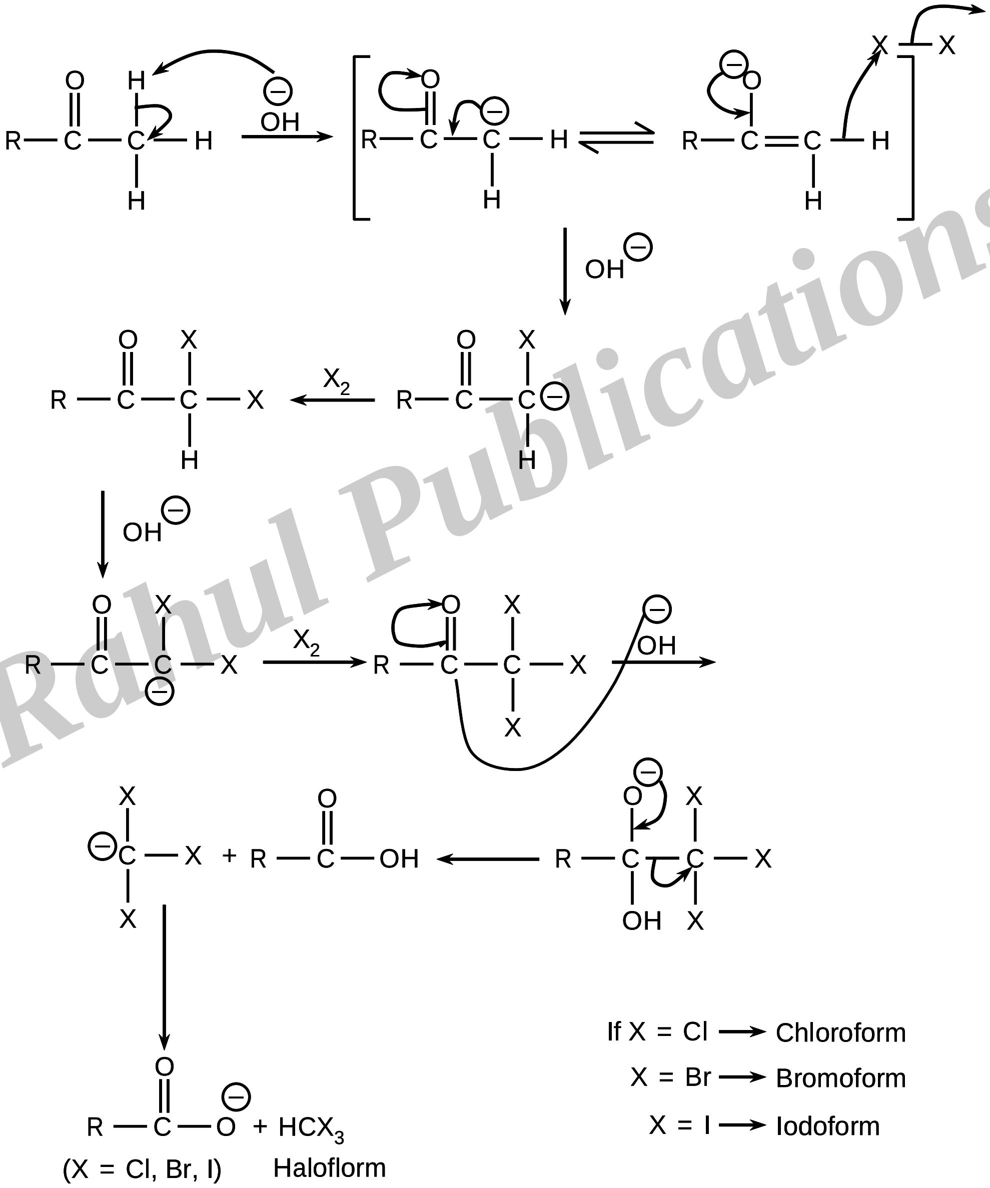
The reaction consists in the cleavage of methyl ketones ( $CH_3-\overset{O}{\overset{\|}{C}}-R$), acetaldehyde, ethanol and secondary methyl carbinols ( $CH_3-\underset{OH}{\underset{|}{CH}}-R$) with halogens and base to give haloforms and salt of carboxylic acid.

Example



$$R-\overset{\overset{\large O}{\|}}{C}-CH_3 + \underset{(X\ =\ \text{halogens})}{4NaOH + 3X_2} \longrightarrow R-\overset{\overset{\large O}{\|}}{C}-ONa + \underset{\text{(Halo form)}}{CHX_3} + NaX + 3H_2O$$

Mechanism



If X = Cl ⟶ Chloroform
X = Br ⟶ Bromoform
X = I ⟶ Iodoform

4.7 CONVERSION OF SMALLER ALKYNES TO HIGHER ALKYNES

Q13. How can you prepare higher alkynes from smaller alkynes?

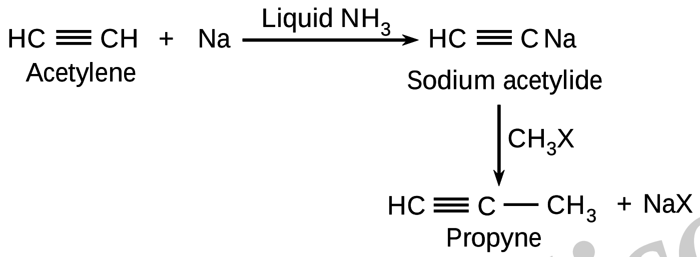
Ans :

(i) From acetylene, Terminal Alkynes

First Acetylene, terminal alkynes can be converted into metal acetylides (or) metal alkynides respectively by treating with sodium in liquid ammonia (or) sodamide the sodium salt thus obtained is treated with an alkyl halide then an higher alkyne is formed.

Example

1.



2.

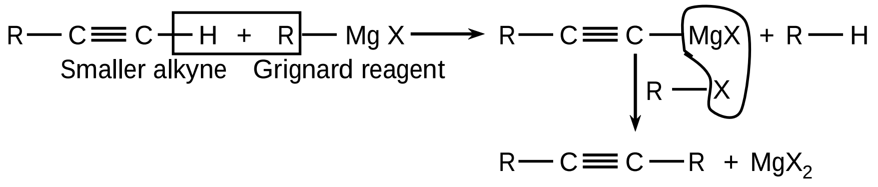
$$\underset{\text{Smaller alkyne}}{R-C\equiv CH} + Na \xrightarrow{\text{Liquid } NH_3} R-C\equiv CNa \xrightarrow{CH_3I} \underset{\text{Higher alkyne}}{R-C\equiv C-CH_3} + NaI$$

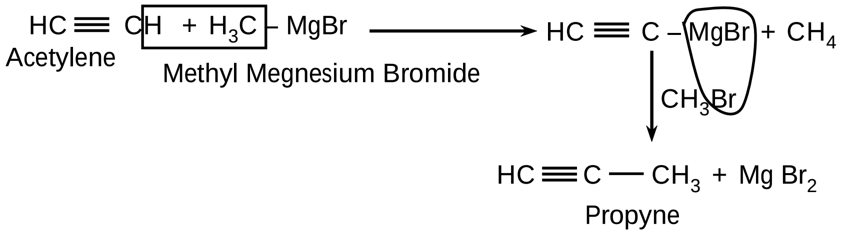
(ii) From grignard reagents

Grignard reagent on treatment with lower alkynes and subsequent treatment with an alkyl halide give higher alkynes.

Example

i)





S3-G-3: PHASE RULE

4.8 STATEMENT AND MEANING OF THE TERMS – PHASE, COMPONENT AND DEGREES OF FREEDOM, GIBB'S PHASE RULE, PHASE EQUILIBRIA OF ONE COMPONENT SYSTEM – WATER SYSTEM

Q14. Explain the terms in phase rule.

Ans :

Definition of The Terms Used in Phase Rule

1. **Phases**

Any heterogeneous system consists of two or more homogeneous parts which are separated from each other by bonding surfaces.

"These homogeneous parts of a heterogeneous system in equilibrium, which are physically distinct and mechanically separable are termed as phases," e.g., in the freezing water system we have three phases, viz., ice (solid), water (liquid) and vapour (gas) in equilibrium.

When calcium carbonate is heated, it decomposes giving calcium oxide and carbon dioxide.

$$\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{CO_2}$$

At the equilibrium we have two solid phases, viz., calcium carbonate and calcium oxide and one gaseous phase viz. carbon dioxide.

2. **Components**

"The minimum number of independently variable constituents by means of which the composition of each phase present in the system can be expressed either directly or in the form of a chemical equation in which zero or negative values are permissible.

Water system has three phases, viz. ice (solid), water (liquid) and water vapour (gaseous). The composition of all the three phases is expressed in terms of only one chemical compound, H_2O. Thus water system has only one component.

3. **Degree of Freedom or Variance**

The minimum number of the variable factors, such as temperature, pressure and composition of the phases which must be arbitrarily fixed in order to define condition of the system completely is termed as degree of freedom of the system. A mixture containing 40% CO_2 and 60% N_2 at 25°C and 760 mm pressure is perfectly defined. Thus a mixture of gases, is a system with three degree of freedom, i.e., it is trivariant.

$$F = C - P + 2$$
$$= 2 - 1 + 2 = 3$$

4. **Equilibrium**

A system is said to be in equilibrium if the properties like temperature, composition etc., of the various phases do not undergo any change with time. This equilibrium may be of two types namely true equilibrium and metastable equilibrium.

In a system, when the same state can be attained by approach from either direction, then this state is called true equilibrium, e.g., the state of ice and water at 1 atm pressure and 0°C. Water at – 4°C can be obtained by fusion of ice but it can be obtained by careful cooling of water. This state of water at – 4°C is called as state of metastable equilibrium.

Q15. Describe the phase rule.

Ans :

The Phase Rule

For the study of the behaviour of the heterogeneous systems an important generalization was put forward by American Physicist Willard Gibbs in 1874. This generalizations commonly known as ‘phase rule’ is applicable to all heterogeneous systems in equilibrium without any exception. This rule cannot be expressed on hypothetical assumptions. This rule cannot be expressed in words. However, it may be stated mathematically as follows:

$$F = C - P + 2$$

where, F is the number of degree of freedom, C is the number of component and P is the phases of the system.

Q16. Draw a phase diagram for one component water system. Label it and discuss the importance of various points lines, and areas in equilibrium.

Ans : **(Imp.)**

The Water System

This is the most common example of the one component system, H_2O is the only chemical individual involved in it. The three phases in the system are

$$\underset{\text{(solid)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Liquid)}}{\text{Water}} \rightleftharpoons \underset{\text{(Gaseous)}}{\text{Vapours}}$$

The above three single phases may occur in four possible combinations in equilibrium as follows.

1. Liquid $\rightleftharpoons$ Vapour
2. Liquid $\rightleftharpoons$ Solid
3. Solid $\rightleftharpoons$ Vapour
4. Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

The number of phases that can exist in equilibrium at any time depends upon the condition of pressure and temperature. These conditions have been determined experimentally. After plotting these on graph paper by taking pressure and temperature on appropriate axis we get a phase diagram.

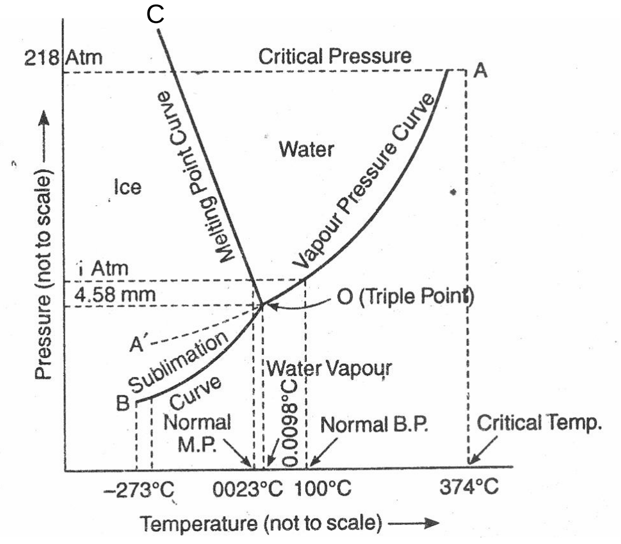


Fig.: Phase Diagram of the Water System

This phase diagram has following parts :

1. The stable curves OA, OB and OC (shown by solid lines)
2. One metastable curve OA (shown by dotted line)
3. Three areas AOC, BOC and AOB
4. Definite point O known as triple point.

Explanation of Curves

1. OA (vapourisation curve) : This is vapour pressure curve of water. It represents the equilibrium between liquid, water and vapour at different temperatures. At every point of the curve, the two phases are present. The starting point of curve, is 0 which is the freezing point of water (0.0098°C at 4.58 mm). This curve ends at A, the critical temperature (374°C at 218 atm) beyond which the two phases merge into each other and thus only one phase is left.

   To define the system completely at any time, it is necessary to mention either pressure or temperature. Thus water vapour system is univariant. It may also be shown by phase rule equation.

$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1$$

2. OA Curve

The dotted curve OA is a continuation of the OA curve and represents the vapour pressure curve of supercooled. This curve is known as metastable curve. When slight disturbance is there, the supercooled phase at once changes to solid ice and the curve merges into OB.

3. OB (the sublimation curve)

It is the vapour pressure curve of ice and gives the various values of temperature and pressure at which ice and vapours can co-exist. It is obtained by studying the effect of pressure on freezing point of water. The curve starts from point O and ends B(– 273°C). For a particular temperature there can be one and only one value of pressure and vice versa, i.e., the system has one degree of freedom.

4. OC (The fusion curve or melting point curve)

The curve shows the equilibrium between ice and liquid water at various pressures. It may be said that it shows the effect of pressure on the melting point of ice. This system is univariant system, at any point of the curve two phases are there (ice and water). The univariant nature of the system may also be shown by phase rule equation.

$$F = C - P + 2 \qquad [\because C = 1, P = 2]$$

$$F = 1 - 2 + 2$$

$$F = 1$$

Areas

Pressure and temperature are the two quantities to define the system completely at any point in an area. Thus the system represented by area has two degrees of variance. As discussed above, in water system there are three areas,

1. AOB – vapours of water only
2. BOC – ice only
3. COA – water in liquid form only.

Number of phases = 1 (Vapour of water of ice)

Number of components = 1 (as all the phases can be represented by chemical formula H_2O).

∵ According to phase rule equation,

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

So these areas are bivariant, i.e., for locating any point in these areas, temperature as well as pressure must be fixed.

Triple Point

It is the point where the three curves OA, OB and OC meet together. At this point, all the three phases are in equilibrium. At point O, temperatures and pressure are fixed at 0.0098°C and 4.58 mm respectively. One of the three phases will disappear, when either pressure or temperature is changed. Since on changing either temperature or pressure, one of the phases disappears, the system has zero degree of freedom at the point O. This can be shown by phase rule equation also.

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 \\ &= 0 \qquad (\because C = 1, P = 3)] \end{aligned}$$

At O, $P = 3$ (Ice, Liquid and water vapour)

$C = 1$ (only H_2O can represent all phases)

Concluding the above discussion, the main features of the phase diagram are as under :

System	Phase	Degree of freedom
Curve (OA, OA', OB, OC)	2	1
Areas (AOB, BOC, COA)	1	2
Triple point (O)	3	0

4.9 PHASE EQUILIBRIA OF TWO-COMPONENT SYSTEM – SOLID-LIQUID EQUILIBRIA, SIMPLE EUTECTIC – Pb- Ag SYSTEM, DESILVERISATION OF LEAD

Q17. Apply the phase rule to silver-led system (Ag-Pb) binary alloy system.

Ans : **(Imp.)**

For a solid-liquid equilibrium, the gas phase is usually absent and the effect of pressure on the equilibrium is negligible. When a two-component system consists of solid and liquid phases only, the effect of pressure may be discarded. Such a system where pressure variable is kept constant is called a condensed system and the new phase equation (reduced phase equation).

$F' = C - P + 1$ (Reduced Phase equation).

Silver-Lead System

It is a two component system, the two components being silver and lead. The various possible phases are:

(i) Solid silver,

(ii) Solid lead,

(iii) Solution of silver and lead in molten state (the two metals are completely miscible in molten state), and

(iv) Vapour.

The phase diagram of the system consists of two curves OA and OB, intersecting at point O.

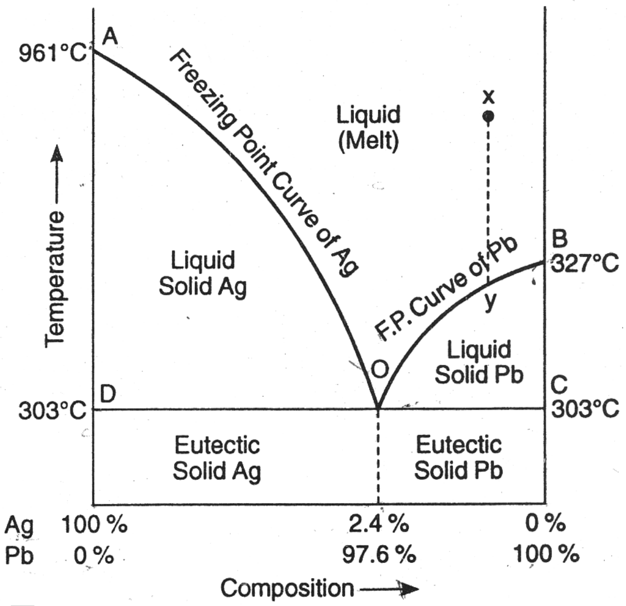


Fig.: Phase Diagram of the Silver-Lead System

Curves (AO and BO)

In the diagram, point A represents the melting point of the pure silver (961°C) and point B that of pure lead (327°C). All the points on the curves AO and BO represents the melting points of various mixtures of silver and lead obtained by the addition of lead to silver (AO curve) or silver to pure lead (BO curve). In other words, curves AO and BO represent the melting point curves of silver and lead respectively. Since addition of metal to another pure metal lowers the melting point of the later, the curves AO and BO are also referred to as the freezing point curves of silver and lead respectively.

All along the curves AO and BO the added metal (Pb in AO and Ag in BO curves) goes into the solution and the separation of the original metal (Ag in AO and Pb in BO curves) occurs till the point O is reached. At the point O no more lead (in case of curve AO) or silver (in case of curve BO) goes into solution because at this point the solution becomes saturated with the added metal and hence the melting point of silver (incase of AO curve) and Pb (in case of BO curve) does not fall further. Thus the point O represents the lowest possible temperature (303° C) in the system and it corresponds to fixed composition have 2.4% Ag and 97.6% Pb. The point O is called the eutectic point.

All along the curves AO and BO, two phases, viz. solid Ag or solid Ag or Pb and melt liquid) of the two metals are present in equilibrium. Therefore, according to reduced phase equation the system along the two curves in univariant.

Eutectic Point O

This is the point where the two curves AO and BO meet together. At this point three phases (solid lead, solid Ag and their liquid solution) co-exist. Therefore, point O has no degree of freedom, i.e., it is invariant. This is also in accordance with the reduced phases equation.

$$F' = C - P + 1$$

$$F' = 2 - 3 + 1 = 0$$

The point O represents the lowest possible temperature (303°C) at which liquid phase can exist and beyond which the liquid phase cannot be enriched in either component by freezing out the other component. Such a point O is called the **eutectic point;** the temperature (303°C) and composition of the components (2.4% Ag^+ 98.6% Pb) corresponding to the eutectic point are called the **eutectic temperature** and **eutectic mixture.** Eutectic mixture may be defined as a liquid mixture of the components which has the lowest freezing point as compared to all other liquid mixtures of the same constituents.

Areas or Regions

There are three regions (i) to (iii) above the line COD; and two regions below the line COD.

(i) The area above the curve AOB. In this region only the liquid alloy (melt of Ag and Pb) exists, i.e., there is only one phase and hence it has two degrees freedom, viz, temperature and composition. For any composition at temperature in this region, we find that the melt of Ag and Pb is stable.

(ii) The area AOD. This region has solid silver and liquid melt. The composition of the liquid melt at any temperature can be obtained from the curve AO.

(iii) The area BOC. This region has solid lead and liquid melt. The composition of the liquid melt at any temperature, can be obtained from the curve OB. Like the AOD, the BOC region also has one degree of freedom (temperature of composition)

(iv) The area DOE and COE. These areas are present below the line COD. Both areas have two phases; viz. solid silver + eutectic in the areas DOE and solid lead + eutectic in the areas COE. Systems in these areas have one degree freedom which is also in accordance with the reduced phase equation.

$$F' = C - P + 1$$

$$= 2 - 2 + 1 = 1$$

Q18. Show how the process of desilversiation of lead by explained with the help of phase rule.

Ans :

Applications of Silver-lead System in the Desilverisation of Lead Patinson's method

Galena (PbS, an ore of lead) is usually associated with silver. During the extraction of lead from galena, a very small amount of silver (less than 0.1%) remains associated with lead because silver is soluble in lead to some extent. The lead thus obtained is with lead because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead. The process of removing these traces of silver from argentiferous lead is known as desilverisation of lead and is based on the phase diagram of silver-lead system.

The argentiferous lead is heated to a temperature well above its melting point so that the system consists only of liquid phase. Now let the point x represents the system 'molten lead' on the diagram in figure. It is then allowed to cool. The temperature of the melt will fall among the line xy without any change in concentration till the point y is reached. As soon as the point y is reached, lead will begin to crystallize out and the solution will contain relatively increasing amount of silver. Further cooling will shift the system along the line Oy. Lead continues to separate out and is constantly removed by be richer and richer in silver till the eutectic point O is reached where percentage of silver increases to 2.4. This alloy containing 2.4% silver and 97.6% lead is treated for the recovery of silver profitably.

The above principle of increasing the relative proportion of silver in the alloy is known as Pattison's process and is commercially used for the disilverisation of lead. The relative increase in the amount of solid lead and in the amount of silver in the residual melt on cooling.

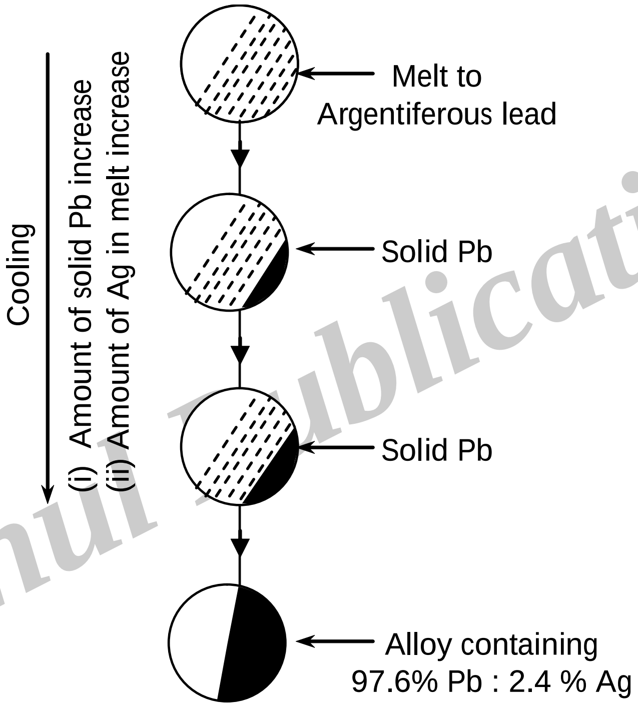


Fig. : Cooling of Melt of Argentiferous Lead

4.10 Solid Solutions – Compound with Congruent Melting Point – (Mg-Zn) System and Incongruent Melting Point – ($NaCl$-H_2O) System

Q19. Construct the phase diagram of Mg Zn_2 system and explain the importance of congruent metting point.

Ans : **(Imp.)**

Systems in which two Components form a Solid Compound (Mg-Zn system)

This is best represented by Mg – Zn system. It is a typical two component system which involves the formation of an intermetallic compound Mg Zn_2 and the liquid solution of Mg and Zn. The complete phase diagram of the Mg – Zn system is shown in figure.

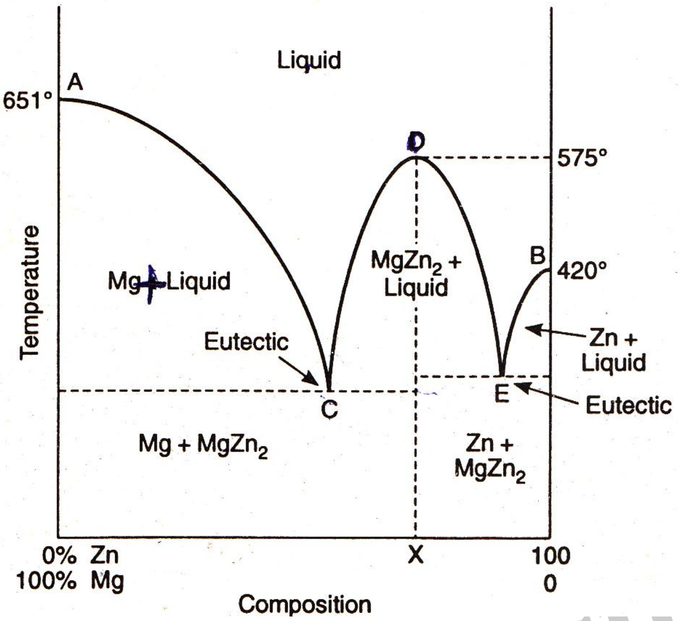


Fig. : Phase Diagram of zinc-magnesium System

The curves AC, CD, DE and BE. The curves AC and BE represent the freezing point curves of Mg and Zn respectively, while CDE represents the curve for the compound $MgZn_2$.

The curve AC shows that the melting point of Mg (651°C) decreases on the addition of Zn till point C is reached where a new phase of solid $MgZn_2$ starts appearing. Thus point C has three phases, solid Mg, solid $MgZn_2$ and a liquid.

The curve CD shows the increases of concentration of Zn in the melt with the rise of temperature till the maximum point D is reached. At point D there are two phases namely melt and the solid compound, the composition of both the phases is same as that of $MgZn_2$ and thus they have identical melting point, such melting point is known as congruent melting point.

The curve DE represents decrease of melting point with the addition of zinc until the lowest point E is obtained where solid Zn starts appearing and thus represents the m.p. of Zn (420° C). The point E is the second eutectic point and has three phases solid Zn, solid Mg Zn_2 and a liquid.

The curve BE represents the decreases of melting point of Zn (420°C) with the addition of Mg. Along the freezing point curves AC, CDE and BE, there are two phases in equilibrium (i) solid phases (Mg, Zn or $MgZn_2$) and (ii) liquid phase. Apply the reduced phase equation, the degree of freedom is found to be 1, i.e., the Mg-liquid Zn-liquid, and $MgZn_2$-liquid are all monovariant.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

Eutectic Points C and E

There are two eutectic points in the phase diagram. The systems at these points have two components and three phases in equilibrium.

Point C	Solid Mg, Solid Mg Zn_2, liquid
Point E	Solid Zn, Solid $MgZn_2$, liquid

Thus these systems are nonvariant.

$$
\begin{aligned}
F &= C - P + 1 \\
&= 2 - 3 + 1 \\
&= 0
\end{aligned}
$$

Congruent Melting Point D

The point D has two phases viz. solid $MgZn_2$ and a melt. Composition of the compound $MgZn_2$ and the melt at D is identical, and this temperature is called congruent melting point of the compound $MgZn_2$ (575°C). Here the system has two phases both of which can be represented by one component ($MgZn_2$) hence the system at D is nonvariant.

$$F = C - P + 1 = 1 - 2 + 1 = 0$$

Q20. Apply the phase rule to salt-water system.

Ans : **(Imp.)**

Salt-Water System

The temperature-composition diagram of sodium chloride ($NaCl.2H_2O$) is shown in figure. Neglecting the vapour phase, the system exhibits four phases : (i) $NaCl.2H_2O$, (ii) NaCl, (iii) ice and (iv) solution.

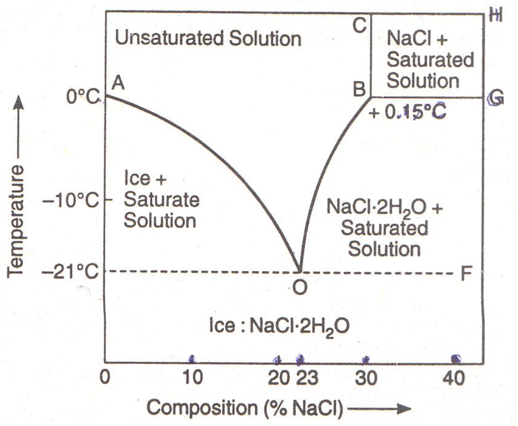


Fig.: Phase Diagram of Sodium Chloride-water System

Let us study the various curves and points of the phase diagram.

Curve AO

Point A is the melting point of ice (or freezing point of water) which is 0°C at 1 atmospheric pressure. When sodium chloride is added to water, its freezing point is lowered.

The temperature at the eutectic point O (eutectic temperature) is the lowest temperature at which an aqueous solution of NaCl can exist at atmospheric pressure. All solutions on cooling ultimately show an arrest in temperature at the eutectic point.

The mixture of NaCl and ice deposited at the eutectic point was at one time considered to be a definite compound of the form of a salt hydrate and was given the name cryohydrate.

Eutectic solid is a mixture and not a compound constancy of composition and melting point alone cannot establish a chemical compound.

The curve AO is called the freezing point curve. The system along the curve two phases (Ice and solution) are in equilibrium.

∴ System along the curve is univariant.

$$F = C - P + 1$$
$$= 2 - 2 + 1 = 1$$

Curve OB

When further amount of NaCl is added at point O and the system is heated, ice disappears. The curve OB represents the effect of temperature on the solubility or the hydrated sodium chloride, $NaCl.2H_2O$. Hence it is called as the solubility curve of the hydrated sodium chloride. Along this curve two phases ($NaCl.2H_2O$ and solution) are in equilibrium and hence the system is univariant.

$$F = C - P + 1$$
$$= 2 - 2 + 1 = 1$$

Point B

It represent the incongruent melting part of the dihydrate.

Curve BC

It is the solubility curve of the anhydrous sodium chloride. Hence curve BC is univariant.

Point O

At this point the solution becomes saturated and the dihydrate, $NaCl.2H_2O$ separates out. Thus the system at the point O consists of 3 phases (Ice, $NaCl.2H_2O$ and solution) in equilibrium. Hence this point is called the eutectic point.

$$F = C - P + 1$$
$$= 2 - 3 + 1 = 0$$

Short Question & Answers

1. What are Significant Figures

Ans :

Significant figures are the total number of digits in a number including the last digit whose value is uncertain.

Example: 876 m has 3 significant figures.

2. What are errors?

Ans :

Every scientific measurement will have some uncertainty. This uncertainty is called errors:

3. What are absolute and relative errors.

Ans :

Absolute Errors

The absolute error of a measurement is the difference between the measured value and the true value.

$E = x_i - x_t$

E = Absolute error

x_i = Measured value

x_t = True value

Relative Errors

The relative error of a measurement is the absolute error divided by the true value.

$$E_R = \frac{x_i - x_t}{x_i}$$

4. Give the expression of Standard Deviation (SD) : ($\bar{d}$).

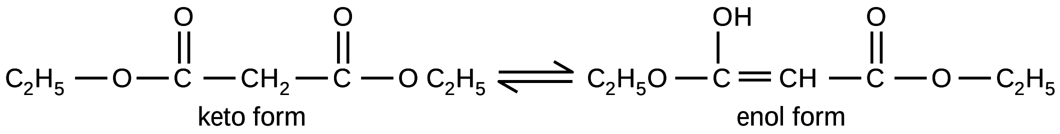
Ans :

Measure of precision is standard deviation.

$$\bar{d} = \frac{\Sigma |x_i - x_t|}{N}$$

5. Give the tautomers of dimethyl malonate.

Ans :



$$C_2H_5-O-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-O\,C_2H_5 \rightleftharpoons C_2H_5O-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-O-C_2H_5$$

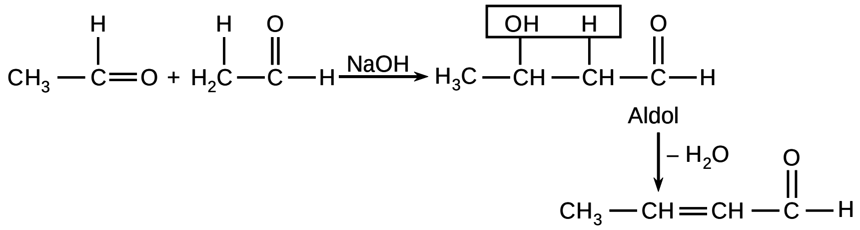
6. Write the Aldol Condensation reaction.

Ans :

Two moles of carbonyl compound having atleast one ‘α’ hydrogen on reaction with alkali converted to ‘aldol’ which is a β-hydroxy carbonyl compound.

Aldol on dehydration converted to α, β unsaturated carbonyl compound.

Example:



$$CH_3-\overset{H}{\overset{|}{C}}=O + H_2\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} H_3C-\boxed{\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-H$$

Aldol

$$\downarrow -H_2O$$

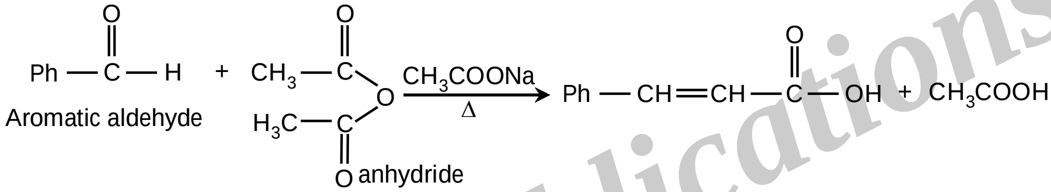
$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H$$

7. Write the Perkin Reaction

Ans :

The reaction of an aromatic aldehyde with an aliphatic acid anhydride in presence of sodium or potassium salt of the acid corresponding to anhydride to give an α, β – unsaturated acid is known as perkin reaction.

Example:



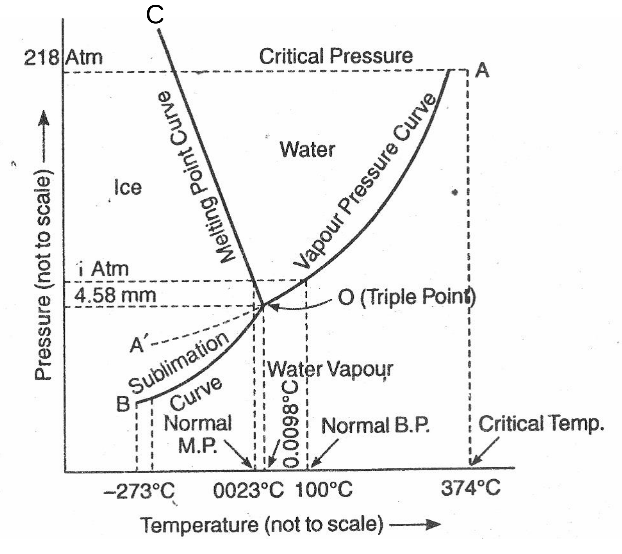
8. What is Degree of Freedom?

Ans :

The minimum number of the variable factors, such as temperature, pressure and composition of the phases which must be arbitrarily fixed in order to define condition of the system completely is termed as degree of freedom of the system.

9. Draw the phase diagram of water system.

Ans :



Choose the Correct Answer

1. 5.400 g has how many number of significant figures. [c]

(a) 2 (b) 3

(c) 4 (d) 5

2. The closeness to true value called [a]

(a) Accuracy (b) Precision

(c) Mean (d) Median

3. Errors can be occur by [d]

(a) Personal Error (b) Instrumental Error

(c) Error of method (d) All

4. Standard deviation is a measure of [b]

(a) Accuracy (b) Precision

(c) Mean (d) Median

5. Absolute error is [c]

(a) Measured value / True value (b) Measured value × True value

(c) Measured value – True value (d) True value / Measured value

6. Carbanion is [b]

(a) An electrophile (b) A nucleophile

(c) Zwitter ion (d) Freeradicals

7. The condensation reaction b/w two ester molecules in presence of a strong base is named as[b]

(a) Reformatsky reaction (b) Claisen condensation

(c) Hofmann reaction (d) Freeradicals

8. When ethylmalonic ester is hydrolysed an heated the product formed is [b]

(a) Acetic acid (b) Propionic acid

(c) Butyric acid (d) Perntanoic acid

9. Hybridisation of carbanion [a]

(a) SP^3 (b) SP^2

(c) SP (d) SP^3d

10. Stability of carbanions [c]

(a) Terallyl > Secalkyl > Prialkyl > Methyl (b) Sec-alkyl > ter-alky > primary > Methyl

(c) Methyl > prim-alkyl > sec-alkyl > ter.alkyl (d) Methyl > sec-alkyl > teralkyl > primary

11. Condensation of Ethyl acetate gives [b]

(a) Malonic ester (b) Ethyl acetate

(c) Acetic acid derivative (d) All the above

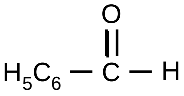
12. Acetoacetic ester undergoes condensation with aldehydes and ketones in presence of a base to form a α, β – unsaturated acids is known as. [d]

(a) Perkin reaction (b) Claisen condensation

(c) Aldd condensation (d) Knoevenagel reaction

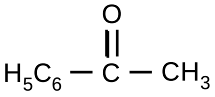
13. Keto - enol tautomerism is observed in [b]

(a)



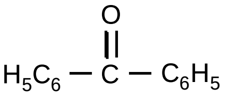
$H_5C_6-\overset{\overset{O}{\parallel}}{C}-H$

(b)



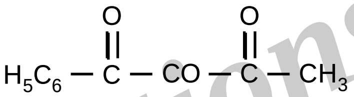
$H_5C_6-\overset{\overset{O}{\parallel}}{C}-CH_3$

(c)



$H_5C_6-\overset{\overset{O}{\parallel}}{C}-C_6H_5$

(d)



$H_5C_6-\overset{\overset{O}{\parallel}}{C}-CO-\overset{\overset{O}{\parallel}}{C}-CH_3$

14. Acetoacetic ester on ketonic hydrolysis gives a main product is [b]

(a) Ethylalcohol (b) Acetone

(c) Carbondioxide (d) Aceticacid

15. Acetoacetic ester on acidic hydrolysis gies a main proudct is [d]

(a) Ethylalcohol (b) Acetone

(c) Carbondioxide (d) Aceticacid

16. Phase rule states that [a]

(a) $P + F = C + 2$ (b) $P + F = C - 2$

(c) $P + C = F + 2$ (d) $P + C = F - 2$

17. The number of phases in a mixture of N_2, O_2 and H_2 will be [b]

(a) 0 (b) 1

(c) 2 (d) 3

18. Number of phases in a mixture of O_2, N_2 and H_2O will be [c]

(a) 0 (b) 1

(c) 2 (d) 3

19. The number of components in the dissociated of NH_4Cl (s) [b]

(a) 0 (b) 1

(c) 2 (d) 3

20. When temperature is constant, the degree of freedom is reduced by [a]

(a) 1 (b) 2

(c) 3 (d) None of these

21. On a phase diagram for a one component system there cannot be a quadruple point because the number of degrees of freedom is : [c]

(a) 3	(b) 4
(c) 1	(d) 0

22. For a one component system, the maximum variables may be [c]

(a) 0	(b) 1
(c) 2	(d) 3

23. A triple point is : [d]

(a) Trivariant	(b) Bivariant
(c) Univariant	(d) Invariant

24. For water system when three phases are under equilibrium the system is [a]

(a) Zero variant	(b) Unvariant
(c) Bivariant	(d) None of these

25. The maximum number of degree of freedom in the phase diagram of an aqueous of NaCl is [c]

(a) 1	(b) 2
(c) 3	(d) 4

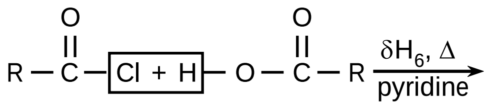
26. The degree of freedom at the eutectic point is [a]

(a) 0	(b) 1
(c) 2	(d) 3

27. A triple point is the temperature where : [b]

(a) Three components are in equilibrium
(b) Three phases are in equilibrium
(c) The number of degree of freedom is 3.
(d) None of these

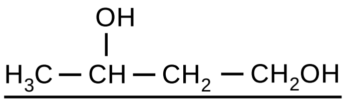
Fill in the blanks

1. Significant number of 0.006 is ________.
2. The errors arises due to instrument called ________.
3. The mathematical expression of mean ($\bar{X}$) is ________.
4. The mathematical expression of standard deviation (SD) ($\bar{d}$) is ________ .
5. Which acid is used as a standard substance in volumetric titrations is ________.
6. The reactionof H_3CMgBr on dry ice followed by acid hydrolysis gives ________.
7. Acetic acid exists in a dimer state in benzene due to ________ ________.
8. $H_3C - COOld \xrightarrow{p/Br2} BrH_2C - COOH$ the reaction is called ________.
9. When acetylchloride reacts with any amine the reaction is known as ________.
10. Alkaline hydrolysis of an ester is called ________.
11. Amides may be converted to amines by the reaction known as ________.
12. Amides are formed by the reaction of acid cholide with ________.
13. 

$$R-\overset{O}{\overset{\|}{C}}-\boxed{Cl + H}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\text{pyridine}]{\delta H_6,\ \Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$ ________.

14. Acetyl chloride reacts with benzene in presence of an hydrous aluminium chloride to form acetophenone. This reaction is an example of ________.
15. Malonic acids on heating gives ________.
16. Acetoacetic ester is a ________ acid than ethyl alcohal.
17. Malonic ester when treated with excess of sodium ethoxide followed by methyl iodide and ethyl iodide gives ________ ________.
18. Acetoacetic ester is heated with concetrate alcoholic KOH to give ________.
19. Crbanions act as ________.
20. A methylene group flanked on both sides by $e^{(-)}$ withdrawing groups is highly reactive and is knwon as ________.
21. The relative stability of carbanioni n alkanes, alkenes, alkynes ________.
22. Shape of the carbanion structure ________.
23. Product in knoevenagel reaction are ________.
24. Aceto acetic ester on reduction with LiAIH gives ________.
25. At the triple point, water has the vapour pressure ________ .
26. For the silver-lead system, the number of phases at a particular point is three, its degree of freedom will be ________.
27. Silver-lead phase diagram is applied in the purification of ________.
28. No mixture of lead and silver has a melting point lower than the ________ temperature.
29. The maximum possible number of phases in water system is ________ .
30. In phase diagram of one component system, areas are ________ curves are ________ and point is ________.

ANSWERS

1. One
2. Instrumental Error
3. $\overline{x} = \sum_{i=1}^{N} \frac{x_i}{N}$
4. $\overline{d} = \frac{\Sigma |x_i - x_t|}{N}$
5. Oxalic acid
6. Acetic acid
7. Hydrogen bonding
8. Hell-volhard - xebnsky reaction
9. Acetylation
10. Esterification
11. Hofman degradation
12. Ammonia
13. Acetic anhydride
14. Friedal-crafts reaction
15. Substituted Acetic acid
16. Stronger
17. Methylethyl Matonic ester
18. Acetic acid
19. Nucleophiles
20. Active methylene compound
21. $HC \equiv \overset{\ominus}{C} > H_2C = \overset{\ominus}{C}H > H_3C - \overset{\ominus}{C}H_2$
22. Pyramidal
23. α, β – unsaturated acid
24. 

$H_3C - \underset{}{\overset{OH}{\overset{|}{C}H}} - CH_2 - CH_2OH$

(1, 3 Butane diaol)

25. 4.58 mm
26. 0
27. Lead
28. Eutectic
29. 3
30. Bivariant, univoriant, non-variant

PRACTICALS

1. **Synthesis of Organic Compounds**

   Acetylation: Acetylation of salicylic acid, Benzoylation of Aniline.

   Aromatic Electrophilic Substitution: Nitration: Preparation of nitro benzene and m-dinitro benzene.

   Halogenation: Preparation of p-bromo acetanilide, Preparation of 2,4,6-tribromo phenol

   Oxidation: Preparation of benzoic acid from benzyl chloride.

   Esterification: Preparation of n-butyl acetate from acetic acid.

   Methylation: Preparation of - naphthyl methyl ether.

   Condensation: Preparation of benzilidine aniline and Benzaldehyde and aniline.

   Diazotisation: Azocoupling of β-Naphthol.

2. **Microwave assisted synthesis of Asprin – DEMO (demonstration only)**

PREPARATION OF ASPIRIN

Aim : To study the Acetylation of Salicylic acid

Principle : Salicylic acid undergoes acetylation with acetic anhydride in presence of acid catalyst which generates acetyl carbonium or acetyl carbocation. The acetylation takes place selectively at weakly acidic group i.e. phenolic group in preference to strong carboxylic group to form aspirin

Type of reaction : Electrophilic substitution reaction (O-acetylation)

Chemicals required : Salicylic acid - 1 gm, acetic anhydride- 3ml, Cone. H_2SO_4 -1 or 2 drops.

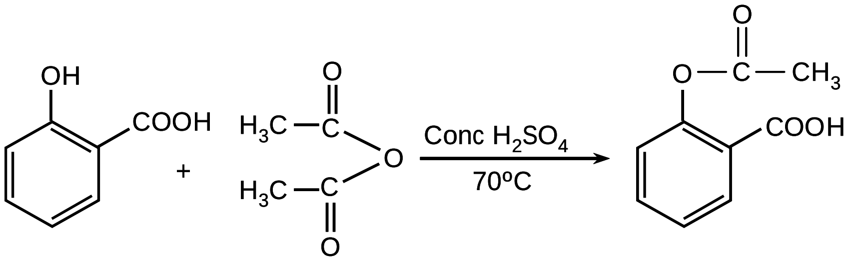
Apparatus : Conical flask, Beaker, Glass rod and Funnel

Procedure : Place 1 gm of salicylic acid in 1.5 ml of acetic anhydride into a 100 ml conical flask. Add slowly 1 or 2 drops of concentrated H_2SO_4 and stir the flask to mix the contents. Heat the reaction mixture on water bath at 40 – 60°C with stirring for 15 minutes. After the completion of heating, allow the reaction mixture to cool and then add 15 ml of water. White crystalline product of aspirin separates out. Filter the product and wash the solid with water and dry it.

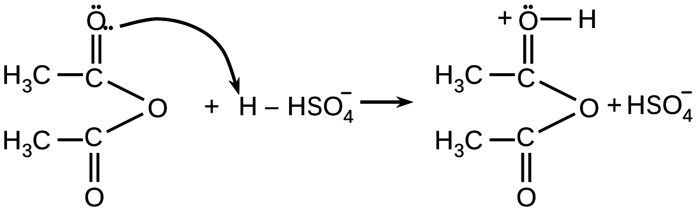
Result : White solid of aspirin is prepared.

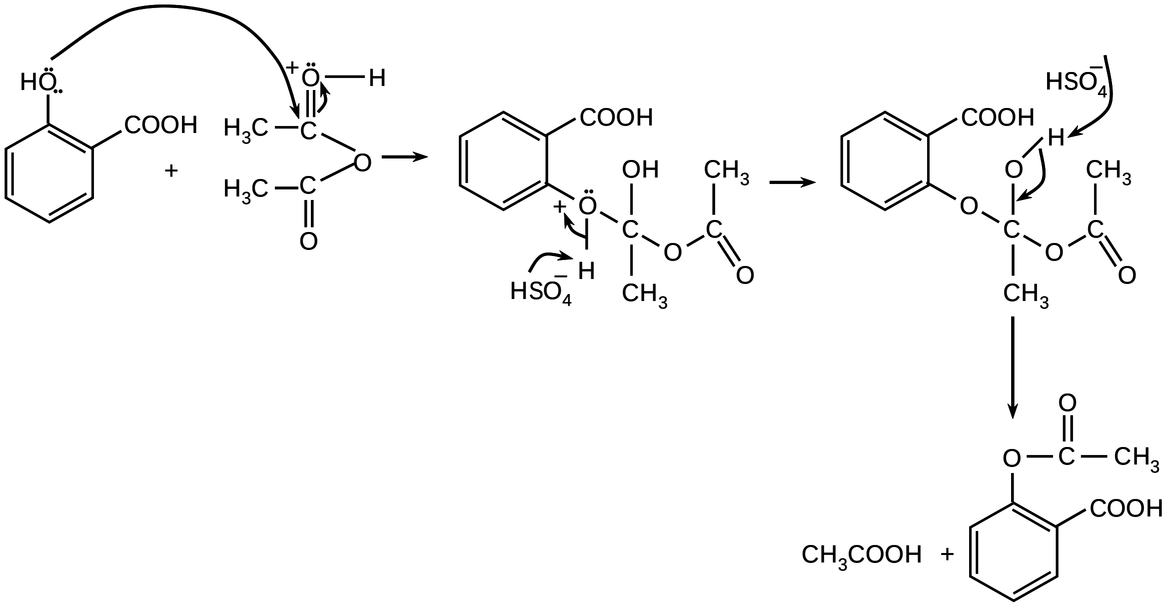
PREPARATION OF ASPIRIN

Reaction



Mechanism





PREPARATION OF BENZANILIDE

Aim : To Study the Benzoylation of Aniline.

Principle : The benzoylation of hydroxy or amino compounds in the presence of excess of cold aqueous base is called Schotten- Baumann reaction. The reaction involves the attack of aniline on the carbonyl group of Benzoyl chloride followed by elimination of HCl to form Benzanilide

Type of Reaction : Condensation reaction (N-Benzoylation)

Chemicals Required : Aniline-lml , Benzoyl Chloride-1.5 ml and Aqueous NaOH- 15 ml

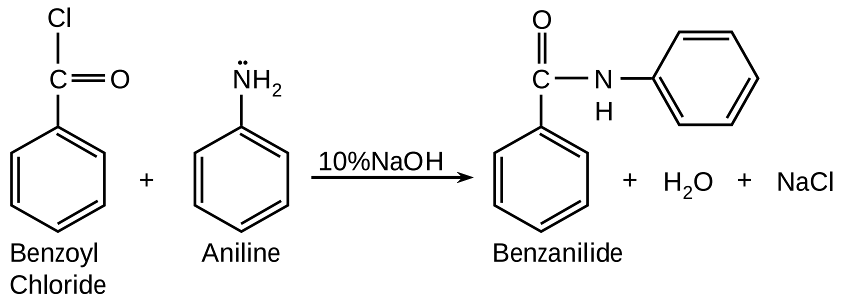
Apparatus : Conical flask, Beaker, glass rod and funnel

Piocedure : Add 1 ml of Aniline to 15 ml of 10% NaOH taken in a clean dry conical flask. Then add 1.5 ml of Benzoyl Chloride, cork the flask and shake the reaction mixture vigorously for 15- 20 minutes. The mixture becomes warm and Benzoyl derivatives separates out as a white precipitate. Filter the product obtained and wash with water.

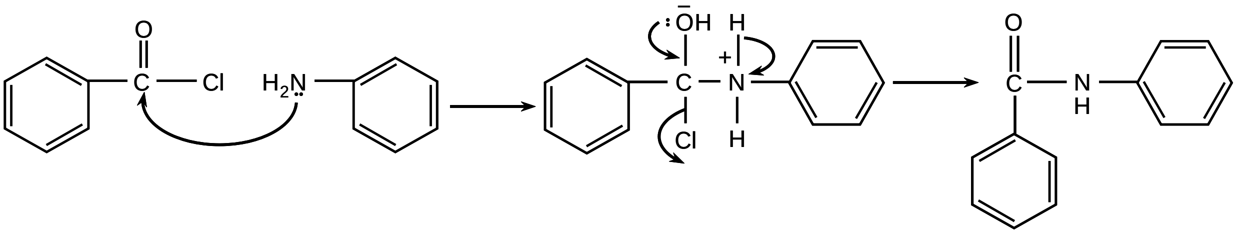
Result : Benzanilide is obtained as white solid.

PREPARATION OF BENZANILIDE

Reaction



Mechanism



Unreacted C_6H_5COCl reacts with NaOH

$$C_6H_5COCl + NaOH \longrightarrow C_6H_5COONa + HCl$$

PREPARATION OF NITROBENZENE

Aim : To study the Nitration of Benzene

Principle : Benzene undergo substitution with electrophile, nitronium ion which can be generated by nitrating mixture (Cone. H_2SO_4 + Cone. HNO_3). The purpose of Cone. H_2SO_4 is to convert the nitric acid into highly reactive electrophile, nitronium ion.

Chemicals Required : Benzene-2ml, Cone. HNO_3-1.5ml, Cone. H_2SO_4-2ml

Type of Reaction : Electrophilic Substitution (Nitration)

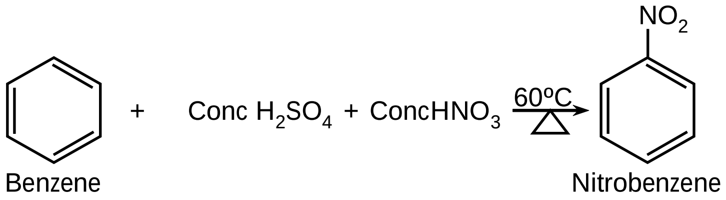
Apparatus : Round bottomed flask, Air condenser, Beaker, glass rod, Separating funnel and measuring cylinder

Procedure : Place 1.5 ml of Cone. HNO_3 in a clean dry round bottomed flask and add 2 ml of Cone. H_2SO_4 drop wise with shaking. During the addition keep the mixture cool by placing the round bottomed flask in ice cold water. Add 1ml of benzene drop wise into the R.B flask with shaking. Fix air condenser to the round bottomed flask and heat on water bath by maintaining the temperature 60°C for 45 mins. During the heating occasionally shake the RB flask from time to time to ensure thorough mixing of the reaction mixture. Pour the contents of the flask into the beaker containing 50 ml of cold water, stir the mixture vigorously and transfer it into a separating funnel. The nitro benzene being heavier settles at the bottom of the funnel. Collect the lower layer of nitro benzene and reject the upper aqueous layer. Repeat the process again with water. Transfer the nitrobenzene to the separating funnel again and shake it vigorously with 10 ml of sodium bicarbonate. Shake the mixture well and separate the nitrobenzene. Repeat the process again with sodium bicarbonate. Collect the nitrobenzene in a dry beaker and add calcium chloride. Allow it to stand for some time and decant it in a dry test tube.

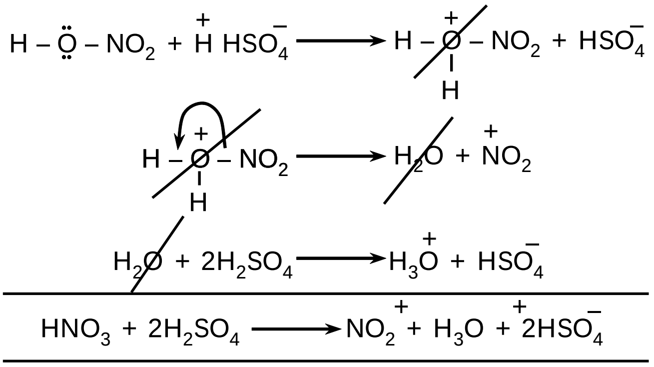
Result : Nitrobenzene is obtained as a clear pale yellow liquid.

PREPARATION OF NITROBENZENE

Reaction



Generation of Electrophile



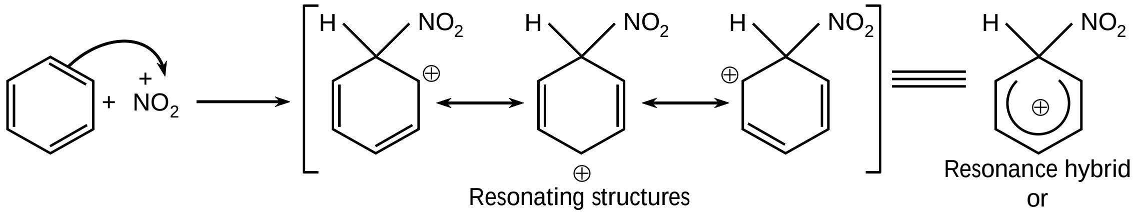
$$H-\ddot{\underset{\cdot\cdot}{O}}-NO_2 + \overset{+}{H}\,HSO_4^{-} \longrightarrow H-\underset{\underset{H}{|}}{\cancel{\overset{+}{O}}}-NO_2 + HSO_4^{-}$$

$$H-\underset{\underset{H}{|}}{\cancel{\overset{+}{O}}}-NO_2 \longrightarrow \cancel{H_2O} + \overset{+}{NO_2}$$

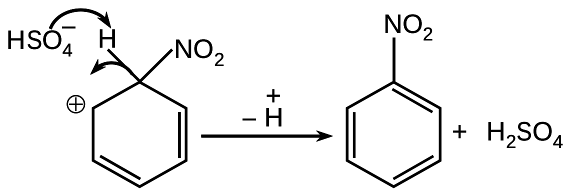
$$\cancel{H_2O} + 2H_2SO_4 \longrightarrow H_3\overset{+}{O} + HSO_4^{-}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{NO_2} + H_3\overset{+}{O} + 2HSO_4^{-}$$

Attack of Electrophile



Loss of Proton



PREPARATION OF M-DINITRO BENZENE

Aim : To study the Nitration of Nitrobenzene.

Principle : The nitro group on benzene ring is a meta direciing strongly ring deactivating group which directs the incoming electrophile, nitronium ion to occupy meta position to give meta dinitrobenzene.

Type of Reaction : Electrophilic substitution reaction (Nitration).

Chemicals Required : Nitrobenzene -1ml, Fuming HNO_3 - 2ml and Cone. H_2SO_4 - 3ml.

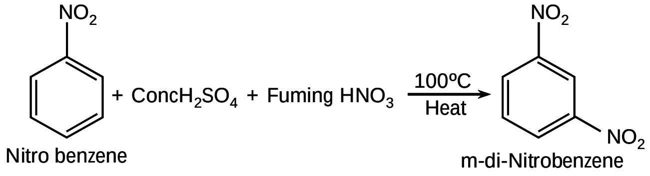
Apparatus : Round bottomed flask, Beaker, Air condenser , glass rod and funnel

Procedure : Take 2ml of fuming nitric acid in a clean round bottom flask and add carefully with shaking 3ml of Cone. H_2SO_4. Add 1 ml of nitrobenzene in small portions with shaking and fix an air condenser. Add 1 or 2 porcelain pieces and heat the reaction mixture on boiling water bath for 45 minutes. After the completion of heating pour the contents of the flask in ice cold water. Pale yellow solid of m- dinitrobenzene separates out. Filter the product and wash with water.

Result : m-Dinitrobenzene is obtained as pale yellow solid.

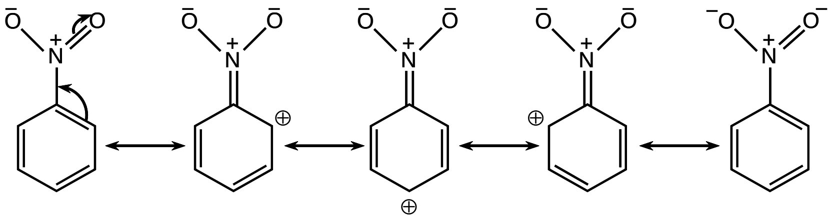
PREPARATION OF m-DINITRO BENZENE

Reaction



Mechanism

Orientation of Nitro benzene



Generation of electrophile (Nitronium ion)

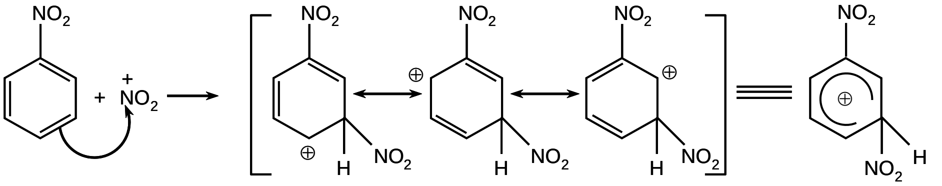
$$H-\ddot{O}-NO_2 + \overset{+}{H}\,HSO_4^- \longrightarrow H-\overset{+}{\underset{\underset{H}{|}}{\cancel{O}}}-NO_2 + HSO_4^-$$

$$H-\overset{+}{\underset{\underset{H}{|}}{\cancel{O}}}-NO_2 \longrightarrow \cancel{H_2O} + \overset{+}{N}O_2$$

$$\cancel{H_2O} + H_2SO_4 \longrightarrow H_3\overset{+}{O} + HSO_4^-$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{N}O_2 + H_3\overset{+}{O} + 2HSO_4^-$$

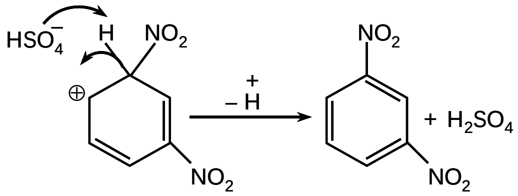
Attack ofelectropile on benzene ring of nitrobenzene



Resonance Structures

Resonance Hybrid

Loss of Proton



PREPARATION OF TRIBROMO PHENOL

Aim : To study the Bromination of Phenol.

Principle : The Phenolic -OH group is a strong ring activating, ortho-para directing group which directs the incoming electrophile, bromonium ion to occupy two ortho and one para positions givina rise to 2,4.6-Tribromo phenol.

Type of Reaction : Aromatic Electrophilic. substitution reaction (Bromination)

Chemicals Required : r-Phenol-2 to 3 drops, Bromine in acetic acid.

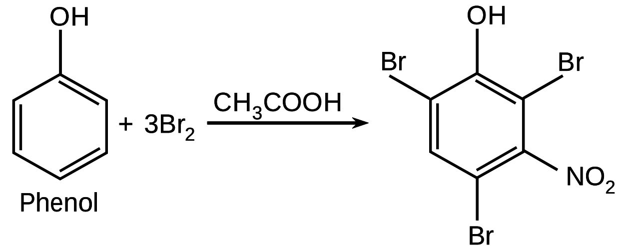
Apparatus : Conical flask. Beaker, glass rod and funnel.

Procedure : Dissolve 2 to 3 drops of Phenol in 10ml of water taken in-a Conical Flask . Add Bromine in acetic acid slowly and drop wise with constant shaking till dark orange colour persist. Allow the reaction mixture to stand at room temperature for 15-20 mins. Then pour the contents of the flask in a beaker containing ice cold water. White coloured solid of 2, 4, 6 - Tribromo phenol separates out. Filter the product at suction pump and wash with water to remove unreacted reagent.

Result : 2, 4, 6 - Tribromo phenol is obtained as white solid.

PREPARATION OF TRIBROMO PHENOL

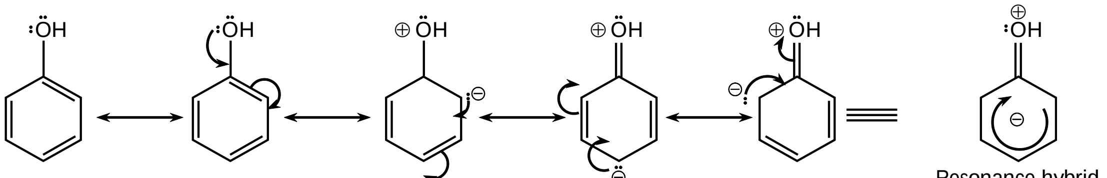
Reaction



Tri Bromo Phenol

Mechanism

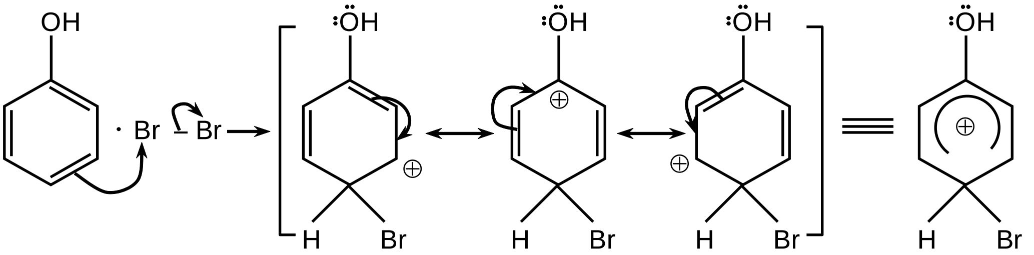
Orientation Effect in Phenol



Resonating Structures

Resonance hybrid
or
Arenium ion

Formation of Arenium ion

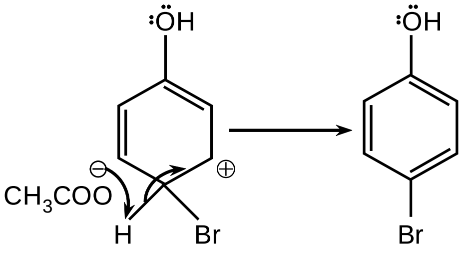


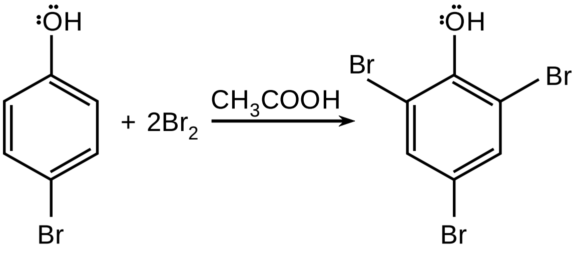
Resonance Structures

Resonance hybrid
or
Arenium ion

Loss of Proton

For di- and tri - substitution mechanism is same as in mono bromination





PREPARATION OF PARA-BROMO ACETANILIDE

Aim : To study the selective Bromination of Acetanilide

Principle : The -NH-CO-CH_3 group in Acetanilide is a moderately ring activating, ortho-para directing group which directs the incoming electrophile, bromonium ion to occupy only para position and not ortho positions due to steric hinderance giving rise to para-bromo acetanlide. The electron-withdrawing carbonyl group of anilide makes the benzene ring less nucleophilic unlike the phenolic -OH group.

Type of Reaction : Electrophilic substitution reaction (Bromination)

Chemicals Required : Acetanilide- 1gm , Glacial acetic acid- 5ml, Bromine in acetic acid.

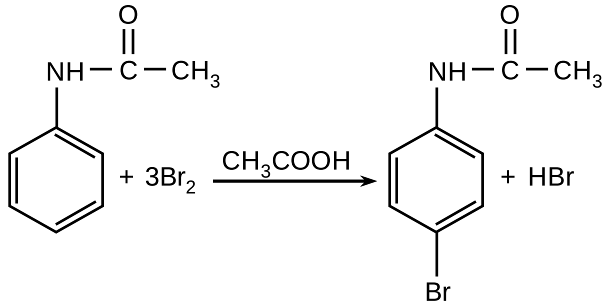
Apparatus : Conical flask, Beaker, glass rod and funnel.

Procedure : Dissolve 1 gm of finely powered Acetanilide in 5ml of Glacial acetic acid in a 150ml Conical Flask. Add very carefully Bromine in acetic acid with constant shaking until the colour of the reaction mixture is bright orange. Allow the mixture to stand at room temp for 15-20 minutes. Pour the mixture in ice cold water. Para-bromo acetanilide crystallizes out as white solid.

Result : Para-bromo acetanilide is obtained as white solid.

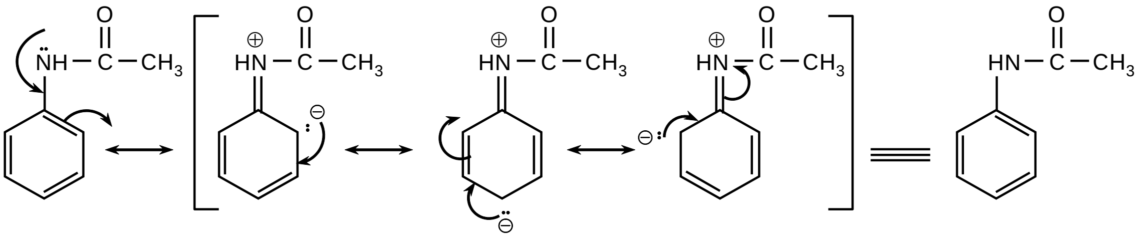
PREPARATION OF PARA-BROMO ACETANILIDE

Reaction



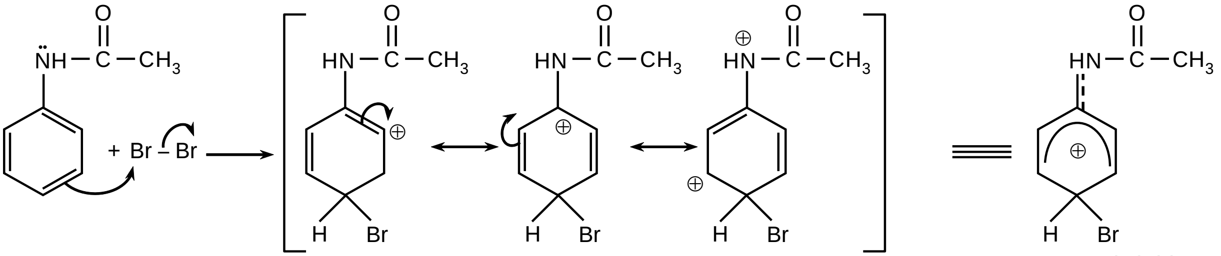
Acetanilide p-brome acetanilide

Orientation effect in acctanilide



Mechanism

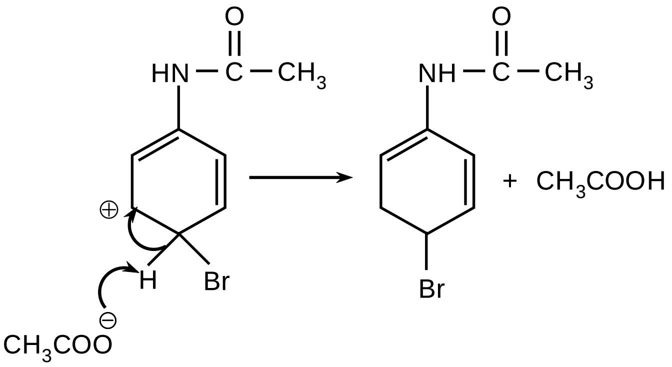
Formation of Arenium ion



Resonance structures

Resonance hybrid

Loss of proton



PREPARATION OF BENZOIC ACID

Aim : To study the Oxidation of Benzyl Chloride to Benzoic acid.

Principle : Benzyl chloride is hydrolyzed to benzyl alcohol which undergoes oxidation leading to the formation of benzaldehyde and then to corresponding acids in the presence of potassium permanganate as an oxidizing agent.

Type of Reaction : Oxidation

Chemicals required : Anhydrous $Na_2 CO_3$ -1gm, potassium pennanganate-2gm, Benzyl chloride- 1.5ml, Sodium Sulphite and Cone. HCl.

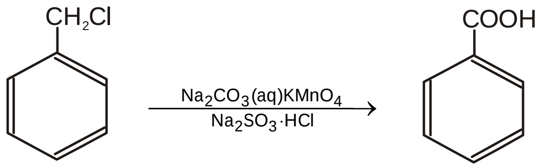
Apparatus : Round bottomed flask, Water condenser, Beaker and glass rod,

Procedure : To 100 ml of water taken in 250ml round bottom flask. Add 1 gm of sodium carbonate and 2gm of Potassium Permanganate and 1.5 ml of Benzyl Chloride. Fix a water condenser and boil the mixture gently for 1 hour until the reaction is complete and liquid running down the condenser contains no oily drops of un-reactive benzyl chloride. During this boiling the permanganate is slowly reduced to Manganese dioxide which separates as dark brown precipitate. Now cool the flask and add about 10ml of concentrated HCl until the mixture is strongly acidic and all the benzoic acid is precipitated. Then add 20% aqueous solution of crystalline $Na2SO_3$ with shaking until manganese dioxide is dissolved and white precipitate of benzoic acid separates out. Filter the benzoic acid at suction pump and wash with water.

Result : Benzoic acid is obtained as white precipitate.

PREPARATION OF BENZOIC ACID

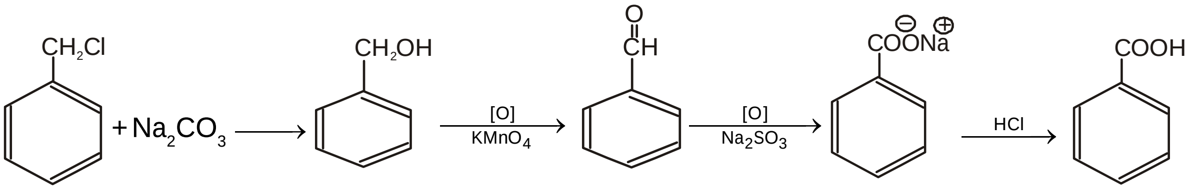
Reaction



Benzylchlorine

Benzoic acis

Mechanism



Dissolving of brown precipitate (MnO_2)

$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$

$MnO_2 + 2SO_2 \rightarrow MnS_2O_6$

$MnS_2O_6 + MnO_2 \rightarrow 2MnSO_4$

PREPARATION OF N-BUTYL ACETATE

Aim : To study the Esterification reaction of n-Butyl alcohol and Acetic acid.

Principle : It is an example of esterification reaction catalyzed by an acid. The mechanism involves protonation of carbonyl group in presence of acetic acid followed by nucleophilic attack of n-butyl alcohol and finally elimination of water resulting in the formation of n-butyl acetate.

Type of reaction : Esterification reaction

Chemicals required : n-Butyl alcohol-5ml, Glacial acetic acid -7.5ml, Cone. H_2SO_4 -5drops.

Apparatus : Round bottomed flask, Air condenser. Beaker, glass rod, Separating funnel and measuring cylinder

Procedure : Take 5ml of n-butyl alcohol, 7.5ml Glacial Acetic Acid and 5 drops of Cone. H_2SO_4 in a Round Bottomed flask. Attach a reflux condenser and heat the reaction mixture on low flame for 1hr. After the completion of heating pour the contents of the flask into 50 ml of water taken in a beaker. Transfer the mixture in a separating funnel and separate the upper layer of ester. Add 10 ml of 10% sodium bicarbonate to the ester taken in a separating and separate the upper layer. Repeat the process once again with 10 ml of 10% sodium bicarbonate and transfer the ester layer into the small beaker, add a pinch of anhydrous sodium sulphate. Keep the mixture aside for 10 mins. and then transfer the ester into a clean test tube.

Result : A pleasant smelling liquid of n-butyl acetate is obtained

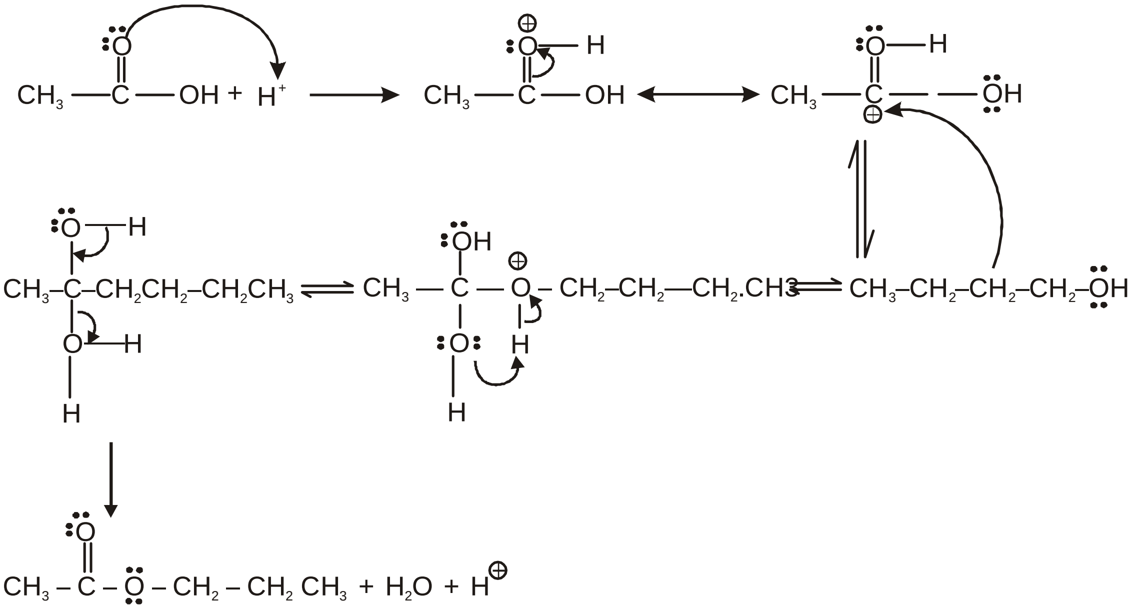
PREPARATION OF N-BUTYL ACETATE

Reaction

$$CH_3COOH + CH_3CH_2CH_2CH_2OH \xrightleftharpoons{\text{Conc } H_2SO_4} CH_3COOCH_2CH_2CH_2CH_3 + H_2O$$

Acetic acid n-butyl alcohol n-butyl acetate

Mechanism



PREPARATION OF β-NAPHTHYL METHYL ETHER (NEROLINE)

Aim : To prepare β-naphthyl methyl ether from β-Naphthol and dimethyl sulphate.

Principle : Napthoxide ion is generated by treating β-Naphthol with 10% NaOH which attacks dimethyl sulphate to form Neroline.

Type of reaction : Nucleophilic substitution reaction (O-methylation)

Chemicals required : β-Naphthol -1 gm. 10% NaOH-7.5ml, dimethyl sulphate-1.5ml.

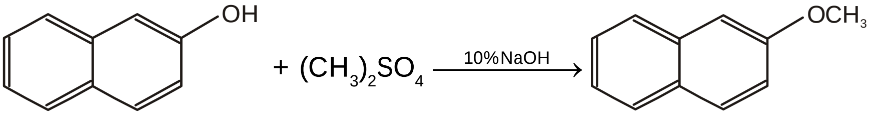
Apparatus : Conical flask, Beaker, glass rod and funnel

Procedure : Dissolve lgm of β-Naphthol in 7.5ml of 10% NaOH in a conical flask and add 1ml of dimethyl sulphate carefully without dropping on hands. Cork the flask and shake well. A pink colored solid separates out. Add 20ml of water, stir the mixture, filter the solid and collect the sample.

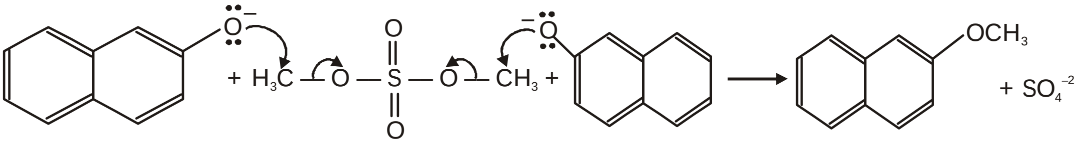
Result : Pink colored β-Naphthyl methyl ether is prepared

PREPARATION OF β-NAPHTHYL METHYL ETHER (NEROLINE)

Reaction



Mechanism



PREPARATION OF BENZAL ANILINE/ BENZYLIDENE ANILINE

Aim : To Study the Condensation Reaction of Benzaldehyde and Aniline.

Principle : It is an example of condensation reaction which involves nucieophilic addition followed by elimination. The aniline acts as a nucleophile which attacks at the carbonyl group of benzaldehyde forming an addition product followed by elimination of water molecule to form Benzal aniline.

Type of reaction : Condensation reaction

Chemicals required : Benzaldehyde-1ml, Aniline-1ml

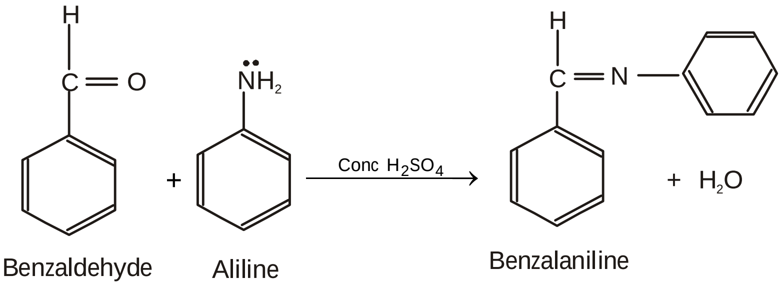
Apparatus : China dish, Beaker and glass rod

Procedure : Take 1ml of Benzaldehyde and 1ml of Aniline in a china dish. Heat the reaction mixture on water bath for 15-20 minutes. Keep it aside for 10 minutes. A cream colored solid separates out. If no solid separates, add 2 drops of Cone. H_2SO_4 and stir the mixture with glass rod. Collect the solid separated and dry it.

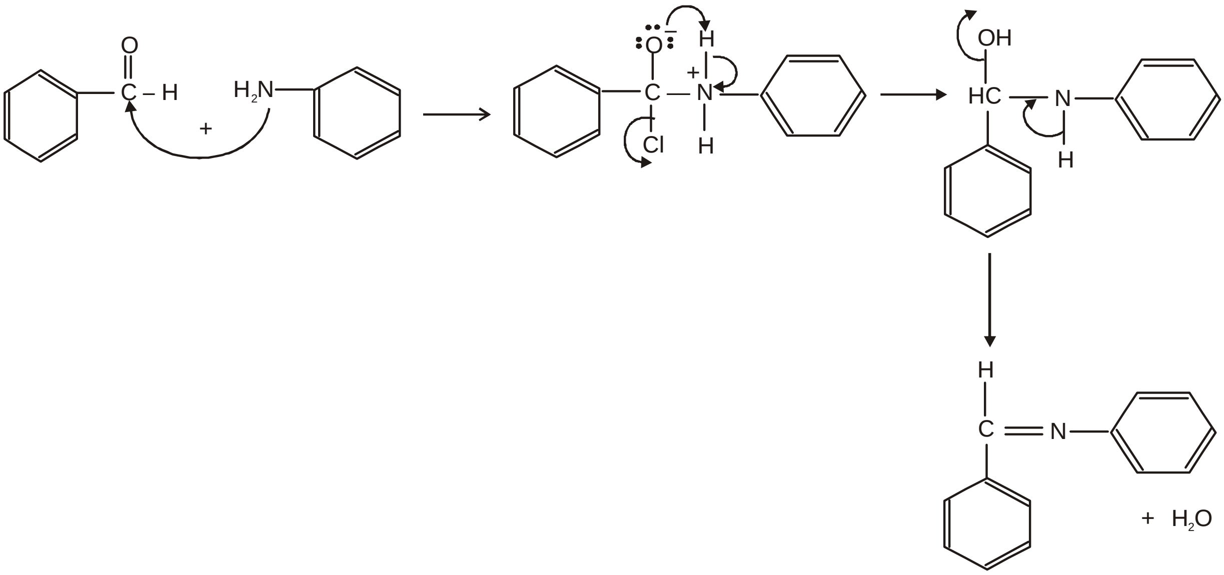
Result : Benzal aniline is obtained as cream colored solid

PREPARATION OF BENZAL ANILINE/ BENZYLIDENE ANILINE

Reaction



Mechanism



PREPARATION OF AZO- β-NAPHTHOL

Aim : To study the Diazotization reaction of Aniline and its coupling with β-Naphthol.

Principle : Aniline on reaction with nitrous acid at 0-5°C undergoes diazotization to give benzene diazonium chloride salt which couples with β-Naphthol at 0-5°C to give azodye.

Type of reaction : Diazotization and Coupling

Chemicals required : Aniline-1 ml, Cone. HCl-2ml, Sodium nitrite-lgm, β-Naphthol-l gm

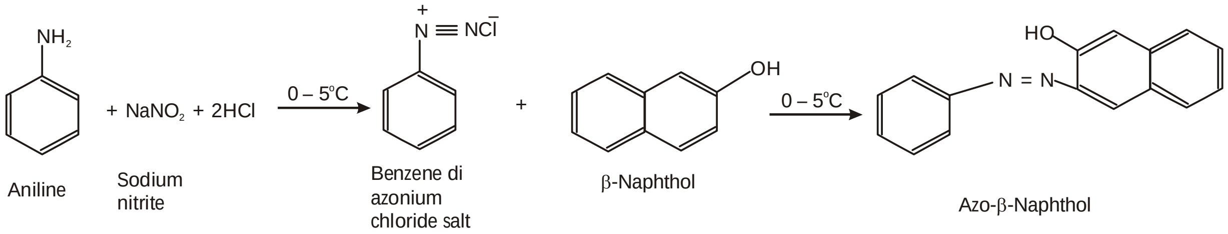
Apparatus : Conical flask, Beaker, glass rod and funnel

Procedure : Dissolve 1ml of Aniline in 2ml of Cone. HC1 in a beaker and keep it for cooling. In another test tube dissolve 1 gm of sodium nitrite in 5ml of H_2O and keep it for cooling at 0-5°C. hi a small beaker take lgm of β-Naphthol and dissolve it in 5ml of NaOH. Keep it for cooling at 0-5°C. Add the cold sodium nitrite solution to aniline with stirring and maintaining the temperature 0-5° C. Add the diazonium chloride salt obtained slowly to cold β-Naphthol solution with occasional stirring and maintaining the temperature 0-5° C. Allow the reaction mixture to stand in ice for some time. Filter the product obtained and dry it.

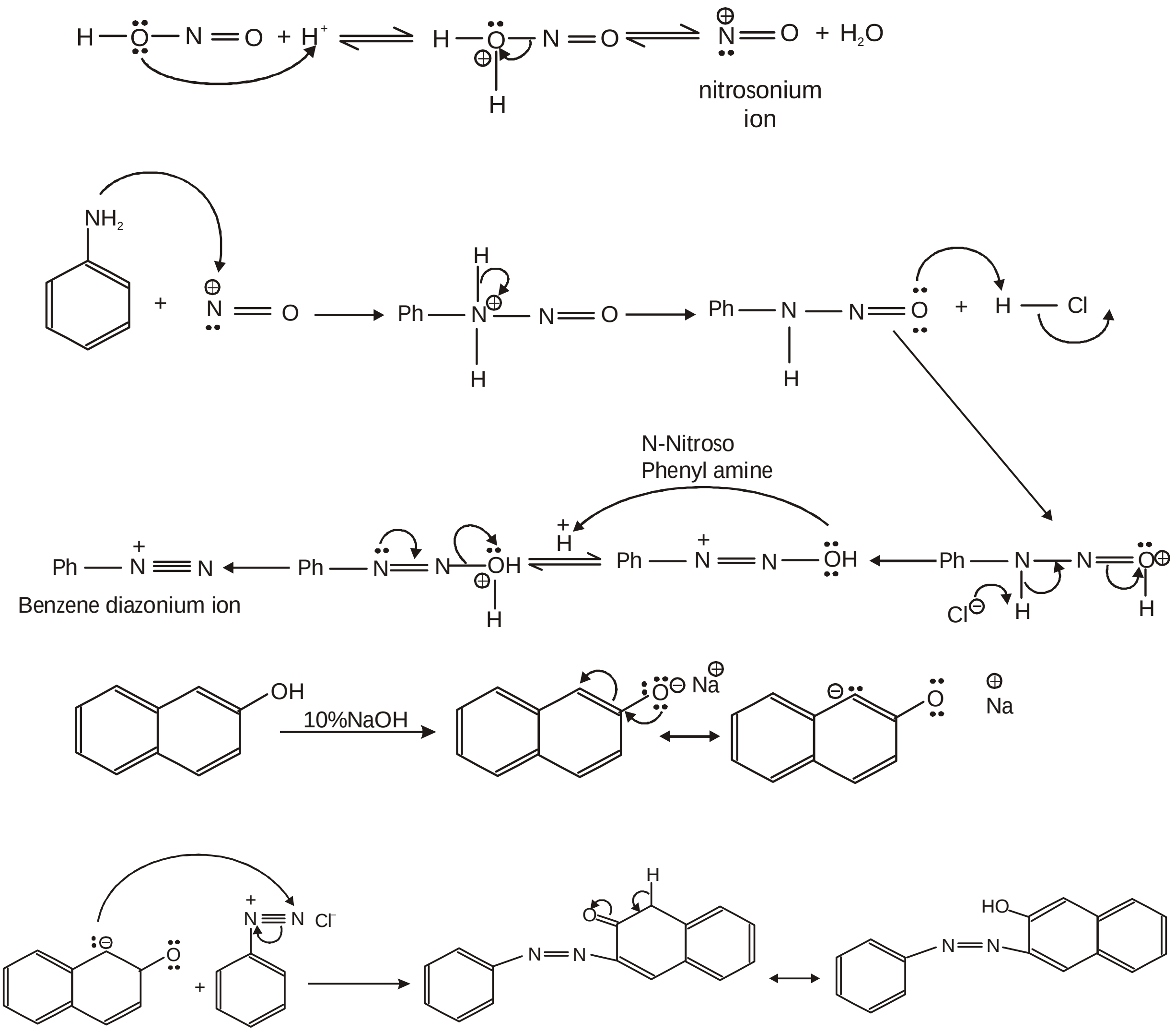
Result : Red colored azo β-Naphthol is prepared.

PREPARATION OF AZO- β-NAPHTHOL

Reaction



Mechanism



MICROWAVE ASSISTED SYNTHESIS OF ASPIRIN

Aim : To study the Acetylation of Salicylic acid by microwave synthesis

Principle : Aspirin can be prepared conventionally by heating the mixture of Salicylic acid, acetic anhydride and Cone. H_2SO_4 for 15-20 minutes. However, in microwave oven the reaction takes only 2 minutes for completion.

Type of reaction : Electrophilic substitution reaction (O-acetylation)

Chemicals required : Salicylic acid - 1gm, acetic anhydride- 1.5ml, 85% phosphoric acid - 1 or 2 drops and ferric chloride

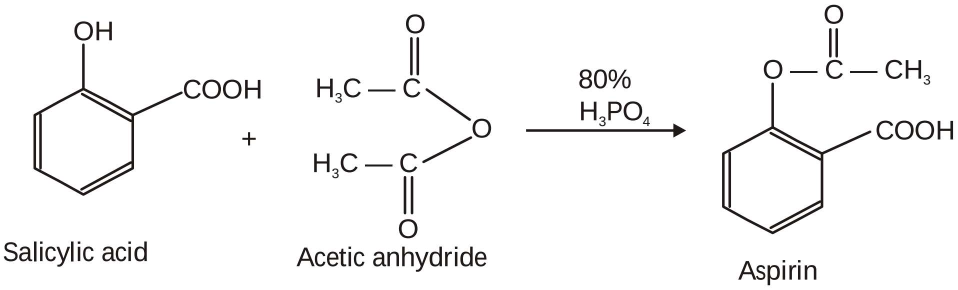
Apparatus : Conical flask, Beaker, glass rod and funnel

Procedure : Place Igm of salicylic acid in 1.5 ml of acetic anhydride and one or two drops of 85% phosphoric acid into a clean dry beaker. Mix the reaction mixture with a glass rod, cover the beaker with a watch glass and place it in a microwave oven at a power level of 30% for 2 minutes. Take out the beaker from the microwave oven, allow it to cool to room temperature and then place in an ice bath for crystallization. Test the compound for salicylic acid by feme chloride test.

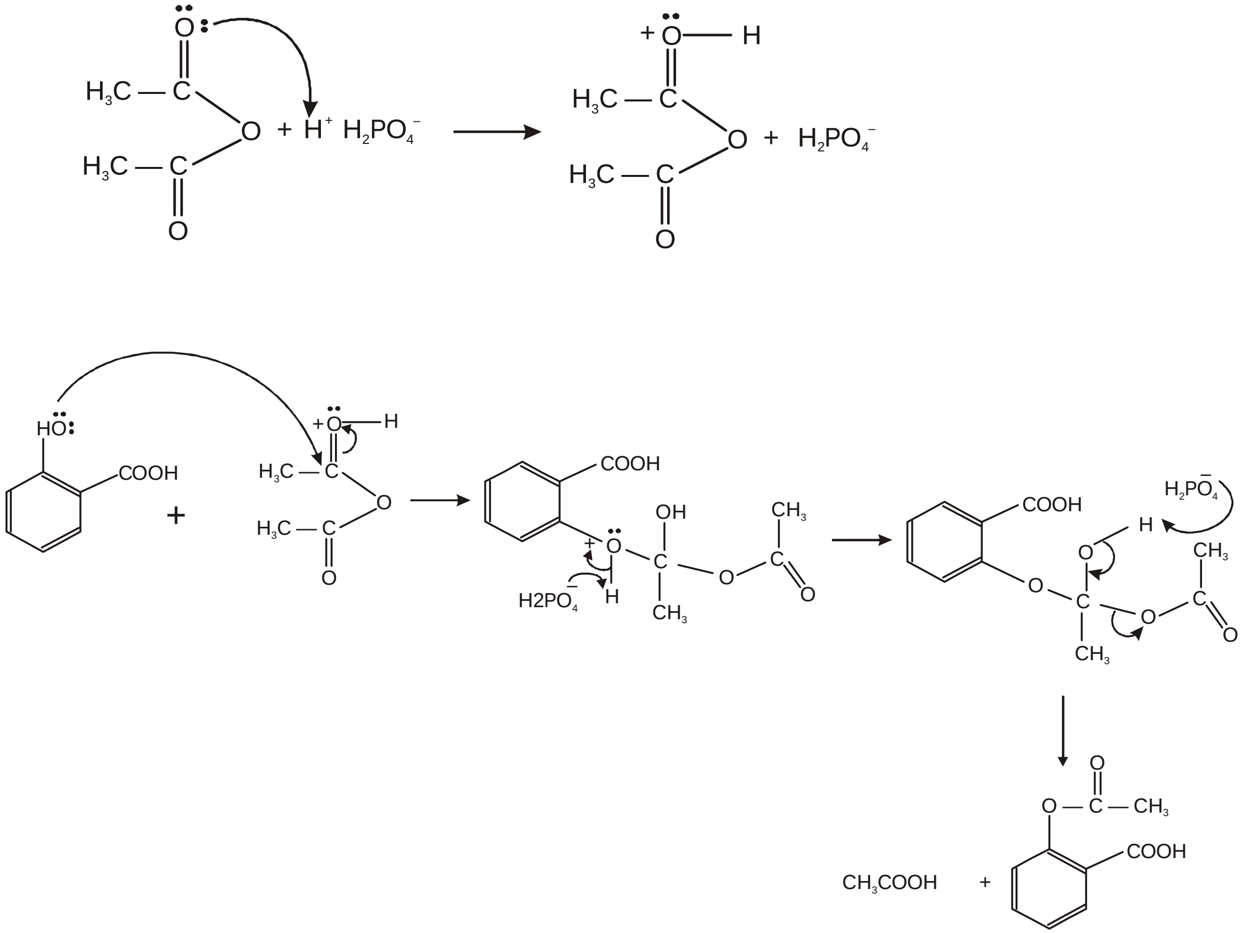
Result : Aspirin is obtained as white solid.

MICROWAVE ASSISTED SYNTHESIS OF ASPIRIN

Reaction



Mechanism



FACULTY OF SCIENCE

B.Sc. III - Semester (CBCS) Examination

Model Paper - I

CHEMISTRY - III

Time : 3 Hours] [Max. Marks : 80

PART – A (8 × 4 = 32 Marks)

(Short Answer Type)

Note: Answer any EIGHT of the following questions.

		Answer
1.	What is Lanthanide contraction?	**(Unit-I, SQA. 1)**
2.	What are Ambidentate Ligands?	**(Unit-I, SQA. 6)**
3.	What is Effective Atomic Number [EAN] ?	**(Unit-I, SQA. 8)**
4.	Give Schmidt reaction.	**(Unit-II, SQA. 3)**
5.	What is diozotisation.	**(Unit-II, SQA. 9)**
6.	Write the Carbylamine Reaction.	**(Unit-II, SQA. 12)**
7.	What are intensive and extensive properties of a system?	**(Unit-III, SQA. 3)**
8.	What is Joule-Thompson coefficient?	**(Unit-III, SQA. 8)**
9.	Draw the carnot cycle.	**(Unit-III, SQA. 11)**
10.	What are absolute and relative errors.	**(Unit-IV, SQA. 3)**
11.	Write the Perkin Reaction.	**(Unit-IV, SQA. 7)**
12.	Draw the phase diagram of water system.	**(Unit-IV, SQA. 9)**

PART – B (4 × 12 = 48 Marks)

(Essay Answer Type)

Note: Answer ALL from the questions.

13.	(a)	Write the separation methods of Lanthanides ion-exchange method and solvent extraction.	**(Unit-I, Q.No. 6)**
		OR	
	(b)	Write about valence bond theory (VBT) and its postulates.	**(Unit-I, Q.No. 18)**
14.	(a)	Discuss the mechanism of Arndt-Eistert synthesis.	**(Unit-II, Q.No. 9)**
		OR	
	(b)	Write the chemical properties of cyanides and isocyanides.	**(Unit-II, Q.No. 33)**
15.	(a)	The work done in an isothermal reversible expansion of an ideal gas is greater than the work done in reversible adiabatic expansion explain.	**(Unit-III, Q.No. 15)**
		OR	

(b) Derive carnot's cycle. Derive an expression for the efficiency of reversible heat engines working between the temperatures between T_2 and T_1. **(Unit-III, Q.No. 22)**

16\. (a) Define the following terms **(Unit-IV, Q.No. 1)**

(i) Significant figures

(ii) Accuracy

(iii) Precision

OR

(b) Apply the phase rule to salt-water system. **(Unit-IV, Q.No. 20)**

FACULTY OF SCIENCE

B.Sc. III - Semester (CBCS) Examination

Model Paper - II

CHEMISTRY - III

Time : 3 Hours] [Max. Marks : 80

PART – A (8 × 4 = 32 Marks)
(Short Answer Type)

Note: Answer any EIGHT of the following questions.

		Answer
1.	What is coordination complex?	**(Unit-I, SQA. 3)**
2.	What are Flexidentate Ligands?	**(Unit-I, SQA. 7)**
3.	What is Linkage isomerism, Give Examples.	**(Unit-I, SQA. 11)**
4.	Give the esterfication reaction.	**(Unit-II, SQA. 1)**
5.	Give Schmidt reaction.	**(Unit-II, SQA. 3)**
6.	Write the Sandmeyer Reaction.	**(Unit-II, SQA. 10)**
7.	Give Kirchoff's reaction.	**(Unit-III, SQA. 9)**
8.	What is heat capacity.	**(Unit-III, SQA. 5)**
9.	State the first law of thermodynamics.	**(Unit-III, SQA. 2)**
10.	What are Significant Figures	**(Unit-IV, SQA. 1)**
11.	Write the Perkin Reaction	**(Unit-IV, SQA. 7)**
12.	What is Degree of Freedom?	**(Unit-IV, SQA. 8)**

PART – B (4 × 12 = 48 Marks)
(Essay Answer Type)

Note: Answer ALL from the questions.

13. (a) Explain the structure and bonding of given octahedral complexes according to Valence Bond Theory. **(Unit-I, Q.No. 22)**

(a) $[Fe(CN)_6]^{3-}$ (b) $[FeF_6]^{4-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[CoF_6]^{3-}$

OR

(b) Describe the optical and geometrical isomerism in octahedral complexes. **(Unit-I, Q.No. 24)**

14. (a) What is Huns Diecker reaction. Explain the mechanism. **(Unit-II, Q.No. 7)**

OR

(b) What is diozotisation. Describe the laboratory method for the preparation of benzene diazorouum chloride. **(Unit-II, Q.No. 26)**

15. (a) Derive an Ideal gas equation $C_p - C_v = R$. **(Unit-III, Q.No. 12)**

OR

(b) The work done in an isothermal reversible expansion of an ideal gas is greater than the work done in reversible adiabatic expansion explain. **(Unit-III, Q.No. 15)**

16. (a) Explain the mechanism or (i) Perkin reaction (ii) Haloform reaction. **(Unit-IV, Q.No. 12)**

OR

(b) Construct the phase diagram of $MgZn_2$ system and explain the importance of congruent metting point. **(Unit-IV, Q.No. 19)**

FACULTY OF SCIENCE

B.Sc. III - Semester (CBCS) Examination

Model Paper - III

CHEMISTRY - III

Time : 3 Hours] [Max. Marks : 80

PART – A (8 × 4 = 32 Marks)

(Short Answer Type)

Note: Answer any EIGHT of the following questions.

		Answer
1.	What is 18 Valence electron rule?	**(Unit-I, SQA. 12)**
2.	What is Geometrical Isomerism give one example?	**(Unit-I, SQA. 10)**
3.	What are Ionic Organometallic Compounds?	**(Unit-I, SQA. 13)**
4.	What is Huns Diecker reaction.	**(Unit-II, SQA. 2)**
5.	Write the HVZ reaction.	**(Unit-II, SQA. 4)**
6.	Give the Gattermann reaction.	**(Unit-II, SQA. 11)**
7.	What is Adiabatic process.	**(Unit-III, SQA. 6)**
8.	Give Kirchoff's reaction.	**(Unit-III, SQA. 9)**
9.	Give the expression for the efficiency of reversible heat engines working between the temperatures between T_2 and T_1.	**(Unit-III, SQA. 10)**
10.	Give the expression of Standard Deviation (SD).	**(Unit-IV, SQA. 4)**
11.	Write the Aldol Condensation reaction.	**(Unit-IV, SQA. 6)**
12.	Give the tautomers of dimethyl malonate.	**(Unit-IV, SQA. 5)**

PART – B (4 × 12 = 48 Marks)

(Essay Answer Type)

Note: Answer ALL from the questions.

13. (a) Discuss the colour and magnetic properties of lanthanides. **(Unit-I, Q.No. 5)**

OR

(b) Explain the structure and bonding in $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ complexes by valance bond theory. **(Unit-I, Q.No. 21)**

14. (a) Discuss the reactions of acid amides and esters. **(Unit-II, Q.No. 11)**

OR

(b) How do you separate primary, secondary, tertiary amines from a mixture, by hinsberg separation method. **(Unit-II, Q.No. 23**

15. (a) Explain joule - Thompson effect what is Thompson coefficient. **(Unit-III, Q.No. 16)**

OR

(b) Give derivation of equation PV^{γ} = constant. Derive the expression for adiabatic changes in ideal gas. **(Unit-III, Q.No. 17)**

16. (a) Explain the mechanism of following reactions. **(Unit-IV, Q.No. 11)**
    (i) Aldol condensation
    (ii) Benzoin condensation

OR

(b) Apply the phase rule to silver-led system (Ag-Pb) binary alloy system. **(Unit-IV, Q.No. 17)**