CAREERS 360

PREPARATION Series

NEET UG 2025

Important Formulas for Chemistry

As per Latest NTA Syllabus

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Contents

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Welcome to **"Important Formulas For Chemistry"**, your essential NEET exam study resource for mastering the fundamental formulas, equations, and laws of all 11th and 12th-class Chemistry chapters. This eBook is designed to meet your needs, whether you're a NEET aspirant aiming for top scores or a teacher looking for a concise reference for your students.

What You'll Find Inside:

Comprehensive Coverage:
This eBook provides a chapter-wise collection of all the important formulas, equations, and laws covered in the Chemistry syllabus for the NEET exam. From P**hysical Chemistry to Organic Chemistry and Inorganic Chemistry,** we've got everything covered to help you prepare efficiently.

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Each formula is presented in an easy-to-understand and concise manner. To ensure a clear understanding of fundamental concepts, we have provided explanations and relevant context alongside each formula.

Visual Aids:
To enhance your comprehension, we've included images and tables where necessary, helping you visualize difficult concepts and equations effectively.

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To help you better grasp the concepts, we've included real-life examples and solved problems. By understanding these examples, you can improve your problem-solving abilities and excel in your NEET exam.

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Some basic concepts in chemistry

Important Formulae

1.Nature and Characteristics of Matter

Anything which has mass and occupies some space is called matter. On the basis of shape, size, and volume, the matter can be classified into solids. liquids and gases.

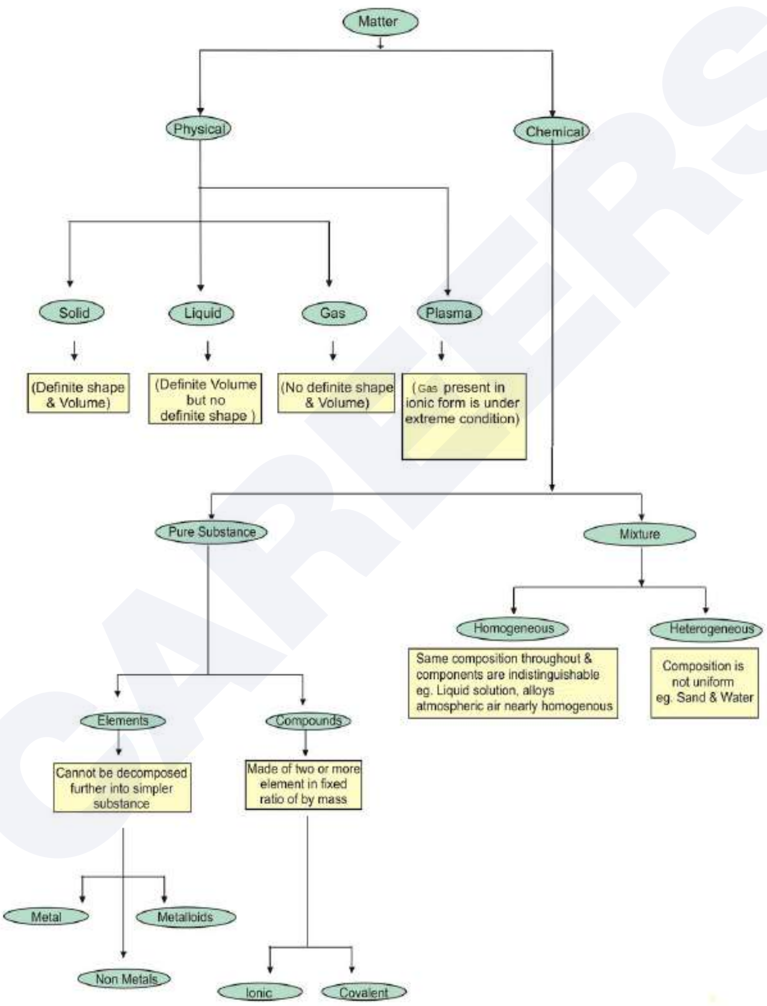
1. Solids have definite volume and definite shape.
2. Liquids have a definite volume but no definite shape. They take the shape of the container in which they are placed.
3. Gases have neither a definite volume nor a definite shape. They completely occupy the container in which they are placed.

These three states of matter are interconvertible by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Gas}$$

On heating, a solid usually changes to a liquid and the liquid on further heating changes to the gaseous (or vapor) state. In the reverse process, a gas on cooling liquifies to the liquid, and the liquid on further cooling freezes to the solid.

Classification of Matter-



1. **Physical Classification:** Based on the physical state under ordinary conditions of temperature and pressure, matter is classified into the following three types-
    1. **Solid:** A substance is said to be solid if it possesses a definite volume and a definite shape.
        - e.g. sugar, iron, gold, wood, etc.
    2. **Liquid:** A substance is said to be liquid if it possesses a definite volume but no definite shape. They take up the shape of the vessel in which they are put.

- e.g. water, milk, oil, mercury, alcohol, etc.

3. **Gas:** A substance is said to be gas if it neither possesses a definite volume nor a definite shape. This is because they fill up the whole vessel in which they are put.

    - e.g. hydrogen(H_2), oxygen(O_2), carbon dioxide(CO_2), etc.

2. **Chemical Classification :**

    1. **Pure Substance:** A material containing only one type of substance. Pure Substances can not be separated into simpler substances by physical methods.

       eg: Element = Na, Mg, Ca, etc. Compound = HCl, H_2O, CO_2, HNO_3, etc.

        1. **Element:** The pure substance containing only one kind of atoms. Depending on the physical and chemical property, these are of three types

            1. Metal
            2. Non-metal
            3. Metalloids

        2. **Compound**: It is defined as a pure substance containing more than one kind of atoms that are combined together in a fixed ratio by weight and which can be decomposed into simpler substances by the suitable chemical method. The properties of a compound are different from those of its components.

            - e.g.: H_2O, HCl, HNO_3, etc.

3. **Mixture Substance**: A material that contains more than one type of substance which are mixed in any ratio by weight is called a mixture. The property of the mixture is the property of its components. The mixture is separated by simple physical method.

    1. **Homogeneous mixture:** The mixture, in which all the components are mixed uniformly is called a homogeneous mixture.

        - e.g. : Water + Salt, Water + Sugar, Water + alcohol.

    2. **Heterogeneous mixture:** The mixture in which the composition is nonuniform is called as Heterogeneous mixture.

        - e.g. : Water + Sand, Water + Oil

2. PROPERTIES OF MATTER AND THEIR MEASUREMENT

3.UNCERTAINTY IN MEASUREMENT

4.LAWS OF CHEMICAL COMBINATIONS

Law of Conservation of Mass :

It states that matter can neither be created nor destroyed. This law formed the basis for several later developments in chemistry. In fact, this was the result of the exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

Law of Definite Proportions :

This law was given by, a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight.

Law of Multiple Proportions :

This law was proposed by Dalton in 1803. According to this law, if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

Gay Lussac's Law of Gaseous Volumes :

This law was given by Gay Lussac in 1808. He observed that when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at the same temperature and pressure.

Avogadro Law :

- According to this law, "Under similar conditions of temperature and pressure, the equal volume of gases the equal number of molecules. "

  It means 10 ml of H_2, O_2, N_2 or a mixture of gases have the same number of molecules.

  It is used in:

  (i) The deriving molecular formula of a gas

  (ii) Determining atomicity of a gas

  (iii) Deriving a relation

  molecular mass = 2 x vapour density

  M=2 X VD

  (iv) Deriving the gram molecular volume

- Avogadro number (N_o or N_A) = 6.023×10^{23}
- Avogadro number of gas molecules occupy 22.4 litre or 22400 ml or cm^3 volume at STP
- The number of molecules in 1 cm^3 of a gas at STP is equal to Loschmidt number, that is, 2.68×10^{19}
- The reciprocal of Avogadro number is known as Avogram.

5.DALTON'S ATOMIC THEORY

1. Matter consists of indivisible atoms.
2. Atom is indivisible and cannot be broken down.

3. All the atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.

4. Compounds are formed when atoms of different elements combine in a fixed ratio.

5. Chemical reactions involve the reorganization of atoms. These are neither created nor destroyed in a chemical reaction.

6.Atomic Mass And Molecular Mass

Atomic Mass :

One atomic mass unit is defined as a mass exactly equal to one-twelfth the mass of one carbon - 12 atom.

And 1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen = 1.6736×10^{-24} g

Thus, in terms of amu, the mass of hydrogen atom

$$= \frac{1.6736 \times 10^{-24}\ \text{gm}}{1.66056 \times 10^{-24}\ \text{gm}}$$

= 1.0078 amu

= 1.0080 amu

Similarly, the mass of oxygen - 16 (^{16}O) atom would be 15.995 amu.

Today, 'amu' has been replaced by 'u' which is known as unified mass.

When we use atomic masses of elements in calculations, we actually use average atomic masses of elements which are explained.

Average Atomic Mass :

Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (percent occurrence), the average atomic mass of that element can be computed.

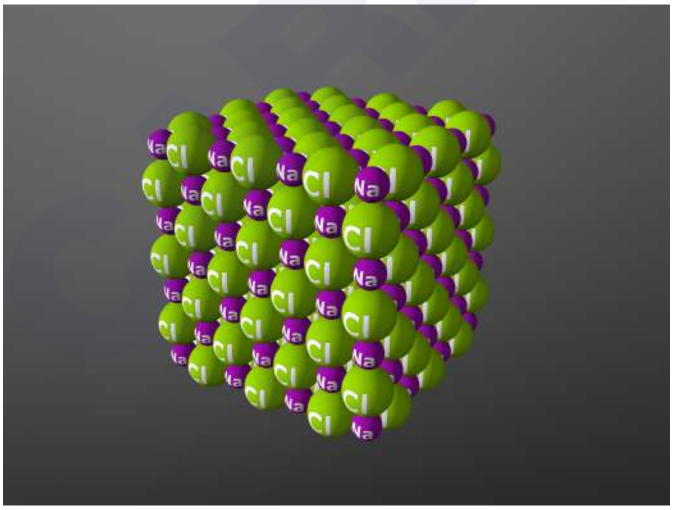
$$\text{Average Atomic Mass} = \frac{\Sigma(\text{Mass of Isotopes})_i \times (\%abundance)_i}{100}$$

In the periodic table of elements, the atomic masses mentioned for different elements actually represented their average atomic masses.

Molecular Mass :

Molecular mass is the sum of the atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

Formula Mass :



It may be noted that in sodium chloride, One Na^+ is surrounded by six Cl^- and vice-versa. The formula such as NaCl is used to calculate the **formula mass** instead of molecular mass as in the solid-state sodium chloride does not exist as a single entity.

Thus. formula mass of sodium chloride = atomic mass of sodium + atomic mass of chlorine

= 23.0 u + 35.5 u = 58.5 u

7.Mole Concept Basic

Mole:

- A mole is a unit that represents 6.023 x 10^{23} particles, atoms, molecules or ions, etc., irrespective of their nature.
- Mole is related to the mass of the substance, the volume of gaseous substance and the number of particles
- $$\text{Mole} = \frac{\text{W}}{\text{M}} = \frac{(\text{Wt. of substance in gm.})}{(\text{Molar mass of substance (G.m.m)})}$$

  Here G.m.m. = Gram molecular mass or molar mass which is the mass of 1 mole of any substance
- $$\text{Mole} = \frac{(\text{Volume of substance in litre})}{22.4 \text{ litre}}$$
- The volume of one mole of any gas is equal to 22.4 litres or dm^3 at STP. It is known as molar volume.
- $$\text{Mole} = \frac{\text{Number of identities}}{\text{Avogadro's number}}$$

Relationship of Mole:

A mole of any substance (like O_2) stands for:

- 6.023 x 10^{23} molecules of O_2
- 2 x 6.023 x 10^{23} atoms of Oxygen
- 32 gm of Oxygen
- 22.4 litre of O_2 at STP.

To Find the Total Number of Identities:

1. Total number of Molecule = mole(n) x N_A
2. Total number of Atoms = mole (n) x N_A x No. of atoms present in one molecule (atomicity).
3. Total number of Electrons = mole (n) x N_A x No. of electron present in one atom.
4. Total charge on any ion = mole (n) x N_A x charge on one ion x 1.6 x 10^{-19} C

8.Percent Composition Formula

Percentage Composition:

The percentage combination of the compound is the relative mass of each of the constituent elements in 100 parts of it.

$$\text{Mass \% of an element} = \frac{\text{Mass of that element in one mole of the compound}}{\text{Molar mass of the compound}} \times 100$$

Let us take an example of water (H_2O), it contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follow:

The molar mass of water = 18.02 g

$$\text{Mass \% of Hydrogen} = \frac{2 \times 1.008}{18.02} \times 100 = 11.18\%$$

$$\text{Mass \% of Oxygen} = \frac{16.00}{18.02} \times 100 = 88.79\%$$

One can check the purity of a given sample by analyzing percentage composition.

Equivalent Weight:

- Equivalent weight is the weight of an element or a compound that combines with or displaces 1 gram of hydrogen or 8 grams of oxygen, or 35.5 part by weight of Chlorine.
- Equivalent weight is a number and when it is denoted in grams, it is called gram equivalent.
- It depends upon the nature of chemical reaction in which substance takes part

How To Find Equivalent Weight:

$$\textbf{Equivalent Weight} = \frac{\textbf{Molecular weight}}{\textbf{n} - \textbf{factor}(\textbf{x})}$$

n-Factor or Valence Factor:

It calculates the molar ratio of the species taking part in reactions that are, reactants. The reciprocal of the n-factor 's ratio of the reactants represents the molar ratio of the reactants. For example, If A (having n-factor = a) reacts with B (having n-factor = b) then its n-factor's ratio is

a: b, so molar ratio of A to B is b: a.
It can be represented as follows:

$$\begin{array}{lll} bA & + & aB \rightarrow \text{Product} \\ (n - \text{factor} = a) & & (n - \text{factor} = a) \end{array}$$

Calculation of n-Factor
Before calculating the n-factor of any of the reactants in a given chemical reaction we must have a clear idea about the type of reaction. The reaction may be any of these types:

(i) Acid-base or neutralization reaction

(li) Redox reaction

- **Acid-Base or Neutralization Reactions:**
  As we know that according to the Arrhenius concept, "An acid provides H^+ ion(s) while a base provides OH^- ion(s) in neutralization these H^+ and OH^- ion/ions combines together".
  The number of H^+ ion(s) and OH^- ion(s) represent n-factor for acid and base respectively, that is, basicity and acidity respectively.
  Example,
  $HCl \rightarrow H^+ + Cl^-$
  $(n = 1)$ that is, monobasic acid

  $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$
  $(n = 2)$ that is, dibasic acid
- **Redox Reactions**
  These reactions involve oxidation and reduction simultaneously. Here the exchange of electrons occurs. To find the n-factor for Oxidizing or agent we must find out the change in the oxidation state of these species.

  You will be learning the following in detail in the chapter of redox. For now, just look at the definition. Sufficient questions will be practiced later.

- **For Redox Reactions:**
  E = (Molecular weight) / (Change in oxidation number),

  x= change in oxidation state
  For Example, for $KMnO_4$
  (a) In acidic medium: E = M/5

  $2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5[O]$
  5 unit change in oxidation number.

  (b) In basic medium: E = M/1

  $2K\overset{+7}{Mn}O_4 + 2KOH \rightarrow 2K_2\overset{+6}{Mn}O_4 + H_2O + [O]$
  one unit change in oxidation number

  (c) In neutral medium: E = M/3

  $2K\overset{+7}{Mn}O_4 + H_2O \rightarrow 2KOH + 2\overset{+4}{Mn}O_2 + 3[O]$
  3 unit change in oxidation number

Formulae for calculation of Equivalent Weight:

- **For Acids:**
  E = (Molecular weight) / (Protocity or Basicity of Acid), x= number of furnishable protons
  For Example, for H_3PO_4, E = M/3
  For H_2SO_4 , E =M/2
- **For Bases:**
  E = (Molecular weight) / (Acidity or number of OH^- ions),x= number of furnishable OH^- ions
  For Example, for $Ca(OH)_2$, E = M/2
  For $Al(OH)_3$, E =M/3
- **For Ions:**
  E = (Molecular weight) / (Charge on ion), x= charge on ion
  For Example, for SO_4^{2-}, E = M/2
  For PO_4^{3-}, E = M/3
- **For Compounds:**
  E = (Molecular weight) / (total positive charge or negative charge present in compound),

  x= total positive charge or negative charge present in compound
  For Example, for $CaCO_3$, E = M/2
  For $AlCl_3$, E =M/3

- **For Acidic Salt:**
  E = (Molecular weight) / (Number of replaceable H-atoms)
  For example, for H_3PO_4

$$2NaOH + NaH_2PO_4 \rightarrow Na_3PO_4 + 2H_2O$$

$$E = M/2$$

- Metal displacement method
  $E_1 / E_2 = W_1 / W_2$

9.Empirical and Molecular Formula

Chemical Formula:
A chemical formula represents the combination of atoms of all the elements which make up a compound. It represents the relative ratio of atoms of its constituent elements. In case of a compound, it represents one molecule, one mole, one gram molecular weight of the compound.
Example, $CuSO_4.5H_2O$ represent one molecule, one mole and one gram molecular weight of hydrated copper sulphate.

Empirical Formula:
It is the simplest ratio of the number of atoms of different elements present in one molecule of a compound. It does not represent the actual number of atoms of different elements present in one molecule of the compound.

How to find out the empirical formula and the molecular formula in case the % composition of the compound is given to us

Step 1. Conversion of a mass percent to grams.

Step 2. Convert grams into the number of moles of each element.

Step 3. Divide the mole value obtained above by the smallest number.

Step 4. Write the empirical formula by mentioning the numbers obtained above after writing the symbols of respective elements.

Step 5. Write molecular formula (Molecular formula) with the help of the information given.

Molecular formula is a whole number multiple of the empirical formula

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

where n is whole number.

Molecular Formula:
It shows the actual number of atoms of different elements present in one molecule of a compound.

- n = (Molecular weight) / (Empirical formula weight)
- Molecular weight can be directly given or some other information like Vapour density can be given which will enable us to calculate the molecular weight.
- Molecular weight = 2 x Vapour Density
- For some compounds the molecular formula and empirical formula may be same also.

10.Stoichiometric Calculations

Stoichiometry:

Stoichiometry deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or the products produced in a chemical reaction, let us study what information is available from the balanced chemical equation of a given reaction.

Stoichiometric Calculations:

Step 1 Write down the correct formulas of reactants and products.

Step 2 Balance the number of atoms on both reactant and product sides.

Step 3 Make the equation balanced.

The coefficients of atoms or molecules are stoichiometric coefficients.

Limiting Reagent:

The reactant is consumed first in the reaction. When we are dealing with the balanced chemical equation, if the number of moles of reactants is not in the ratio of the stoichiometric coefficient of the balanced chemical equation, then there should be one reactant that should be limiting reactant.

% yield

Sometimes, experimentally, the reaction does not undergo 100% completion because of many factors which are involved in the actual industrial processes. So in such cases, we need the concept of % yield.

It is defined as the ratio of actual moles of product(s) formed to the number of moles that should have been theoretically formed assuming 100% completion of the reaction.

$$\% \text{ yield} = \frac{\text{Actual number of moles formed}}{\text{Theoretical moles that should have formed}}$$

11.Gravimetric Analysis

Gravimetric Analysis:
It is an analytical technique based on the measurements of the mass of solid substances or the volume of the gaseous species. It is divided into three categories:

- **Mass-Mass (weight-weight) relation**

  This relationship relates to the mass of a reactant or product with the mass of another reactant or product.

  1. Write down the balanced equation to represent the chemical change.
  2. Write the number of moles below the formula of reactants and products.
  3. Finally, apply the unitary method to calculate the unknown factor.

- **Mass-volume relation**
  This relationship relates the mass of a reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction.

  1. Write down the relevant balanced chemical equation.
  2. Write the weights of various solid reactants and products.
  3. Gases are normally expressed in terms of volume. In case the volume of the gas is measured at room temperature and pressure, convert it into N.T.P. by applying gas laws.
  4. The volume of a gas at any temperature and pressure can be converted into its weight and vice versa by using the relation,
     PV = (g/M) x RT
     Here g is the weight of the gas, M is the molecular weight of gas and R is the gas constant.
  5. Finally, calculate the unknown factor (n or s) by unitary method.

- **Volume-Volume relation**
  This relationship relates the volume of a gaseous reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction.

  1. First, write down the relevant balanced chemical equation.
  2. Now write down the volume of the reactants and the products below the formula to each reactant and product using the fact that one gram molecules of every gaseous substance occupies 22.4 liters at N.T.P. (22.7 Litre at STP)
  3. If the volume of the gas is measured under particular or room temperature, convert it to N.T.P. with the help of the ideal gas equation.
  4. Now use Avogadro's hypothesis gases under similar conditions of temperature and pressure contain the same number of molecules. Thus under similar conditions of temperature and pressure, the number of moles of the gases in the balanced equation.

12.Reactions in Solutions

1. Solution:

The solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

2. Solute and Solvent:

The solution is present in the same physical state as that of the solvent.

In case the species forming a solution are all present in the same physical state then the component which is present in a smaller amount is called the **solute** and the other present in a larger amount is called the **solvent**.

3. Concentration:

The **concentration of a solution** is a measure of the amount of solute that has been dissolved in a given amount of solvent or **solution**

4. Types of concentration terms:

(I) Mass fraction or % (w/w)

The mass percentage of a component of a solution is defined as:

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, a commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

(II) Mole fraction: Commonly used symbol for mole fraction is x and subscript used on the right-hand side of x denotes the component.
It is defined as:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

It is expressed by X for example, for a binary solution with two components A and B.

$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

Here n_A and n_B represent moles of solvent and solute respectively. Mole fraction does not depend upon temperature as both solute and solvent are expressed by weight.

(III) Molality
It is the number of moles or gram moles of solute dissolved per kilogram of the solvent. It is denoted by 'm'.

$$\mathrm{m} = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{wt. of solvent in Kg}}$$

- If molality is one solution, it is called molal solution.
- One molal solution is less than one molar solution.
- Molality is preferred over molarity during experiments as molality is temperature independent while molarity is temperature-dependent.

(IV) Mass by volume percentage (w/V): Another unit that is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

(V) Molarity:
It is the number of moles or gram moles of solute dissolved per litre of the solution. Molarity is denoted by 'M'.

$$\mathrm{M} = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{volume in litre}}$$

- When the molarity of a solution is one, it is called a molar solution and when it is 0.1, the solution is called decimolar solution.
- Molarity depends upon temperature and its unit is mol/litre.
- Number of moles of solute if the Molarity and the **Volume in litres** are given, is calculated as

  Moles = M × V

  In case the volume is given in ml then the millimoles of solute will be given by the above formula

- On dilution water is added and the final volume is made to V_2 , then the moles of solute will remain constant and hence the following formula can be used (V_1 is the volume before dilution, V_2 is the volume after dilution)

  $M_1V_1 = M_2V_2$

- When a mixture of different solutions having different concentrations are taken the molarity of the mixture is calculated as follows:
  $$\mathrm{M} = \frac{M_1V_1 + M_2V_2 \ldots..}{V_1 + V_2 \ldots..}$$
- When density and % by weight of a substance in a solution are given, molarity is found as follows:
  $$\mathrm{M} = \frac{\% \text{ by weight} \times d \times 10}{\text{Molecular weight}}$$
  Here d = density

(VI) Normality
It is the number of gram equivalents of solute present in one litre of the solution and it is denoted by 'N'.

$$\mathrm{N} = \frac{\text{Weight of solute in gram}}{\text{Equivalent mass} \times \text{volume in litre}}$$

- When the normality of a solution is one, the solution is called a normal solution and when it is 0.1, the solution is called a decinormal solution.

Normality Equation:

$$N_1V_1 = N_2V_2$$

- Volume Of water added = V_2 - V_1
  Here V_2 = volume after dilution
  V_1 = volume before dilution
- When density and % by weight of a substance in a solution are given, normality is found as follows:

  $$\mathrm{N} = \frac{\% \text{ by weight} \times d \times 10}{\text{Equivalent weight}}$$
  Here d = density of solution

  When a mixture of different solutions having different concentrations are taken the normality of the mixture is calculated as follows:
  $$\mathrm{N} = \frac{N_1V_1 + N_2V_2 \ldots..}{V_1 + V_2 \ldots..}$$

(VII) Strength :
It is the amount of solute present in one litre of solution. It is denoted by C or S.

$$\text{C or S} = \frac{\text{Weight of solute in gram}}{\text{Volume in litre}}$$

$$\text{C} = \text{N} \times \text{E}$$

$$\text{Here N} = \text{normality and E} = \text{Eq. wt.}$$

(VIII) The relation between Normality and Molarity :
N = molarity x n-factor

N x Eq wt. = molarity x molar mass

13.Law of Equivalence

Laws of Equivalence
According to the law of equivalence, for each and every reactant and product,
Equivalents of each reactant reacted = Equivalents of each product formed.

Example,
Suppose the reaction is taking place as follows:
$P + Q \rightarrow R + S$

According to the law of equivalence,

Equivalents of P reacted = Equivalents of Q reacted = Equivalents of R produced = Equivalents of S produced

Equivalents of any substance = (Weight of substance (in g)) / (Equivalent weight)
= Normality (N) x Volume (V) (In litre)
Normality (N) = n-Factor x Molarity (M)

Law of Equivalence finds great importance in Acid base Neutralisation Reactions as well as Redox Titrations.

14.Oleum and its % labelling

Oleum and its % labelling-

Oleum is a mixture of SO_3 dissolved in 100% H_2SO_4. The strength of the Oleum sample is expressed in terms of % labelling and it is defined as the grams of pure H_2SO_4 that can be obtained from 100 g of the Oleum sample upon dilution with water.

For example, if an Oleum sample is labelled as 109%, it means that upon addition of 9g water to 100 g of Oleum sample, the amount of H_2SO_4 obtained is 109 g.

We can calculate the % of free SO_3 in the sample by simple stoichiometry as follows:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Weight of H_2O added = 9 g

Moles of H_2O added = 0.5

$\therefore$ Moles of SO_3 present = 0.5 (from reaction stoichiometry)

$\therefore$ Weight of SO_3 in the 100g Oleum sample = 0.5 $\times$ 80 = 40 g

$\therefore$ % of free SO_3 in Oleum = 40 %

Let us also discuss a general case

Let us suppose that the % labelling of Oleum sample is y %. This means that (y-100) g of water is added to 100g Oleum sample

$$\therefore \text{moles of water} = \frac{y - 100}{18} = \text{moles of } SO_3$$

$$\therefore \% \text{ of free } SO_3 \text{ in Oleum} = \frac{80 \times (y - 100)}{18}$$

In this manner, the % of free SO_3 in Oleum sample can be calculated.

15. Smart Tips

Heating of Carbonates

- Group II metal carbonates like $MgCO_3$, $CaCO_3$ and other bivalent metal carbonates ($PbCO_3$, $ZnCO_3$) liberate CO_2 on heating and leave their oxide as residue

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

- Group 1 metal carbonates like Na_2CO_3, K_2CO_3 are resistant to decomposition upon heating (except Li)

Heating of Bicarbonates

- **Group II metal bicarbonates like $Ca(HCO_3)_2$ liberate CO_2 and H_2O on heating and leave their oxide as residue**

$$\mathrm{M(HCO_3)_2 \xrightarrow{\Delta} MO + 2\,CO_2 + H_2O}$$

- **Group I metal bicarbonates like $NaHCO_3$ liberate CO_2 and H_2O on heating and leave their carbonate as residue**

$$\mathrm{2\,Na(HCO_3) \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O}$$

Acid-Base Titrations involving Multiple acids or bases

Sometimes, the problems involving neutralisation reactions involve more than one acids or bases. In such cases too, the underlying principle is the law of equivalence. i.e.

meq. of acid 1 + meq. of acid 2 + ... = meq of base 1 + meq. of base 2 + ...

Atomic Structure

Important Formulae

1. Thomson atomic model

2. Rutherford atomic model and its limitations

3.Atomic Number(Z), Mass number(A), Isotopes and Isobars

Atomic number (z) = number of protons in the nucleus of an atom

Mass number (A) = sum of neutrons and protons in the nucleus

Isotopes = Atoms having the same atomic number but a different mass number.

Isobars = Atoms with same mass number but different atomic number

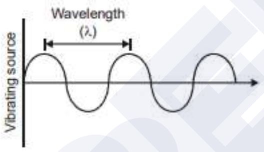
4.Electromagnetic radiation

EM radiation -

According to electromagnetic wave theory, energy is emitted continuously from a source in the form of radiations (or waves), known as electromagnetic radiation. Electromagnetic radiations have both magnetic field as well as electric field components which oscillate in the phase perpendicular to each other as well as perpendicular to the direction of wave propagation. These waves do not require any medium for propagation and can propagate through vacuum. There are many types of electromagnetic radiations which constitute what is known as electromagnetic spectrum.

There are several parameters required to characterise or define a wave. These parameters are defined below:

1. Wavelength (λ): It is the distance travellled by the wave during one complete oscillation.



The maxima are called as Crests and the minima are called as Troughs. Alternatively, the distance between two consecutive crests or two consecutive troughs is also called as the wavelength.

2. Time Period (T): It is the time required for one complete oscillation or one complete cycle by a wave.

3. Frequency (ν): It is number of waves produced by the source in one second

It is the inverse of the time period. Its SI unit is Hertz (Hz).

$$\nu = \frac{1}{\mathrm{T}}$$

4. Speed (c): It is the distance travelled by the wave in one second.

In one time period, the wave travels a distance equal to its wavelength.

$$\mathrm{c} = \frac{\text{distance}}{\text{time}} = \frac{\text{Wavelength}}{\text{Time Period}} = \frac{\lambda}{\mathrm{T}}$$

$$\because \nu = \frac{1}{\mathrm{T}}$$

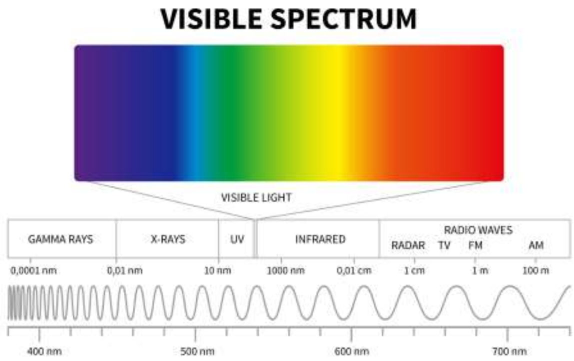
$$\therefore \mathrm{c} = \nu \times \lambda$$

The speed of all the different components of light is the same i.e. they travel with the speed of 3×10^8 m/s. Their frequency and wavelength are different

5. Wave number ($\bar{\nu}$) : It is the inverse of the wavelength. It can also be defined as the number of wavelengths present in unit length.

$$\bar{\nu} = \frac{1}{\lambda}$$

- List of wavelengths for the electromagnetic spectrum



The rays present on the left extreme of the spectrum have the greatest frequency, least wavelegth and the greatest energy,

As the frequency increases, wavelength decreases and energy increases.

5. Planck's quantum theory

Atoms and molecules could emit (or absorb) energy only in discrete quantities known as quanta and not in a continuous manner. The following are certain phenomena which could not be explained by the wave nature of electromagnetic radiation and are explained by the particle nature:

1. The nature of emission of radiation from hot bodies (black-body radiation).
2. Ejection of electrons from a metal surface when radiation strikes it (photoelectric effect).
3. Variation of heat capacity of solids as a function of temperature.
4. Line spectra of atoms with special reference to hydrogen.

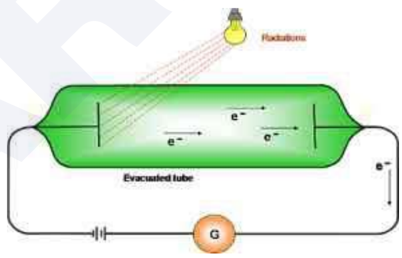
Max Planck suggested that the energy which is emitted or absorbed by the black body is not continuous but discontinuous in the form of small discrete packets of energy. Each such packet of energy is called a ‘quantum’. In case of light, the quantum of energy is called a ‘photon’. The energy of radiation is proportional to its frequency (ν) and is expressed by the following equation:

$$E = h\nu = \frac{hc}{\lambda}$$

where h is the Planck's constant and it has a value equal to 6.63×10^{-34} J-s

6.Photoelectric effect

Whenever a metal surface is exposed to light radiation of suitable energy or frequency, it was observed that some electrons get ejected from the metal surface. This phenomenon is called as Photoelectric effect and the ejected electrons are called as photoelectrons.



There were certain observation in the photoelectric effect experiment.

(1) There was a requirement of a minimum energy for each metal for the photoelectric effect to occur. This minimum energy is known as work function (W_0) and it can be closely associated with the ionisation energy of the metal.

- Corresponding to the work function, there is a minimum frequency of light required for photoelectric effect. This minimum frequency is called as Threshold frequency.
- Corresponding to the work function, there is a maximum wavelength of incident light above which Photolelectric effect cannot occur. This maximum wavelength is called as the Threshold wavelength.

Mathematically, the work function, threshold frequency and threshold wavelength can be associated as

$$\mathrm{W}_0 = \mathrm{h}\nu_0 = \frac{\mathrm{hc}}{\lambda_0}$$

Note: hc is approximately equal to 2×10^{-25} J-m or 12400 eV-nm. (eV is the energy in electron volts)

(2) The number of electrons ejected is proportional to the intensity (brightness) of light striking the metal but does not depend upon the frequency of light.

(3) There was almost no time lag between the striking of light and ejection of photo electrons

(4) The kinetic energy of the ejected electrons (photoelectrons) depend upon the frequency of the light used.

Einstein's photoelectric equation

From conservation of energy

$$E_p = W_0 + KE$$

$$\therefore h\nu = h\nu_0 + \frac{1}{2}mv^2$$

where

m is the mass of the electron

v is the velocity associated with the ejected electron.

h is planck’s constant.

v is frequency of photon,

v_0 is threshold frequency of metal.

(5) The Kinetic energy of ejected photoelectron is also sometimes associated to **Stopping Potential**. It is defined as the minimum opposing potential applied due to which kinetic energy of electron becomes zero.

$$\frac{1}{2}mv^2 = eV_s$$

where,

V_s = Stopping potential

e = Charge on electron

7.Hydrogen Spectrum

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. These radiations are emitted because of electronic transitions upon de-excitation to different energy levels and on the basis of the final energy level of transition, the hydrogen spectrum consists of several series of lines named after their discoverers like Lyman series, Balmer Series, Paschen Series, Bracket Series, Pfund Series.

Line Spectrum of Hydrogen-like atoms

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where R is called Rydberg constant, R = 109677cm^{-1}, Z is atomic number

n_1= final orbit occupied after de-excitation= 1, 2, 3….

n_2= initial orbit occupied before de-excitation

Lyman Series spectrum:

Transition of electrons from higher orbits to n=1 result in the Lyman Series

n_1= 1 and n_2= 2, 3, 4....

For H atom, this lies in Ultraviolet region. For elements with higher Z, the Balmer lines lie in the Ultraviolet region

Balmer Series Spectrum:

Transition of electrons from higher orbits to n=2 result in the Balmer Series

Where n_1= 2 and n_2= 3, 4, 5, 6....

For H atom, this generally lies in visible region.

Paschen, Bracket and Pfund Series spectrums:

Transition of electrons from higher orbits to n=3, 4 and 5 respectively result in the Paschen, Bracket and the Pfund Series

These lines lie in the Infrared Region for H atom.

Discovery of the line spectrum gave the evidence for quantised electronic energy levels in atoms and laid the foundation for the development of the Bohr's model.

8.Bohr's Model Of An Atom

Bohr's model and its postulates:

1. The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states and are arranged concentrically around the nucleus. Force of attraction between the nucleus and an electron provides the centripetal force required by the electron to carry out the circular motion.

2. The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state

3. Energy can be absorbed or emitted when electron transitions between two different orbits and the frequency of photon involved can be calculated using the formula:

$$|E_1 - E_2| = h\nu$$

4. The angular momentum of an electron is quantised. In a given stationary state it can be expressed as

L= mvr= nh/2π, n = orbit number

So only those energy states (or orbits) are allowed in which the above equation holds true for the angular momentum.

Note: Bohr's model is only valid for Hydrogen like species or unielectronic species which contain only a single electron

According to Bohr's theory for hydrogen atom:

(1) The stationary states for electron are numbered n = 1,2,3.......... These integral numbers are known as Principal quantum numbers.

(2) Bohr radius of nth orbit:

$$\mathrm{r_n} = 0.529\frac{\mathrm{n}^2}{\mathrm{Z}}\mathrm{A}^0$$

where Z is atomic number and radius is calculated by the formula in angstrom (A^0) ($1A^0=10^{-10}$ m)

(3) Velocity of electron in nth orbit:

$$\mathrm{V_n} = (2.18 \times 10^6)\frac{\mathrm{Z}}{\mathrm{n}}\ \mathrm{m/s}$$

where Z is atomic number

(4) Total energy of electron in nth orbit:

$$\mathrm{E_n} = -13.6\frac{\mathrm{Z}^2}{\mathrm{n}^2}\mathrm{eV} = -2.18 \times 10^{-18}\frac{\mathrm{Z}^2}{\mathrm{n}^2}\mathrm{J}$$

where Z is atomic number

Depending upon the units given in the question, the respective formula can be used

(5) Time Period and Frequency of Revolution

Although the precise equations for time period and frequency of revolution are not required but still it is a good idea to look at the variations of these with the atomic number (Z) and the orbit number (n).

We know that Time period (T) is the time required for one complete revolution and that Frequency (ν) is inverse of the time period

$$\therefore T = \frac{distance}{time} = \frac{2\pi r}{v}$$

$$\because \mathrm{r} \propto \frac{\mathrm{n}^2}{\mathrm{Z}} \mathrm{and\ v} \propto \frac{\mathrm{Z}}{\mathrm{n}}$$

$$\therefore T \propto (\frac{n^2}{Z} \times \frac{n}{Z}) \propto (\frac{n^3}{Z^2})$$

$$\therefore \nu = (\frac{1}{T}) \propto (\frac{Z^2}{n^3})$$

Limitation of Bohr theory:

1. It does not explain the spectra of the atom with more than one electron.

2. Failed to explain Zeeman and stark effect.

3. Failed to explain the basis of stationary orbit.

Zeeman effect:

Splitting of spectral lines in the presence of magnetic field

Stark effect:

Splitting of spectral lines in the presence of the electric field.

9.De Broglie Relationship

De-broglie wavelength

(1) de-Broglie proposed that just like light, matter should exhibit both particle and wave-like properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, and he proposed the following mathematical relationship:

$$\lambda=\frac{h}{mv}=\frac{h}{p}=\frac{h}{\sqrt{2mKE}}=\frac{h}{\sqrt{2mqV}}$$

where m is the mass of the particle, v its velocity, p its momentum,

KE is the Kinetic Energy of the particle,

V is the voltage across which the Charged particle having charge q is accelerated.

(2) de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves.

(3) It needs to be noted that according to de Broglie, every object in motion has a wave character. This wavelength is quite significant for the subatomic particles which have very small masses. The wavelengths associated with ordinary objects are however so short that their wave properties cannot be detected as they have large masses.

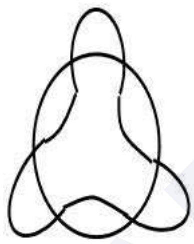
(4) Bohr's model and the de Broglie's relation: Number of standing waves made by an electron in n^{th} Bohr orbit

According to Bohr's model,

$$mvr=\frac{nh}{2\pi}$$

According to de Broglie's Relation,

$$p=\frac{h}{\lambda}$$



Combining the two

$$2\pi r=n\lambda$$

So, the number of waves made by any electron in the nth orbit is equal to the principal quantum number of the orbit i.e. n.

10. Heisenberg Uncertainty Principle

Heisenberg's uncertainty principle:

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

If an attempt is made to ensure that any one of these two quantities are measured with a higher accuracy, then the other quantity becomes less accurate.

Mathematically, the product of uncertainty in position(Δx) and uncertainty in momentum(ΔP) is equal to or greater than h/4π

$$\Delta x.\Delta P\geq\frac{h}{4\pi}$$

It can be proved mathematically that the uncertainty principle is only significant to subatomic particles but not insignificant for everyday large sized objects.

11. Orbital frequency

Time Period and Frequency of Revolution of an Electron in the n^{th} Bohr orbit

We know that Time period (T) is the time required for one complete revolution and that Frequency (ν) is inverse of the time period

$$\therefore T = \frac{distance}{time} = \frac{2\pi r}{v}$$

$$\because \mathrm{r} \propto \frac{\mathrm{n}^2}{\mathrm{Z}} \text{and } \mathrm{v} \propto \frac{\mathrm{Z}}{\mathrm{n}}$$

$$\therefore T \propto (\frac{n^2}{Z} \times \frac{n}{Z}) \propto (\frac{n^3}{Z^2})$$

$$\therefore \nu = (\frac{1}{T}) \propto (\frac{Z^2}{n^3})$$

12. Quantum Numbers

Quantum numbers:

They are the set of four numbers which explain the state of electron i.e., location, energy, type of orbital, orientation of orbital, etc. in an atom. Various quantum numbers are as follows:

1. Principal quantum number(n)
2. Azimuthal quantum number(l)
3. Magnetic quantum number(m)
4. Spin quantum number(s)

Principal quantum number(n):

It represents the principal shell of an atom. It can have integral values except zero like 1,2,3,.... Also denoted as K,L,M,.....etc.

Maximum number of electrons in a principal shell can be $2n^2$ where n is principal quantum number.

This quantum number gives information about :

- Distance of electron from nucleus i.e., size of electron cloud.
- Energy of electron in any shell in unielectronic species

$$\mathrm{E_n} = -\frac{1312 \times \mathrm{Z}^2}{\mathrm{n}^2} \ \mathrm{kJ/mol}$$

Where, Z is atomic number and n is principal quantum number.

- **In case of multielectronic species, the energy of an electron is given by Aufbau's Principle, which we shall be studying later.**

Azimuthal quantum number(l):

It gives us an idea of the three dimensional shape of the orbitals.

Azimuthal quantum number represents the subshell or subenergy shell in an atom.

l has values from 0 to (n-1).

e.g. for n=2 ; l= 0, 1

Subshell notation for l = 0, 1, 2, ... is s, p, d ...

Maximum number of electrons that can be accomodated in a subshell with azimuthal quantum number 'l' is given by [2(2l+1)]:

e.g. for s subshell = 2; for p subshell = 6.

Magnetic quantum number(m):

It gives us information about the spatial orientation of the orbitals in the subshell with respect to the standard set of coordinate axes.

Every value of m represents a possible orientation of the orbital

It represents the number of orbitals present in a subshell.

m has values ranging from -l to +l including zero.

For eg: for ‘s’ subshell :

1. Value of l is 0
2. m has value=0

It means that there is only one possible orientation for the s orbital

For ‘p’ subshell :

1. Value of l is 1

2. m has value= -1, 0, +1

It means that there are three possible orientation for the p orbital

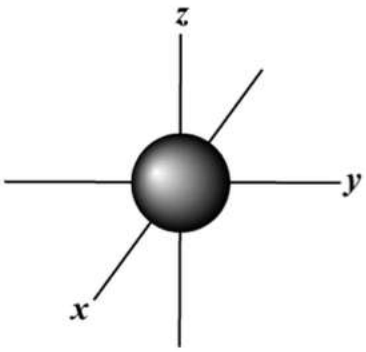
Spin quantum number(s):

Electron in an orbital can spin in either clockwise or anticlockwise direction. The spin quantum number has no classical analogue and any spin direction can be assigned +1/2 and the opposite spin will be automatically assigned -1/2. These values of +1/2 or -1/2 are not fixed for a particular spin direction.

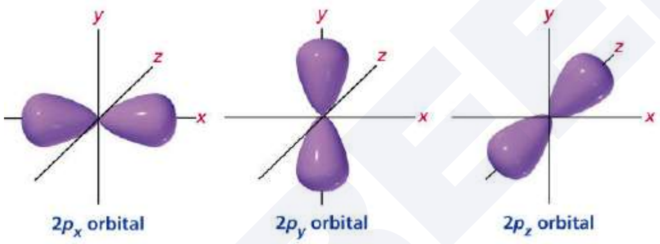
Thus, an electron can have only two possible values of this quantum number, either $+\frac{1}{2}$ or $-\frac{1}{2}$ respectively.

13. Shape of Orbitals

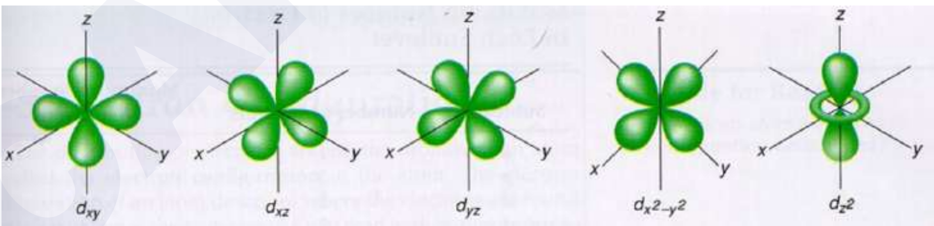
Shape of s orbital: spherical



Shape of p orbital: Dumb-bell



Shape of d orbital: Double Dumb-bell



14.Radial nodes and planar nodes

Nodes:

Total number of nodes = (n - 1)

Radial node is a spherical surface where the probability of finding an electron is zero. The number of radial nodes increases with the principle quantum number (n).

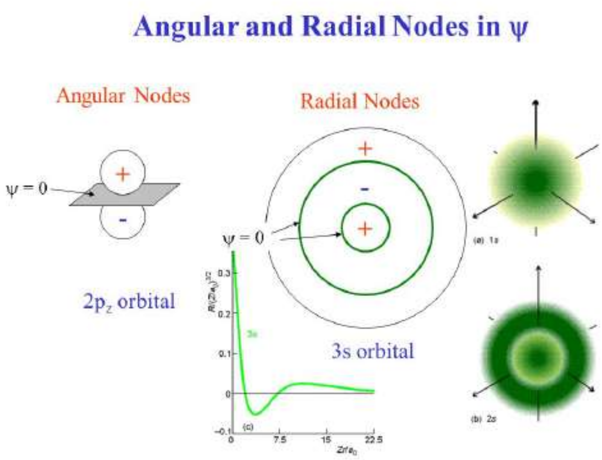
No. of radial nodes = (n- l- 1)

where n is the principal quantum number, l is the azimuthal quantum number.

Angular node is also called nodal plane. Angular node is a plane that passes through the nucleus. Angular node is equal to the azimuthal quantum number (l).

no. of planar nodes = l

where l is the azimuthal quantum number.



15.Hund's Rule, Pauli Exclusion Principle, and the Aufbau Principle

Stability of completely filled and half-filled subshells

The completely filled or half-filled subshells have the symmetrical distribution of electrons in them and are therefore more stable.

1.Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have the symmetrical distribution of electrons in them and are therefore more stable.

2. Exchange Energy: The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled. As a result, the exchange energy is maximum and so is the stability.

For eg: The valence electronic configurations of Cr and Cu are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$.

Aufbau Principle -

According to this rule, “orbitals are filled in the increasing order of their energies starting with the orbital of lowest energy”.

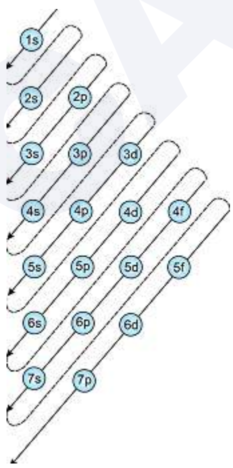
Energy of various orbitals are compared with (n+l) rule.

- The orbitals having lower value of (n+l), has lower energy.
- If value of (n+l) is same for two orbitals, then orbital with lower value of ‘n’ would have lower energy and filled first.

For eg: 3p and 3d.

For 3p : n=3, l=1 so n+l= 4   For 3d : n=3, l=2 so n+l=5

Thus energy of 3p is lower than that of 3d.



Pauli Exclusion Principle -

“No two electrons in an atom can have the same set of four quantum numbers" .

Hund’s Rule of Maximum Multiplicity -

"pairing of electrons in the orbitals belonging to the same subshell (p,d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e. It is singly occupied".

16. Electronic Configuration of Elements

Writing of electronic configuration of any element is based on three rules as told in previous concepts. They are:

1. Aufbau principle
2. Pauli's exclusion principle
3. Hund's rule of maximum multiplicity

The distribution of electrons into orbitals of an atom is called its electronic configuration.

The electronic configuration of the different elements can be represented in two ways:

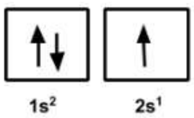
1. Subshell notation
2. Orbital diagram

Let's understand with the help of examples:

1. The hydrogen atom has only one electron which goes in the orbital with lowest energy, namely 1s.The E.C of hydrogen is $1s^1$ (subshell notation)

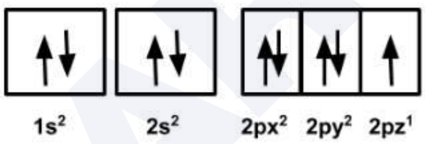
Orbital diagram:

2. The electronic configuration of lithium is $1s^2\ 2s^1$. Lithium has 3 electrons as atomic number is 3. 2 electrons filled in 1s orbital and 1 electron filled in 2s orbital.



let us consider fluorine (Z = 9) :

F(Z = 9) = $1s^2$, $2s^2$, $2px^2$, $2py^2$, $2pz^1$ or



The importance of knowing the exact electronic configuration of an element lies in the fact that the chemical properties of an element are dependent on the behavior and relative arrangement of its electrons.

Stability of completely filled and half-filled subshells

The completely filled or half-filled subshells have the symmetrical distribution of electrons in them and are therefore more stable.

1.Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have the symmetrical distribution of electrons in them and are therefore more stable.

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For eg: The valence electronic configurations of Cr and Cu are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$.

Classification of Elements and Periodic table

Important Formulae

1. Introduction of Periodic Table

Introduction:

A periodic table helps us systematically study the various elements found in nature, without it, it would have been impossible for us to study all the elements. By classifying the elements into various groups and periods a comparative study of the elements and their compounds can be done. It also helps us to analyze the periodic trend in various properties such as ionization potential, electron affinity, electronegativity, etc.

Development of Periodic Table:

1. **PROUT'S HYPOTHESIS**

He simply assumed that all the elements are made up of hydrogen, so we can say that

Atomic weight of elements = n (Atomic weight of one hydrogen atom)

Atomic weight of H = 1 , where n = number of hydrogen atom = 1, 2, 3,..

Drawback or Limitation:

1. Every element can not be formed by Hydrogen.
2. The atomic weights of all elements were not found as whole numbers.

Ex. Chlorine (atomic weight 35.5) and Strontium (atomic weight 87.5)

2. **DOBEREINER TRIAD RULE**

J.W. Dorbereiner pointed out that within a group of three elements having similar chemical and physical properties, the atomic weight of the middle element is the mean of the other two. Some examples of such triads are given below. He also pointed out the triad - iron, cobalt and nickel in which the atomic weights of the elements are almost the same.

Some representative triads of Dobereiner

Triads Elements	Li Na K	Ca Sr Ba	S Se Te	Cl Br I
Atomic Weight	7 23 39	40 88 137	32 80 128	35.5 80 127
Mean Value	23	88.5	80	81.25

Other examples. (K, Rb, Cs), (P, As, Sb) (H, F, Cl) (Sc, Y, La).

Though it was the first successful attempt to rationalize the problem, it could not be generalised or extended.

Drawback or Limitation: All the known elements could not be arranged as triads.

3. **NEWLAND'S Octave LAW**

John Alexander Reina Newland in England made the first attempt to correlate the chemical properties of the elements with their atomic weight. According to him -

1. If the elements are arranged in order to their increasing atomic weights, every eighth element had similar properties to first one like the first and eighth note in music. For example

Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	2	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

2. Inert gases were not discovered till then.
3. All the elements could not be classified on this basis.

2.Mendeleev's Periodic table

Dmitri Mendeleev:

Mendeleev proposed the Periodic Law and constructed his Periodic Table of elements. At that time, the structure of atoms was unknown and Mendeleev's idea to consider that the properties of the elements were in some way related to their atomic masses was a very imaginative one. To place certain elements into the correct group from the point of view of their chemical properties, Mendeleev reversed the order of some elements as they did not fit the scheme classification if the order of atomic weights has strictly followed. Mendeleev also had the foresight to leave gaps in the Periodic Table for elements unknown at that time and predict their properties from the trends that he observed among the properties of related elements. Mendeleev's predictions were proved to be astonishingly correct when these elements were discovered later. Mendeleev's Periodic Law spurred several areas of research during the subsequent decades.

MENDELEEV'S PERIODIC TABLE:

1. Mendeleev's periodic law: The physical and chemical properties of elements are the periodic function of their atomic weight
2. Characteristic of Mendeleev's periodic table :
    1. It is based on atomic weight
    2. 63 elements were known, noble gases were not discovered.

3. He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.

4. Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.

5. Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.

6. Each group upto VIIth is divided into A & B subgroups.'A' sub groups elements are called normal elements and 'B' sub groups elements are called transition elements.

7. The VIIIth group was consisting of 9 elements in three rows (Transitional metals group).

8. The elements belonging to the same group exhibit similar properties.

3. Merits or Advantages of Mendeleev's periodic table :

1. Study of elements: First time all known elements were classified into groups according to their similar properties. So study of the properties of elements becomes easier.

2. Prediction of new elements: It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium) Ga (Gallium) Ge (Germanium) Tc (Technetium)

These were the elements for whom position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

Ex. Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element discovered later was named Germanium.

Similarly, other elements discovered after Mendeleev periodic table was.

Eka aluminium – Gallium(Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

3. **Correction of doubtful atomic weights:** Correction was done in the atomic weight of some elements.

Atomic weight = Valency × Equivalent weight.

Initially, it was found that the equivalent weight of Be is 4.5 and it is trivalent (V = 3), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent (V = 2). So, the weight of Be became 2 × 4.5 = 9 and there was a space between Li and B for this element in Mendeleev's table.

– Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

4.Defects of Mendeleev's Periodic Table:

1. The position of hydrogen is uncertain. It has been placed in lA and VII-A groups because of its resemblance with both the groups.

2. No separate positions were given to isotopes.

3. It is not clear whether the lanthanides and actinides are related to IIA or IIB group.

4. Although there is no resemblance except valency of subgroups A and B, they have been put in the same group.

5. Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For e.g. – Co (At. wt. 58.9) is placed before I (127) and Ar (39.9) before K (39).

Lother Meyer:

1. He plotted a curve between atomic weight and the atomic volume of different elements.

2. The following observations can be made from the curve –

   1. Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak positions on the curve.

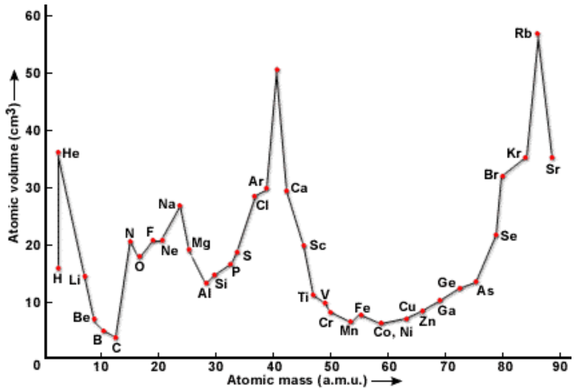
   2. Less electropositive i.e. alkali earth metals (Be, Mg, Ca, Sr, Ba) occupy the descending position on the curve.

   3. Metalloids (B, Si, As, Te, At etc.) and transition metals occupy the bottom part of the curve.

   4. Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending position on the curve.

   Note: Elements having similar properties occupy similar positions on the curve.

   Conclusion: On the basis of this curve Lother Meyer proposed that the physical properties of the elements are periodic functions of their atomic wt. and this becomes the base of Mendeleev's periodic table.

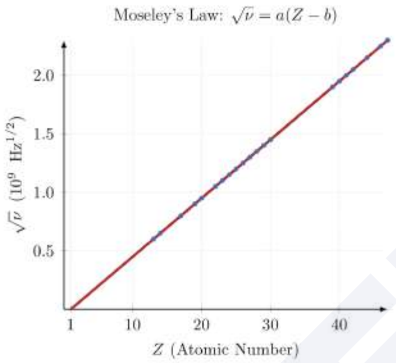


3. Modern periodic table

Modern Periodic Table (modified Mendeleev Periodic Table) :

1. It was proposed by Moseley.
2. The modern periodic table is based on the atomic number.
3. Moseley did an experiment in which he bombarded high-speed electrons on different metal surfaces and obtained X-rays.

   He found out that



   where v = frequency of X-rays, Z = atomic number.

4. Modern periodic law : The physical & chemical properties of elements are the periodic function of their atomic number.

Characteristics of Modern Periodic Table

1. 18 vertical columns called groups.
2. IA to VIIA group, IB to VIIB, and zero group of inert gases.
3. Inert gases were introduced in the periodic table by Ramsay.
4. 7 horizontal series called periods.

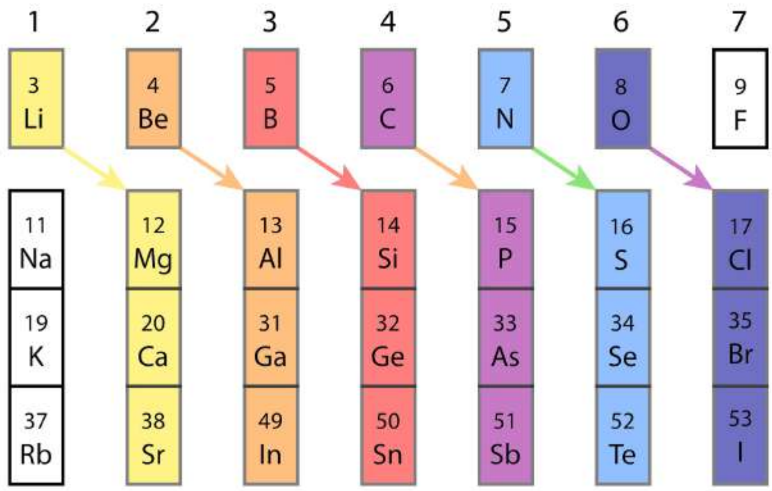
Magic Number

The magic number of neutrons is the number of neutrons that are present in stable isotopes (non-radioactive). These magic numbers are: **2, 8, 20, 28, 50, 82, 126, and 184**.

LONG FORM / PRESENT FORM OF MODERN PERIODIC TABLE :

(It is also called as 'Bohr, Bury & Rang, Werner Periodic Table)

1. It is based on the Bohr-Bury electronic configuration concept and atomic number.
2. This model is proposed by Rang & Werner
3. 7 periods and 18 vertical columns (groups)
4. According to I. U. P. A. C. 18 vertical columns are named as Ist to 18th group.
5. Elements belonging to the same group have the same number of electrons in the outermost shell so their properties are similar.
6. Elements belonging to the same group have same no. of electrons in the outermost shell so their properties are similar.



Important Points :

1. 2nd period elements (Li, Be, B) Shows diagonal relationship with 3rd period elements (Mg, Al, Si) so (Li, Be, B) are called Bridge elements. Because of same ionic potential value they shows similarity in properties. (Ionic potential = Charge/Radius)Li Be B Na Mg Al Si

2. 3rd period elements (Na, Mg, Al, Si, P, S, Cl) are called typical elements because they represent the properties of other element of their respective group.

3. Atomic number of last inert gas element is 86.
4.
   - Number of Gaseous elements – 11 (H, N, O, F, Cl + Noble gases)
   - Number of Liquid elements – 6 (Cs, Fr, Ga, Hg, Br, Uub)
   - Bromine is the only non-metal which exists in liquid form.
   - Number of Solid elements – 95 (if discovered elements are 112)
5. 2nd period contains a maximum number of gaseous elements. They are 4 (N, O, F, Ne)

4. Electronic Configuration in Periods and Groups

Period

The period of any element is determined by the last shell in which the last electrons enter. For example, Fe atomic number is 26. The electronic configuration can be written as:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Now, the last electron enters into the d-subshell but electrons are also present in 4th subshell. Therefore, Fe belongs to fourth period.

Block

The block of any element is determined by the last subshell in which the last electron enters. For example, Na has atomic number 11, thus its electronic configuration can be written as:

$1s^2 2s^2 2p^6 3s^1$

Now, its last electron enters into the s-subshell, therefore, Na belongs to the s-block.

Group

The group of any element is determined in different ways.

- **For s-block**

  If the last electron of any element enters into the s-subshell, then the group number is equal to the number of electrons in the last s-subshell.

  For example, K has atomic number 19, thus its electronic configuration can be written as:

  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

  Now it has 1 electron in the s-subshell, therefore K belongs to **Group 1**.

- **For p-block**

  If the last electron of any element enters into the p-subshell, then the group number is equal to (12 + the number of electrons in the last p-subshell).

  For example, Ge has atomic number 32, thus its electronic configuration can be written as:

  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

Now, it has 2 electrons in the last p-subshell, therefore its group number is:

12 + 2 = 14

Thus, Ge belongs to **Group 14**

- **For d-block**

  If the last electron of any element enters into the d-subshell, then the group number is equal to (2 + the number of electrons in (n-1)d-subshell.

  For example, Mn has atomic number 25, thus its electronic configuration can be written as:

  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

  Now it has 5 electrons in the d-subshell, therefore its group number is:

  2 + 5 = 7

  Thus, Mn belongs to **Group 7**.

- **For f-block**

  There are only two series of f-block i.e, lanthanide and actinide. If the last electron of any element enters into the f-subshell and if the atomic number is between 57-71, then the element belongs to lanthanide series i.e, 6th period. Further, if the last electron of any element enters into the f-subshell and if the atomic number is between 89-103, then the element belongs to the actinide series i.e, 7th period. All the elements from both these series belong to group 3.

5. Nomenclature Of Elements With Atomic Number

IUPAC proposed a system for naming elements with Z > 100. By using these rules as follows.

- The names are derived by using roots for the three digits in atomic number of the element and adding the ending-ium. The roots for the numbers are:

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

- In some cases the names are shortened; bi ium and tri ium are shortened to bium and trium respectively, and enn nil is shortened to ennil.
- The symbol for the element is made from the first letters from the roots which make up the name. The strange mixture of Latin and Greek roots has been chosen to ensure that the symbols are all different.

Nomenclature of Elements with Atomic Number Above 100

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nn
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

6. Classification of Elements and Periodicity in Properties

Classification of Elements : s-block

- The elements having ns^1 and ns^2 electronic configurations in their outermost shell are called s-block elements.
- Elements with ns^1 configuration are called group 1 (alkali elements).
- Elements with ns^2 configuration are called group 2 (alkaline earth elements).
- They are highly reactive and readily form univalent or bivalent positive ions by losing the valence electrons.
- The elements of this block are soft, malleable and good conductors of heat and electricity.
- The elements have largest atomic and ionic radii but lowest ionization energies.
- They show fix valency and oxidation states.
- The loss of the outermost electrons(s) occurs readily to form M^+ (in case of alkali metals) or M^{2+} ions (in case of alkaline earth elements).
- Except beryllium compounds all other compounds of this block elements are predominantly ionic.
- They are soft metals having low melting points and boiling points.
- These metals and their salts impart characteristic colour to the flame. For example, sodium salt imparts a golden yellow colour to flame.
- The elements of this group have large size, strong reducing nature, high electropositive nature, very low electronegativity values, ionization energy and electron affinity.

s-BLOCK

	1	2
1*s*		
2*s*	Li	Be
3*s*	Na	Mg
4*s*	K	Ca
5*s*	Rb	Sr
6*s*	Cs	Ba
7*s*	Fr	Ra

Classification of Elements : p-block

- The elements whose last electron enters into any p-orbital are known as p-block elements.
- The general outer electronic configuration for these elements is ns^2np^{1-6}.
- Group 13 or III A have one electron in p-orbital whereas group 18 or VIII A (inert gas) have 6 electrons in their outer p-orbitals. The outer p-orbitals in an inert gas are fully-filled with electrons.
- They include both metals and nonmetals but there is a regular change from metallic to non-metallic character as we move from left to right across the period.
- These elements do not impart colour to the flame test.
- Except F and inert gases, all other elements of this block show variable oxidation states.
- They have quite high ionization energies and the values tend to increase as we move from left to right across the period.
- They form covalent compounds mostly like oxides, halides, sulphides, carbonates, etc.
- Except metals, the other elements of this block are nonconductors.
- A number of elements of this block show catenation property and allotropy like C, Si, Ge, S, O etc.
- As we move from left to right, there is a gradation from reducing to oxidizing properties.

p- BLOCK

	13	14	15	16	17	18
						He
2p	B	C	N	O	F	Ne
3p	Al	Si	P	S	Cl	Ar
4p	Ga	Ge	As	Se	Br	Kr
5p	In	Sn	Sb	Te	I	Xe
6p	Ti	Pb	Bi	Po	At	Rn
7p	Uut	Fi	Uup	Lv	Uus	Uuo

Classification of Elements : d-block

- The d-block is in between s and p blocks. In these elements, their last electron enters into any of the d-orbitals. These elements are also known as transition elements as their properties are in between s and p-block elements.
- The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$.
- These elements are in between 2-13 groups in the periodic table.
- They show variable valency and oxidation state in their chemical bond formation.
- These metals have high values of melting points, boiling points, densities, thermal stability and hardness.
- They are ductile and malleable.
- They are good conductors of heat and electricity due to the presence of free electrons.
- They form coloured ions and complexes.
- Metals and their ions are generally paramagnetic in nature because of the presence of unpaired electrons.
- These metals form a number of alloys as they have almost similar sizes.
- These metals and their compounds are widely used as catalysts.
- These metals also form nonstoichiometric and interstitial compounds with small-size atoms like H, C, N, and O which can be easily fitted in the vacant sides of the lattices of these metals. For example, $Fe_{0.93}O$.

d-block

	3	4	5	6	7	8	9	10	11	12
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6d	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

Classification of Elements : f-block

- The elements placed in two separate rows at the bottom of the periodic table are f-block elements.
- These elements have their last electron entering into the f-orbital.
- The elements from cerium to lutetium having incomplete 4f-orbitals are known as lanthanoids.
- The elements from thorium to lawrencium having incomplete 5f-orbitals are known as actinides.

- The general electronic configuration of f-block elements is $(n-2)f^{1-14}(n-1)d^{1-2}ns^2$.
- Many of actinide elements have been made only in nanogram quantities or less by nuclear reactions and their chemistry is not fully studied.
- Many of them are synthetic elements.
- The elements coming after uranium are called transuranium elements.
- They are metals having high melting and boiling points.
- They show variable oxidation states however their most common and stable oxidation state is +3.
- They form coloured ions and complexes.
- Actinides are radioactive in nature.

f-BLOCK

Lanthanoids 4*f*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids 5*f*	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

7. Metals, Non-metals and Metalloids

The elements can be divided into three categories i.e., metals and non-metals and metalloids. Metals comprise more than 78% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature except mercury which is liquid at room temperature and even gallium and caesium also have very low melting points (303K and 302K respectively). Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable and ductile.

Non-metals are placed at the top right side of the Periodic Table. In a period, the properties of elements change from metallic on the left to non-metallic on the right. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we move from top to bottom in a group and the non-metallic character increases as we move from left to right in a period.

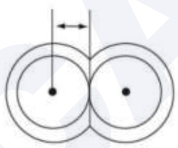
There are some elements whose properties are in between the metals and non-metals. They are known as metalloids. There are a total of 8 metalloids in the periodic table i.e, boron(B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), polonium (Po) and astatine (At).

8. Atomic Size & Atomic Radius

There are various physical properties that follow the trend according to the atomic numbers of elements.

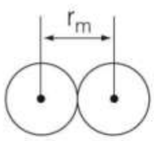
- **Atomic Radius**
  Atomic radius is the distance from the centre of the nucleus to the outermost shell of electrons. It can be measured by the x-ray diffraction, electron diffraction techniques and other spectroscopic methods. As it cannot be measured in absolute form thus it is measured in various definitions such as covalent radius, Van der Waal's radius, metallic radius and ionic radius.

- **Covalent Radius**
  It is half of the total length between two successive nuclei covalently bonded to each other in a molecule. Suppose there are two same atoms' A' and 'A' in a molecule and their bond length is 'a', then covalent radius is half of the covalent bond length between A and A. Thus, covalent radius = (a/2).



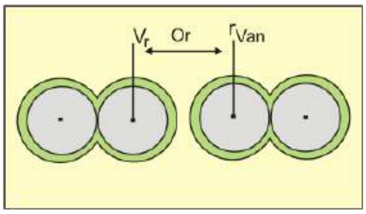
- **Metallic Radius**

  It is defined as half of the distance between nuclei of two adjacent metal atoms that are closely packed in the metallic crystal lattice. For example, there are two metals atoms 'A' and 'A' that are closely packed to each other and bond length is 'a' then the metallic radius is half of the distance between these two metallic atoms i.e, a/2.



- **Van der Waal's Radius**

  It is half of the distance between two nuclei of the adjacent non-bonded atoms of different molecules. For example, if 'a' is the distance between two adjacent atoms i.e, A and B, then the Van der Waals's radius is the half of the distance between these two atoms A and B, i.e, a/2.



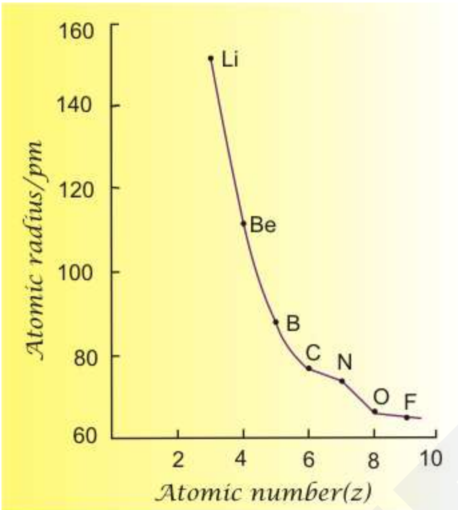
- **Ionic Radius**

  It is the effective distance from the centre of the nucleus of an ion up to which it has the influence over the electrons.

Comparison of the ionic radii and atomic radii

Variation in a Period

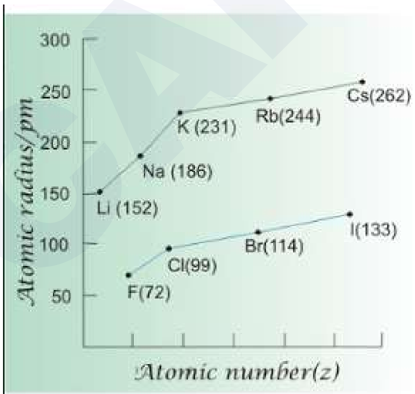
In moving from left to right in a period, the nuclear charge increases and the last electron enters into the same shell, thus the effective nuclear charge increases. Thus in this way, the atomic size decreases in the period.



Variation of atomic radius with atomic number across the second period

Variation in a Group

In moving from top to bottom in a group, the number of shells increases due to which the atomic size increases.



Variation of atomic radius with atomic number for alkali metals and halogens

- The size of the cation is always smaller than its parent atom. In the case of cations, the number of electrons in the ion decrease and the nuclear charge remains the same, thus the effective nuclear charge increases and the size decreases.
- The size of the cation decreases as effective nuclear charge increases
- $M^{+3} < M^{+2} < M^{+} < M$

- The size of the anion is always greater than its parent atom. In the case of anions, the number of electrons in the ion increase and the nuclear charge remains the same, thus the effective nuclear charge decreases and the size increases.

- $M^{-3} > M^{-2} > M^{-} > M$

Atomic Properties

Atomic properties are the physical properties of elements that are related to the atomic number of the elements. These properties can be divided into two categories:

1. Properties of individual atoms: These are the properties of individual atoms that are directly dependent on their electronic configurations. Some examples include ionisation enthalpy, electron gain enthalpy, screening effect, effective nuclear charge, etc.

2. Properties of the group of atoms: These are properties of the group of atoms together that are indirectly related to their electronic configurations. Some examples include the melting point, boiling point, the heat of fusion, density, etc.

The Screening effect or Shielding effect

The decrease in the force of attraction between the outer electrons and the nucleus due to the presence of inner electrons is called the screening effect or shielding effect. Actually, these inner electrons generate the repulsion between these inner electrons and the outer electrons due to which the net force of attraction between the nucleus and the outer electrons decreases.

Calculation of the screening effect

- **For ns or np orbital electrons**
  - All electrons in the (ns, np) group contribute to 0.35 each to the screening effect constant. Except for 1s electrons which contribute by 0.30.
  - All electrons in the (n-1) shell contribute by 0.85 each to the screening effect constant.
  - All electrons in (n-2) shell or lower contribute by 1.0 each to the screening effect constant.
- **For d- or f-electrons**
  - All electrons in the (ns, np) group contribute to 0.35 each to the screening effect constant.
  - All the electrons in groups lower than (nd, nf) contribute by 1.0 each to the screening effect.

Effective Nuclear Charge

Due to the screening effect of the inner or the same shell electrons, the net force of attraction between the nucleus and the outer electrons decreases. This decreased force of attraction is known as effective nuclear charge. It is represented by Z*. Mathematically, it can be formulated as:

Z* = (Z- σ), where σ is the screening effect constant.

- In a period, the effective nuclear charge increases in moving from left to right.

II Period	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
σ	1.7	2.05	2.40	2.75	3.10	3.45	3.80	4.15
Z*	1.3	1.95	2.60	3.25	3.90	4.55	5.20	5.85

- In a group, the effective nuclear charge almost remains the same.

Group I	Li	Na	K	Rb	Cs
Z	3	11	19	37	55
σ	1.7	8.8	16.8	34.8	52.8
Z*	1.3	2.2	2.2	2.2	2.2

Isoelectronic species -

A series of atoms, ions and molecules in which each species contains the same number of electrons but a different nuclear charge.

e.g. $N^{3-}, O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, Al^{3+}$

9. Ionisation Enthalpy or Ionisation Potential

Ionisation Enthalpy

Ionisation enthalpy may be defined as the minimum energy required to remove the most loosely bound electron from an isolated gaseous atom to convert it into a gaseous monovalent positive ion.

$$M(g) \xrightarrow{IE_1} M^{+}(g) + e$$

IE_1 is ionisation enthalpy or also known as first ionisation enthalpy.

Ionisation Potential

Ionisation enthalpy is also expressed in terms of ionisation potential. It is the minimum potential difference required to remove the outermost electron from a gaseous atom to form a cation. As the ionisation energy increases, the ionisation potential also increases.

Factors Affecting Ionisation Enthalpy

The ionisation enthalpy of any atom is affected by the following factors.

- **Size of the atom:** The larger the size of an atom, the lower is the ionisation enthalpy. As the atomic size increases, the distance between the outermost electrons and the nucleus increases due to which the force of attraction between the nucleus and these outermost electrons decreases, thus it becomes easy to remove an electron from the atom and hence the ionisation enthalpy decreases. Thus,

  Ionisation enthalpy decreases as Atomic size increases

- **Screening effect:** The higher is the value of the screening effect, the lower is the ionisation enthalpy. As the screening effect increases, the repulsion between the electrons increases, and thus the removal of an electron from the atom becomes easier. Thus,

  Ionisation enthalpy decreases as the Screening effect increases

- **Nuclear charge:** As the nuclear charge increases, the force of attraction between the nucleus and electrons also increases and thus the removal of electrons from the atom becomes difficult and hence the ionisation enthalpy increases. Thus,

  Ionisation enthalpy increases as Nuclear charge increases

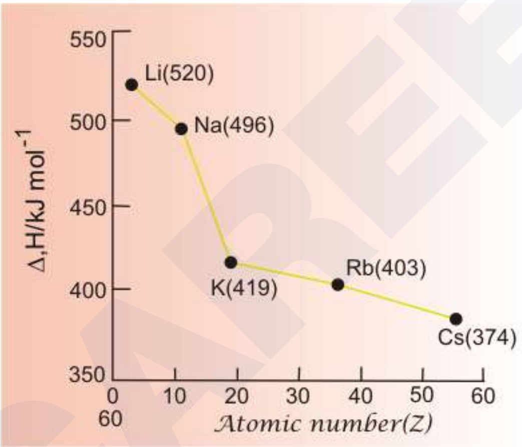
- **Half filled and fully filled orbitals:** The atoms with half-filled and fully filled orbitals are more stable than other atoms. Thus removing an electron from these atoms requires a little more energy. Thus for these atoms with half-filled and fully filled orbitals, the ionisation enthalpy is higher than others.

- **The shape of orbital:** The ionisation enthalpy also depends on the shape of the orbital in which the last electron enters. The more the orbital is close to the nucleus, the more energy is required to remove the electron in the same orbit. Thus, the ionisation enthalpy for the orbitals from the same orbit follows the given order:

  s > p > d > f

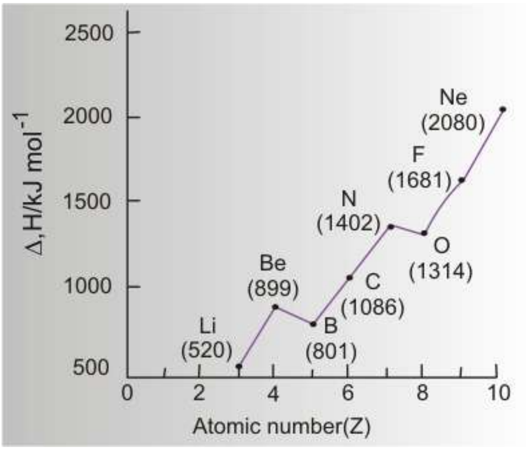
Variation of Ionisation Enthalpy

- In moving down the group, the ionisation enthalpy decreases. As we move down in the group, the number of shells increases due to which the force of attraction between the nucleus and the outer electrons decreases, thus removing an electron from the atom becomes easy and hence ionisation enthalpy decreases. There are some exceptions after the element with atomic number 72. The elements with atomic numbers from 73 to 82 have higher ionisation enthalpy than the earlier elements in their respective group. This deviation of behaviour is because of the lanthanide contraction.



- In moving from left to right in a period, the ionisation enthalpy increases. In the period, the nuclear charge increases but the number of shells remains the same, thus the force of attraction between the nucleus and the outer electrons increases, and hence the ionisation enthalpy increases. In a period, some elements like Be, Mg, N, and P have exceptionally higher ionisation enthalpies than expected. This is because of their half-filled or fully-filled outer orbital configuration.

- For every element, the successive ionisation energy increases. This is because of the increase in the nuclear charge due to the successive removal of electrons.



Importance of Ionisation Enthalpy

Ionisation enthalpy is an important factor for determining the nature of an element. The elements with low ionisation enthalpies are metals while the elements with higher ionisation enthalpies are non-metals.

The stability of oxidation states of an element can also be determined on the basis of the value of ionisation enthalpies.

- **Comparison of IE_1 and IE_2 of oxygen and nitrogen**

  Oxygen has an electronic configuration as $1s^22s^22p^4$. After IE^1, its electronic configuration becomes $1s^22s^22p^3$. Now nitrogen has the electronic configuration as $1s^22s^22p^3$. After IE_1, its electronic configuration becomes $1s^22s^22p^2$.

  Thus in the case of oxygen, after IE_1, O^+ has achieved the stable half-filled electronic configuration and hence more energy is required in IE_2 to remove an electron further. Similarly, nitrogen already has a stable half-filled electronic configuration, thus more energy is required for IE_1 to remove the first electron.

  Therefore, the order of different ionisation enthalpies is followed as mentioned below:

  (i) $N(IE_1) > O(IE_1)$ (ii) $O(IE_2) > N(IE_2)$

- **Comparison of IE_1 and IE_2 of chromium and manganese**

  Chromium has an electronic configuration as $[Ar]3d^54s^1$. After IE_1, its electronic configuration becomes $[Ar]3d^5$. Now manganese has the electronic configuration as $[Ar]3d^54s^2$. After IE_1, its electronic configuration becomes $[Ar]3d^54s^1$. Thus in the case of chromium, after IE_1, Cr^+ has achieved the stable half filled electronic configuration, and hence more energy is required in IE_2 to remove an electron further. Similarly, manganese already has stable half-filled d-orbitals and fully filled 4s orbitals, thus more energy is required for IE_1 to remove the first electron.

  Therefore, the order of different ionisation enthalpies is followed as mentioned below:

  (i) $Mn(IE_1) > Cr(IE_1)$ (ii) $Cr(IE_2) > Mn(IE_2)$

- **Comparison of different ionisation enthalpies of N and N^+**

  Nitrogen has an electronic configuration as $1s^22s^22p^3$. After IE_1, nitrogen becomes N^+ and has the electronic configuration as $1s^22s^22p^2$. Every time some amount of energy has to supply to remove the electron. But the nuclear charge remains the same, thus removing the second and third electron from the atom becomes very difficult. Thus for any atom, multiple ionisation enthalpies follow the order given below:

  $IE_3 > IE_2 > IE_1$

- **Group exception**

  In moving from top to bottom in a group, the ionisation enthalpy decreases but there are some exceptions as mentioned below.

  (i) In group 13, the **expected** ionisation enthalpy is as follows:

  B > Al > Ga > In > Tl

  But Thallium and Gallium have inner f and inner d electrons respectively due to which there is poor shielding and thus the size reduces and ionisation enthalpy increases. Thus the **real order** of ionisation enthalpy is:

  B > Tl > Ga > Al > In

  (ii) In group 14, the **expected** ionisation enthalpy is as follows:

  C > Si > Ge > Sn > Pb

But lead(Pb) has inner f-orbitals due to which it has the lanthanoid contraction and thus its size reduces and ionisation enthalpy increases. Thus the **real order** of ionisation enthalpy is:

C > Si > Ge > Pb > Sn

10. Electron Gain Enthalpy or Electron Affinity

Electron Gain Enthalpy $(\Delta_{eg}H)$

Electron gain enthalpy is the energy change that occurs when an electron is added to a neutral gaseous atom to form a negative ion. It is also known as electron affinity.

$$A(g) + e \rightarrow A^{-}(g) + \Delta_{eg}H$$

Factors affecting electron gain enthalpy

The electron gain enthalpy or electron affinity depends upon various factors such as:

- **Atomic Size**

With the increase of atomic size, the distance between the nucleus and the last shell electrons also increases due to which the force of attraction between the nucleus and the incoming electron decreases. Hence, the electron gain enthalpy becomes less negative.

- **Nuclear Charge**

With the increase of nuclear charge, the force of attraction between the nucleus and the incoming electron increases. Thus, the electron gain enthalpy becomes more negative.

- **Electronic Configuration**

Elements that have half-filled or completely filled orbitals are more stable than others. In these cases Generally, energy has to be provided to add an electron. Thus, their electron gain enthalpy generally has large positive values.

Variation of Electron Gain Enthalpy

- The electron gain enthalpy becomes less negative in going from top to bottom in a group.
- In moving from top to bottom in a group, both the atomic size and the nuclear charge increase. However, the effect of the increase in atomic size is more dominant than the nuclear charge.
- With the increase in atomic size, the attraction of the nucleus for the incoming electron decreases. Hence, the electron gain enthalpy becomes less negative. But in moving from left to right in a period, the attraction of the nucleus and the incoming electron increases and thus electron gain enthalpy becomes more negative.
- Halogens have the most negative electron gain enthalpies. In moving down from chlorine to iodine, the electron gain enthalpies become less negative due to the increase in their atomic radii.
- Chlorine has the most negative electron gain enthalpy value than fluorine. Because fluorine is very small in size due to which there is a very strong inter-electronic repulsion for the incoming electron, thus its electron gain enthalpy is less than chlorine.
- Generally, Members of the 2nd period in p-block elements show the anomalous value of electron gain enthalpy.

Importance of Electron Gain Enthalpy

Some properties of the elements can be predicted on the basis of the electron gain enthalpy values.

- The elements with high negative electron gain enthalpy values accept electrons easily and form ionic compounds. For example NaCl.
- The elements with high negative electron gain enthalpy values are strong oxidising agents. For example, F, Cl, O.
- The electron affinity term was used for the gain of electrons in older times, the use of which has been replaced by electron gain enthalpy nowadays. It is generally defined as the negative of the electron gain enthalpy. Electron efficiency values for noble gases are, however, defined to be zero. Other species like Be, Mg, Zn Cd, Hg, N etc. have positive values of eletrons affinity due to their half-filled r fully filled orbital configuration.

11. Electronegativity

Electronegativity

The tendency of an atom to attract the shared pair of electrons towards itself is called electronegativity. It is a relative quantity. This concept was introduced in 1932 by Pauling. It has no units. Fluorine is the most electronegative element known so far and its value is arbitrarily assigned as 4.0. In moving from left to right in a period, the electronegativity increases while in moving to the top to bottom in a group, the electronegativity decreases.

Factors affecting Electronegativity

There are various factors which affect electronegativity.

- **Atomic Size:** As the atomic size increases, the electronegativity decreases.
- **Effective Nuclear Charge:** With the increase of effective nuclear charge, the electronegativity of the atom increases.

- **Oxidation State:** As the oxidation state of an atom increases, the electronegativity also increases. For example, Fe^{3+} is more electronegative than Fe^{2+}.

Variation of Electronegativity

- In moving from top to bottom in a group the atomic size increases thus the force of attraction decreases and hence the electronegativity decreases.
- In moving from left to right in a period, the atomic size decreases and effective nuclear charge increases, thus the electronegativity increases.
- Halogens are the most electronegative elements and fluorine has the highest electronegativity.
- For transition elements, the electronegativity values vary between 1.1 to 1.3.
- Metals have lower electronegativity values while non-metals have higher electronegativity values.

Importance of Electronegativity

The following predictions can be made out of the information of the electronegativities of atoms.

- **Nature of Element:** The elements with lower electronegativity values are metals while the elements with higher electronegativity values are non-metals. The elements with intermediate electronegativity values are metalloids. Fluorine has the highest electronegativity value, thus it is the most non-metallic element. Similarly, caesium has the lowest electronegativity value, thus it is the most metallic element.
- **Nature of Oxides:** The nature of the oxides formed by the elements can also be predicted by electronegativity. When M_O - M_A difference is lower, then the oxide is acidic in nature but when this difference M_O - M_A is large, then the oxide is basic in nature. M_O here is the electronegativity of oxygen.

Scales for measuring electronegativity

There are various following scales to measure the electronegativity of elements.

- **Pauling Scale: The electronegativity of the elements in Pauling scale is given by the following formula:**

  $M_A - M_B = 0.208[E_{A-B} - (E_{A-A} \times E_{B-B})^{½}]^{½}$

  Where E_{A-B} is the bond energy of A-B

  E_{A-A} is the bond energy of A-A

  E_{B-B} is the bond energy of B-B

  This formula is used only when the energy is taken in kcal/mol.

  When bond energy is taken in kJ/mol, then:

  $M_A - M_B = 0.102[E_{A-B} - (E_{A-A} \times E_{B-B})^{½}]^{½}$

- **Mulliken Scale:** Mulliken considered electronegativity as the average of the ionisation potential and electron gain enthalpy of an atom.

  (i) When ionisation potential and electron gain enthalpy are taken in electron volts:

  Electronegativity = (IE + EA)/2

  (ii) When ionisation potential and electron gain enthalpy are taken in kJ/mol.

  Electronegativity =(IE + EA)/(2 x 96.48)

- **Allred and Rochow Scale:** In this scale, the electronegativity is given by the following formula:

  Electronegativity = 0.744 + (3590 Z/r^2)   Where Z is the effective nuclear charge and r is the covalent radius in pm.

Applications of Electronegativity

The following predictions can be made out of the information of the electronegativities of atoms.

- **Nomenclature:** The nomenclature of binary compounds can be done using the electronegativity value of the atoms. The atom with higher electronegativity is written with ide as suffix. For example, in HCl, the chlorine atom has higher electronegativity, thus it is written as chloride and the complete name is hydrogen chloride.
- **Nature of Bond:** From the electronegativity values of respective atoms, the nature of the bond can be estimated.

  (i) When the electronegativity difference between two atoms i.e., M_A- M_B = 0, then the bond is purely covalent.

  (ii) When M_A- M_B is small, then the bond is polar but covalent.

  (iii) When M_A- M_B is 2.1, then the bond is 50% ionic and 50% covalent.

  (iv) When M_A- M_B is more than 2.1, the bond is very much ionic and less covalent.

  The percentage of ionic character is given by the following formula:

Percentage of ionic character = $16(M_A - M_B) + 3.5(M_A - M_B)^2$

Where M_A and M_B are the electronegativities of two bonded atoms i.e, A and B.

- **Nature of Element:** The elements with lower electronegativity values are metals while the elements with higher electronegativity values are non-metals. The elements with intermediate electronegativity values are metalloids. Fluorine has the highest electronegativity value, thus it is the most non-metallic element. Similarly, caesium has the lowest electronegativity value, thus it is the most metallic element.
- **Nature of Oxides:** The nature of the oxides formed by the elements can also be predicted by electronegativity. When $M_O - M_A$ difference is lower, then the oxide is acidic in nature but when this difference $M_O - M_A$ is large, then the oxide is basic in nature. M_O here is the electronegativity of oxygen.
- **Bond Strength:** The more the electronegativity difference between the atoms, the stronger the bond. Thus,

  H-F > H-Cl > H-Br > H-I
- **Acidic Nature:** When the electronegativity difference is less, then the bond between the atoms is weaker and thus it is easier to lose the proton. Thus,

  H-I > H-Br > H-Cl > H-F

12. Physical and chemical properties of elements

Atomic Volume-

In moving from left to right in a period the atomic volume first decreases and then increases because of the following reasons:

- As we move in a period from left to right, first the increase in nuclear charge overcomes the increase in the number of electrons. Thus, the atomic volume decreases.
- But on moving further in a period, newly added electrons enter into the p orbitals and because of the high shielding power of s and p orbitals, atomic volume increases.

Li	Be	B	C	N	O	F	Ne
13	5	5	5	14	11	15	17
Na	Mg	Al	Si	P	S	Cl	Ar
24	14	10	12	17	16	19	24

In moving from top to bottom in a group, the atomic volume increases due to the increase of the number of shells.

Density

The density of elements also follows almost the same order as the atomic volume. In moving from left to right in a period, the density increases first and becomes maximum till some middle elements thereafter it starts decreasing gradually.

Melting Points and Boiling Points

The melting points of elements show a general trend with their atomic numbers. The elements with low atomic numbers have high melting points while the elements with higher atomic numbers have low melting points. In a period from left to right, the melting points of elements first increase and become maximum till some middle elements and then it decreases gradually.

Value of melting point of elements-

Li	Be	B	C	N	O	F	Ne
454	1550	2303	4000	63	54	53	24
Na	Mg	Al	Si	P	S	Cl	Ar
370.8	924	933	1693	317	392	172	83.6

The boiling points of elements also show similar trends as the melting points but the trend is not that much regular.

In moving down the group, melting and boiling points follow the regular trend but the trend is different for different groups. For example for the alkali group, the melting and boiling points decrease in moving from top to bottom but for halogens, the melting and boiling points increase in moving down the group.

Chemical Properties of Elements-

Valency

The number of electrons that an atom donates or takes from another atom to form a compound is known as valency. In the case of representative elements, the valency is equal to the number of valence electrons or eight minus the number of electrons. In the case of transition elements, they show variable valency involving the valence electrons and d electrons of the penultimate shell. In moving from left to right in a period, the valency first increases to 4 and then decreases to 0.

Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0

But in the group, all the elements have the same number of valence electrons thus all the elements have the same valency.

Nature of Oxides

When the oxygen atom combines with any other atom and forms a compound, then it is known as as oxide. In moving from left to right in a period, the nature of oxide changes from basic to acidic while in moving down the group, the basic nature of oxides increases and acidic nature decreases. The oxides of metals are basic in nature, oxides of non-metals are acidic in nature and oxides of metalloids are amphoteric in nature.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Strongly acidic

If an element forms a number of oxides, then the acidic nature of oxides increases with the increase of oxygen atoms.

MnO	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7
Basic	Basic	Neutral	Acidic	Acidic

Nature of Oxy-acids

- The strength of oxyacids formed by non-metals increases in moving from left to right in a period. Thus, oxyacid strength increases as shown below:

  $HNO_3 > H_2CO_3 > H_3BO_3$

- In moving from top to bottom in a group, the strength of oxyacids decreases. Thus, the order is followed as given below:

  $HNO_3 > H_3PO_4 > H_3AsO_4$

- If any non-metal forms a number of oxyacids, then the strength of oxyacids increases with the increase of oxygen atoms. Thus, chlorine forms a number of oxyacids and strength follows the given order:

  $HClO_4 > HClO_3 > HClO_2 > HClO$

Nature of Hydrides

Hydrides are basically compounds with hydrogen atoms or atoms and some other element.

In a period, the nature of hydrides changes from basic to acidic in moving from left to right.

NH_3	H_2O	HF
Weak base	Neutral	Weak acid

In a group, the acidic nature of hydrides increases in moving from top to bottom. Thus,

$HI > HBr > HCl > HF$

Anomalous Behaviour of Elements of Second Period

The elements of the second period or the first elements in each group of the representative elements show anomalous behaviour in many aspects from the other elements in their respective groups. This anomalous behaviour of these elements is due to the following reasons:

- Small atomic size of the atom.
- Higher electronegativity
- The d-orbitals in their valence shell are absent.
- High charge-to-radius ratio.
- Capability to form multiple bonds by carbon, nitrogen and oxygen.

13. Modern periodic table trend

General Trends of Some Properties in the periodic table

The general trends of some properties of elements in the periodic table are mentioned below:

Property	Variation from top to bottom in a group	Variation from left to right in a period
Atomic radius	Increases	Decreases
Ionisation enthalpy	Decreases	Increases
Electron gain enthalpy	Decreases	Increases
Electronegativity	Decreases	Increases
Metallic character	Increases	Decreases
Electropositive nature	Increases	Decreases
Oxidising nature	Decreases	Increases
Reducing nature	Increases	Decreases

Some important facts about elements

There are some important facts about the elements as mentioned below:

- Bromine is the only non-metal which is liquid at room temperature.
- Mercury is the only metal that is liquid at room temperature.
- Tungsten has the highest melting point among metals around 3410^{o}C.
- Carbon has the highest melting point among non-metals around 4100^{o}C.
- Among metals, aluminium is the most abundant metal.
- Among all the elements in the periodic table, hydrogen is the most abundant element in the universe.
- Iron is the most abundant transition metal.
- Boron has the lowest atomic volume.
- Francium has the highest atomic volume.
- Silver is the best conductor of electricity.
- Fluorine is the most electronegative element.
- Chlorine has the maximum negative electron gain enthalpy.
- Helium has the maximum ionisation enthalpy.
- Diamond is the hardest substance in the universe.
- Plutonium is the most poisonous metal.
- The members of the actinide series are radioactive and most of them are not found in nature.
- Tin is the element that has the maximum number of isotopes i.e, 10 isotopes.

Chemical Bonding and Molecular Structure

Important Formulae

1. Chemical Bonding

A chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule or as a force that holds a group of two or more atoms together and makes them function as a unit. For example, in water, the fundamental unit is the H-O-H molecule, which is described as being held together by the two O-H bonds.

Cause of Chemical Combination

Atoms combine with each other on the basis of the following reasons:

(i) Decrease in energy: All systems in the universe tend to lose potential energy and achieve more stability. It is an observed fact that a bonded state is more stable than an unbonded state because the bonded state has lower potential energy than the unbonded state. Thus when two atoms approach each other, they combine only under the condition that there is a decrease in potential energy. When two atoms approach each other, new kinds of forces of attraction and repulsion start acting. These forces are:

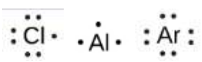
1. **Electrons and nuclei attract each other:** Attractive forces are always energetically favourable, thus an electron attracted to a nucleus is of lower energy and therefore more stable than a free electron.
2. **Electrons repel each other:** Because of this repulsion, the energy is raised and the stability reduced.
3. **Nuclei repel each other:** The repulsion exists between the nuclei and this also reduces the stability.

Among all these above forces, If the net result is the attraction, then the total potential energy of the system decreases and a chemical bond formation takes place. No chemical bonding is possible if the net result is repulsion.

(ii) Lewis Octet Rule: The atoms of all elements during the bond formation try to attain the stable noble gas configuration, i.e., they try to obtain either 2 electrons (when only one energy shell) or 8 electrons in their outermost energy level which is of maximum stability and hence of minimum energy. Thus, the tendency of atoms to achieve eight electrons in their outermost shell is known as the Lewis octet rule. The octet rule is the basis of the electronic theory of valency. All the noble gases like helium, neon, etc. are not active towards the bond formation because of their already filled outermost shell, in other words, their octet is already complete and thus these elements do not need to combine with other elements to complete its octet.

Lewis's symbol of elements

For explaining the formation of bonds, the Lewis symbol representation of atoms is necessary. To write the Lewis symbol for an element, we write down its symbol surrounded by a number of dots that are equal to the number of valence electrons. Paired and unpaired valence electrons are also indicated. The Lewis symbols for some of the elements like Chlorine, Aluminium, and Argon are mentioned below:

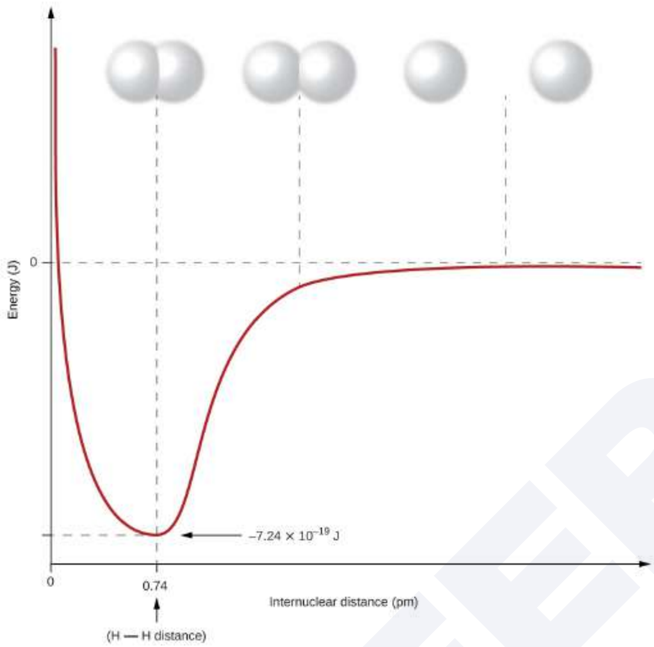


Theory of chemical bonding-

A type of bonding that results from the mutual attraction of atoms for a shared pair of electrons. are known as covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves. For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Formation of Covalent Bonds

The figure given below shows the explanation of this bond. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.



The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

Coordinate Bonds

It is a special type of covalent bond in which both the shared electrons are contributed by one atom only. Such a bond is also known as a dative bond. A coordinate or a dative bond is established between two such types of atoms, out of which one has a complete octet and while the other is short of a pair of electrons. This bond is represented by "→".

The atom which donates the electron pair is called the donor while the atom which accepts the electron pair is called the acceptor. The compounds in which the coordinate bond exists are known as complex or coordination compounds. Some example include $[Pt(en)_2]CO_3$, $[Ni(H_2O)_6]Cl_2$, etc.

Characteristics of Coordination Compounds

The main properties of the coordination compounds are mentioned below:

- **Melting and boiling points:** The melting and boiling points of these compounds are higher than purely covalent compounds but lower than purely ionic compounds.
- **Solubility:** These compounds are sparingly soluble in polar solvents like water but readily soluble in non-polar solvents.
- **Stability:** The stability of these compounds is similar to the covalent compounds.
- **Conductivity:** Like covalent compounds, these are also bad conductors of electricity.
- **Dielectric constant:** The compounds containing coordinate bonds have high values of the dielectric constants.

2. Lewis Electron Dot Structures

Lewis Symbols of Elements-

The number of electrons present in the outermost shell is known as valence electrons. For example, the electronic configuration of sodium (Na) is 2, 8, 1, thus, sodium has one valence electron. According to the long form of the periodic table, in the case of representative elements, the group number is equal to the number of valence electrons. The valence electrons in atoms are shown in terms of Lewis symbols. To write the Lewis symbol for an element, we write down its symbol surrounded by a number of dots or crosses equal to the number of valence electrons. Paired and unpaired valence electrons are also indicated. The Lewis symbols for some of the important elements are shown below:

Atoms	Electronic Configuration	Lewis Symbol
sodium	[Ne]$3s^1$	Na •
magnesium	[Ne]$3s^2$	• Mg •
aluminum	[Ne]$3s^2 3p^1$	• Al •
silicon	[Ne]$3s^2 3p^2$	• Si •
phosphorus	[Ne]$3s^2 3p^3$	• P •
sulfur	[Ne]$3s^2 3p^4$	: S •
chlorine	[Ne]$3s^2 3p^5$	: Cl •
argon	[Ne]$3s^2 3p^6$	: Ar :

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding also known as lone pairs of electrons and one shared pair of electrons. A dash (or line) is sometimes used to indicate a shared pair of electrons:

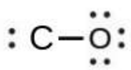
A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

To draw the Lewis structure for any molecule like CO, we follow the following five steps:

1. Determine the total number of valence (outer shell) electrons. The sum of the valence electrons is 4 (from C) + 6 (from O) = 10.
2. Draw a skeleton structure of the molecule. We can easily draw a skeleton with a C–O single bond:

   C–O

3. Distribute the remaining electrons as lone pairs on the terminal atoms. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

4. Place all remaining electrons on the central atom. Since there are no remaining electrons, this step does not apply.
5. Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible. In this case, carbon has only four electrons around it. To move to an octet for carbon, we take two of the lone pairs from oxygen and use it to form a CO triple bond.

   This satisfies the Octet condition for both atoms

3. Formal Charge And Its Properties

Formal Charge-

The formal charge of an atom in a molecule is the hypothetical charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. In other words, formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate the formal charge as follows:

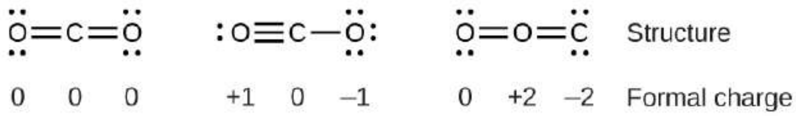
formal charge = valence shell electrons − lone pair electrons − 1/2 bonding electrons

Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bonds and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

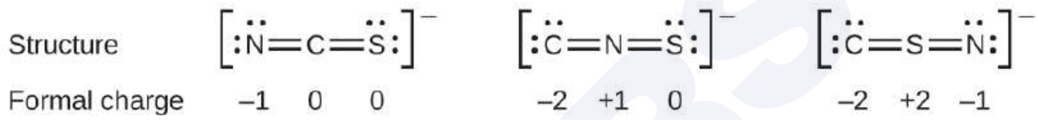
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure has non-zero formal charges, the arrangement with the smallest non-zero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

Let us consider some possible structures for carbon dioxide, CO_2, and thiocyanate. We know that the less electronegative atom typically occupies the central position, but formal charges allow us to understand why this occurs. We can draw three possibilities for the structure: carbon in the centre and double bonds, carbon in the centre with a single and triple bond, and oxygen in the centre with double bonds:



Comparing the three formal charges, we can identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

In the case of thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, three different molecular structures: CNS–, NCS–, or CSN– are possible as shown below. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown below:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges. Also, it places the least electronegative atom in the centre and the negative charge on the more electronegative element.

4. Limitations of The Octet Rule

Limitations to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

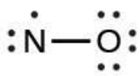
- Odd-electron molecules have an odd number of valence electrons and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

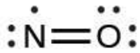
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for odd-electron molecules like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. Determine the total number of valence (outer shell) electrons. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. Draw a skeleton structure of the molecule. We can easily draw a skeleton with an N–O single bond:
   N–O
3. Distribute the remaining electrons as lone pairs on the terminal atoms. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

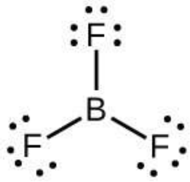


4. Place all remaining electrons on the central atom. Since there are no remaining electrons, this step does not apply.
5. Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

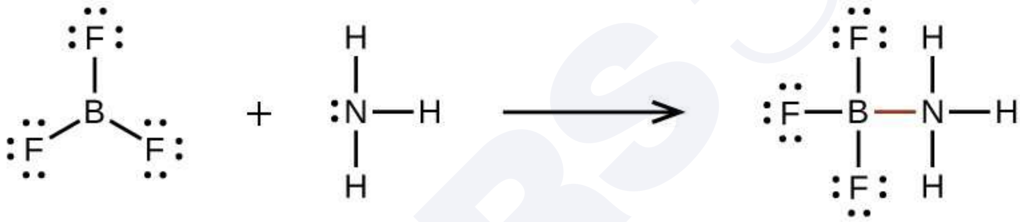


Electron-deficient Molecules

These are a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron-deficient boron. The reactivity of the compound is also consistent with an electron-deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

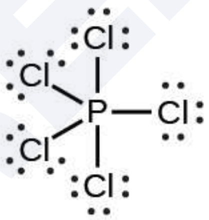


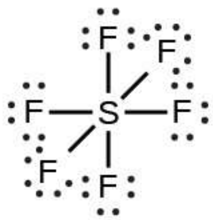
An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



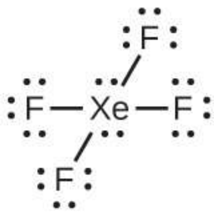
Hypervalent Molecules

Elements in the second period of the periodic table (n = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2s and three 2p orbitals). Elements in the third and higher periods (n ≥ 3) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d-orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figures given below show the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.





In some of the hypervalent molecules, like IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

5. Ionic Bond or Electrovalent Bond

Ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell. Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds or electrostatic forces of attraction between oppositely charged cations and anions. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are poor conductors of electricity as the strength of ionic bonds is very strong and it prevents the ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because, in the liquid state, these ions can move freely.

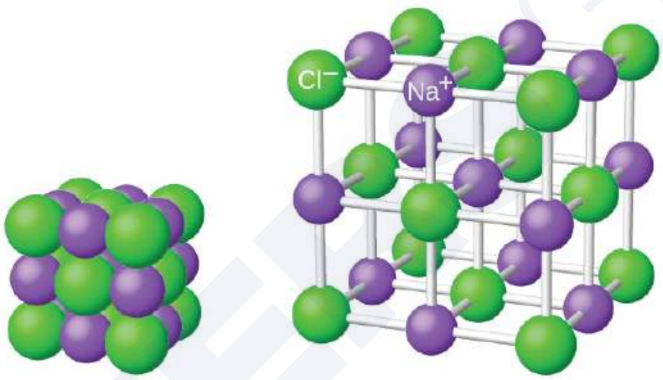
Neutral atoms and their associated ions have very different physical and chemical properties. For example, sodium atoms form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine atoms form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium cations and chloride anions. The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.

The Formation of Ionic Compounds

Binary ionic compounds are composed just of two elements i.e., a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must be equal to the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges.

It is important to consider that the formula for an ionic compound does not represent the physical arrangement of its ions. For example, sodium chloride (NaCl) "molecule", because there is not a single ionic bond between any particular pair of sodium and chloride ions. The attractive forces between ions are isotropic i.e., the same in all directions in other words, any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions as shown in the figure.



(a) (b)

The strong electrostatic force of attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\mathrm{kJ}$$

6. Lattice Energy

The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$\mathrm{MX}(s) \longrightarrow \mathrm{M}^{n+}(g) + \mathrm{X}^{n-}(g) \quad \Delta H_{\mathrm{lattice}}$$

The lattice energy ΔHlattice of an ionic crystal can be expressed by the following equation:

$$\Delta \mathrm{H}_{\mathrm{lattice}} = \frac{\mathrm{C}\left(\mathrm{Z}^{+}\right)\left(\mathrm{Z}^{-}\right)}{\mathrm{R}_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions, and Ro is the interionic distance. Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease.

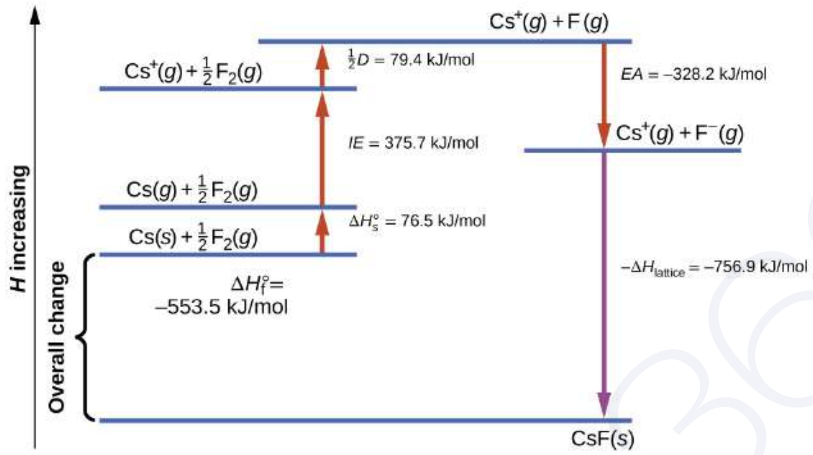
The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- $\Delta H_f°$, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal

- $\Delta H_s°$, the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

The figure given below shows the Born-Haber cycle for the formation of solid cesium fluoride.



The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

Enthalpy of sublimation of Cs(s)	$Cs(s) \longrightarrow Cs(g)$	$\Delta H = \Delta H_s° = 76.5 kJ/mol$
One-half of the bond energy of F_2	$\frac{1}{2}F_2(g) \longrightarrow F(g)$	$\Delta H = \frac{1}{2}D = 79.4 kJ/mol$
Ionization energy of Cs(g)	$Cs(g) \longrightarrow Cs^+(g) + e^-$	$\Delta H = IE = 375.7 kJ/mol$
Negative of the electron affinity of F	$F(g) + e^- \longrightarrow F^-(g)$	$\Delta H = -EA = -328.2 kJ/mol$
Negative of the lattice energy of CsF(s)	$Cs^+(g) + F^-(g) \longrightarrow CsF(s)$	$\Delta H = -\Delta H_{lattice} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H_f° = \Delta H_s° + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{lattice})$ $Cs(s) + \frac{1}{2}F_2(g) \longrightarrow CsF(s)$	$\Delta H = -553.5 kJ/mol$

For Caesium fluoride, the lattice energy can be calculated using the given values as follows:

$$\Delta H_{\text{lattice}} = (553.5 + 76.5 + 79.4 + 375.7 + 328.2) \text{kJ/mol} = 1413.3 \text{kJ/mol}$$

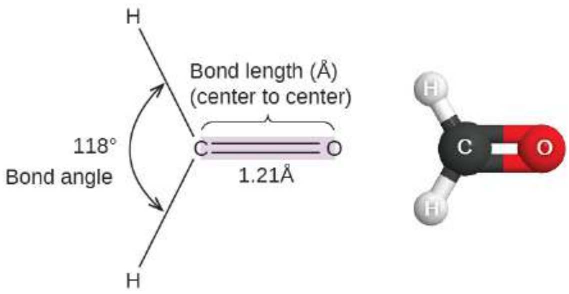
7. Bond Parameters - Bond Order, Angle, Length, and Energy

Bond length-

It is the distance between the nuclei of two bonded atoms when the lowest potential energy between the atoms is achieved.

Bond angle-

It is the angle between any two covalent bonds that share a common atom as shown in the figure.



Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

Bond energy-

It is the energy required to break one mole of bonds between two atoms in a gaseous state. For example, the bond enthalpy of the H-H bond is 435.8 kJ/mol.

$H_2(g) \rightarrow H(g) + H(g) : \Delta_a H' = 435.8 kJmol^{-1}$

Bond Strength-

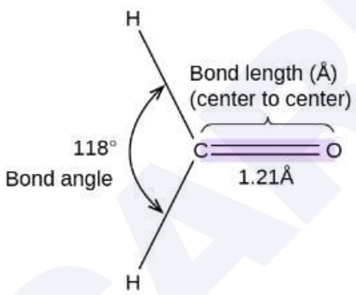
It is the strength by which the bonded atoms are held together in a molecule. It is measured in terms of the bond energy, in other words, it is the amount of energy required to break the bond.

Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

Bond Angle-

The bond angle is the angle between two bonds that form between two atoms. The figure given below illustrates the concept.



Drago's Rule-

Drago's rule is an empirical rule that is used to explain the bond angles of hydrides of groups 14, 15 and 16 and 2nd members of each of these three groups.

According to Drago's rule when the various conditions are satisfied as mentioned below, then the energy difference will be very high between the participating atomic orbitals and hence no mixing of orbitals or hybridization takes place.

- At least one lone pair must be present on the central atom.
- The central atom must be off or below 3rd period.
- The electronegativity of the surrounding atoms must be less than or equal to 2.1.
- For these hydrides, hybridization does not take place and thus bonding takes place only through pure atomic p orbitals like in PH_3 and hence the bond angle will be approximately 90^0.

For example, the bond angle for H_2O is 104.50 but for S_2H, Se_2H and Te_2H, the bond angles are approximately 90^0.

Bond Order-

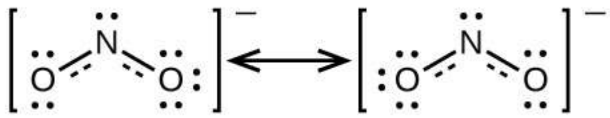
Bond order is defined as the number of bonds between the two atoms in a molecule. For example, in an H-H or H_2 molecule, there is only a single bond present thus its bond order is 1. Further, in O=O or O_2, the bond order is 2 as it has 2 bonds between the oxygen atoms.

Resonance-

The nitrite anion can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions as shown below.

If nitrite ions do indeed contain a single and a double bond, we would expect the two bond lengths to be different. A double bond between two atoms is shorter than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO^{2-} have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO^{2-} in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an average of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO^{2-} is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO^{2-} ion is shown as:



Resonance Hybrid-
It is the average of the resonance forms shown by the individual Lewis structures or canonical structures.

8. Fajan's Rule and Covalent Character in Ionic Bond

The covalent character in ionic bonds is determined by Fajan’s rule. It simply says that no ionic bond is completely ionic, there is always some covalent character in ionic bond. When a cation approaches an anion, then the electron cloud of the anion is distorted and shifted towards the cation, this distortion is known as the polarisation of the anion.

The ability of the cation to distort the anion is known as polarising power and the ability of the anion to get distorted is known as polarisability.

The covalent character in ionic bonds depends on the following factors:

- **Size of the cation:** The smaller the size of the cation, the larger will be its polarisability.
- **Size of the anion:** The larger the size of the anion, the larger will be its polarisability.
- **Charge on cation and anion:** The more the charge on a cation more polarising power. Further, the more the charge on the anion, the more will be its polarisability.

Thus covalent character for chlorides follows this order:

$NaCl < MgCl_2 < AlCl_3$

In this case, the charge on the cation increases, thus its polarising power also increases.

Further, for cation size, the covalent character follows the below order:

LiCl > NaCl > KCl > CsCl

In this case, as the size of the cation increases, its polarising power decreases.

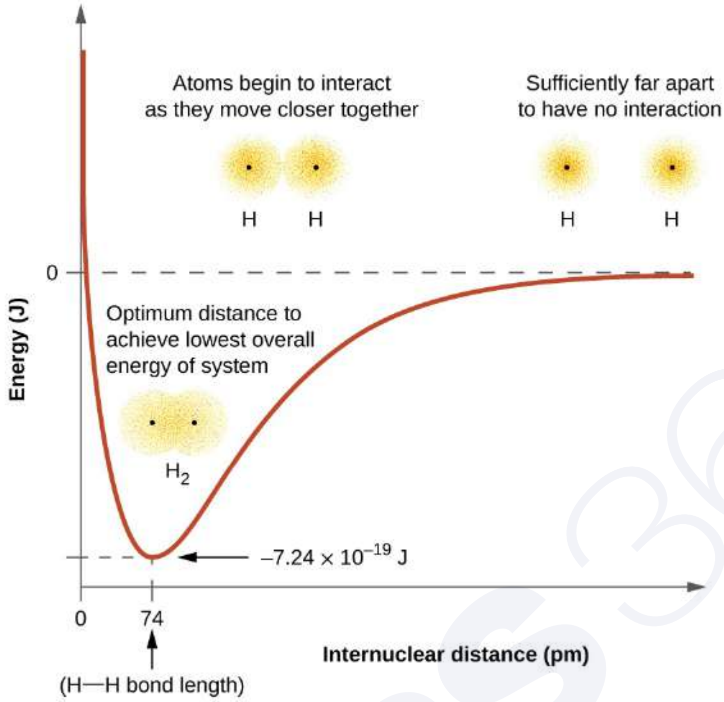
9. Valence Bond Theory

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

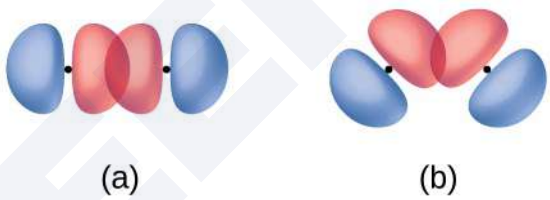
- An orbital on one atom overlaps an orbital on a second atom.
- The single electrons in each orbital combine to form an electron pair.

The mutual attraction between these negatively charged electron pairs and the two positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. The figure given below shows how the sum of the energies of two hydrogen atoms (the coloured curve) changes as they approach each other.

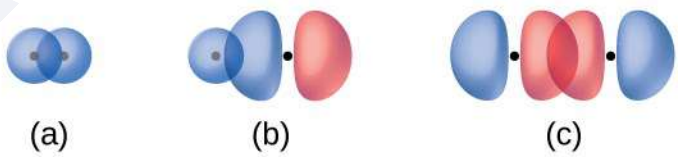


In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap. Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. The figure given below shows this for two p orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.



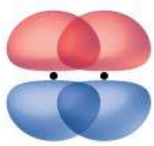
(a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two s orbitals, the overlap of an s orbital and a p orbital, and the end-to-end overlap of two p orbitals all produce sigma bonds (σ bonds), as given in the figure below. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.



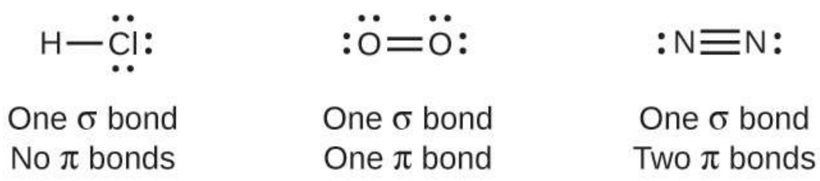
Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two p orbitals. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.



Pi (π) bonds form from the side-by-side overlap of two p orbitals.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bonds, there will be one σ bond, and the remaining one or two bonds will be π bonds.



$p\pi - p\pi$ *Bonding*

When one p-orbital of one atom contains one electron and the other atom also has one electron in the p-orbital, both perpendicular to the plane of the molecule then the type of bond formed is known as $p\pi - p\pi$ bonding.

$p\pi - d\pi$ *Bonding*

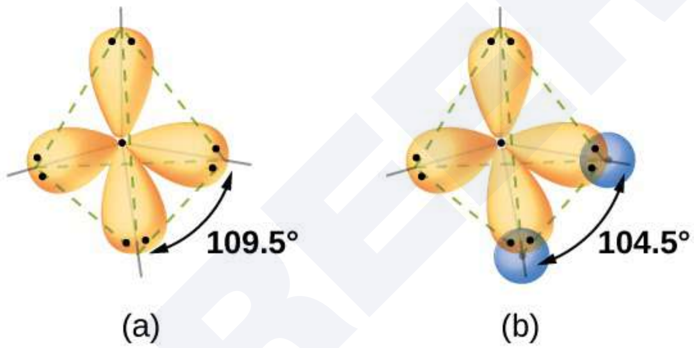
When one p-orbital of one atom contains one electron and the other atom also has one electron then the type of bond formed is known as $p\pi - p\pi$ bonding. In other words, $p\pi - d\pi$ bond is formed when the p orbital of one atom and the d orbital of another atom overlap laterally.

For example, PO_4^{3-} has a $p\pi - d\pi$ bonding because the lateral overlap of the p-orbital of the oxygen atom with the d-orbital of the sulphur atom occurs.

10. Hybridisation

When atoms are bound together in a molecule, the individual atomic orbitals combine to produce new forms of orbitals that are the same in energy and have the same size and shape. This process of combining atomic orbitals is called hybridization and is mathematically accomplished by the linear combination of atomic orbitals, LCAO. The new orbitals that result are called hybrid orbitals.

For example, the valence orbitals in an isolated oxygen atom are a 2s orbital and three 2p orbitals. However, the valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron as shown in the figure given below. Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°) but the real bond angle in a water molecule is 104.5°, this is because of the presence of the lone pairs of electrons in two of the hybrid orbitals.

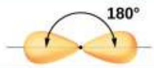
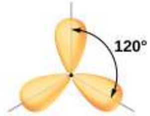
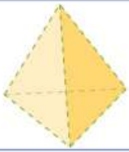
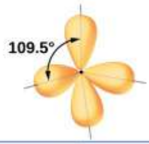
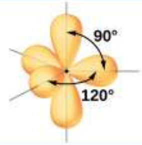
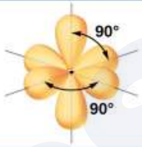


The salient features and conditions for hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

Types of Hybridisation

The hybridisation can be of several types depending on the number of hybrid orbitals involved in the formation of molecules. The table given below describes all types of hybridisation and their geometries.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

How to find Hybridisation-

The hybridisation depends upon sigma bonds and a lone pair of electrons.

Thus,

Hybridisation = Number of sigma bonds + Number of lone pairs present on the central atom

For example, hybridisation for NH_3 is sp^3 and its molecular geometry is tetrahedral.

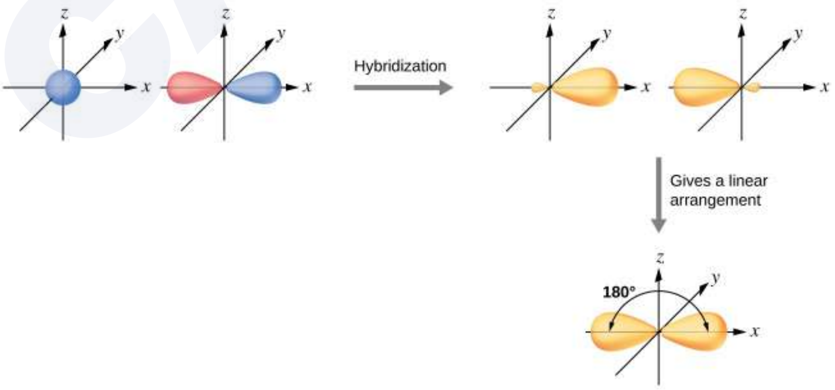
NH_3 has 3 sigma bonds and 1 lone pair, thus hybridisation for NH_3:

3 sigma bonds + 1 lone pair = 4

Thus hybridisation for NH_3 is sp^3 and its geometry is tetrahedral.

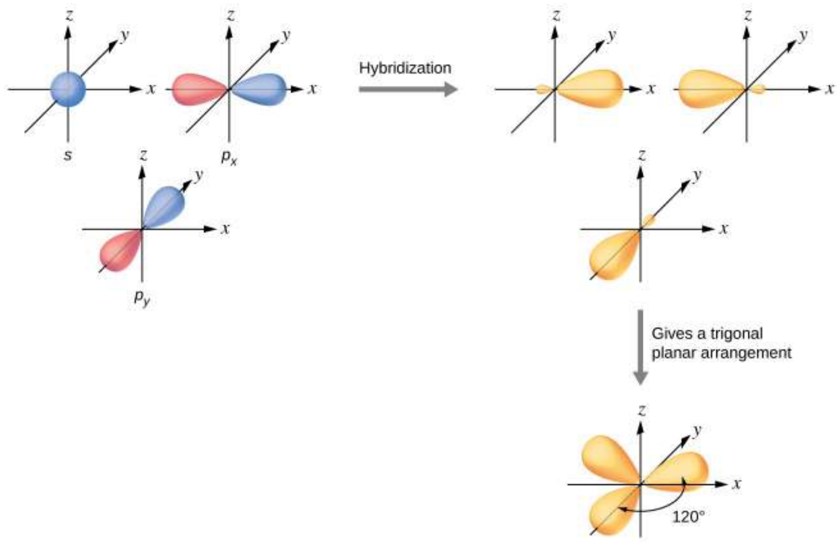
sp Hybridization-

This hybridization process involves mixing the valence s orbital with one of the valence p orbitals to yield two equivalent sp hybrid orbitals that are oriented in a linear geometry as shown in the figure. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The p orbital is one orbital that can hold up to two electrons. The sp set is two equivalent orbitals that point 180^{o}C from each other. The two electrons that were originally in the s orbital are now distributed to the two sp orbitals, which are half-filled.



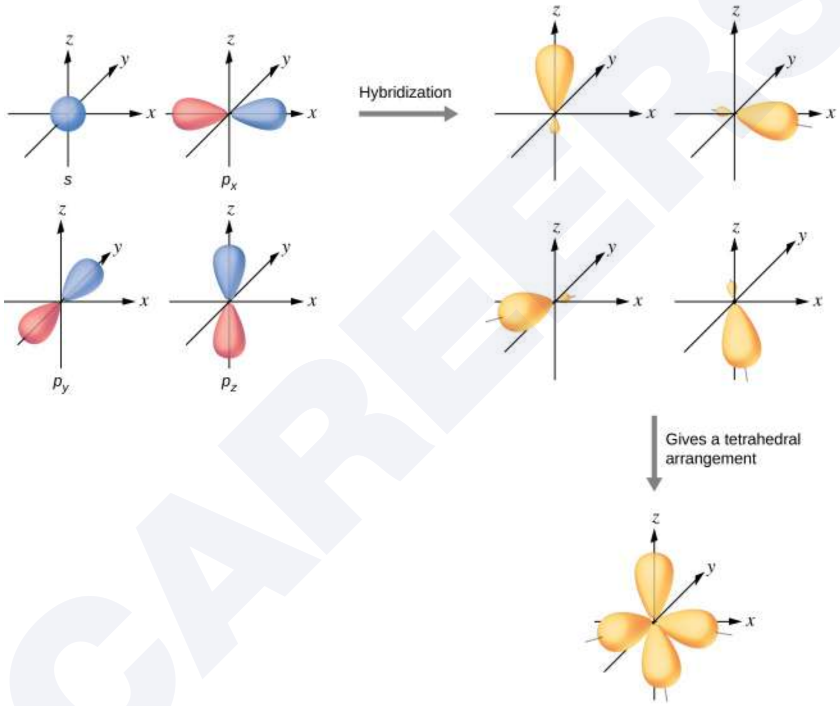
sp^2 Hybridization-

When 1 s-orbital and 2 p-orbitals are involved in the molecule formation then the equivalent set of orbitals are known as sp^2 hybrid orbitals. These hybrid orbitals arrange themselves at an angle of 120^{o}C as shown in the figure.



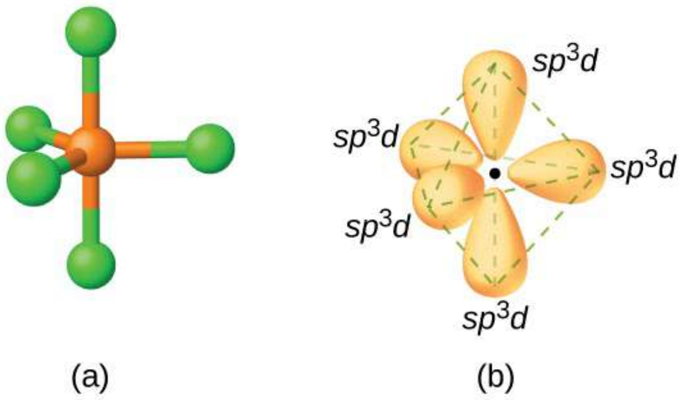
sp3 Hybridization-

When 1 s-orbital and 3 p-orbitals are involved in the molecule formation then the equivalent set of orbitals are known as sp^3 hybrid orbitals. The bond angle between these hybrid orbitals is 109°C as shown in the figure.



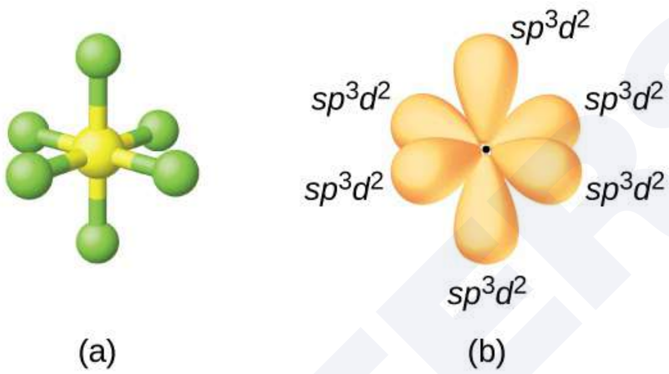
sp^3d Hybridisation-

When 1 s-orbital, 3 p-orbitals and 1 d-orbital are involved in the molecule formation then the equivalent set of orbitals are known as sp^3d hybrid orbitals. There are two kinds of bonds formed for sp^3d hybridisation, i.e, 2 axial bonds and 3 equatorial bonds. The angle between the axial bond and the equatorial plane is 90°C while the bond angle between the equatorial bonds is 120°C as shown in the figure given below:



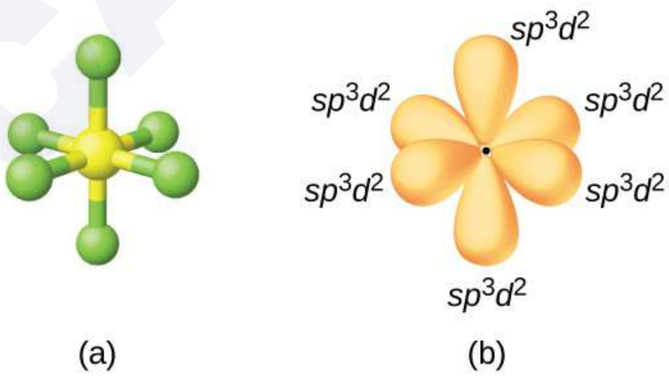
sp^{3}d^2 Hybridization-

When 1 s-orbital, 3 p-orbitals and 2 d-orbitals are involved in the molecule formation then the equivalent set of orbitals are known as sp^{3}d^2 hybrid orbitals. There are two kinds of bonds formed for sp^{3}d^2 hybridisation, i.e, 2 axial bonds and 4 equatorial bonds. The angle between the axial bond and the equatorial plane is 90^{o}C while the bond angle between the equatorial bonds is 90^{o}C as shown in the figure given below:



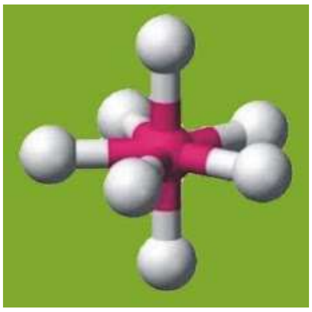
d^{2}sp^3 hybridisation-

When 2 d-orbital, 1 s-orbital and 3 p-orbitals are involved in the molecule formation then the equivalent set of orbitals are known as d^{2}sp^3 hybrid orbitals. There are two kinds of bonds formed for sp^{3}d^2 hybridisation, i.e, 2 axial bonds and 4 equatorial bonds. The angle between the axial bond and the equatorial plane is 90^{o}C while the bond angle between the equatorial bonds is 90^{o}C as shown in the figure given below:



sp^{3}d^3 hybridization-

When 1 s-orbital, 3 p-orbitals and 3 d-orbitals are involved in molecule formation then the equivalent set of orbitals are known as sp^{3}d^3 hybrid orbitals. The sp^{3}d^3 hybridization has a pentagonal bipyramidal geometry i.e., five bonds in a plane, one bond above the plane and one below it.



11. VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom of a molecule from the estimation of the number of bonds and lone pairs of electrons in its Lewis structure.

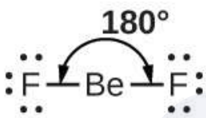
The main postulates of VSEPR theory are:

- The actual shape of a molecule depends upon the number of electron pairs (bonded or non–bonded) around the central atom.
- The electron pairs tend to repel each other due to their negative charge.
- Electron pairs arrange themselves in such a way that there exists a minimum repulsion between them.
- The valence shell is considered as a sphere with the electron pairs placed at a distance.
- A multiple bond is treated as if it is a single electron pair & the electron pairs which constitute the bond as a single pair.
- The repulsive interaction of electron pairs decreases in the order as mentioned below:

  Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp).

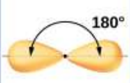
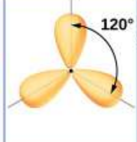
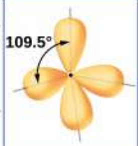
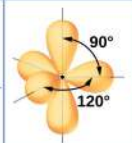
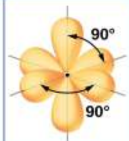
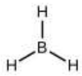
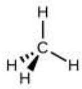
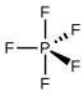
- Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than double bonds. This repulsion decreases sharply with increasing bond angle between the electron pairs.

Let us understand VSEPR theory using a gaseous BeF_2 molecule. In the Lewis structure of BeF_2, as shown in the figure, there are only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom, thus the bond angle is 180°.



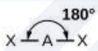
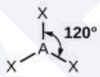
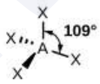
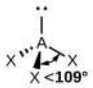
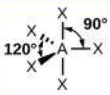
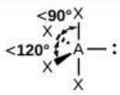
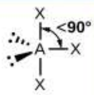
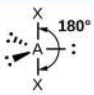
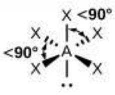
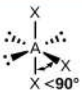
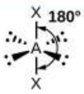
The BeF_2 molecule adopts a linear structure in which the two bonds are at maximum distance from each other and maintain an angle of 180°.

As given in the table below, two regions of electron density around a central atom in a molecule form a linear geometry, three regions form a trigonal planar geometry, four regions form a tetrahedral geometry, five regions form a trigonal bipyramidal geometry, and six regions form an octahedral geometry.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

12. Shapes of Molecules

The ideal shapes of molecules, which are predicted on the basis of electron pairs and lone pairs of electrons are mentioned in the table below:

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

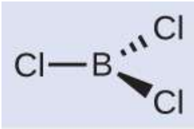
Predicting the geometry of molecules-

The following procedure uses VSEPR theory to determine the geometry of the molecules:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral

4. Use the number of lone pairs to determine the molecular structure. If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

For example, BCl_3 has three electron pairs and no lone pairs of electrons. Thus these three electron pairs will arrange themselves in a trigonal planar geometry as shown below. The bond angle between each B-Cl bond is 120^oC.



13. Molecular Orbital Theory

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. The table given below explains the major differences between the valence bond theory and molecular orbital theory.

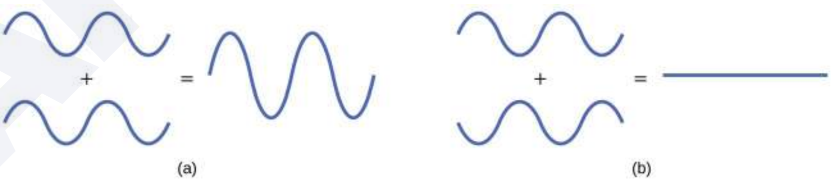
Comparison of Bonding Theories

Valence Bond Theory	**Molecular Orbital Theory**
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from the overlap of atomic orbitals (s, p, d…) and hybrid orbitals (sp, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behaviour of an electron in a molecule is still described by a wave function, Ψ, analogous to the behaviour in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs as shown in the figure below. In orbitals, the waves are three-dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.



(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

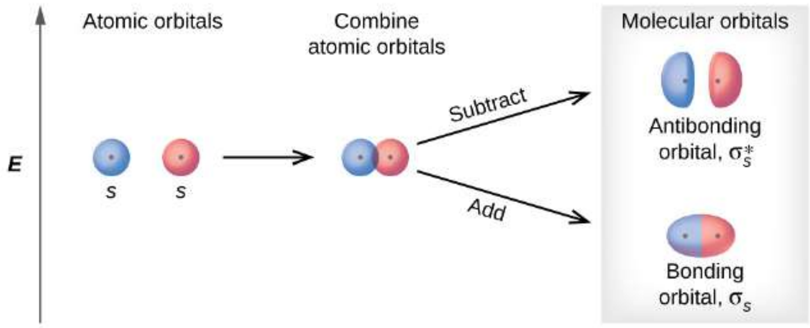
Types of Molecular Orbitals-

Molecular orbitals from s-atomic orbitals-

There are two types of molecular orbitals that can form from the overlap of two atomic s orbitals on adjacent atoms. The two types are described below:

- σ molecular orbital: The in-phase combination with lower energy orbitals in which most of the electron density is directly between the nuclei.
- σ* molecular orbital: The out-of-phase addition produces a higher energy molecular orbital in which there is a node between the nuclei.

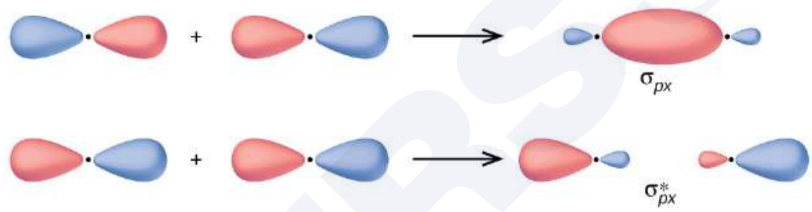
Electrons in a σ orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the σ* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.



Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

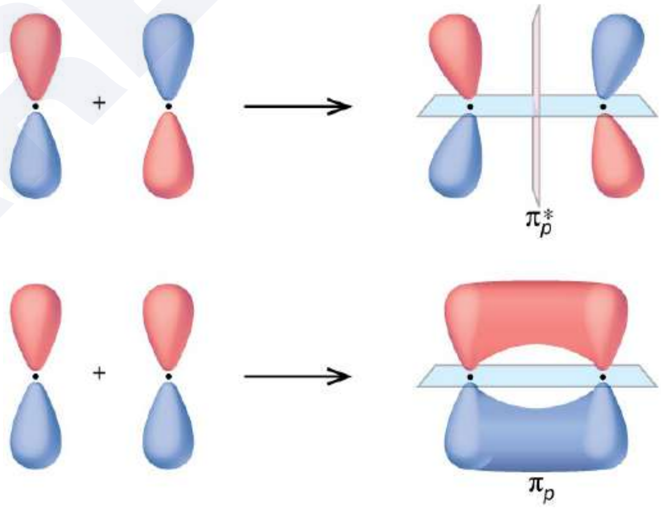
Molecular orbitals from p-atomic orbitals-

In p orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes in different colours. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phases overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ* orbitals. If two atoms are located along the x-axis in a Cartesian coordinate system, the two px orbitals overlap end to end and form σ_{px} (bonding) and σ_{px}* (antibonding).



Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp and σp*.

The side-by-side overlap of two p orbitals gives rise to a pi (π) bonding molecular orbital and a π* antibonding molecular orbital. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the p orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.



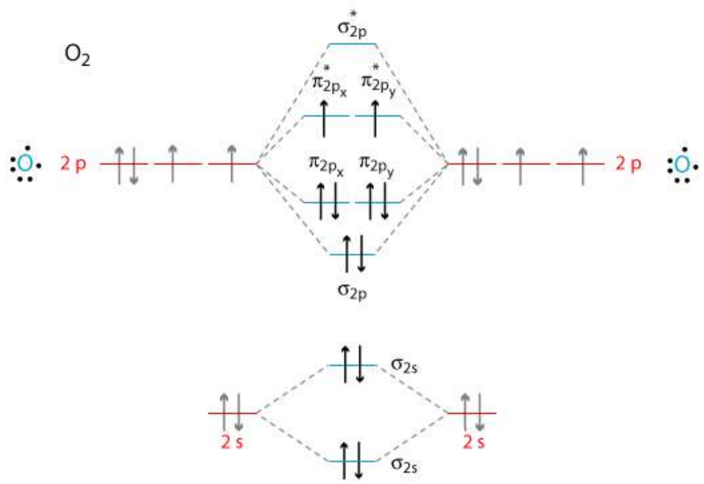
Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals.

In the molecular orbitals of diatomic molecules, each atom also has two sets of p orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and π_{py}* orbitals are oriented at right angles to the π_{pz} and π_{pz}* orbitals. Except for their orientation, the πpy and πpz orbitals are identical and have the same energy; they are degenerate orbitals. The π_{py}* and π_{pz}* antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ_{px}*, π_{py} and π_{py}*, π_{pz} and π_{pz}*.

Electronic Configuration and Molecular Behaviour-

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by using the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins. Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital.

For example, the electronic configuration of the O_2 molecule is given below:



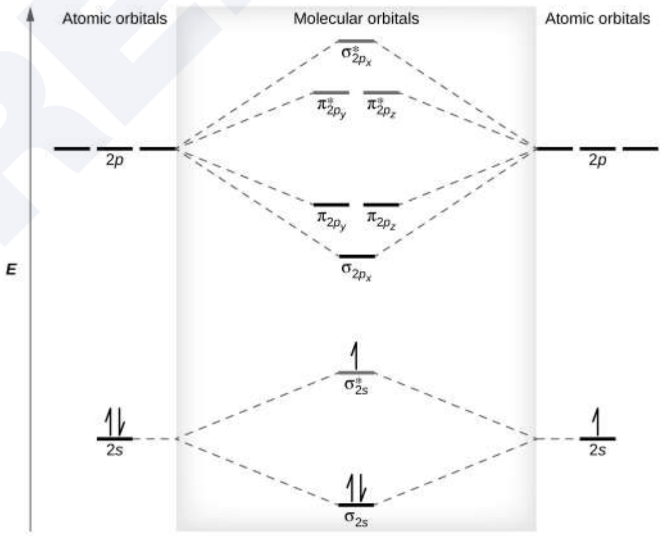
Thus, the electronic configuration of O_2 molecule can be written as:

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$$

14. Energy Level Diagram

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram. As given in the figure below, for a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the centre. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2p atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).



22

molecular orbital diagram

The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order-

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

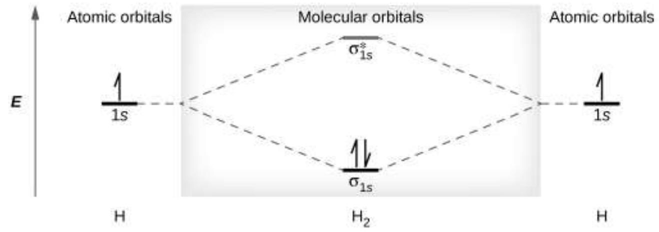
The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

bond order = [(number of bonding electrons)−(number of antibonding electrons)]/2

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form.

For example, the bond order of the H_2 molecule is given as follows:



The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have:

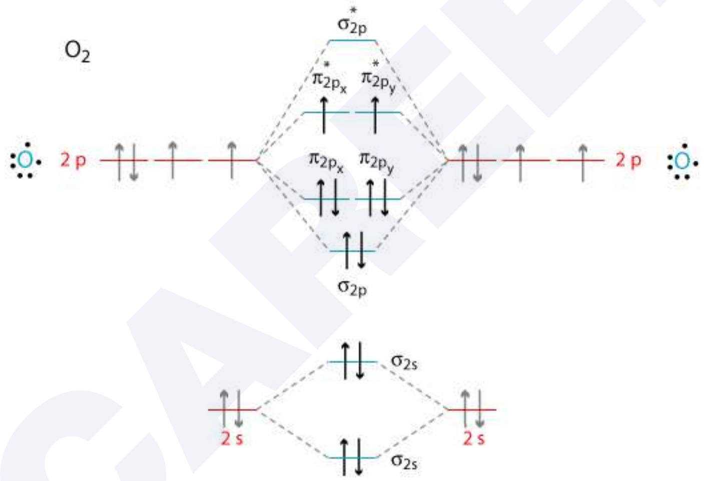
bond order in H_2=(2−0)/2=1

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

Magnetic Moment

The magnetic behaviour of any molecule can be determined from the number of unpaired electrons in the bonding and antibonding orbitals. The molecule is said to be diamagnetic as there is no unpaired electron present in the orbitals and not attracted by the magnet. But if any unpaired electron is present then the molecule is paramagnetic.

For example, O_2 molecule has 2 unpaired electrons can be seen from the diagram below:



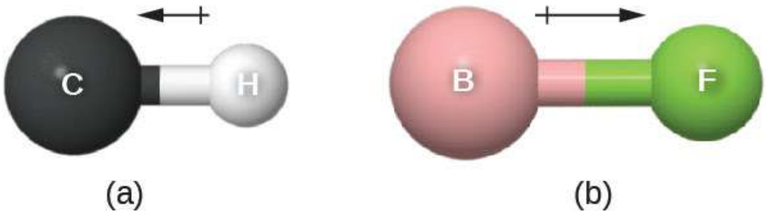
Therefore, the O_2 molecule is paramagnetic.

15. Dipole Moment

When the covalent bond forms between two different atoms then because of the difference in electronegativity the electrons get shifted towards the more electronegative atom and thus form the polar covalent bond and this polar molecule is known as a dipole molecule. The more electronegative atom occupies a partial negative charge (δ-) and the other atom possesses a partial positive charge (δ+). This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula as shown below, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude as shown in the figure. Dipole vectors are shown as arrows pointing along with the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

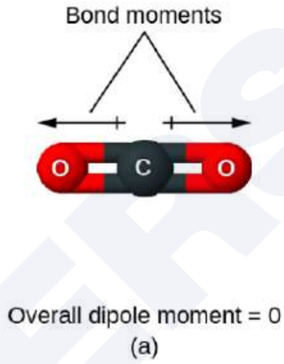


(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

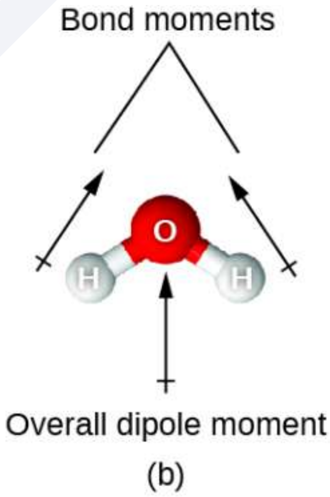
The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their dipole moments cancel, then the molecule is non-polar. For example, in the case of CO_2 as shown in the figure given below. Each of the bonds is polar, but the molecule as a whole is non-polar. The dipole moments cancel each other because they are pointed in opposite directions.



In the case of the water molecule, the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).



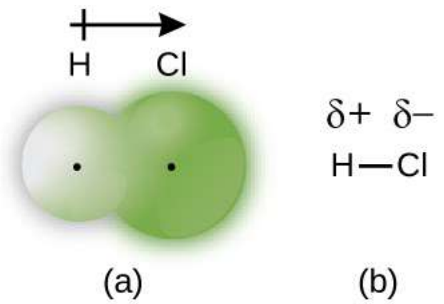
16. Ionic Character in Covalent Bond

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

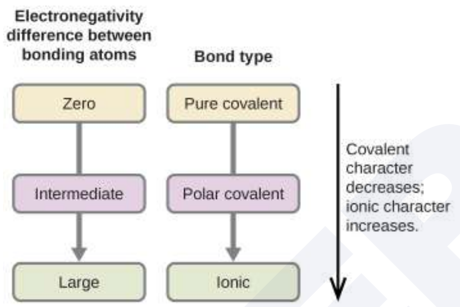
$$Cl + Cl \rightarrow Cl_2$$

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule are shifted towards chlorine. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge as shown in the figure given below.



(a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

When the electronegativity difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). The figure below shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

As the electronegativity difference increases between two atoms, the bond becomes more ionic.

17.Van Der Waals Forces

Van der Waal Forces

Van der Waal's force of attraction is the force of attraction between the molecules. This force is weaker compared to bonds like covalent and ionic bonds.

Van der Waal forces can be divided into various categories as follows:

- Ion-dipole interaction: This type of interaction exists between an ion and a polar molecule like HF, HCl, H_2O, etc. The ion can be like Na^+. This type of interaction is responsible for the dissolution of ions in solution.
- Dipole-Dipole interaction: This type of interaction exists between two or more polar molecules. These dipoles can be H-Cl and H-Cl, NH_3 and NF_3, etc. Hydrogen bonding is a special type of dipole-dipole interaction.
- Ion-induced dipole interaction: This type of interaction exists between the ion and non-polar molecule. The charge on the ion causes the distortion in the electron cloud of the non-polar molecule and thus induces a dipole in the non-polar molecule. Then the ion and the induced dipole attract each other.
- Dipole-induced dipole interaction: This kind of interaction exists between a polar and a non-polar molecule. For example, CCl_4 in H_2O. One of the dipole molecules distorts the electron cloud in the non-polar molecule and thus creates the dipole in the non-polar as well.
- Instantaneous dipole-dipole interaction: This type of interaction exists between two non-polar molecules. This force is also known as London forces. At any instant, electrons in one non-polar molecule come closer to each other and then this molecule becomes a dipole for instance. This instantaneous dipole distorts the electron cloud in another non-polar molecule and thus both behave like polar molecules. For example CCl_4 and CCl_4.

The strength of these forces follows the given order:

Ion-Dipole > Dipole-Dipole > Ion-Induced Dipole > Dipole-Induced Dipole > London Forces

18. Hydrogen Bonding

Hydrogen Bonding

Hydrogen bonds are strong forces which occur when a hydrogen atom bonded to an electronegative atom approaches a nearby electronegative atom such as O, N, F, etc. Greater electronegativity of the atom will result in an increase in hydrogen-bond strength. The hydrogen bond is a stronger intermolecular force, but it is weaker than a covalent or an ionic bond. Hydrogen bonds are responsible for holding together DNA, proteins, and other macromolecules.

Formation of Hydrogen Bond

A hydrogen bond is an electromagnetic attraction that occurs between a partially positively charged hydrogen atom attached to a highly electronegative atom and another nearby electronegative atom. A hydrogen bond is a type of dipole-dipole interaction; it is not a true chemical bond. This hydrogen bond attraction can occur between different molecules (intermolecularly) or within different parts of a single molecule (intramolecularly).

Types of Hydrogen Bonding

There are two types of hydrogen bonding, i.e.:

- **Intermolecular Hydrogen Bonding:** Intermolecular hydrogen bonding occurs when the H-atom of one molecule and an electronegative atom of another molecule are close to each other. For example, hydrogen bonds between the molecules of hydrogen fluoride. Intermolecular hydrogen bonding results in the association of molecules. Thus, it increases the melting point, boiling point, solubility, etc.
- **Intramolecular Hydrogen Bonding:** Intramolecular hydrogen bonding occurs when the hydrogen atom and an electronegative atom of the same molecule are close to each other. Intramolecular hydrogen bonding results in the cyclization of the molecules and prevents their association. Thus, the properties of these compounds like melting point, boiling point, etc. are usually low. For example, intramolecular hydrogen bonding is present in molecules such as o-nitrophenol, o-nitrobenzoic acid, etc.

19. Smart Tips

- A formal charge is given by using the following formula:

  Formal charge = V - N - (1/2)B

  V = Total number of valence electrons

  N = Total number of lone pair of electrons

  B = Total number of shared electrons or bonded electrons.
- Banana bonding is shown by boron hydride, i.e., diborane.
- Molecular solids have low heat of fusion.
- When the energy gap is very small, conduction occurs while when the energy gap is large no conduction occurs.
- C_2 molecule has no σ bonds but only π bonds.
- The bond length of CO > CO^+ because the bond order of CO is 3 and for CO^+ is 3.5.

Chemical Thermodynamics

Important Formulae

1. THERMODYNAMICS

Thermodynamics is the branch of science which deals with the quantitative relationships between different forms of energy or it deals with the energy changes accompanying physical and chemical transformations.

Main objectives of Thermodynamics

Its main objectives are as follows:

- To decide the feasibility of a given transformation.
- To derive various energy changes and their interrelations.
- To derive laws like—phase rule, Law of mass action, etc.
- Presentation of experimental data in a correct manner.

Terms Related to Thermodynamics

System

It is the region or space to be investigated or the origin at which study of pressure, temperature etc., are to be made and which is isolated from the rest of the universe with a bounding surface.

Surroundings

It is a region apart from the system which might be in a position to exchange energy and mass with the system.

It is to be noted that the system and surroundings together constitute the universe.

Homogeneous and Heterogeneous Systems

Homogeneous Systems

It is all over-uniform that is made of one phase only. For example, pure liquid pure solid, or pure gas present alone.

Heterogeneous Systems

It is non-uniform as it consists of two or more phases. For Example, ice, and water, are solid in contact with a liquid.

Type of Systems

Systems are divided into three parts-

(i) Open System: In such a system, both matter and energy can be exchanged with the surroundings.

For example, Boiling water in a beaker, Limekiln or ice in an open beaker, Zinc granules reacting with dilute HCI to give hydrogen gas is also an example of an open system as hydrogen gas escapes and the heat of reaction is transferred to the surroundings.

(il) Closed System: In such a system, the exchange of energy takes place only with the surroundings.

For example, Heating liquid in a sealed tube or ice in a closed beaker

(iii) Isolated System: In such a system, there is no exchange of matter or energy with the surroundings.

For example, Liquid in a sealed thermos flask or ice m thermos flask.

2. Thermodynamic Property

Properties of System

All macroscopic properties of a system irrespective of the fact whether they are state variables or not are divided into two types:

1. Intensive Properties

Such properties remain the same on any division in the system that is, do not depend upon the amount of substance present in the system.

Example: Temperature, pressure, concentration, density, viscosity, surface tension, specific heat, refractive index, pH, EMF of the dry cell, vapour pressure, dipole moment etc.

2. Extensive Properties

Such properties depend upon the amount of substance that is, their values are different in the divided system than in the entire system

Examples, Mass, volume, energy, work, internal energy, entropy, enthalpy, heat capacity, and length.

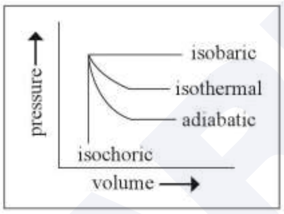
An extensive property can be made intensive specifying it in unit amount of matter.

$\text{Example, Density} \approx \left(\frac{\text{Mass}}{\text{Volume}}\right)$

3. State Functions

Path and state function
It is the path along which a change of state occurs. It is a path of change of a system from one equilibrium state or another which is usually accompanied by a change in energy or mass.

Types of Thermodynamic Process



1. Isothermal Process

Here the temperature is kept constant during each step of the process. Example,

$\Delta T = 0, \Delta E = 0$

- It is achieved by using a thermostatic control.
- Heat can be absorbed or evolved here that is, can be exchanged with the surroundings.

For example, Freezing, melting, evaporation, and condensation.

2. Isobaric Process

Here the pressure is kept constant $(\Delta P = 0)$ during each step of the process.

For example, the Expansion of gas in an open system.

- Vaporization and heating of water up to its boiling point occur at the same atmospheric pressure.

3. Isochoric Process

Here volume is kept constant. $(\Delta V = 0)$ during each step of the process.

For example, the Heating of substance in a closed vessel (system) or non-expanding chamber.

4. Adiabatic Process

- Here no exchange of heat takes place between the system and the surroundings that is, ($Q = 0$)
- It is achieved by insulating the system or in closed insulated containers (thermos).

5. Cyclic Process

- Here the System undergoes a series of changes but finally comes back to the initial state.
- $\Delta E = 0, \Delta H = 0$

4. Reversible, Irreversible, Polytropic Process

Reversible or Quasi-Static Process

It is carried out in such a way that the system remains in a state of equilibrium. All changes occurring at any part of the process will be exactly reversed when the change is carried out in the opposite direction.

- It involves slow changes during operation.
- This process may occur in any direction.
- Here driving force and opposing force differ with each other by a very small value.

Irreversible Process

Here the direction of change can not be reversed by small changes in variables. All processes occurring naturally are reversible

- It involves fast changes during operation.
- It is a unidirectional process.
- Here, driving and opposing forces differ by a large amount.

Polytropic Process

PV^m = constant is known as a general or polytropic process

If m= 0, the process is constant pressure.

If m = 1, the process is isothermal.

If m = γ , the process is adiabatic.

5.Thermodynamic Equilibrium

Thermodynamic Equilibrium

A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

If a system is heterogeneous and is in equilibrium, the macroscopic properties in the various phases remain unchanged with time.

Types: It is of three types-

(i) Mechanical Equilibrium

Here no mechanical work is done by one of the systems on another part of the system and it is possible if the pressure remains the same throughout the system that is, there is no flow of matter from one part to another

(ii) Thermal Equilibrium

There is no flow of heat from one part to another that is, the temperature is constant.

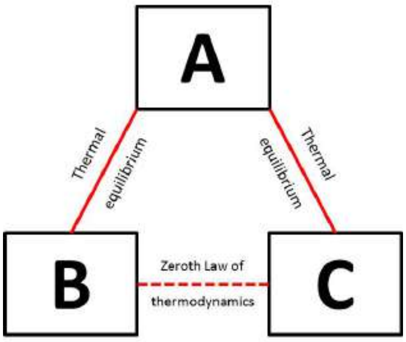
(iii) Chemical Equilibrium

There is no change in the composition of any part of the system with time.

The Zeroth Law of Thermodynamics-

If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.

If system B is in thermal equilibrium with system A and system C is also in thermal equilibrium with system A, system B, and system C are in thermal equilibrium with each other.



A hot body has a higher temperature than a cold body. The temperature of two bodies decides the direction of heat flow when the two bodies are put in contact. The heat flows from the hot body to the cold body till the bodies are at the same temperature it is known as thermal equilibrium.

6.Introduction To Heat, Internal Energy And Work

Heat

Heat is the energy transfer due to the difference in temperature. Heat is a form of energy which the system can exchange with the surroundings if they are at different temperatures. The heat flows from higher temperature to lower temperature.

Heat is expressed as 'q'

Heat absorbed by the system = +q

The heat evolved by the system = - q

Work

It is the energy transfer due to the difference in pressure that is, the mode of energy transfer.
Types of work

(i) Mechanical Work (Pressure volume work) = Force x Displacement

(ii) Electrical Work = Potential difference x charge flow , VQ = EnF

(iii) $\text{Expansion Work} = P \times \Delta V = -P_{ext.}[V_2 - V_1]$

$$P = \text{external pressure And } \Delta V = \text{increase or decrease in volume.}$$

(iv) Gravitational Work = mgh

Here m = mass of body,

g = acceleration due to gravity

h = height moved.

Units: dyne cm or erg (C.G.S.)

Newton meter (joule)

(i) If the gas expands, [$V_2 > V_1$] and work is done by the system and W is negative.

(ii) If the gas [$V_2 < V_1$] and work is done on the system and W is positive.
Different Types of Works and the Formulas

(i) Work done in a reversible isothermal process

$$W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$
$$W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

(ii) Work done in an irreversible isothermal process

$$\text{Work} = -P_{ext.}(V_2 - V_1)$$
$$\text{That is, Work} = -P \times \Delta V$$

Internal Energy or Intrinsic Energy

The energy stored within a substance is called its internal energy. The absolute value of internal energy cannot be determined.

Or

It is the total energy of a substance depending upon its chemical nature, temperature, pressure, and volume, amount of substrate. It does not depend upon path in which the final state is achieved.

$E = E_t + E_r + E_v + E_e + E_n + E_{PE} + E_B$
$E_t =$ Transitional energy
$E_r =$ Rotational energy
$E_{PE} =$ Potential energy
$E_B =$ Bond energy

The exact measurement of it is not possible so it is determined as ΔE as follows:

$\Delta E = \Sigma E_p - \Sigma E_R$
$\Delta E = E_f - E_i$
Here $E_f =$ final internal energy
$Ei =$ Initial internal energy
$Ep =$ Internal energy of products
$Er =$ Internal energy of reactants

Facts about Internal Energy

- It is an extensive property.
- Internal energy is a state property.
- The change in internal energy does not depend on the path by which the final state is reached.
- Internal energy for an ideal gas is a function of temperature only so when the temperature is kept constant ΔE is zero for an ideal gas.

  $E \propto T$

  $\Delta E = nC_v\Delta T[\ C_v$ is the heat capacity at constant volume$]$
- For a cyclic process ΔE is zero. (E = state function), $E \propto T$
- For an ideal gas, it is totally kinetic energy as there is no molecular interaction.
- Internal energy for an ideal gas is a function of temperature only hence, when the temperature is kept constant it is zero.
- At constant volume (Isochoric) $Q_v = \Delta E$
- For exothermic process, ΔE is negative as $E_R > E_P$ but For endothermic process ΔE is positive as $E_R > E_P$.
- It is determined by using a Bomb calorimeter of the system.

  $\Delta E = \frac{Z \times \Delta T \times m}{W}$
  $Z =$ Heat capacity of Bomb calorimeter
  $\Delta T =$ Rise in temperature
  $w =$ Weight of substrate (amount)
  $m =$ Molar mass of substrate

7. First Law of Thermodynamics

First Law or Law of Conservation of Energy

It was introduced by Helmholtz and according to it "Energy can neither be created nor destroyed but can be converted from one form to another or the total energy of the universe is constant",

It can also be written as:

- The energy of an isolated system must remain constant, although it may be transformed from one form to another.
- Energy in one form, if it disappears will make its appearance in an exactly equivalent in another form.
- When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.
- It is never possible to construct a perpetual motion machine that could produce work without consuming any energy.

  Thus if heat is supplied to a system it is never lost but it is partly converted into internal energy and partly in doing work in the system that is,

  Heat supplied = Work done by the system + Increase in internal energy

  So increase in internal energy = Heat supplied - work done by the system

  ie. $\Delta E = q + w \qquad [\because$ work done by the system is -w$]$

Mathematical Formulation of the First Law

If a system absorbs 'q' amount of heat and its state changes from X to Y this heat is used up.

(i) On increasing the internal energy of the system

$\Delta E = E_Y - E_X$

(ii) In order to do some external work (W) on the surroundings by the system.

From the first law, we get the relation

$\Delta E = Q - W$ (that is, work done by the system $= W$)
$dE = dQ - dW$ or $dE = dQ - PdV$)
Work done by the system or in expansion

OR

$\Delta E = Q + W$ (that is, work done by the system $= W$)
$dE = dQ + dW$ or $dE = dQ + PdV$)
Work done by the system or in compression

For the sake of simplicity, remember the formula $\Delta E = Q + W$ and when the work is done by the system, work is negative, and when the work is done on the system.

8. Isothermal Expansion of an Ideal Gas

Isothermal reversible and irreversible

Let us consider a cylinder fitted with a frictionless and weightless piston having an area of cross-section as 'A'. If the external pressure (P) is applied on this piston and the value of P is slightly less than that of the internal pressure of the gas When the gas undergoes a little expansion and the piston is pushed out by a small distance dx the work done by the gas on the piston is given by as

$$\begin{aligned}
&dw = \text{ force } \times \text{ distance } = \text{ pressure } \times \text{ area } \times \text{distance} \\
&dw = PA \cdot dx \\
&\text{ As } A.dx = dV \\
&dw = PdV
\end{aligned}$$

When the volume of the gas changes from
$V_1 - V_2$, the total work done (W) can be given as
$W = P. \int \cdot dV$
If we consider the external pressure (P) to be constant, than
$W = P \int dV = P(V_2 - V_1) = P \cdot \Delta V$
$W = P \cdot \Delta V$

Isothermal irreversible expansion of an ideal gas

When a gas expands against a constant external $(P_{\text{ext}} = \text{ constant })$. There is a considerable difference between the gas pressure (inside the cylinder) and the external pressure. The temperature does not change during the process.

$$W = -\int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$\begin{aligned}
&= -P_{ext} \int_{V_1}^{V_2} \\
&= -P_{ext}(V_2 - V_1) \\
W &= -P_{ext} \cdot \Delta V
\end{aligned}$$

Work done in Isothermal reversible expansion of an ideal gas

As a small amount of work done dW on the reversible expansion of a gas through a small volume dV against an external pressure 'P' can be given as

$dW = -PdV$

So the total work done when the gas expands from initial volume V_1 to final volume V_2 is given as

$$\int dW = \int_{v_1}^{v_2} -PdV$$

As according to ideal gas equation $PV = nRT$
$P = \frac{nRT}{V}$

So $W_{rev} = \int \frac{nRT}{V} dV$ (as temp. is constant)

So $W_{rev} = -nRT \ln \frac{V_2}{V_1}$

$W_{rev} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$

$W_{rev} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$

Here negative sign indicates work of expansion and it is generally greater than work in the irreversible process

As in such a case, the temperature is kept constant and internal energy depends only on temperature so it internal energy is constant.

$$\text{So } \Delta E = 0$$
$$\Delta E = q + W$$
$$q = -W$$

Hence, during isothermal expansion, work is done by the system at the expense of heat absorbed.

Here ΔH can be found out as follows:

$\Delta H = \Delta E + \Delta n_g RT$

As, for isothermal process, $\Delta E = 0, \Delta T = 0$
So $\Delta H = 0$

9. Adiabatic Process

Adiabatic Reversible Expansion of An Ideal Gas

(1) Process Equations for Reversible Adiabatic Process

$PV^\gamma = \text{constant}$

$TV^{\gamma-1} = \text{constant}$

$T^\gamma \ P^{1-\gamma} = \text{constant}$

As in an adiabatic change, there is no transfer of heat that is, q = 0 or dq = 0.

$$\Delta E = W$$
$$dE = dW$$

W can be written as

$$W = \Delta E = nC_V \Delta T = n\frac{R}{\gamma - 1}\Delta T = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \longrightarrow (1)$$

Alternatively, the Work can also be derived from the formula

$$W = \int P_{ext}\ dV \text{ and } PV^\gamma = \text{constant}$$

(2)Irreversible Adiabatic Process

The process equations mentioned above for the Reversible Adiabatic Process do not hold for the Irreversible Adiabatic Process.

However, the First Law of Thermodynamics and the Ideal Gas equation hold true for the Irreversible Adiabatic Process and the work can be calculated using Equation (1) as given above

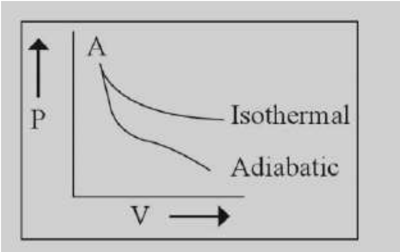
(3)Irreversible Adiabatic Free Expansion

In a free expansion, the expansion is carried out against the Vacuum in an isolated container. Thus, the value of external pressure is zero so work done is zero and also Q is zero as the system is Isolated (Adiabatic).

Thus, it can be said that

$$\Delta E = W = 0$$
$$\Delta T = 0, \Delta H = 0$$

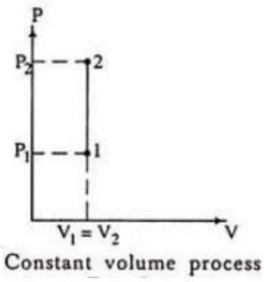
Comparison between Isothermal and Adiabatic Curves



10. Graphical Comparison of Thermodynamic Processes

1. Constant Volume Process:

Representation on P-V diagram:



This process is represented on the P-V diagram by a vertical straight line as shown in the figure, since $V_1=V_2$.

Work done during the process:

$$W=\int_{V_1}^{V_2} P dv$$

But $dv=0$ for an isochoric process

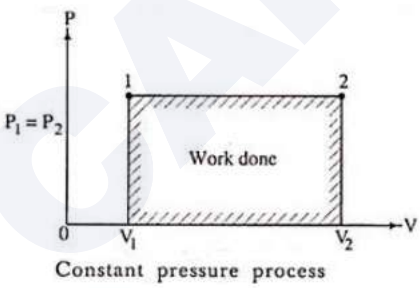
$\therefore W=0$

Thus, work done during the constant volume process is zero which is also evident from the P-V diagram as no area is enclosed by the vertical line on the P-V diagram.

2. Constant Pressure Process:

Representation on P-V diagram:

During this process the pressure or the gas remains constant therefore it is represented by a horizontal line on P-V diagram. See figure.



Work done during the process:

$$W=\int_{V_1}^{V_2} P dv$$

But P is constant.

$$\therefore \text{ Work done } = P \int_{V_1}^{V_2} dv = P\left(V_2-V_1\right)$$

The work done by the gas during the constant pressure process is represented by a rectangle on the P-V diagram.

11. Heat Capacity

Heat Capacity

The heat capacity of a system is defined as "The quantity of heat required for increasing the temperature of one mole of a system through 1^0C". It is given as follows:

$$C = \frac{dq}{dT} \quad \ldots.(1)$$

(i) Heat capacity at constant volume

According to the first law of thermodynamics,

$$dq = dE + PdV$$

On substituting the value of dq in equation (2)

$$C = \frac{dE+PdV}{dT}.......(3)$$

If volume is constant then

$$C_v = (dE/dT)_v \quad .....(4)$$

Hence the heat capacity at constant volume of a given system may be defined as the rate of change of internal energy with temperature.

(ii) Heat capacity at constant pressure

If pressure is constant, equation (3) becomes as follows:

$$C_P = \frac{dE + PdV}{dT}$$

$$\text{or} \quad C_P = (dq/dT)_P = \frac{dH}{dT} \; . \; . \; . \; . \; . \; .(5)$$

Hence the heat capacity at constant pressure of a system may be defined as the rate of change of enthalpy with temperature.

For the proof of equation (5), we have to learn the relation between Enthalpy (H) and Internal energy (E)

Relation between Enthalpy and Internal Energy

Enthalpy (H) and Internal energy (E) are related as

$$H = E + PV$$

$$\therefore dH = dE + d(PV)$$

$$\therefore dH = dE + PdV + VdP$$

At constant pressure, dP =0

$$dH = dE + PdV = (dq)_p$$

Hence, the heat supplied at constant pressure is equal to the Enthalpy

Relation Between Cp And Cv -

For one mole of a gas C_p and C_v are known as molar heat capacities and the difference between them is equal to the work done by one mole of gas in expansion on heating it through 1^oC.

We know that

$$H = U + PV$$

$$\Rightarrow dH = dU + d(PV)$$

$$\Rightarrow nC_pdT = nC_vdT + nR\ dT\ [\because PV = nRT]$$

$$\Rightarrow C_p - C_v = R$$

Other Relation between C_p and C_v

$$\gamma = \frac{C_P}{C_V}$$

Now, C_V and C_P can be represented as

$$C_V = \frac{f\,R}{2} \text{and } C_P = (\frac{f}{2} + 1)R$$

where f is the degree of freedom

(1) For Monoatomic Gas:

$$f=3, C_V=\frac{3R}{2}, C_P=\frac{5R}{2}, \gamma=\frac{5}{3}$$

(2) For Diatomic Gas:

$$f=5, C_V=\frac{5R}{2}, C_P=\frac{7R}{2}, \gamma=\frac{7}{5}$$

(3) For Polyatomic Gas:

$$f=6, C_V=3R, C_P=4R, \gamma=\frac{4}{3}$$

12. Thermochemistry And Enthalpy For Chemical Reaction

Thermochemistry

It deals with the heat changes during chemical reactions. It is called chemical energetics and is based on the first law of thermodynamics.

Exothermic Reaction

$$\begin{aligned}
&\text{Heat is evolved here.}\\
&\Delta \mathrm{H} \text{ is -ve as } \mathrm{H_R} > \mathrm{H_P}\\
&\Delta \mathrm{H} = \mathrm{H_P} - \mathrm{H_R} = - \text{ ve} \quad \text{(at constant pressure)}\\
&\text{At constant volume,}\\
&\Delta \mathrm{E} = (\mathrm{E_P} - \mathrm{E_R}) = -\text{ve}\\
&\text{that is. } \mathrm{E_R} > \mathrm{E_P}
\end{aligned}$$

Endothermic Reaction

$$\begin{aligned}
&\text{Here heat is absorbed.}\\
&\Delta H \text{ or } \Delta E = + \text{ ve for endothermic}\\
&\Delta H = H_p - H_R = + \text{ ve (at constant pressure as)}\\
&\text{ as } H_p > H_R \text{ or } E_p > E_R\\
&\text{At constant volume}\\
&\Delta E = (E_p - E_R) = +ve
\end{aligned}$$

Heat or Enthalpy of Reaction

It is the change in enthalpy (amount of heat evolved or absorbed) when the number of gm-moles of the substance indicated by a chemical reaction have undergone complete reaction.

$$\begin{aligned}
&\text{It is determined by water and Bomb calorimeters.}\\
&\text{Mathematically, it is given as}\\
&= \Sigma \mathrm{H_p} - \Sigma \mathrm{H_R}\\
&\text{It can be express by } [\Delta \mathrm{H}]_\mathrm{p} \text{ or } [\Delta \mathrm{E}]_\mathrm{v} \text{ at constant}\\
&\text{pressure and volume respectively.}
\end{aligned}$$

13. Standard Enthalpy And Enthalpy Of Formation

Heat of Formation

The amount of heat evolved or absorbed or changed in enthalpy when 1 mole of a substance is obtained from its constituents or free elements.

$$\Delta \mathrm{H}^\circ = \sum \mathrm{H^\circ p} - \sum \mathrm{H^\circ r}$$

Once the value of H^o at 25^o C for any species has been assigned the value of H^o at other temperatures Can be found out by using Kirchoff's equation as follows.

$$\int_{298}^{\mathrm{T}} \mathrm{dH}^\circ = \int_{298}^{\mathrm{T}} \mathrm{CpdT}$$

$$\mathrm{H_T^\circ} - \mathrm{H_{298}^\circ} = \int_{298}^{\mathrm{T}} \mathrm{CpdT}$$

1. Standard heat of formation of a free element is taken as zero.

   For example, In carbon—graphite form is taken as the standard state and in sulphur, the monoclinic form is the standard state.

2. The heat of formation may be +ve or -ve.

$$\begin{aligned}
&\text{If } \Delta \mathrm{H} \text{ is -ve compound is exothermic.}\\
&\text{If } \Delta \mathrm{H} \text{ is +ve compound is endothermic.}
\end{aligned}$$

3. The stability of the exothermic compound is more than that of the endothermic compound hence, the greater the liberated energy greater is the stability of the compound.

Example, HF > HCI > HBr > HI

14. Enthalpy Of Combustion

Heat of Combustion

1. It is, changes in enthalpy when one mole of a substance is completely oxidized or combusted or burnt.

2. ΔH is - ve here as heat is always evolved here that is, exothermic process.

3. Heat of combustion is useful in calculating the calorific value of food and fuels.

4. It is also useful in confirming the structure of organic molecules having C, H, O, N, etc.

5. Enthalpy change by combustion of 1 gm solid or 1 gm liquid or 1 cc gas is called calorific value.

$$\text{calorific value} = \frac{\text{Heat of combustion}}{\text{Molecular wt.}}$$

$$\Delta H \text{ (heat of reaction) } = -\Sigma \Delta H_P^o - \Sigma H_R^o$$

Enthalpy of Dissociation or Ionization

It is defined as, "The quantity of heat absorbed when one mole of a substance is completely dissociated into its ions". Example,

$$H_2O\ (l) \rightarrow H^+ + OH^- \quad \Delta H = 13.7 \text{ Kcal}$$

Heat of Atomization

It is the enthalpy change (heat required) when bonds of one mole of a substance are broken down completely to obtain atoms in the gaseous phase (isolated) or it is the enthalpy change when one mole of atoms in the gas phase is formed from the corresponding element in its standard state. In the case of diatomic molecules, it is also called bond dissociation enthalpy.

It is denoted by ΔH_a or $\Delta H^\bullet$.

Example,

$H_2\ (g) \rightarrow 2H\ (g) - 435 \text{ kJ}$

$\Delta H = +435 \text{ kJ/mol}$

$CH_4\ (g) \rightarrow C\ (g) + 4H\ (g) + 1665 \text{ kJ}$

$\Delta H = +1665 \text{ kJ/mol}$

Phase Transition and Transition Energy

- The change of matter from one state (solid, liquid, or gas) to another state is called Phase Transition.
- Such changes occur at definite temperatures such as melting point (solid to liquid), boiling point (liquid to vapours) etc., and are accompanied by absorption or evolution of heat. The enthalpy change during such phase transitions is called heat of transition or transition energy.

Example,

$C\ (\text{diamond}) \rightarrow C\ (\text{amorphous})$

$\Delta H = 3.3 \text{Kcal}$

15. Lattice Enthalpy, Hydration Enthalpy And Enthalpy Of Solution

Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound is formed from its ions in the gaseous state.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s), \Delta H = -788 \text{ kJmole}^{-1}$$

Heat of Hydration

The enthalpy change during hydration of one mole of any gaseous ion is called heat of hydration.

$$Na^+(g) \longrightarrow Na^+(aq), \Delta H = \Delta H_{hyd_{Na+}}$$

$$Cl^-(g) \longrightarrow Cl^-(aq), \Delta H = \Delta H_{hyd_{Cl-}}$$

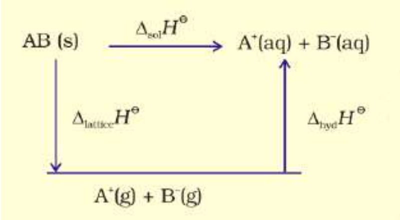
Heat of Solution

It is a change in enthalpy when one mole of a solid solute is dissolved in excess of solvent.

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq), \Delta H = \Delta H_{sol_{NaCl}}$$

Solubility of an Ionic Compound in water

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. The enthalpy of solution of any ionic solid, in water is, therefore, determined by the selective values of the lattice enthalpy and enthalpy of hydration of ions. This will be more clear with the help of the diagram given below:



Thus, the enthalpy of solution, enthalpy of hydration and the lattice energy can be related as

$$\Delta_{sol} H^0 = \Delta_{lattice} H^0 + \Delta_{hyd} H^0$$

For most of the ionic compounds, $\Delta_{sol} H^0$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all.

16. Enthalpy of Neutralization of Strong Acid and Strong Base

Heat of Neutralization

It is an enthalpy change during the neutralization of 1 equivalent of an acid and base.

Case of Strong Acid and Strong Base:

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

The enthalpy change of the above reaction is equal to -13.7 kcal eq^{-1} or -57.3 kJ eq^{-1}.

It is to be noted that the enthalpy of neutralisation of 1 equivalent of any strong acid or strong base is equal to -13.7 kcal eq^{-1} or -57.3 kJ eq^{-1}.

$$H^+ + OH^- \longrightarrow H_2O, \Delta H = -13.7 \text{ kcal mol}^-$$

Case in which any one of the Acids or Bases (or Both) are weak:

In case one of the acids or base is weak, then some part of the heat will be used up for ionisation of the weak component and the heat liberated will be lesser than the above values

For example

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O, |\Delta H| < 13.7 \text{ kcal eq}^{-1}$$

Properties of enthalpy of neutralisation:

- It is always exothermic $\Delta H = -ve$
- The heat of neutralization of strong acid and strong base is always 13.7 Kcal/mole or 57 kJ/mole.
- It is independent of the nature of strong acid or strong base.
- If one electrolyte is weak then ΔH will be less than —13.7 Kcal as some amount of heat will be absorbed in the ionisation of the weak electrolyte.
- In the case of HF, ΔH is more due to more hydration of F^- ions.

17. Ionization And Electron Gain Enthalpy

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account.

$$M(g) \rightarrow M^+(g) + e^-(\text{for ionization})$$
$$M(g) + e^- \rightarrow M^-(g) \text{ (for electron gain)}$$

at temperature, T is

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(0) + \int_0^T \Delta_r C_p^{\ominus} dT$$

The value of C_p for each species in the above reaction is 5/2 R (C_V = 3/2R)

$$\text{So, } \Delta_r C_p^{\ominus} = +5/2R \text{ (for ionization)}$$
$$\Delta_I C_p^{\ominus} = -5/2R \text{ (for electron gain)}$$

Therefore,

$$\Delta_r H^{\ominus}(\text{ ionization enthalpy })= E_0(\text{ ionization energy })+5/2RT$$
$$\Delta_r H^{\ominus}(\text{ electron gain enthalpy})=-A(\text{ electron affinity})\ -5/2RT$$

18. Resonance Energy

Resonance Enthalpy:

The theoretical difference in molecular energy between a resonance hybrid and the 'most stable' resonance contributor (if this resonance contributor existed as a real molecule). In other words, the stability gain by electron delocalization is due to resonance versus the absence of such delocalization. The resonance energy of benzene is 36 kcal mol^{-1} .

Calculation of Resonance Energy:

(1) Resonance energy can be calculated in terms of the heat of the formation data:

$$\text{ResonanceEnergy}=\Delta_f H^o_{\text{theoretical}}-\Delta_f H^o_{\text{actual}}$$

(2) Resonance energy can be calculated in terms of the heat of combustion data:

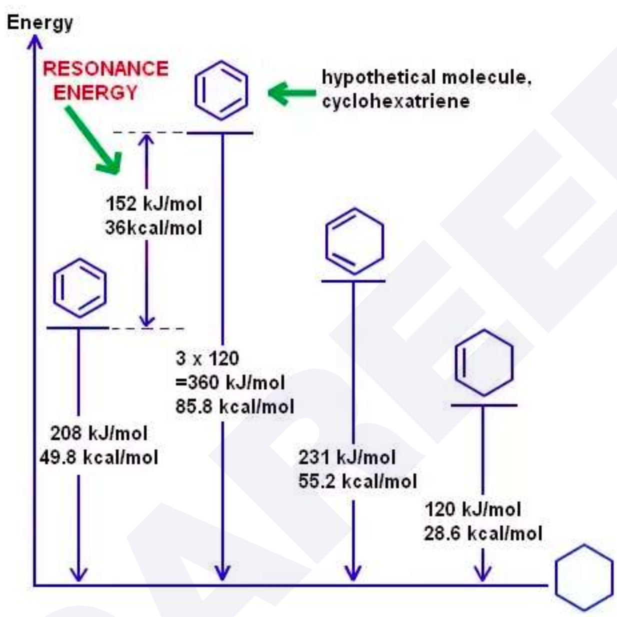
$$\text{ResonanceEnergy}=\Delta_c H^o_{\text{actual}}-\Delta_c H^o_{\text{theoretical}}$$

(3) Resonance energy can be calculated in terms of the heat of hydrogenation data:

$$\text{ResonanceEnergy}=\Delta_{\text{hydrogenation}} H^o_{\text{actual}}-\Delta_{\text{hydrogenation}} H^o_{\text{theoretical}}$$

Note: Resonance Energy is always a Positive Number. Use this fact to quickly calculate Resonance Energy using the above formulae.

The calculation of Resonance energy in terms of Heat of hydrogenation is given below:



19. Kirchoff’s Equation

Kirchhoff's Law describes the variation of enthalpy of a reaction with changes in temperature. In general, the enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to the change in enthalpy divided by the change in temperature.

$$c_p=\frac{\Delta H}{\Delta T} \text{...............1}$$

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

$$\Delta H_{T_f}=\Delta H_{T_i}+\int_{T_i}^{T_f}\Delta C_p\,dT \text{...........2}$$

If the heat capacity is temperature-independent over the temperature range, then Equation 1 can be approximated as

$\Delta H_{T_f} = \Delta H_{T_i} + \Delta C_p (T_f - T_i)$..............3

where

- ΔC_p is the change in heat capacity of the reaction and is defined as

  $\Delta C_P = \sum_{f(P)} i_P C_p - \sum_{f(R)} i_R C_p$

  It has exact same treatment for Cp as we have for the calculation of change in enthalpy

- H_{Ti} and H_{Tf} are the enthalpy at the respective temperatures.

Equation 3 can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

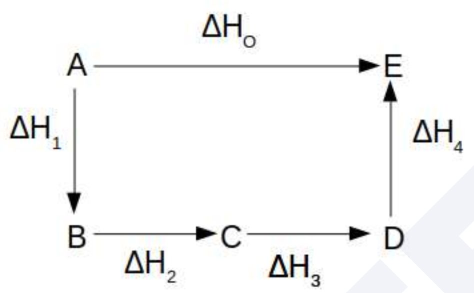
In case the variation of C_p with temperature is given then we can use equation 2 and integrate the function of Cp as f(T) with respect to T and obtain the result.

20. Hess's Law

Hess's Law

This rule is a consequence of the Enthalpy or Internal energy being a state function.

According to Hess's Law, "The enthalpy change for a process is independent of path or way of a process. The enthalpy change (ΔH or ΔE for any physical or chemical process remains the same whether the process is carried out in one step or in many steps. "



$\Delta H_O = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

Let us consider the following example

$C + O_2 \rightarrow CO_2; \Delta H_1 = -94.3 \text{kcal}$
$C + \frac{1}{2} O_2 \rightarrow CO; \Delta H_2 = -68.3 \text{kcal}$
$CO + \frac{1}{2} O_2 \rightarrow CO_2; \Delta H_3 = -26 \text{kcal}$

It can be seen that $\Delta H_1 = \Delta H_2 + \Delta H_3$

Hence it proves that

- ΔH or ΔE is not proportional to the path or way of reaction
- ΔH or ΔE is a state function that depends only on the initial and final state (state function).

Applications of Hess Law:-

It has the following applications:
1. It helps in finding enthalpy changes for those reactions which are experimentally not possible.

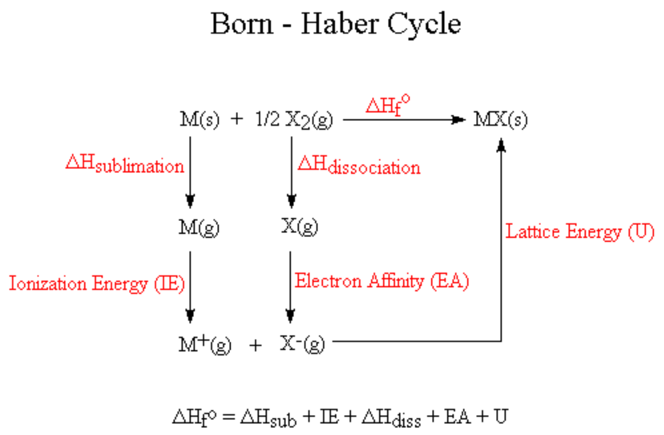
2. It also helps in finding $\Delta H_{formation}$, $\Delta H_{combustion}$ etc.

3. For the determination of resonance energy and lattice energy.

4. For the determination of enthalpies of reactions occurring very slowly.

21. Born Habers Cycle

The diagram below is the Born-Haber cycle for the formation of an ionic compound from the reaction of an alkali metal (Li, Na, K, Rb, Cs) with a gaseous halogen (F_2, Cl_2). The Born-Haber thermochemical cycle is named after the two German physical chemists, Max Born and Fritz Haber, who first used it in 1919.



22. Bomb Calorimeter

In the laboratory, the heat released during combustion is measured in a bomb calorimeter.

It consists of an insulated vessel containing water and a rigid, constant-volume container (called a bomb) inside it.

The combustion process is carried out isochorically in the bomb and the heat released during combustion is trapped in the vessel and is used to raise the temperature of the calorimeter system.

The change in temperature can be measured with the help of a thermometer and knowing the heat capacity of the system, the heat released due to combustion can be calculated.

Suppose T_1 and T_2 are initial and final temperatures and C be the heat capacity of the system, then

$$Q = C(T_2 - T_1)$$

Now, since the combustion occurs in the rigid bomb, therefore the heat liberated is at constant volume and thus knowing the amount of substance undergoing combustion, the internal energy change during combustion can be calculated.

- If 1 mole of substance undergoes combustion then

  $$Q = |\Delta E| = C(T_2 - T_1)$$

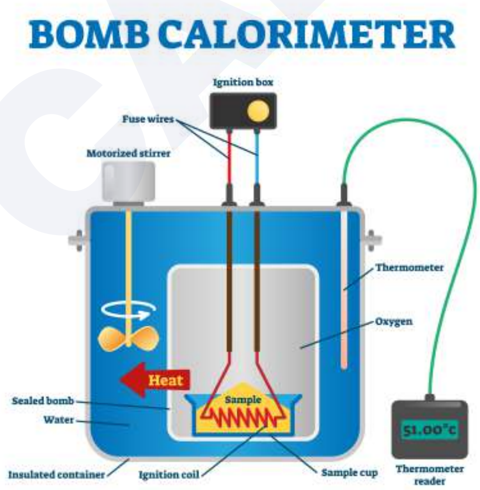
- If x g of substance (molar mass M) undergoes combustion then

  $$Q = |\Delta E| \times \frac{w}{M} = C(T_2 - T_1)$$

Once, the value of ΔE is calculated, we can calculate the ΔH of the reaction using the following relation:

$$\Delta H = \Delta E + (\Delta n_g)RT$$

The pictorial representation of a calorimeter system is given below



23. Entropy

ENTROPY

It is a thermodynamic state quantity which is used to measure the disorder or randomness of the molecules in a system The disorder or randomness in a system is measured in terms of entropy (S). The absolute value of 'S' is not determined so most change In entropy ΔS is measured.

Randomness $\propto$ Entropy

It is a state function that depends only on the initial and final state of the system that is, it is independent of the path used in going from the initial to the final state.

$\Delta S = S_{Final} - S_{Initial}$

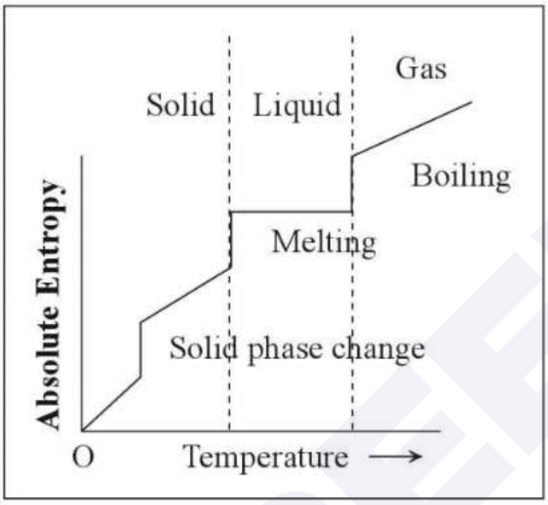
For a general chemical reaction at 298K and 1 atm:

$$m_1P + m_2Q \rightarrow n_1R + n_2S$$
$$\Delta S^\circ = \left[(n_1S^\circ_R + n_2S^\circ_s) - (m_1S^\circ_P + m_2S^\circ_Q)\right]$$
$$\Delta S^\circ = \sum S^\circ_P - \sum S^\circ_R$$

It is an extensive property and a state function that depends on state variables like T, P, V and n which govern the state of a system.

Entropy and Temperature

Entropy increases with the increase of temperature as it is associated with molecular motion which Increases with the increase of temperature due to the increase in the average kinetic energy of the molecules. The entropy of a perfectly ordered Crystalline substance is taken as zero at Zero Kelvin (0K). It is the third law of Thermodynamics. However, in the case of N_2O, NO, Solid CI_2, etc. the value of entropy is not found to be zero at O Kelvin also.



24. Calculation Of Changes In S For Different Processes

Mathematical Definition of Entropy

For a reversible isothermal process, Clausius defined it as the integral of all the terms involving heat exchange (q) divided by the absolute temperature T.

$$dS = \frac{dq_{rev}}{T} \text{ or } \Delta S = \frac{q_{rev}}{T}$$

$$\text{Unit of entropy is } \frac{J}{mol - K}$$

Here mol^{-1} is also used as entropy being an extensive property that depends upon the amount of the substance.

Entropy Changes in different processes:

1. Isothermal reversible process

For a reversible isothermal process, $\Delta E = 0$

So $q = -w$

$$\therefore \Delta S = \frac{-w}{T} = \frac{2.303 \text{ nRT} \log(\frac{V_2}{V_1})}{T}$$

$$\therefore \Delta S = 2.303 \text{ nR} \log(\frac{V_2}{V_1}) = 2.303 \text{ nR} \log(\frac{P_1}{P_2})$$

2. Adiabatic reversible process

As $q = 0$, so $\Delta S = 0$

Note: Reversible adiabatic process is also called an Isentropic process

3. Isobaric process:

$$\Delta S = 2.303\ nC_P\ \log(\frac{T_2}{T_1}) = 2.303\ nC_P\ \log(\frac{V_2}{V_1})$$

4. Isochoric process:

$$\Delta S = 2.303\ nC_V\ \log(\frac{T_2}{T_1}) = 2.303\ nC_V\ \log(\frac{P_2}{P_1})$$

5. Entropy change in a process where both the Temperature, as well as Volume or Pressure, is changing

$$\Delta S = \int \frac{dq}{T} = \int \frac{(dE - dw)}{T}$$

$$\Delta S = \int \frac{nC_v dT + PdV}{T} = \int_{T_1}^{T_2} \frac{(nC_v dT)}{T} + \int_{V_1}^{V_2} \frac{(nRdV)}{V}$$

$$\Delta S = nC_v \ln(\frac{T_2}{T_1}) + nR\ln(\frac{V_2}{V_1})$$

The above equation can also be written in terms of Pressure as

$$\Delta S = nC_p \ln(\frac{T_2}{T_1}) + nR\ln(\frac{P_1}{P_2})$$

6. Entropy change in irreversible processes:

Suppose a system at higher temperature T_1 and its surroundings is at lower temperature T_2. 'q' amount of heat goes irreversibly from the system to the surroundings.

$$\Delta S_{system} = -\frac{q}{T_1}$$

$$\Delta S_{surroundings} = +\frac{q}{T_2}$$

$$\Delta S_{process} = \Delta S_{system} + \Delta S_{surroundings} = -\frac{q}{T_1} + \frac{q}{T_2} = q\frac{[T_1 - T_2]}{T_1 T_2}$$

$$\because T_1 > T_2$$

$$\therefore T_1 - T_2 > 0$$

$$\therefore \Delta S_{process} > 0$$

So entropy increases in an irreversible process like conduction, radiation, etc.

7. Entropy changes during phase transition:

$$\Delta S = S_2 - S_1 = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$$

8. Entropy change when liquid is heated:

When a definite amount of liquid of mass 'm' and specific heat 's' is heated

Let us suppose a small amount of heat dq is added and as a result, the temperature of the body increases by dT temperature

$$dq = m \times s \times dT$$

$$\therefore dS = \frac{dq}{T} = \frac{m \times s \times dT}{T}$$

$$\therefore \Delta S = m \times s \times \log\frac{T_2}{T_1}$$

9. Entropy Change in Mixing of Ideal Gases:

Suppose n_1 mole of gas 'P' and n_2 mole of gas Q' are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R\,[n_1 \log_{10} X_1 + n_2 \log_{10} X_2]$$

Here X_1 and X_2 are mole fractions of gases P and Q respectively.

$$\Delta S/mol = -2.303R\frac{[n_1 \log_{10} X_1}{n_1 + n_2} + \frac{n_2 \log_{10} X_2]}{n_1 + n_2}$$

$\Delta S/mol = -2.303R\,[X_1 \log_{10} X_1 + X_2 \log_{10} X_2]$

It can be seen that the above expression is always positive for ΔS.

25. Spontaneity in Thermodynamics

Entropy and criteria of the spontaneity of a chemical process:

The entropy change of a chemical reaction together with the entropy change of surroundings determine the spontaneity of a chemical process under a given set of conditions.

$$\Delta S_{Total} = \Delta_r S - \frac{\Delta_r H}{T}$$

1. In nature, all processes are Irreversible followed by an increase in entropy. The entropy of the universe tends towards a maximum.

$$S_{Universe} > 0$$

2. $\Delta S_{sys} + \Delta S_{surr} = 0$ for reversible process and $S_{sys} + \Delta S_{surr} > 0$ for irreversible process

3. ΔS for a cyclic process and at the equilibrium state is zero.

4. For a reversible process

$$S_{Total} \text{ or } \Delta S_{Universe} = 0$$
$$\text{So,} \quad \Delta S_{system} = \Delta S_{surrounding}$$

5. For the adiabatic reversible process entropy change is zero.

$$\Delta S_{Total} = 0 \text{ so}$$
$$\text{Hence } \Delta S_{system} = \Delta S_{surrounding}$$

6. Entropy change associated with change in temperature from T_2 to T_1 at constant pressure P is given as

$$\Delta S = 2.303 \times C_P \log \frac{T_2}{T_1}$$

$C_p =$ Molar heat capacity at constant pressure.

Some Examples Of Entropy Change

1. When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence arranged in a more ordered manner that is randomness decreases.

2. When an egg is boiled, the entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

3. Molecule kept in large volume containers will have high entropy.

4. Cases of increase in entropy—(l) dissolution of a solute in water (2) decomposition of compound (3) vaporization and fusion (4) expansion of ideal gas from one container to an evacuated chamber.

4. The decrease of entropy cases are crystallization, combination.

5. Entropy is directly proportional to atomic weight for example—$I_2 > Br_2 > Cl_2$

6. Entropy is directly proportional to the number of bonds example—Ethane > ethylene > ethylene

Spontaneity Criteria Through Enthalpy (H) And Entropy (S)-

Criteria for Spontaneous Change

Processes that involve an increase in entropy of the system ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include the surroundings, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} > 0 \text{ spontaneous}$$
$$\Delta S_{univ} < 0 \text{ nonspontaneous (spontaneous in opposite direction)}$$
$$\Delta S_{univ} = 0 \text{ reversible (system is at equilibrium)}$$

Entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$
$$\Delta S_{toal} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. This is always observed to occur spontaneously. Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. This is never observed to occur spontaneously. Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

3. The temperature difference between the objects is infinitesimally small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. This process involves no change in the entropy of the universe.

Criteria of spontaneity in terms of Gibb's Free energy change

The Gibb's free energy function is defined as

$G = H - TS$

For any general process, change in Gibb's free energy can be defined as

$\Delta G = \Delta H - \Delta(TS)$

For reactions which occur at constant Temperature and pressure, Gibb's free energy change can be defined as

$\Delta G = \Delta H - T\Delta(S)$

Gibb's Free energy change can be defined as the following **(for reactions only)**

$\Delta G = -T\Delta S_{\text{universe}}$

Thus, the condition of spontaneity in terms of Gibb's free energy change is

$\Delta G < 0 \quad [\because \Delta S_{\text{universe}} > 0]$

Spontaneous and non Spontaneous

Sign of ΔH	Sign of ΔS	Comment	Example	ΔH_{298}	ΔS_{298}
–	+	spontaneous at all temperature	$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $C(s) + O_2(g) \longrightarrow CO_2(g)$	-185 -394	14.1 3
–	–	spontaneous at low temperature	$H_2(g) + 1/2\ O_2 \longrightarrow H_2O(\ell)$ $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	-44 -198	-119 -187
+	+	spontaneous at high temperature	$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	176 180	284 25
+	–	non spontaneous at all temperature	$3O_2 \longrightarrow 2O_3$ $2H_2O(\ell) + O_2(g) \longrightarrow 2H_2O_2(\ell)$	286 196	-137 -126

26. Second Law of Thermodynamics

Second Law of Thermodynamics

It is not possible to convert heat into work without compensation.

- Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.
- It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency (Clausius statement).
- The heat of the coldest body among those participating In a cyclic process cannot serve as a source of work (Thomson statement).
- It is Impossible by means of the inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects (Kelvin-Planck statement)
- Nature tends to pass from a less probable to a more probable state (Ludwig Boltzmann statement).
- Whenever a spontaneous process takes place it is accompanied by an increase in the total entropy of the universe.

27. Gibbs Energy Change And Criteria For Equilibrium

Gibbs Energy And Change In Gibbs Energy-

It was introduced in order to relate H, and S and to explain spontaneity. According to J. Willard Gibb's Free energy of a system is defined as the maximum amount of energy available to a system during a process that can be converted into useful work.

or

It is the thermodynamic quantity, especially characterizing the system, the decrease in whose value during a process is equal to the useful work done by the system.

It is denoted by G and it is given mathematically as follows:

$$\mathrm{G=H-TS}$$

Here,

H = Enthalpy

T = Absolute Temperature

S = Entropy

Also, we learnt that

$$\mathrm{H=E+PV}$$
$$\mathrm{G=E+PV-TS}$$

Therefore, Free energy change at constant temperature and pressure is given as:

$$\Delta\mathrm{G}=\Delta\mathrm{E}+\mathrm{P}\Delta\mathrm{V}-\mathrm{T}\Delta\mathrm{S}$$

$$\text{As }\ \Delta\mathrm{H}=\Delta\mathrm{E}+\mathrm{P}\Delta\mathrm{V}$$

$$\text{So, }\ \Delta\mathrm{G}=\Delta\mathrm{H}-\mathrm{T}\Delta\mathrm{S}$$

At standard conditions that is, 298 K and 1 atm pressure

$$\Delta\mathrm{G}^{\mathrm{o}}=\Delta\mathrm{H}^{\mathrm{o}}-\mathrm{T}\Delta\mathrm{S}^{\mathrm{o}}$$

It is called the Gibbs equation and it is used to explain the criterion of spontaneity, driving force etc.

It is a state function and an extensive property.

Gibb's Free Energy Change for a Reaction

For a general reaction, it can be given as follows:

$$\mathrm{pA+qB\rightarrow rC+sD}$$

$$\Delta\mathrm{G}^{\circ}=\sum\Delta\mathrm{G}_{\mathrm{P}}^{\circ}-\sum\Delta\mathrm{G}_{\mathrm{R}}^{\circ}$$

$$=\left[\left(\mathrm{r}\sum\mathrm{G}_{\mathrm{C}}^{\circ}+\mathrm{s}\sum\Delta\mathrm{G}_{\mathrm{D}}^{\circ}\right)-\left(\mathrm{p}.\sum\Delta\mathrm{G}_{\mathrm{A}}^{\circ}+\mathrm{q}\sum\Delta\mathrm{G}_{\mathrm{B}}^{\circ}\right)\right]$$

This requires the exact same treatment as $\Delta\mathrm{H}$ or $\Delta\mathrm{S}$

Gibb's Free Energy Change for small changes in a Reversible process

$$\mathrm{G=H-TS}$$
$$\mathrm{dG=dH-TdS-SdT}\qquad\rightarrow(1)$$

Now,

$$\mathrm{dH=dE+PdV+VdP}\qquad\rightarrow(2)$$

Using equations (1) and (2), we can write

$$\mathrm{dG=dE+PdV+VdP-TdS-SdT}\qquad\rightarrow(3)$$

Now,

$$\mathrm{dE=dq+dw}\ ;\ \mathrm{dq=TdS}\ ;\mathrm{dw=-PdV}$$

Putting these values in the above expression (3), we have

$$\mathrm{dG=VdP-SdT}$$

Note: Remember this important formula for small changes in dG values

Spontaneity Criteria With Gibbs Energy (G)-

$\Delta\mathrm{G}$ and Criteria of Spontaneity

Suppose we consider a system that is not isolated from its surroundings then for such a system $\Delta\mathrm{S}$ is given as:

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$

If we consider that q_p amount of heat is given by the system to the surroundings at constant temperature and constant pressure then

$$(q_p)_{surroundings} = -(q_p)_{system} = -\Delta H_{system}$$

$$\Delta S_{surroundings} = \frac{(q)_{p\ surroundings}}{T} = \frac{-\Delta H_{system}}{T} \ldots (ii)$$

From equation (i) and (ii)

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

Or

$$T\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$$

$$-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system}$$

According to the Gibb-Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

So, $\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$

$$\Delta G_{system} = -T\Delta S_{total}$$

As for the spontaneous process

$$\Delta S_{total} > 0$$

Hence $\Delta G = -ve$

Thus for a spontaneous process $T\Delta S_{total}$ must be positive.

Or ΔG must be negative.

Case I. Suppose both energy and entropy factors oppose a process that is,

$$\Delta H = +ve \text{ and } T\Delta S = -ve$$

$$\Delta G = \Delta H - T\Delta S = (+ve) - (-ve) = +ve$$

Thus, ΔG is positive for a non-spontaneous process.

Case II. Suppose both tendencies are equal in magnitude but opposite, that is,

$$\Delta H = +ve \text{ and } T\Delta S = +ve$$

$$\Delta H = T\Delta S$$

$$\Delta G = \Delta H - T\Delta S = 0$$

Thus, the process is said to be at equilibrium.

Case III. Suppose entropy and energy, are both factors that are favourable for a process, that is,

$$\Delta H = -ve \text{ and } T\Delta S = +ve$$

$$\Delta G = \Delta H - T\Delta S = (-ve) - (+ve) = -ve$$

Thus, this process is spontaneous at every temperature.

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Remark
-	+	Always -ve	Spontaneous
+	-	Always +ve	Non-spontaneous
+	+	+ ve at low temp	Non-spontaneous
		- ve at a high temp	Spontaneous
-	-	- ve at low temp	Spontaneous
		+ ve at a high temp	Non-spontaneous

- $\Delta G = \text{negative}$, Spontaneous process
- $\Delta G = \text{positive}$, Non-spontaneous process
- $\Delta G = 0$, Process in equilibrium

- In exergonic reaction $\Delta G = \text{negative}$
- In endergonic reaction $\Delta G = \text{positive}$
- Temperature also plays an important role in deciding the spontaneity of a process. A process that is not spontaneous at low temperature can become spontaneous at high temperature and vice-versa.

Gibbs Energy At Equilibrium-

Relationship between $\Delta \mathbf{G}^{\circ}$ and Equilibrium constant $(\mathbf{K}_{eq})$

for a reversible reaction

$$P + Q \rightleftharpoons R + S$$

$\Delta G, \Delta G^{\circ}$ and Reaction Quotient (Q) are related as follows

$$\Delta G = \Delta G^{\circ} + RT \log_e Q$$

as at equilibrium $\Delta G = 0$

$$Q = Keq$$
$$0 = \Delta G^{\circ} + RT \log_e Keq$$
$$\Delta G^{\circ} = -RT \log_e Keq$$
$$\Delta G^{\circ} = -2.303RT \log_{10} Keq$$

Relationship between ΔG or ΔG^{o} with E or E^{o}:-

Free energy change ΔG in an electrochemical cell can be related to electrical work done (E) in cell as follows

$$\Delta G = -nFE$$

when we use standard conditions than

$$\Delta G^{o} = -nFE^{o}$$

Here E^{o}= standard E.M.F of the cell

n = No. of moles of e- transferred

F = Faraday's constant

28. Third Law Of Thermodynamics

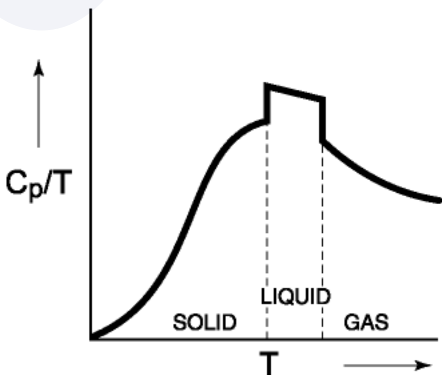
The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called the third law of thermodynamics.

- At any pressure, the entropy of every crystalline solid in thermodynamic equilibrium at absolute zero is zero.
- It is impossible to reduce the temperature of any system to absolute zero by any process.
- As the absolute temperature approaches zero, the increment in entropy for the isothermal process in crystalline solids approaches zero,

  i.e. S=0 at T=0

  Or $\lim_{T \to 0}, S \to 0$

  If the molar heat capacities of a substance (Cp) are measured at different temperatures and a graph between Cp/T vs T is drawn and it shows this type of behavior.



Now let S^{o}_{M} be the entropy of the substance at zero Kelvin and S_M is its molar entropy at Kelvin then

$$\Delta S = S_M - S_M^o$$
$$\therefore \Delta S = S_M$$
$(\because S_M^o = 0$, according to 3rd Law of thermodynamics)
$$\Delta S = \frac{q}{T}$$
$$\Delta S = \int_0^T \frac{C_p.dT}{T}, \quad \because q = 1 \times C_p.dT$$
$$\therefore \Delta S = S_M = \int_0^T \frac{C_p.dT}{T}$$

The area under the curve or graph of Cp/T vs T determined from zero Kelvin to any desired temperature would be molar entropy change going from zero to desired T.

29. Smart Tips

Ideal gas

Gas equation: $pV = nRT = Nk_BT$
Internal energy. $U = nC_VT$

Speed of molecule: $v = \sqrt{\frac{3kT}{m}}$

Capacities: $C_P = C_V + R$, Ratio: $\gamma = \frac{C_P}{C_V}$

Degree of Freedom

Monoatomic: (f =3)

$$C_V = \frac{3}{2}R$$
$$C_p = R\left(\frac{3}{2}+1\right) = \frac{5R}{2}$$

Diatomic: (f =5)

$$C_V = \frac{5}{2}R$$
$$C_p = R\left(\frac{5}{2}+1\right) = \frac{7R}{2}$$

Polyatomic: (f =6)

$$C_V = \frac{6}{2}R$$
$$C_p = R\left(\frac{6}{2}+1\right) = 4R$$

Thermodynamic process

First law: $\Delta U = Q - W$

Work: $W_{A\to B} = \int_A^B pdV$

Entropy: $\Delta S = \int_A^B \frac{dQ}{T}$

Special processes

	Isochoric	Isobaric	Isothermal	Adiabatic
Definition	$\Delta V = 0$	$\Delta P = 0$	$\Delta T = 0$	$Q = 0$
Ideal gas	$pV = nRT$	$pV = nRT$	$pV = nRT$	$pV = nRT,\ pV^\gamma = \text{const}$
Work	$W = 0$	$W = p(V_2 - V_1)$	$W = nRT \ln \frac{V_2}{V_1}$	$W = nC_V(T_1 - T_2) = \frac{1}{1-\gamma}(p_2V_2 - p_1V_1$
Heat	$Q = nC_V\Delta T$	$Q = nC_P\Delta T$	$Q = W$	$Q = 0$
Internal E	$\Delta U = Q$	$\Delta U = Q - W$	$\Delta U = 0$	$\Delta U = -W$
Entropy	$\Delta S = nC_V \ln \frac{T_2}{T_1}$	$\Delta S = nC_P \ln \frac{T_2}{T_1}$	$\Delta S = nR \ln \frac{V_2}{V_1}$	$\Delta S = 0$

Constants

Gas: $R = 8.31 \mathrm{J/K.mol}$

Boltzmann: $k_B = 1.38 \times 10^{-23} \mathrm{J/K}$

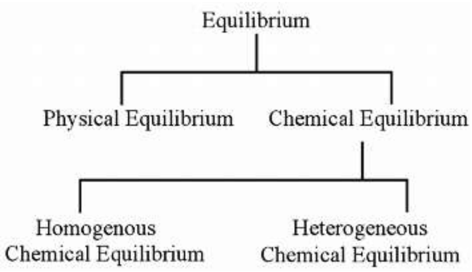
Avogadro: $N_A = 6.02 \times 10^{23}/\mathrm{mol}$
Stefan-Boltzmann: $\sigma = 5.67 \times 10^{-8} \mathrm{W/m^2 \cdot K^4}$

Equilibrium

Important Formulae

1. Equilibrium

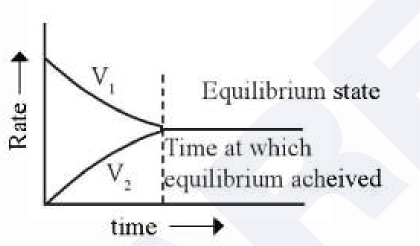
The word "equilibrium" in a physical sense is explained as the "No change of state of the body". When the two opposing processes (reaction) occur simultaneously at equal rates, the system is in a state of equilibrium. Equilibrium is classified as follows



When an equilibrium exists between the same chemical species, it is called physical equilibrium. For example:
$H_2O(s) \rightleftharpoons H_2O(l)$

When an equilibrium exists between different chemical species, it is called chemical equilibrium.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If a chemical equilibrium has only one phase, it is called homogenous, and if more than one phase it is called heterogeneous.
Chemical Equilibrium
"It is the state of a reversible reaction at which measurable properties like colour, density, pressure concentration are nearly unchangeable.



Here V_1 and V_2 are the rates of forward and backward reactions respectively. i.e., equilibrium is the state in a reversible reaction at which the rate of forward and backward reactions or two opposing reactions are the same.

Types of reactions
Chemical reactions are of two types:
Irreversible Reaction: Such reactions occur in one direction only and are completed.
For example:
(i) When unreactive products or solid products are formed.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

(ii) All precipitate reactions are irreversible.

$$\underset{aq.}{BaCl_2} + \underset{aq.}{H_2SO_4} \rightarrow \underset{ppt.}{BaSO_4} + \underset{aq.}{2HCl}$$

(iii) Neutralisation reactions are also irreversible.

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

(iv) Redox reactions are also irreversible.

$$2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$$

(v) Combustion reactions are also irreversible.

$$2Mg + O_2 \rightarrow 2MgO$$

Reversible Reactions: Such reactions occur in both directions i.e., forward and backward direction however never complete as the products can give back the reactants under the same or different conditions. For example:

$N_2 + O_2 \rightleftharpoons 2NO$

- The vaporization of water in an open flask is an irreversible reaction while in a closed flask, it is reversible.
- The decomposition of $CaCO_3$ in the open flask is an irreversible reaction while in a closed flask, it is reversible.

Characteristics of Chemical Equilibrium-

The following are the important characteristics of equilibrium:

- It is obtained only when the reversible reaction is carried out in a closed space.
- Here the rate of forward reaction is equal to the rate of backward reaction.
- Here both forward and backward reactions are taking place at the same rate hence the relative amounts of the reactants and products present at equilibrium do not change with time.
- At constant temperature, it is characterized by properties like colour, density, pressure, etc.
- It is possible from both sides.
- It is dynamic in nature. It means the reaction or process is not going to cease as the reaction occurs in both directions at equal rates.
- A catalyst cannot alter the positive of equilibrium as it accelerates both the forward and backward reactions to the same extent this means the same state of equilibrium is the reaction i.e., a positive catalyst can set up equilibrium in less time but can not change it.
- At equilibrium, ΔG is equal to zero i.e.,
  $\Delta G = \Delta H - T\Delta S$
  So,
  $\Delta H = T\Delta S$
- Under similar conditions of temperature, concentration, and pressure, the same state of equilibrium is reached.

2. Law Of Mass Action

It was introduced by Guldberg and Waage. It states that "the rate at which a substance reacts is directly proportional to its activity and the rate at which substances react together is directly proportional to the product of their activity each raised to a power which is equal to the corresponding stoichiometric number the substance present in the chemical reaction".

$$mA + nB \rightleftharpoons pC + qD$$

Activity is generally represented in terms of concentration or pressure of species involved

If active masses of A, B, C and D are represented in terms of their concentrations [A], [B], [C] and [D] respectively, then:

Rate of reaction of A $\propto [A]^m$

Rate of reaction of B $\propto [B]^n$

$R_1 \propto [A]^m [B]^n = K_1 [A]^m[B]^n$

$R_2 \propto [C]^p [D]^q = K_2 [C]^p [D]^q$

NOTE: For pure solids or pure liquids, activity is always unity (1).

3. Equilibrium Constant

It is the ratio of the rate of forward and backward reaction at a particular temperature or it is the ratio of active masses of the reactants to that of active masses of products at a particular temperature raised to their stoichiometric coefficients. It is denoted by K_c or K_p. The distinction between K_{eq} and K_c is that the expression of K_{eq} involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the expression K_c involves only those species whose concentration is a variable (gases and solution). It means K_c is devoid of pure components (like pure solids and pure liquids) and solvents.

Let us look at the definition of Equilibrium constant in terms of concentration and partial pressure

(1) Equilibrium constant in terms of Concentration

For a reaction:

$$mA + nB \rightleftharpoons pC + qD$$

$$r_{forward} \propto [A]^m[B]^n = K_f[A]^m[B]^n$$

$$r_{backward} \propto [C]^p[D]^q = K_b[C]^p[D]^q$$

We know that at equilibrium

$$r_f = r_b$$

$$K_f[A]^m[B]^n = K_b[C]^p[D]^q$$

$$\frac{K_f}{K_b} = \frac{[C]^p[D]^q}{[A]^m[B]^n} \quad \text{(at constant temperature)}$$

$$\frac{K_f}{K_b} = \frac{[C]^p[D]^q}{[A]^m[B]^n} = K_c$$

The above expression gives us the value of Kc as the activity or the active mass is expressed in terms of the concentrations (c) or the molarity

(2) Equilibrium constant in terms of Partial pressure

In this case, the equilibrium constant is known as K_p. It is applicable only for gaseous systems.
For the reaction:

$$mA + nB \rightleftharpoons pC + qD$$

$$r_{forward} \propto P_A^m\ P_B^n = K_{f_1} P_A^m\ P_B^n$$

$$r_{backward} \propto P_C^p\ P_D^q = K_{b_1} P_C^p\ P_D^q$$

At equilibrium

$$r_f = r_b$$

$$K_{f_1} P_A^m\ P_B^n = K_{b_1} P_C^p\ P_D^q$$

$$K_P = \frac{K_{f_1}}{K_{b_2}} = \frac{P_C^p\ P_D^q}{P_A^m\ P_B^n}$$

The above expression gives us the value of K_P as the activity is expressed in terms of partial pressures.

Note: This is generally used for gaseous systems or systems where gases are in equilibrium with liquids or solids

4. Relation between Kp and Kc

Relation between K_p and K_c

Let us suppose we have a reaction :

$$n_1A(g) + n_2B(g) \leftrightharpoons n_3C(g) + n_4D(g)$$

The equilibrium constant K_c for this reaction is given as:

$$K_c = \frac{[C]^{n_3}[D]^{n_4}}{[A]^{n_1}[B]^{n_2}}$$

For the reaction:

$$n_1A(g) + n_2B(g) \leftrightharpoons n_3C(g) + n_4D(g)$$

The equilibrium constant K_p is given as:

$$K_P = \frac{(P_C)^{n_3}(P_D)^{n_4}}{(P_A)^{n_1}(P_B)^{n_2}}$$

Now, from Ideal gas Equation

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

$$P = CRT$$

Putting the value of P in terms of C in the expression for K_P

$$K_p = \frac{[C]^{n_3}(RT)^{n_3}[D]^{n_4}(RT)^{n_4}}{[A]^{n_1}(RT)^{n_1}[B]^{n_2}(RT)^{n_2}}$$

$$K_P = \frac{[C]^{n_3}[D]^{n_4}}{[A]^{n_1}[B]^{n_2}}[RT]^{(n_3+n_4)-(n_1+n_2)}$$

Putting $\Delta n_g = (n_3 + n_4) - (n_1 + n_2)$, we have

$$K_P = K_C(RT)^{\Delta n_g}$$

It can be seen that:

- When $\Delta n_g = 0$, then $K_P = K_C$
- When $\Delta n_g > 0$, then $K_P > K_C$
- When $\Delta n_g < 0$, then $K_P < K_C$

Characteristics of Equilibrium Constant

The equilibrium constant has the following characteristics:

- The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start of the direction from which the equilibrium is approached.
- If the reaction is reversed. The value of the equilibrium constant is inversed.
- If the equation is divided by 2, the equilibrium constant for the new equation is the square root of K, i.e $\sqrt{K}$.
- If the equation is multiplied by 2, the equilibrium constant for the new equation is the square of K, i.e K^2.
- If the equation is written in two steps, then $K = K_1 \times K_2$.
- The magnitude of the equilibrium constant gives an idea of the relative amounts of reactants and the products.
- The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

5. Degree of Dissociation

Degree of dissociation: It is the extent to which any reactant gets dissociated. It is denoted by α.

$$\alpha = \frac{\text{number of molecules dissociated}}{\text{total number of molecules}}$$

If "a" be the initial number of moles and the number of moles dissociated be "x" then

$$\alpha = \frac{\mathrm{x}}{\mathrm{a}}$$

Relation between degree of dissociation and Observed Molar mass/Vapor density

Due to dissociation, the total number of moles at equilibrium can be determined. Knowing the number of moles at equilibrium, the observed molar mass can be calculated.

Conversely, if the degree of dissociation is not known but the Observed Vapor density is available, then we can calculate the degree of dissociation.

We know about the law of conservation of mass

$$\text{Mass initially taken} = \text{Mass after dissociation at equilibrium}$$

$$\therefore \text{Theoretical moles} \times \text{Theoretical molar mass} = \text{Observed Moles} \times \text{Observed Molar mass}$$

Using the above equation, we can calculate the unknown term required to be calculated.

Observed Density and Molar Mass-

In equilibrium, the observed molar mass or average molar mass of the reactant is the total mass of the mixture divided by the total number of moles.

	A	$\rightleftharpoons$	nB
Initially:	1		0
Equil:	$1 - \alpha$		$\mathrm{n}\alpha$

$$\mathrm{M_{observed}} = \frac{\text{Total mass of mix}}{\text{Total number of moles of mix}}$$

$$\mathrm{M_{obs}} = \frac{\mathrm{M_{real}}}{1-\alpha+\mathrm{n}\alpha} = \frac{\mathrm{M_{real}}}{1+\alpha(\mathrm{n}-1)}$$

In the equilibrium system, the observed molar mass of the reactant is always different from the actual mass. Thus, when the reaction is reversible, the observed mass varies. In a chemical reaction, some amount of this reactant gets converted into a product, thus observed mass is different from than actual mass.

For example:

$$\mathrm{N_2O_4(g)} \rightleftharpoons \mathrm{2NO_2(g)}$$

In this reaction, the original molar mass of N_2O_4 = 92g/mol. However, the observed molar mass at equilibrium is 80g/mol. The observed molar mass is less than the original molar mass as during the reaction some amount of N_2O_4 is converted into NO_2.

Vapour Density

Similarly, the observed density of the substance is different from the actual density.

Thus, we know:

Vapour density = Molar mass/2

$$\text{Thus, } 2\,\mathrm{x}\,(\mathrm{V.D})_{\mathrm{obs}} = \frac{2\,\mathrm{x}\,(\mathrm{V.D})_{\mathrm{real}}}{1+\alpha(\mathrm{n}-1)}$$

$$\Rightarrow \mathrm{d} = \frac{\mathrm{D}}{1+\alpha(\mathrm{n}-1)}$$

6. Le Chatelier's Principles on Equilibrium

Reaction coefficient/quotient-

It is defined as the ratio of the concentration of products to the concentration of the reacting species raised to their stoichiometric coefficient at any point of time other than the equilibrium stage. It has the exact same expression as that of the Equilibrium constant except that the concentration values are at any instant. Mathematically, it can be determined as follows:
If we consider a reaction
$\mathrm{mA + nB \rightleftharpoons pC + qD}$

$$\mathrm{Q} = \frac{[\mathrm{C}]^{\mathrm{p}}[\mathrm{D}]^{\mathrm{q}}}{[\mathrm{A}]^{\mathrm{m}}[\mathrm{B}]^{\mathrm{n}}}$$

Q can be denoted as Q_c or Q_p if we use concentration in terms of mole per litre or partial pressure respectively.

The value of Q is useful to determine the direction in which the equilibrium will shift at any instant for a particular set of activities of the species involved.

- When Q = K, the reaction is at equilibrium and the rate of forward and backward reactions are equal.
- When Q > K, the reaction will proceed or favour a backward direction. This means products convert into reactants to attain equilibrium.
- When Q < K, the reaction will proceed or favour a forward direction. This means that the reactants convert into products to attain equilibrium.

Relation between K, q and ΔG

$$\Delta \mathrm{G} = \Delta \mathrm{G}^0 + \mathrm{RTlnQ} \quad \rightarrow (1)$$

where

$\Delta \mathrm{G} = \text{Change in Gibbs Free energy}$

$\Delta \mathrm{G}^0 = \text{Change in Gibbs Free energy under Standard Conditions}$

$\mathrm{Q} = \text{Reaction quotient}$

Now, we know that

$$\Delta \mathrm{G}^0 = -\mathrm{RTlnK_{eq}}$$

Putting this value in equation (1)

$$\Delta \mathrm{G} = -\mathrm{RTlnK_{eq}} + \mathrm{RTlnQ}$$

which can be simplified to

$$\Delta \mathrm{G} = \mathrm{RTln}\left(\frac{\mathrm{Q}}{\mathrm{K_{eq}}}\right) \quad \rightarrow (2)$$

From Equation (2) it is clear that

- $\text{When } \mathrm{Q} = \mathrm{K_{eq}},\ \Delta \mathrm{G} = 0 \text{ and the reaction is at equilibrium}$
- $\text{When } \mathrm{Q} < \mathrm{K_{eq}},\ \Delta \mathrm{G} < 0 \text{ the reaction will move in the forward direction}$
- $\text{When } \mathrm{Q} > \mathrm{K_{eq}},\ \Delta \mathrm{G} > 0 \text{ the reaction will move in the backward direction}$

Le Chatelier's principle-

It describes the effect of change in concentration, pressure and temperature on the reversible system.
According to it, "If the system at equilibrium is subjected to a change of concentration or temperature or pressure, the system adjusts itself in such a way as to null the effect of that change i.e., the effect of these changes can be neglected or minimized."

Effect of Concentration

- An increase in the concentration of any substance favours the reaction in which it is used up i.e., in the opposite direction.
- An increase in concentration of reactant favours the formation of more product i.e., forward reaction. Increase in concentration of product favours.
- An increase in the concentration of product favours a backward reaction. I.e., its continuous removal is essential for more formation of it.

Effect of Pressure

- High pressure is favourable for the reaction in which there is a decrease in volume or $n_r > n_p$.
- Low pressure is favourable for the reaction in which there is an increase in volume or $n_r < n_p$.
- Pressure is kept constant when the volume is constant or $n_r = n_p$.

Here n_r = moles of gaseous reactant

n_p = moles of gaseous product

Effect of change in temperature

On increasing the temperature, equilibrium shifts to that direction which proceeds with the absorption of heat.

- $A + B + \Delta \rightleftharpoons C + D$
  This is an endothermic reaction. Thus, on increasing the temperature, equilibrium shifts in the forward direction.
- $A + B :\rightleftharpoons C + D + \Delta$
  This is an exothermic reaction. Thus on increasing the temperature, equilibrium shifts in the backward direction.

For example:

$H_2 + I_2 \rightleftharpoons 2HI + 3000\,\text{calories}$
In this reaction, the product formed is HI and the release of 3000 calories of energy. Thus if temperature is increased then equilibrium will shift backward and form the reactants.

Effect of Adding Inert Gas on Equilibrium

- When n_p is equal to n_r there is no effect of adding an inert gas either at constant volume or pressure.
- When $n_p \neq n_r$ there is no effect of adding an inert gas at constant volume.
- When $n_p \neq n_r$ at constant pressure on adding inert gas equilibrium will shift towards more volume side. e.g., the dissociation of ammonia will be more at constant pressure by adding inert gas like argon (Ar).

7. Ionic Equilibrium

Types of substances

Substances are of two types:

- Non-Electrolyte: Their aqueous solution or molten state does not conduct electricity. For example, a solution of urea, glucose, sugar, glycerine etc.
- Electrolyte: Their aqueous or molten state conducts electricity.

Strong Electrolyte: These are much ionized in water, and hence show more conduction. For example, Strong acids like HCI, H_2SO_4, HNO_3, strong bases like MOH, MOH_2. For example, KOH, NaOH, etc. and salt of strong acid or strong base like NaCl, CH_3COONa, NH_4X, etc.
Weak Electrolyte: These are less ionized in water so show less conduction. For example, weak acids like CH_3COOH, HCN, H_3PO_4, H_2CO_3, weak bases like NH_4OH and their salts like NH_2CN, CH_3COONH_4, etc.
Degree of ionization: It is the extent to which an electrolyte gets ionized in a solvent. It is shown by α or x.

$$\alpha = \frac{\text{number of molecules dissociated}}{\text{total number of molecules}}$$

α depends on the following factors:

- Nature of solute and solvent: For strong electrolytes, α is more than that for weak electrolytes.
- α is directly proportional to the dielectric constant of the solvent.
- The degree of dissociation of weak electrolyte $\propto$ Dilution
- $\alpha \propto$ 1/Concentration
- $\alpha \propto$ Temperature

8. Bronsted Lowry and Lewis Acid-Base Theory

Bronsted-Lowry Acids and Bases

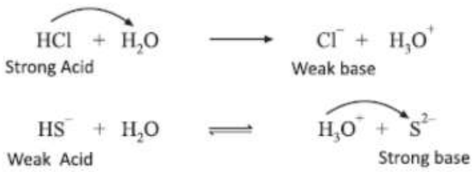
According to this concept, an acid and a base can defined as follows :
Acid: It is a substance that can donate a proton.
Base: It is a substance that can accept a proton.

Some examples include:

- When HCl is dissolved in water, it donates a proton to H_2O which behaves as a base.
  $HCl(aq) + H_2O(\ell) \rightarrow Cl^-(aq) + H_3O^-(aq)$
- When HCO_3^- is dissolved in water, it donates a proton to NH_3 which behaves as a base.
  $HCO_3^-(aq) + NH_3(aq) \rightleftharpoons CO_3^{2-}(aq) + NH_4^+(aq)$

The base formed from an acid is known as the conjugate base of the acid. Correspondingly, the acid formed from a base is called the conjugate acid of the base.
$HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$
In the above reaction, Cl^- is the conjugate base of HCl and NH_4^+ is the conjugate acid NH_3.

Strength of Bronsted-Lowry Acid and Bases:
The strength of an acid or base is measured by its tendency to lose or gain a proton. A strong acid is a substance which loses a proton easily to a base. Consequently, the conjugate base of a strong acid is a weak base.



The ability of an acid to lose a proton is experimentally measured by its equilibrium constant known as K_a. The larger the value of K_a, the more complete the reaction or the higher the concentration of H_3O^+ and the stronger is the acid. Similarly, for bases, we have the equilibrium constant, K_b which determines the extent of the completion of the reaction.

Amphiprotic Compounds:
The compounds which can act either as acids or as bases, NaSH, $NaHCO_3$ etc. are some of the examples.

Lewis Acid and Bases:
Acid: It is a substance that can form a covalent bond by accepting a shared pair of electrons.
Base: It is a substance that possesses at least one unshared pair of electrons.

Substances that are based on the Bronsted system are also based according to the Lewis concept. However, the Lewis definition of an acid considerably expands the number of substances that are classified as acid. A Lewis acid must have an empty orbital capable of receiving the electron pair of the base.
Lewis acids include molecules or atoms that have incomplete octets. For example molecules like BF_3, $AlCl_3$, etc. act as Lewis Acid.

Many simple cations can act as Lewis acids:
$$\mathrm{Cu^{2+} + 4NH_3 \rightarrow Cu\,(NH_3)_4^{2+}}$$

Some metal atoms can function as acids in the formation of compounds such as:
$$\mathrm{Ni\ +\ 4CO \rightarrow Ni(CO)_4}$$

Compounds that have central atoms capable of expanding their valence shells are Lewis acids in reactions in which this expansion occurs.
$$\mathrm{SnCl_4 + 2Cl^- \rightarrow SnCl_6^{2-}}$$

9. Ionization Of Acids And Bases

Ionisation Constant of Acids and Bases and pH of strong Acids and Bases-

The ionisation constant of acid is also known as the dissociation constant or equilibrium constant at the dissociation of acid. Thus, the ionisation constant equation of acid is given as follows:

$$\mathrm{K_a\ =\ K_c\ =\ \frac{[H+][A^-]}{[HA]}}$$

Thus, K_a is very small for weak acids and it is very high for strong acids. For example:

$$\mathrm{HCl\ \rightarrow\ H^+\ +\ Cl^-}$$

$$\mathrm{Thus,\ K_a\ =\ K_c\ =\ \frac{[H+][Cl^-]}{[HCl]}}$$
Since HCl concentration is low after the reaction due to 100% dissociation, K_a for Strong acids is very high.

Hence, as K_a increases, the strength of the acid increases.

Similarly, for bases, we have:

$$\mathrm{MOH \rightleftharpoons M^+ + OH^-}$$

Again, the equilibrium constant K_b or K_c is given as follows:

$$\mathrm{K_b\ =\ K_c\ =\ \frac{[M]^+[OH]^-}{[MOH]}}$$

Again, K_b is very small for weak bases and it is very high for strong bases like NaOH.

Hence, as K_b increases, the strength of the base increases.

pH and Strong Acids/Bases

pH is also referred to as the potential or power of hydrogen. Mathematically, it can be represented as follows:

$$\mathrm{pH\ =\ -\log_{10}[H^+]}$$

If the solution is neutral, then:
$$\mathrm{k_w = [H^+][OH^-] = 10^{-14}}$$
On Solving we have,

$$\mathrm{[H^+] = [OH^-] = 10^{-7}}$$
$$\mathrm{Thus,\ pH = 7}$$

For Acidic solutions:
For acidic solutions, we must have $[H^+] > [OH^-]$
Thus, $[H^+] > 10^{-7}$
Thus, $[H^+]$ for acids can be 10^{-6}, 10^{-5}, 10^{-4}, etc.

For Basic solutions:
For basic solutions, we must have $[H^+] < [OH^-]$
Thus, $[H^+] < 10^{-7}$
Thus, $[H^+]$ for bases can be 10^{-8}, 10^{-9}, 10^{-10}, etc.

Thus, pH of acids can be 6, 5, 4, etc.
Hence, pH of acidic solutions is less than 7

Thus, pH of basics can be 8, 9, 10, 11, etc.
Hence, pH of basic solutions is greater than 7

pH of Strong Acids
Strong acids are those acids which dissociate completely in solutions. For example:

- 2×10^{-3} M HNO_3

  Since HNO_3 is a strong acid, thus it will dissociate completely into H^+ and OH^- ions as follows:

  $$HNO_3 \rightarrow H^+ + NO_3^-$$

  $$\text{Thus, } [H^+] = 2 \times 10^{-3}\text{M} \quad \text{(given)}$$

  $$\Rightarrow pH = -\log_{10}(2 \times 10^{-3})$$

  $$\Rightarrow pH = -\log_{10}(2) - \log_{10}(10^{-3})$$

  $$\Rightarrow pH = -0.30 + 3 = 2.7$$

  Thus, pH of HNO_3 is 2.7

- 10^{-4} M H_2SO_4

  Since H_2SO_4 is a strong acid, thus it will dissociate completely into H^+ and OH^- ions as follows:

  $$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

  $$\text{Thus, } [H^+] = 2 \times 10^{-4}\text{M} \quad \text{(given)}$$

  $$\Rightarrow pH = -\log_{10}(2 \times 10^{-4})$$

  $$\Rightarrow pH = -\log_{10}(2) - \log_{10}(10^{-4})$$

  $$\Rightarrow pH = -0.30 + 4 = 3.7$$

  Thus, pH of H_2SO_4 is 3.7

pH of Weak Acids
Weak acids are those acids which dissociate partially in solutions. For example:

- **8 M HA (K_a = 2 x 10^{-8})**

  The chemical equation for the dissociation of weak acid HA is as follows:

  $$HA \rightleftharpoons H^+ + A^-$$

  Initial: 8M 0 0
  Equil: 8 - 8α 8α 8α

  The equilibrium constant K_a for the weak acid is given as follows:

  $$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{8\alpha\,.\,8\alpha}{8(1-\alpha)} = \frac{8\alpha^2}{1-\alpha}$$

  $$K_a = 8\alpha^2 \quad (\text{as } (1-\alpha) \approx 1)$$

  $$\text{Thus, } \alpha = \sqrt{\frac{K_a}{8}} = \sqrt{\frac{2 \times 10^{-8}}{8}} = \sqrt{\frac{10^{-8}}{4}} = 0.5 \times 10^{-4}$$

  $$[H^+] = 8 \times 0.5 \times 10^{-4} = 4 \times 10^{-4}$$

  $$pH = -\log_{10}4 + 4$$

  $$pH = -0.60 + 4 = 3.4$$

  Thus, pH of this given acid = 3.4

- **0.002N CH_3COOH(α = 0.02)**

  The chemical equation for the dissociation of CH_3COOH is as follows:

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

  Initial: c 0 0
  Equil: c - cα cα cα

  The equilibrium constant K_a for the weak acid is given as follows:

$$K_a = \frac{[CH_3COOH^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \,.\, c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = c\alpha^2 \quad (\text{as } (1-\alpha) \approx 1)$$

Now, as we have given :

$c = 0.002N$ or $0.002M$ (Normality = Molarity, as n factor = 1)

$$\alpha = \frac{2}{100} = 0.02$$

Thus, $[H^+] = 0.002 \times 0.02 = 4 \times 10^{-5}$

$$pH = -\log_{10}(4 \times 10^{-5})$$

$$pH = 5 - \log 4 = 4.4$$

Thus, pH of acetic acid = 4.4

Ostwald's Dilution Law

This is an application of law of mass action for weak electrolyte dissociation equilibria. Consider ionisation of a weak electrolyte say a monoprotic acid, acid HA.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Thus,

	HA	$\rightleftharpoons H^+$	$+ A^-$
Moles before dissociation	1	0	0
Moles after dissociation	$1-\alpha$	α	α

α is the degree of dissociation of weak acid HA and c is the concentration.

Thus, according to the equilibrium constant equation, we have:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha . c\alpha}{c(1-\alpha)}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

For weak electrolytes, α is small, thus $1 - \alpha = 1$

$$K_a = c\alpha^2 \text{ or } \alpha = \sqrt{\left(\frac{K_a}{c}\right)}$$

A similar expression can be made for a weak base as BOH:

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

Similarly, for the base BOH, the expression of K_b can be written as

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{c\alpha^2}{(1-\alpha)}$$

Thus, if $1 - \alpha = 1$, then

$$K_b = c\alpha^2 \text{ or } \alpha = \sqrt{\left(\frac{K_b}{c}\right)}$$

From the expression for Ka or K_b it is evident that

(1) As the value of concentration decreases, the degree of dissociation increases

(2) As the value of concentration increases, the degree of dissociation decreases

This is called as Ostwald's dilution law for weak electrolytes

Ionization Constant of Water / Ionic Product of Water-

The ionisation of water occurs as follows:

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The equilibrium constant here is defined in a different way, and is called as ionic product K_w of water and is given by:

$$K_w = [H^+][OH^-]$$

At 25^0C, $K_w = 1.0 \times 10^{-14}$

Experimentally it has been seen that the K_w value changes on increasing or decreasing the temperature. At 63^0C, $K_w = 10^{-13}$ and at 11^0C, $K_w = 0.3 \times 10^{-14}$

since pure water is neutral, $[H^+] = [OH^-] = \sqrt{K_W} = 10^{-7} M$ at $25°C$

- If a strong acid is added to it, $[H^+]$ increases and hence $[OH^-] < 10^{-7}$M at 25^0C and the solution is said to be acidic.
- If a strong base is added to it, $[OH^-]$ increases and hence $[H^+]$ must decrease in order to keep K_w constant. Now $[OH^-] > 10^{-7}$M and the solution is basic (or alkaline).

Temperature Dependence of Equilibrium Constant: Vant Hoff's Equation

$$\ell n\left[\frac{K_{T_2}}{K_{T_1}}\right]=\frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\Rightarrow 2.303\log_{10}\left[\frac{K_{T_2}}{K_{T_1}}\right]=\frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Using the above equation, the value of Keq at any unknown temperature can be calculated if the Keq value at a particular temperature and ΔH is known.

Conversely, the above equation can also be used to calculate the value of ΔH if the values of Keq at two different temperatures are known.

10. K_a and K_b Relationship

The relation between K_a,K_b and K_w can be understood by the following reaction.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Base Conjugate acid

The equilibrium constant K_b for base NH_3 is given as:

$$K_b = \frac{[NH_4^+][OH^-]}{NH_3}$$

Again, the reaction is:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

The equilibrium constant K_a for conjugate acid NH_4^+ is given as:

$$K_a = \frac{[NH_3][H_3O^+]}{NH_4^+}$$

Thus, $K_a \times K_b = [H_3O^+]\,[OH^-] = K_w$

Thus, $K_a \propto 1/K_b$ at a given temperature

Therefore, if K_a of acid increases, then K_b of the conjugate base decreases. In other words, the conjugate base of strong acid is a weak base and vice-versa.

11.pH Of Acids And Bases

pH of Solutions: Strong Acids-

pH is also referred to as potential or power of hydrogen. Mathematically, it can be represented as follows:

$$pH = -\log_{10}[H_3O^+]$$

If solution is neutral, then:

$K_w = [H_3O^+][OH^-]$

From the ionic product of water, we know:

$K_w = 10^{-14}$

$[H_3O^+] = [OH^-] = x$ (since solution is neutral)

Thus, $10^{-14} = K_w = x^2$

$x = 10^{-7}$

Now, $[H_3O^+] = 10^{-7}$

Thus, pH = $-\log_{10}(H_3O^+) = -\log_{10}(10^{-7}) = 7$

For Acidic solutions:

For acidic solutions, we must have $[H_3O^+] > [OH^-]$

Thus, $[H_3O^+] > 10^{-7}$

Thus, $[H_3O^+]$ for acids can be 10^{-6}, 10^{-5}, 10^{-4}, etc.

Thus, pH of acids can be 6, 5, 4, etc.

Hence, pH of acidic solutions is less than 7

For Basic solutions:

For basic solutions, we must have $[H_3O^+] < [OH^-]$

Thus, $[H_3O^+] < 10^{-7}$

Thus, $[H_3O^+]$ for basics can be 10^{-8}, 10^{-9}, 10^{-10}, etc.

Thus, pH of basics can be 8, 9, 10, 11, etc.

Hence, pH of basic solutions is greater than 7

pH depends upon temperature

We know from ionic product of water that at 63^0C, the value of $K_w = 10^{-13}$.

For neutral solution we know:

$$[H_3O^+] = [OH^-]$$

$$\Rightarrow K_w = x^2$$

$$\Rightarrow x = \sqrt{10^{-13}} = 10^{-6.5}$$

$$\Rightarrow [H_3O^+] = 10^{-6.5}$$

$$\Rightarrow pH = -\log_{10}(10^{-6.5}) = 6.5$$

Hence, pH depends upon temperature

pH of Strong Acids
Strong acids are those acids which dissociate completely in solutions. For example:

- 2×10^{-3} M HNO_3
  Since HNO_3 is a strong acid, thus it will dissociate completely into H^+ and OH^- ions as follows:

  $$HNO_3 \rightarrow H^+ + NO_3^-$$

  $$\text{Thus, } [H^+] = 2 \times 10^{-3} M \qquad \text{(given)}$$

  $$\Rightarrow pH = -\log_{10}(2 \times 10^{-3})$$

  $$\Rightarrow pH = -\log_{10}(2) - \log_{10}(10^{-3})$$

  $$\Rightarrow pH = -0.30 + 3 = 2.7$$

  Thus, pH of HNO_3 is 2.7
- 10^{-4} M H_2SO_4
  Since H_2SO_4 is a strong acid, it will dissociate completely into H^+ and OH^- ions as follows:

  $$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

  $$\text{Thus, } [H^+] = 2 \times 10^{-4} M \qquad \text{(given)}$$

  $$\Rightarrow pH = -\log_{10}(2 \times 10^{-4})$$

  $$\Rightarrow pH = -\log_{10}(2) - \log_{10}(10^{-4})$$

  $$\Rightarrow pH = -0.30 + 4 = 3.7$$

  Thus, pH of H_2SO_4 is 3.7

NOTE: If molarity(N) of solution is not given but normality(N) is given, then molarity can be calculated using the following formula:

$$N = M \times n$$

where, n is the number of moles

pH of Solutions: Weak Acids-

pH of Weak Acids
Weak acids are those acids which dissociate partially in solutions. For example:

- **8 M HA (K_a =2 x 10^{-8})**
  The chemical equation for the dissociation of weak acid HA is as follows:

  $$HA \rightleftharpoons H^+ + A^-$$

  Initial: 8M 0 0
  Equil: 8 - 8α 8α 8α

  The equilibrium constant K_a for the weak acid is given as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{8\alpha . 8\alpha}{8(1-\alpha)} = \frac{8\alpha^2}{1-\alpha}$$

$$K_a = 8\alpha^2 \quad (\text{as } (1-\alpha) \approx 1)$$

$$\text{Thus, } \alpha = \sqrt{\frac{K_a}{8}} = \sqrt{\frac{2 \times 10^{-8}}{8}} = \sqrt{\frac{10^{-8}}{4}} = 0.5 \times 10^{-4}$$

$$[H^+] = 8 \text{ x } 0.5 \text{ x } 10^{-4} = 4 \times 10^{-4}$$

$$pH = -\log_{10} 4 + 4$$

$$pH = -0.60 + 4 = 3.4$$

Thus, pH of this given acid = 3.4

- **0.002N CH_3COOH(α = 0.02)**

  The chemical equation for the dissociation of CH_3COOH is as follows:

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

  Initial: c 0 0
  Equil: c - cα cα cα

  The equilibrium constant K_a for the weak acid is given as follows:

  $$K_a = \frac{[CH_3COOH^-][H^+]}{[CH_3COOH]} = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

  $$K_a = c\alpha^2 \quad (\text{as } (1-\alpha) \approx 1)$$

  Now, as we have given :
  $$c = 0.002N \text{ or } 0.002M \quad (\text{Normality} = \text{Molarity, as n factor} = 1)$$
  $$\alpha = \frac{2}{100} = 0.02$$

  $$\text{Thus, } [H^+] = 0.002 \text{ x } 0.02 = 4 \times 10^{-5}$$

  $$pH = -\log_{10}(4 \times 10^{-5})$$

  $$pH = 5 - \log 4 = 4.4$$

  Thus, pH of acetic acid = 4.4

pH of Solutions: Strong Bases-

Strong bases
Strong bases are those bases that dissociate completely in solution. For example:

- **0.1M NaOH**

  Since NaOH is a strong base, thus it will dissociate completely into Na^+ and OH^- ions. The chemical equation for the dissociation of NaOH is as follows:

  $$NaOH \rightarrow Na^+ + OH^-$$

  $$[OH^-] = 10^{-1} M$$

  $$\text{Thus, } pOH = -\log_{10}(OH^-) = -\log_{10}(10)^{-1} = 1 \quad ....(1)$$

  For any solution, we know :
  $$pH + pOH = 14$$

  Thus, from equation(1), we have :
  $$pH = 13$$

  Hence, pH of 0.1M NaOH solution is 13.

- **0.05M $Ba(OH)_2$**

  Since $Ba(OH)_2$ is a strong base, thus it will dissociate completely into Ba^{2+} and $2OH^-$ ions. The chemical equation for the dissociation of $Ba(OH)_2$ is as follows:

$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

$[OH^-] = 2 \times 5 \times 10^{-2}\,M = 10 \times 10^{-2} = 10^{-1}$

Thus, $pOH = -\log_{10}(OH^-) = -\log_{10}(10)^{-1} = 1$ ....(1)

For any solution, we know :
$pH + pOH = 14$

Thus, from equation(1), we have :
$pH = 13$
Hence, pH of 0.05M $Ba(OH)_2$ solution is 13.

pH of solution/mixture-

- **Mixture of Strong Acids:**

$$\mathbf{10^{-2}M\ HCl(1L) + 10^{-2}M\ HNO_3(2L)}$$

The chemical equation for HCl is as follows :
$HCl \rightarrow H^+ + Cl^-$
Thus, moles of $H^+ = 10^{-2}\,M$

Similarly, for HNO_3, we have :
$HNO_3 \rightarrow H^+ + NO_3^-$
Thus, moles of $H^+ = 2 \times 10^{-2}\,M$ (since volume is 2L)

Thus, total moles of $H^+ = 3 \times 10^{-2}$ and total volume $= 3L$
Thus, $[H^+] = \dfrac{3 \times 10^{-2}}{3} = 10^{-2}\,M$

$$\mathbf{pH = -\log_{10}(10^{-2}) = 2}$$

NOTE: Shortcut only for monobasic acids and monoacidic bases:

$$[H^+] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} \quad \text{(for acids)}$$
$$[OH^-] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} \quad \text{(for bases)}$$

- **Mixture of Strong Bases:**

$$\mathbf{10^{-3}M\ NaOH(2L) + 10^{-2}M\ KOH(1L)}$$
Using the shortcut formula for bases as given above, we get:
$$[OH^-] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{10^{-3} \times 2 + 10^{-2} \times 1}{3}$$
$$\Rightarrow \frac{10^{-3}(2+10)}{3} = \frac{12 \times 10^{-3}}{3} = 4 \times 10^{-3}$$
$$pOH = -\log 4 + 3 = -0.60 + 3 = 2.40$$
$$\text{Thus, } pH = 14 - pOH = 14 - 2.40 = 11.60$$

- **Mixture of Strong Acid and Strong Base:**

$$\mathbf{10^{-2}M\ HCl(2L) + 10^{-3}M\ NaOH(1L)}$$
Clearly, moles of $(H^+) = 2 \times 10^{-2}$ moles and moles of $(OH^-) = 1 \times 10^{-3}$ moles.
Since moles of (H^+) is greater than moles of (OH^-), therefore the solution medium will be acidic.
Now, remaining moles of $H^+ = 2 \times 10^{-2} - 10^{-3} = 19 \times 10^{-3}$
Thus, $[H^+] = \dfrac{19 \times 10^{-3}}{3} = 6.3 \times 10^{-3}$

Thus, pH of mixture $= -\log_{10}(6.3 \times 10^{-3})$

$pH = 3 - \log_{10}6.3 = 3 - 0.79 = 2.2$
Thus, the pH of the mixture = 2.2

12. Common ion effect

Common ion effect-

The value of the degree of dissociation for a weak electrolyte is decreased by the addition of a strong electrolyte having a common ion. As a result of this effect, the concentration of the uncommon ion of the weak electrolyte decreases.
For example:

- $NH_4OH \rightleftharpoons NH_4^+ + OH^-$
  weak electrolyte

  $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$
  Common ion
  Here α for NH_4OH will be decreased by NH_4Cl
- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
  $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$
  Here α for CH_3COOH will be decreased by CH_3COONa

Applications of Common Ion Effect

- The solubility of a partially soluble salt decreases due to the common ion effect. For example, the presence of $AgNO_3$ or KCl decreases the solubility of AgCl in water.
- Salting out of soap by addition of NaCl.
- Purification of NaCl by passing HCl gas.

Isohydric Solution: These are the solutions having the same concentration of common ions.

pH of weak acid + strong acid-

The pH of a mixture of a weak acid and a strong acid can be understood using the following example.

Weak acid: H_2S (0.1M)
Strong acid: HCl (0.3M)
The K_a value for this mixture = 1.2×10^{-20}

The chemical equation for H_2S is given as follows:

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

Initial: c 0 0
Equil: c - cα cα cα

Thus, the equilibrium constant K_a is given as follows:

$$K_a = \frac{[c\alpha]^2.c\alpha}{c(1-\alpha)} = \frac{[H^+]^2.c\alpha}{c(1-\alpha)}$$

$$1.2 \times 10^{-20} = \frac{[c\alpha + 0.3].c\alpha}{c(1-\alpha)} = (0.3)^2 = 0.09\alpha$$

$$\textbf{Thus}, \alpha = \frac{1.2 \times 10^{-20}}{0.09} = 13.3 \times 10^{-20}$$

Again, the chemical equation for HCl is given as follows:

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

Initial: 0.3 0 0
Equil: 0 0.3 0.3

Thus, total $[H^+]$ for the mixture = c α + 0.3
$[H^+] = 3 \times 10^{-1}$ (α is very small for weak acids)

Now, the pH for the mixture is given as follows:

$$pH = -\log[H^+] = -\log[3 \times 10^{-1}] = -\log 3 + 1 = -0.47 + 1$$

$$pH = 0.53$$

13. Buffer Solution

A solution whose pH does not change very much when $H^+(H_3O^+)$ or OH^- are added to it is referred to as a buffer solution.
A buffer solution is prepared by mixing a weak and its salt having a common anion(i.e HA + HB forms an acidic buffer) or a weak base and its salt having common cation(i.e BOH + BA forms a basic buffer).
It can be prepared to have a desired value of pH by controlling the amounts of acids and their salts in case of acidic buffer and of bases and their salts in basic buffer.

$$\begin{array}{ll} \text{Acidic buffer :} & CH_3COOH + CH_3COONa \\ \text{Basic buffer :} & NH_4OH + NH_4Cl \end{array}$$

Consider an acidic buffer containing an acid HA and say common ions A^-. Now any H^+ added to this solution within certain limits are neutralized by A^- ions as:

$$H^+ + A^- \rightleftharpoons HA$$

While the addition of OH^- ions externally (within certain limits) are neutralised by acid HA as:

$HA + OH^- \rightleftharpoons H_2O + A^-$

Hence in both cases, the effect of the addition of H^+ or OH^- is almost compensated for (i.e. pH almost remains constant).

Such a system (which may be acidic or basic) finds enormous use not only in industrial processes but also most importantly in biological reactions. Like the pH of normal blood is 7.4 and for good health and even for survival, it should not change below 7.1 or greater than 7.7, the body maintains it through a buffer system made of carbonate and bicarbonate ions and $H_2PO_4^-$ and HPO_4^{2-}. Similarly, the pH of gastric juice is kept constant in order to operate good digestive functions.

Types of Buffers-

Buffer solutions are obtained if the acids and bases are mixed in different amounts (equivalents).

Buffer solutions are those, which resist a change in pH upon the addition of a small amount of acid or base. this does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer

Buffer solutions can be classified into three types:

(1) Acidic Buffer Solutions

Acidic buffer solutions are the solutions that are made from **a weak acid and one of its salt with a strong base**.

For example: Solution of CH_3COOH and CH_3COONa

It is to be noted that the pH of an acidic buffer may not be always less than 7. It depends upon the Ka values of the acid and also the concentration of the acid and the salt

(2) Basic Buffer Solutions

Basic buffer solutions are the solutions that are made from **a weak base and one of its salt with a strong acid**.

For example: Solution of NH_4OH and NH_4Cl

It is to be noted that the pH of an basic buffer may not be more less than 7. It depends upon the Kb values of the base and also the concentration of the salt and base

(3) Simple Buffer Solutions

Simple buffer solutions are the solutions that are made from the **salt of a weak acid and weak base**.

For example: Solution of CH_3COONH_4

It is to be noted that the pH of simple buffer may be less than, greater than or equal to 7. It depends upon the Ka and Kb values of the acid and the base.

Buffer Action:

A buffer solution resists a change in its pH on addition of small amount of acid or base. This is because there is one component which can neutralise the acid and the other component can neutralise the base

e.g $CH_3COOH \text{ and } CH_3COONa$

When small amount of base is added, then it is the acid which neutralises it

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

When small amount of acid is added, then it is the acetate ion which neutralises it

$HCl + CH_3COO^- \rightleftharpoons CH_3COOH + Cl^-$

as neutralisation occurs, the $[H^+] \text{ or } [OH^-]$ does not alter much in the solution and pH change is almost negligible

Cases which are not a buffer solution

(1) Solutions of Strong Acid and its salt e.g. $H_2SO_4 \text{ and } KHSO_4$

(2) Solutions of Strong Base and its salt e.g. $NaOH \text{ and } NaCl$

For a solution to be classified as a buffer solution, there must be one weak acid or base and its respective conjugate base or acid

Calculating pH of a Buffer Solution(acidic)-

When a solution contains CH_3COOH and CH_3COONa, then the following equilibrium will be established:

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

The equilibrium equation for the given system can be calculated using the following equation:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[Salt][H^+]}{[Acid]}$$

$[CH_3COO^-]$ is the concentration of salt
$[CH_3COOH]$ is the initial concentration of acid

Rearranging the above equation, we get

$$[H^+] = K_a \frac{[Acid]}{[Salt]}$$

$$-\log_{10}[H^+] = -\log_{10}K_a - \log_{10}[Acid] + \log_{10}[Salt]$$

$$pH = pK_a + \log_{10}\frac{[Salt]}{Acid}$$

This equation is also known as the **Henderson-Hasselbalch** equation.

Some examples

- Find the pH of a solution having 0.1M $CH_3COOH(K_a = 10^{-5})$ and 0.2M CH_3COONa.

  We know that pH of a solution is given as:

  $$pH = pK_a + \log_{10}\frac{[Salt]}{Acid}$$

  $$\text{Thus, } pH = -\log_{10}K_a + \log_{10}\frac{[0.2]}{[0.1]}$$

  $$\Rightarrow pH = -\log_{10}10^{-5} + \log_{10}2$$

  $$\Rightarrow pH = 5 + 0.30 = 5.30$$

- Find the pH of a solution containing 0.25 moles of $HCN(K_a = 10^{-5})$ and 0.10 moles of NaCN present in 1 litre solution.

  We know that pH of a solution is given as:

  $$pH = pK_a + \log_{10}\frac{[Salt]}{Acid}$$

  $$\text{Thus, } pH = -\log_{10}K_a + \log_{10}\frac{[Salt]}{[Acid]}$$

  $$\Rightarrow pH = -\log_{10}10^{-5} + \log_{10}\frac{0.10}{0.25}$$

  $$\Rightarrow pH = 5 + \log_{10}\frac{2}{5}$$

  $$\Rightarrow pH = 5 - 0.39 = 4.6$$

Working of Acidic Buffer -

Acidic buffer solutions are the solutions that are made from a weak acid and one of its salt mainly sodium salt.

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

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

- **On addition of acid**

  $$H^+ + CH_3COO^-(\text{solution}) \rightarrow CH_3COOH$$

  Although on the addition of acid concentration of CH_3COOH increases, so it wants to go in the forward direction but due to common ion effect CH_3COOH cannot dissociate back.
  CH_3COO^- concentration decreases but we have an abundant amount of CH_3COO^-. So the decrease is negligible.

- **On addition of base**

  $$OH^- + H^+(\text{from solution}) \rightarrow H_2O$$

  In this case, $[H^+]$ concentration decreases and CH_3COOH goes in the forward direction to dissociate into H^+ so as to restore the concentration of $[H^+]$

Buffer Capacity-

The property of a buffer solution to resist a change in pH is known as buffer capacity. It is defined as the number of moles of acids or bases added in one litre of solution to change the pH by unity, i.e. Thus, buffer capacity is given as:

$$\begin{aligned}\text{Buffer capacity } &= \frac{\text{Mole of acid or base added to 1 litre of buffer}}{\text{Change in pH}}\\ &= \frac{n}{\Delta pH}\end{aligned}$$

Note: The greater is the buffer capacity, the greater is its capacity to resist change in pH

Salient Features of Buffer Solutions

- It has a definite pH.
- Its pH does not change on standing.
- Its pH does not change on dilution.
- Its pH does not change significantly with the addition of a small amount of acid or base.
- The pH of the buffer solution depends upon pK_a and on the relative molar amount of weak acid and its conjugate base.
- Buffer solutions are used in:
    1. Qualitative analysis of mixture, for example, removal of phosphate.
    2. Quantitative analysis of estimations.
    3. Industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc.
    4. Digestion of food.
    5. Preservation of foods and fruits.
    6. Agriculture and dairy products preservations.

Basic Buffers-

A basic buffer solution contains a weak base and its salt with strong acid. Some examples of basic buffers are:

- $NH_4OH + NH_4Cl$
- $NH_4OH + (NH_4)_2SO_4$
- $CH_3\text{-}NH_2 + [CH_3\text{-}NH_3^+]Cl^-$

The pH of the basic buffer is given as:

$$pOH = pK_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}$$

We already know that pH = 14 - pOH. This can be calculated using this equation.

For example: the basic buffer we have:

$$NH_4OH \rightleftharpoons NH_4^+ + Cl^-$$
$$NH_4Cl \rightarrow NH_4^+\ Cl^- \quad \text{(Strong electrolyte)}$$

$$\text{Thus, } K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

In this system:

- **[NH_4OH]**: The initial concentration of [NH_4OH] is taken as at equilibrium negligible dissociation of NH_4OH is there because of the common-ion effect.
- **[NH_4^+]**: The concentration of NH_4OH is mostly from 100% dissociation of NH_4Cl.

Again, as we know:

$$K_b = \frac{[\text{Salt}][OH^-]}{\text{Base}}$$

$$\text{Thus, } [OH^-] = K_b\frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{Using log on both sides, we get :}$$

$$-\log_{10}[OH^-] = -\log_{10}K_b + \log_{10}[\text{Salt}] - \log_{10}[\text{Base}]$$

$$\textbf{Hence}, \ pOH = pK_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}$$

The action of Basic Buffer-

A basic buffer solution contains equimolar quantities of a weak base and its salt with strong acid. For example ammonium hydroxide i.e. NH_4OH and ammonium chloride i.e. NH_4Cl.

On Adding Acid: H^+ release and combines with OH^- of the base.

On Adding Base: OH^- releases and combines with NH_4^+ of salt.

- On adding acid to the basic buffer, its H^+ ions react with OH^- ions of the base and form H_2O. Thus, in this case, the solution feels that its $[OH^-]$ has decreased, thus to neutralize this effect, NH_4OH dissociate in small amounts and gives $[OH^-]$ so as to restore the concentration of $[OH^-]$
- On adding base to the basic buffer, its $[OH^-]$ ions react with NH_4^+ ions and form NH_4OH. In this case, the solution feels that its NH_4OH concentration is increased. Thus, in this case, the reaction will not proceed forward because of the common ion effect.

14. Salt Hydrolysis

Salt Hydrolysis

When a salt is added to water ions of the salt interact with water to cause acidity or basicity in an aqueous solution. This ionic interaction is called salt hydrolysis. Interaction of cation is cationic hydrolysis and interaction of anion is anionic hydrolysis.

- Hydrolysis is the reverse of neutralization and an endothermic process.
- If the hydrolysis constant is K_h and the neutralization constant is Kn. Then,
  $Kn = 1/K_h$
- A solution of the salt of strong acid and weak base is acidic and for it pH < 7 or $[H^+] > 10^{-7}$. For example, $FeCl_3$ (weak base + strong acid): The solution is acidic and involves cationic hydrolysis.
- A solution of the salt of strong base and weak acid is basic and for it pH > 7 or $[H^+] < 10^{-7}$. For example, KCN (strong base + weak acid): The solution is basic and involves anionic hydrolysis.
- A solution of the salt of weak acid and weak
  base, then:
  If $K_a > K_b$, it is acidic
  If $K_a < K_b$, it is basic
  If $K_a = K_b$, it is neutral
- CH_3COONH_4 (weak acid + weak base): The solution is neutral and involves both cationic and anionic hydrolysis.
- A solution of the salt of strong acid and strong base is neutral or pH = 7 or $[H^+] = 10^{-7}$
- A salt of strong acid and strong base is never hydrolyzed however, ions are hydrated. For example, K_2SO_4 (however, strong base + strong acid).

Degree of Hydrolysis: It is defined as the fraction of total salt that has undergone hydrolysis on attainment of equilibrium. It is denoted by h.
Let c be the concentration of salt and h be its degree of hydrolysis.

$$A^- + H_2O \rightleftharpoons OH^- + HA$$

c
c - ch ch ch

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{(ch)(ch)}{c - ch} = \frac{ch^2}{1-h}$$

$$\text{Thus, } K_h = ch^2 \quad (\text{assuming } h << 1)$$

$$h = \sqrt{\frac{K_h}{c}}$$

Salt hydrolysis: Weak Acid and Strong Base-

Such salts give alkaline solutions in water. Some of such salts are: CH_3COONa, Na_2CO3, K_2CO_3, KCN, etc. For our discussion, we consider CH_3COONa (sodium acetate) in water. When CH_3COONa is put in water, it completely ionises to give CH_3COO^- (acetate) ions and Na^+ ions. Now acetate ions (CH_3COO^-) absorb some H^+ ions from weakly dissociated H_2O molecules to form undissociated CH_3COOH. Na^+ remains in the ionic state in water. Now for K_w (ionic product) of water to remain constant, H_2O further ionises to produce more H^+ and OH^- ions. H^+ ions are taken up by CH_3COO^- ions leaving OH^- ions in excess and hence an alkaline solution is obtained.

Let BA represents such a salt. As it is put in water;

$$BA(aq) + H_2O(aq) \rightleftharpoons BOH(aq) + HA(aq)$$

BA dissociates into ions and BOH being strong base also ionises.

$$B^+ + A^- + H_2O \rightleftharpoons B^+(aq) + OH^-(aq) + HA(aq)$$

Thus, the net reaction is:
$$A^-(aq) + H_2O \rightleftharpoons OH^-(aq) + HA(aq)$$

Thus, the hydrolysis constant(K_h) is given as:
$$K_h = \frac{[OH^-][HA]}{[A^-]}$$

pH of Solution

pH of a basic solution is given as:

$$\mathrm{pH} = 14 + \log\left[\mathrm{OH}^-\right] \quad \text{and} \quad \left[\mathrm{OH}^-\right] = \mathrm{ch} = \sqrt{\mathrm{K_h c}}$$

Thus, substituting for K_h, we get:

$$\left[\mathrm{OH}^-\right] = \sqrt{\frac{\mathrm{K_w c}}{\mathrm{K_a}}}$$

$$\mathrm{pH} = 14 + \log_{10}\sqrt{\frac{\mathrm{K_w c}}{\mathrm{K_a}}}$$

$$\text{Thus, pH} = \frac{1}{2}(\mathrm{pK_w} + \mathrm{pK_a} + \log_{10}\mathrm{c})$$

$$\text{Hence, pH} = 7 + \frac{1}{2}(\mathrm{pK_a} + \log_{10}\mathrm{c})$$

Salt hydrolysis: Weak Base and Strong Acid-

Such salts give acidic solutions in water. Some of such salts are NH_4Cl, $ZnCl_2$, $FeCl_3$, etc. For the purpose of discussion, we will consider the hydrolysis of NH_4Cl. When NH_4Cl is put in water, it completely ionises in water to give NH_4^+ and Cl^- ions. NH_4^+ ions combine with OH^- ions furnished by weakly dissociated water to form NH_4OH (a weak base). Now for keeping K_w constant, water further ionises to give H^+ and OH^- ions, where OH^- ions are consumed by NH_4^+ ions leaving behind H^+ ions in solution to give an acidic solution.
Let BA be one of such salts. When it is put into water, the reaction is as follows.

$$\mathrm{B^+ + A^- + H_2O \rightleftharpoons BOH + H^+(aq) + A^-(aq)}$$

Thus the net reaction of hydrolysis is as follows:

$$\mathrm{B^+ + H_2O \rightleftharpoons BOH(aq) + H^+(aq)}$$

c - ch ch ch

$$\mathrm{K_h} = \frac{[\mathrm{BOH}][\mathrm{H^+}]}{[\mathrm{B^+}]} = \frac{(\mathrm{ch})(\mathrm{ch})}{\mathrm{c - ch}} = \frac{\mathrm{ch^2}}{1 - \mathrm{h^2}} = \mathrm{ch^2} \quad (\text{assuming } \mathrm{h} << 1)$$

$$\textbf{Thus}, \ \mathrm{h} = \sqrt{\frac{\mathrm{K_h}}{\mathrm{c}}}$$

Considering ionisation of weak base BOH and H_2O.

$$\mathrm{BOH \rightleftharpoons B^+ + OH^-} \quad \Rightarrow \quad \mathrm{K_b} = \frac{[\mathrm{B^+}][\mathrm{OH^-}]}{[\mathrm{BOH}]}$$

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-} \quad \Rightarrow \quad \mathrm{K_w} = [\mathrm{H^+}][\mathrm{OH^-}]$$

From expressions for K_h, K_b and K_w, we have :

$$\mathrm{K_h} = \frac{\mathrm{K_w}}{\mathrm{K_b}} \quad \Rightarrow \quad \mathrm{h} = \sqrt{\frac{\mathrm{K_w}}{\mathrm{K_b c}}}$$

pH of Solution
Now, pH = - log $[H^+]$

$$\text{and} \ \left[\mathrm{H^+}\right] = \mathrm{ch} = \mathrm{c}\sqrt{\frac{\mathrm{K_h}}{\mathrm{c}}} = \sqrt{\mathrm{K_h c}} \quad \Rightarrow \quad \left[\mathrm{H^+}\right] = \sqrt{\frac{\mathrm{K_W c}}{\mathrm{K_b}}}$$

$$\Rightarrow \quad \mathrm{pH} = -\log_{10}\sqrt{\frac{\mathrm{K_w c}}{\mathrm{K_b}}}$$

$$\Rightarrow \quad \mathrm{pH} = \frac{1}{2}(\mathrm{pK_w} - \mathrm{pK_b} - \log_{10} c)$$

$$\textbf{Hence}, \ \mathrm{pH}(\text{ at } 25°\mathrm{C}) = 7 - \frac{1}{2}(\mathrm{pK_b} + \log_{10} c)$$

Salt hydrolysis: Weak Acid and Weak Base-

Let us consider ammonium acetate (CH_3COONH_4) for our discussion. Both NH_4^+ ions and CH_3COO^- ions react respectively with OH^- and H^+ ions furnished by water to form NH_4OH (a weak base) and CH_3COOH (acetic acid).

Let BA represent such a salt.

$$\mathrm{B^+ + A^- + H_2O \rightleftharpoons \underset{\text{weak base}}{BOH} + \underset{\text{weak acid}}{HA}}$$

Initially: c c 0 0
At equilibrium: c - ch c - ch ch ch

$$\Rightarrow \quad K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{(ch)(ch)}{(c - ch)^2}$$

$$\Rightarrow \quad K_h = \frac{h^2}{(1-h)^2}; \quad \text{Taking square root on both sides to get:}$$

$$\Rightarrow \quad h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

Hence, the degree of hydrolysis of such salts is independent of the concentration of salt solution.

Now consider the dissociation of both weak base and acid.

$$HA \rightleftharpoons H^+ + A^- \quad ; \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$BOH \rightleftharpoons B^+ + OH^- \quad ; \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+][OH^-]$$

Combining K_h, K_b, K_a and K_w, we get:

$$K_h = \frac{K_W}{K_a K_b} \quad \text{and} \quad h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

pH of Solution

Considering K_a for acid, we have:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [H^+] = K_a \frac{[HA]}{[A^-]}$$

Since, base and acids are weaker, hence,

$$[BOH] = [HA] \quad \Rightarrow \quad [B^+] = [A^-]$$

$$\Rightarrow \quad K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{[HA]^2}{[A^-]^2} \quad \Rightarrow \quad [H^+] = K_a\sqrt{K_h} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$pH = -\log[H^+] = -\log\sqrt{\frac{K_W K_a}{K_b}}$$

$$\Rightarrow \quad pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

$$\textbf{Hence},\ pH(\text{at } 25°C), \quad pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

15. Solubility and Solubility Product

Solubility-

The maximum amount of a particular solute in grams, which can dissolve in 100 grams of solvent at a given temperature is called **solubility**. It is denoted by 's' and is expressed in g. The number of moles of solute in 1 L of saturated solution is known as molar solubility.

Solubility decreases with the increase in the concentration of common ion. It increases with temperature and increases in case the ions formed from the sparingly soluble salt undergo some sort of reaction like complexation.

For example, The solubility of AgCl in water in the presence of $AgNO_3$

Solubility increases due to complex ion formation. For example, AgCl has more solubility in ammonia due to complex formation
$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2Cl$

Solubility Product: It is the product of the molar concentrations of ions of an electrolyte in a saturated solution at a particular temperature. It is denoted by Ksp or S.

General Representation
$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$

$Ksp = [A^{+y}]^x \times [B^{-x}]^y$

Relation between Solubility(s) and Solubility Product (Ksp)
$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$
s 0 0

- xs ys

$$\text{Thus, } K_{sp} = x^x y^y (s)^{x+y}$$

Solubility Product and Precipitation

- If K_{sp} ≈ Ionic product
  The solution is saturated and for precipitation, more solute is to be added.
- If Ionic product > K_{sp}
  The solution is supersaturated so easily precipitated.
- If Ionic product < K_{sp}
  The solution is unsaturated so no precipitation takes place.

Redox Reaction and Electrochemistry

Important Formulae

1. Oxidation Number and Oxidation State

Oxidation
It is a process that involves the loss of electrons by the atoms or ions.
Reduction
It is a process that involves the gain of electrons by the atoms or ions.

Any reaction, in which the electrons are exchanged between atoms or ions, represents a simultaneous process of oxidation and reduction and is called a Redox Reaction.

In a Redox Reaction, the species that loses electrons (i.e., gets oxidised) is known as the reducing agent or reductant, (since it causes reduction of other species), the species which accepts electrons from reductant (i.e., gets reduced) is known as an oxidising agent or oxidant (as it causes oxidation of other species).

Oxidation State (O.S.): It refers to the hypothetical charge on atoms in a compound if all the bonds were assumed to be 100% ionic.

Oxidation state, many times, is also referred to as Oxidation Number.
This means the oxidation number of an element in a compound is equal to the oxidation state of that element multiplied by the total atoms of that element in a particular compound.
(i) In ionic compounds, it is simply the charge on the corresponding cation and anion which is expressed as the oxidation state of that particular element. For example, the oxidation state of potassium and chlorine in potassium chloride (KCl) is simply +1 and –1 respectively as KCl is treated as K^+Cl^-.

Refer to the following examples where oxidation states are written above the atoms:

+2-1	+2-2	+3-1	+1+6-2
$MgCl_2$	CaS	$AlCl_3$	K_2SO_4

NOTE: (a) In $MgCl_2$ and $AlCl_3$, -1 is the oxidation state of Cl.
(b) In each of the cases, the sum of the oxidation number of all atoms of all kinds is equal to zero since the compound is neutral.

(ii) In Covalent Compounds, it is not so easy to assign the oxidation state of an atom. In order to simplify the concept, we are going to define a set of rules which would enable us to assign an oxidation state to every element in any compound.

Rules for Assigning Oxidation State (O.S.) and Oxidation Number (O.N.):

- Any element in a free state is assigned an oxidation state of zero. For example, the O.S. of H, P, S, and O in H_2, P_4, S_8, and O_2 respectively is zero.
- The oxidation state of any cation or anion (of form A^+ or B^-) is equal to the magnitude of its charge. For example: O.S of Ca in Ca^{2+} = +2 and O.S of Al in Al^{3+} = +3.
- The algebraic sum of the oxidation number of all atoms in a neutral compound is equal to 0. The algebraic sum of the oxidation numbers of all atoms in an ion (like PO_4^{3-}) is equal to the charge on the ion.
- The oxidation state of Alkali Metals (Group IA) is +1 in all of their compounds and that of Alkaline Earth elements (Group IIA) is +2 in all of their compounds.
- Hydrogen in almost all of its compounds is assigned an oxidation state of +1. The exception occurs when hydrogen forms compounds with strong metals like KH, NaH, MgH_2, CaH_2, etc. In all of these, the oxidation state of hydrogen is -1.
- Oxygen in almost all of its compounds is assigned an oxidation state of -2. But in certain compounds like Peroxides(H_2O_2), the oxidation state of oxygen is -1. Another exception is OF_2, where O.S. is +2. O_2F_2, where O.S. is +1 and KO_2 in which O.S. is -1/2.
- Fluorine is the most electronegative element and is assigned an O.S. of -1, in all its compounds. For other halogens, O.S. is generally -1 except when they are bonded to a more electronegative halogen or oxygen. O.S. of iodine in IF_7 is +7, O.S. of chlorine in $KClO_3$ is +5.
- Generally, an element with greater electronegativity is assigned -1 by the hypothetical breaking of one covalent bond.

2. Redox Reactions

The different types of redox reactions are:

- Decomposition Reaction
- Combination Reaction
- Displacement Reaction
- Disproportionation Reactions

Decomposition Reaction
This is the reaction that involves the breakdown of a compound into different compounds. Some examples of this type of reaction are:

$$2H_2O(l) \xrightarrow{\Delta} 2H_2(g) + O_2(g)$$
$$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$$

This must be noted here that all decomposition reactions are not redox reactions. For example, the decomposition of calcium carbonate is not a redox reaction.
$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Combination Reaction
These types of reactions are the opposite of decomposition reactions and hence involve the combination of two species to form a single compound. Some examples include:

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

Displacement Reaction
Displacement reactions, also known as replacement reactions, involve compounds and the replacement of elements. They occur as single and double replacement reactions. In other words, in these type of reactions, an atom or an ion in a compound is substituted by another element.

Some examples include:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)(\text{Metal displacement})$$
$$Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)(\text{Non} - \text{Metal displacement})$$

Disproportionation Reactions

Disproportionation reactions are those reactions in which a single element in one oxidation state is simultaneously oxidized and reduced. Some examples include:

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-$$
$$S_8(s) + 12OH^-(aq) \rightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$$

Displacement Reaction-

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:

$$X + YZ \rightarrow XZ + Y$$

Displacement reactions fit into two categories: metal displacement and non-metal displacement.

- **Metal Displacement:** A metal in a compound can be displaced by another metal in an uncombined state. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:

  $$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$
  $$V_2O_5(s) + 5Ca(s) \xrightarrow{\Delta} 2V(s) + 5CaO(s)$$
  $$TiCl_4(l) + 2Mg(s) \xrightarrow{\Delta} Ti(s) + 2MgCl_2(s)$$

  In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

- **Non-metal displacement:** The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.
- Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:

  $$2Na(s) + 2H_2O(l) \quad \rightarrow \quad 2NaOH(aq) + H_2(g)$$
  $$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

  $$Mg(s) + 2H_2O(l) \xrightarrow{\Delta} Mg(OH)_2(s) + H_2(g)$$

Balancing of Redox Reaction: Ion Electrode Method-

1. Identify the oxidation and reduction half-reactions and write them separately in ionic form.
   For example:
   Mn in MnO^-_4 in an acidic medium generally goes to $MnSO_4$ or Mn^{2+}

Write an equation like this:
$MnO_4^- \longrightarrow Mn^{2+}$

2. Balance each half-reaction separately. This is done according to the following procedure.
   1. Balance all the atoms of both reactions except 'O' and 'H'.
   2. Now balance O and H atoms depending upon the medium of reaction:

Acidic Medium

$MnO_4^- \longrightarrow Mn^{2+} \quad \text{(acidic medium)}$

$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

Now to balance H atoms, add as many H+ ions required to the side that is deficient in H atoms.

$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

Basic Medium

To balance O atoms, add a same number of H_2O molecules to the side having excess of O atoms and add the double the number of OH^- ions to the other side (i.e., to the side deficient in O atoms).

$NO_3^- \longrightarrow NH_4^+ \quad \text{(basic medium)}$

$NO_3^- + 3H_2O \longrightarrow NH_4^+ + 6OH^-$

Now to balance H atoms, add same number of OH^- ions to the side in excess of H atoms and then add same number of water molecules to the other side (i.e., the side deficient in H atoms).

$NO_3^- + 3H_2O + 4H_2O \longrightarrow NH_4^+ + 6OH^- + 4OH^-$
$NO_3^- + 7H_2O \longrightarrow NH_4^+ + 10OH^-$

Alternatively, for balancing in the basic medium, you can first balance in the acidic medium and then add as many OH^- ions on both sides such that all the H^+ on one side is consumed to give water. Now complete the net number of water molecules after the above operation.

$NO_3^- + 10H^+ \longrightarrow NH_4^+ + 3H_2O$

$NO_3^- + 10H^+ + 10OH^- \longrightarrow NH_4^+ + 3H_2O + 10OH^-$

$NO_3^- + 10H_2O \longrightarrow NH_4^+ + 3H_2O + 10OH^-$

$NO_3^- + 7H_2O \longrightarrow NH_4^+ + 10OH^-$

3. Now add electrons to the side deficient in negative charge in order to balance the charge on both sides.

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
$NO_3^- + 7H_2O + 8e^- \longrightarrow NH_4^+ + 10OH^-$

These are balanced half-reactions in acidic and basic medium respectively.

4. Now add two half-reactions together in such a manner that electrons from both sides cancel. So multiply by coefficients so that number of electrons produced in oxidation equals the number of electrons used in reduction.

Balancing of Disproportionation Redox Reaction: Ion Electrode Method-

Disproportionation reactions are those reactions in which one species having some oxidation state converts into two different oxidation states, one oxidation state is higher and the other is lower.

The balancing of the disproportionation reaction by the ion electrode method can be understood by the following example.
The chemical reaction is as follows:

$Cl_2 + OH^- \rightarrow ClO_3^- + Cl^- + H_2O$

In this reaction, Cl on the reactant side has zero oxidation state but on the product side, its oxidation states are +5(in ClO_3^-) and -1 in Cl^-.

STEP 1: Write oxidation half-reaction

$Cl_2 \rightarrow ClO_3^-$

Now balance the chlorine atoms on both sides. Thus the balance equation is as follows:

$Cl_2 \rightarrow 2ClO_3^-$

Now chlorine atoms are changing its oxidation states from 0 to 5. Thus, there is a total exchange of 10 electrons. So, write the complete balanced equation as follows:

$Cl_2 \rightarrow 2ClO_3^- + 10e^- \qquad \text{............(i)}$

STEP 2: Write the reduction half-reaction

$Cl_2 \rightarrow Cl^-$

Now balance the chlorine atoms on both sides. Thus the balance equation is as follows:

$Cl_2 \rightarrow 2Cl^-$

Now in this equation, chlorine atoms are changing its oxidation states from 0 to -1. Thus, there is a total exchange of 2 electrons. So, write the complete balanced equation as follows:

$Cl_2 + 2e^- \rightarrow 2Cl^-$ ....(ii)

Now balance the electrons exchange of equations (i) and (ii) and then add them both. Thus the final added equation is as follows:

$6Cl_2 \rightarrow 2ClO_3^- + 10Cl^-$ ....(iii)

STEP 3: Balance the charge
In equation(iii), there is a total of -12 charge on the product side and zero charge on the reactant side. Thus, to balance the charge on both sides, add the required number of OH^- ions on the deficient side. Thus,

$$12OH^- + 6Cl_2 \longrightarrow 2ClO_3^- + 10Cl^-$$

STEP 4: Balance the oxygen atoms
To balance the oxygen atoms, add the required number of H_2O molecules on the deficient side.

$$12OH^- + 6Cl_2 \longrightarrow 2ClO_3^- + 6H_2O + 10Cl^-$$

This is the final balanced equation for the given disproportionation reaction by the ion-electrode method.

Balancing of Redox Reaction: Oxidation Number Method-

While balancing a given reaction by this method, the following steps are to be followed :

1. Assign the oxidation state to each element (atom) on both sides of the equation and identify which element has been oxidised and which reduced.
2. Calculate the increase or decrease in the oxidation number per atom.
3. Multiply by suitable integers so as to equalise the total increase or decrease in the oxidation state of the species involved.
4. Balance atoms undergoing oxidation and reduction apart O and H.
5. Balancing of the total charge in the equation using H^+ or OH^- depending upon the medium.

- In the Acidic medium, count the total charge on both sides and balance it by adding H^+ ions to the required side (i.e., to the side deficient in positive charge). Finally, add enough water molecules to balance H and O atoms to the required side.

- In a Basic medium, balance the charge by adding OH^- ions to the side with an excess of positive charge and finally add the required number of H_2O molecules to the appropriate side to balance O and H.

3. Introduction to Electrochemistry

ELECTROCHEMISTRY
Electrochemistry is the branch of science that deals with the transformation of chemical energy into electrical energy and vice versa or it deals with the relationship between electrical and chemical energy produced in a redox reaction.

Galvanic Cell (or Voltanic Cell)
Consider the following redox reaction:

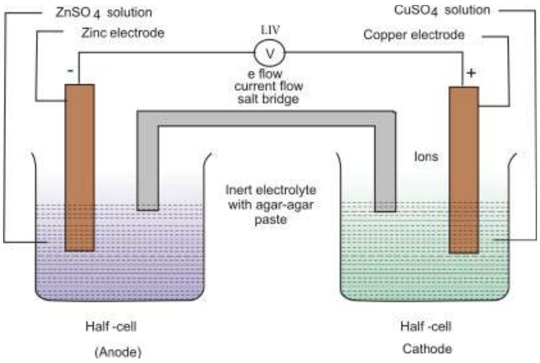
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

In the above reaction, Zn displaces copper ions (Cu^{2+}) from aqueous solution. This reaction can be achieved very easily in practice. Put a Zn rod into a solution of $CuSO_4$ (containing Cu^{2+} ions). It is observed that the blue colour of the $CuSO_4$ solution disappears after some time. In this situation, Zn loses 2 electrons per atom and Cu^{2+} ions in the solution accept them. Cu^{2+} ions from the solution in this manner are deposited in the form of solid Cu and Zn goes into the solution as Zn^{2+} (colourless). The reaction can be understood in terms of two half-reactions:

$$\text{Oxidation :} \quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

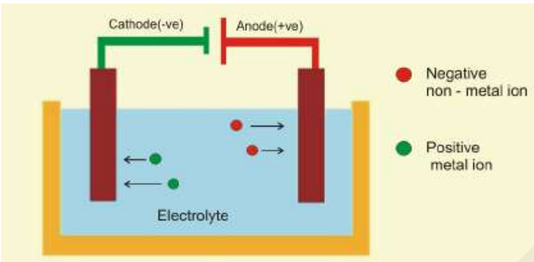
$$\text{Reduction :} \quad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Now, we can make the same reaction take place even if the copper ions and zinc rod are not in direct contact. If we put the Cu^{2+} ions and Zn rod in two separate containers connect the two by a conducting metallic wire and introduce an inverted U shape instrument (called a salt bridge), then electrons will still be transferred through the connecting wires. The electrons from the Zn rod travel to Cu^{2+} ions through the connecting wires and the same reaction takes place. This flow of electrons through the wire generates electricity.



Electrolysis

It is a process by which an electric current is passed through a substance to effect a chemical change. A chemical change is one in which the substance loses or gains an electron (oxidation or reduction). The process is carried out in an ***electrolytic cell***, an apparatus consisting of positive and negative electrodes held apart and dipped into a solution containing positively and negatively charged ions. The substance to be transformed may form the electrode, may constitute the solution or may be dissolved in the solution. Electric current enters through the negatively charged electrode (cathode); positively charged components of the solution travel to this electrode, combine with the electrons and are transformed to neutral elements or molecules. The negatively charged components of the solution travel to the other electrode (anode), give up their electrons and are transformed into neutral elements or molecules. If the substance to be transformed is the electrode, the reaction is generally one in which the electrode dissolves by giving up electrons.



4.Electrochemical Series

Li^+/Li	$Li^+(aq.) + e^- \longrightarrow Li(s)$	-3.04
K^+/K	$K^+(aq.) + e^- \longrightarrow K(s)$	-2.93
Ca^{2+}/Ca	$Ca^{2+}(aq.) + 2e^- \longrightarrow Ca(s)$	-2.87
Na^+/Na	$Na^+(aq.) + e^- \longrightarrow Na(s)$	-2.71
Mg^{2+}/Mg	$Mg^{2+}(aq.) + 2e^- \longrightarrow Mg(s)$	-2.37
$Pt, H_2/H^-$	$H_2(g) + 2e^- \longrightarrow 2H^-(aq.)$	-2.25
Al^{3+}/Al	$Al^{3+}(aq.) + 3e^- \longrightarrow Al(s)$	-1.66
Mn^{2+}/Mn	$Mn^{2+}(aq.) + 2e^- \longrightarrow Mn(s)$	-0.91
$OH^-/H_2, Pt$	$2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$	-0.83
Zn^{2+}/Zn	$Zn^{2+}(aq.) + 2e^- \longrightarrow Zn(s)$	-0.76
Cr^{3+}/Cr	$Cr^{3+}(aq.) + 3e^- \longrightarrow Cr(s)$	-0.74
Fe^{2+}/Fe	$Fe^{2+}(aq.) + 2e^- \longrightarrow Fe(s)$	-0.44
$Cr^{3+}/Cr^{2+}, Pt$	$Cr^{3+}(aq.) + e^- \longrightarrow Cr^{2+}(aq.)$	-0.41
Cd^{2+}/Cd	$Cd^{2+}(aq.) + 2e^- \longrightarrow Cd(s)$	-0.40
Co^{2+}/Co	$Co^{2+}(aq.) + 2e^- \longrightarrow Co(s)$	-0.28
Ni^{2+}/Ni	$Ni^{2+}(aq.) + 2e^- \longrightarrow Ni(s)$	-0.25
$I^-/AgI/Ag$	$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq.)$	-0.15
Sn^{2+}/Sn	$Sn^{2+}(aq.) + 2e^- \longrightarrow Sn(s)$	-0.14
Pb^{2+}/Pb	$Pb^{2+}(aq.) + 2e^- \longrightarrow Pb(s)$	-0.13
Fe^{3+}/Fe	$Fe^{3+}(aq.) + 3e^- \longrightarrow Fe(s)$	-0.04
$H^+/H_2, Pt$	$2H^+(aq.) + 2e^- \longrightarrow H_2(g)$	0.00
$Br^-/AgBr/Ag$	$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq.)$	0.10
$Cu^{2+}/Cu^+, Pt$	$Cu^{2+}(aq.) + e^- \longrightarrow Cu^+(aq.)$	0.16
$Sn^{4+}/Sn^{2+}, Pt$	$Sn^{4+}(aq.) + 2e^- \longrightarrow Sn^{2+}(aq.)$	0.15
$SO_4^{2-} + H_2SO_3$	$SO_4^{2-}(aq.) + 4H^+ + 2e^- \longrightarrow H_2SO_3(aq.) + H_2O(\ell)$	0.17
$Cl^-/AgCl/Ag$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq.)$	0.22
$Cl^-/Hg_2Cl_2/Hg(Pt)$	$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(\ell) + 2Cl^-(aq.)$	0.27
Cu^{2+}/Cu	$Cu^{2+}(aq.) + 2e^- \longrightarrow Cu(s)$	0.34

$Pt, O_2/OH^-$	$O_2(g) + 2H^+(aq.) + 2e^- \longrightarrow H_2O_2(aq.)$	0.40
Cu^+/Cu	$Cu^+(aq.) + e^- \longrightarrow Cu(s)$	0.52
$I_2/I^-, Pt$	$1/2I_2(s) + e^- \longrightarrow I^-(aq.)$	0.54
$Pt, O_2/H_2O_2$	$O_2(g) + 2H^+(aq.) + 2e^- \longrightarrow H_2O_2(aq.)$	0.68
$Fe^{3+}/Fe^{2+}, Pt$	$Fe^{3+}(aq.) + e^- \longrightarrow Fe^{2+}(aq.)$	0.77
$Hg_2^{2+}/Hg(Pt)$	$1/2Hg_2^{2+}(aq.) + e^- \longrightarrow Hg(s)$	0.79
Ag^+/Ag	$Ag^+(aq.) + e^- \longrightarrow Ag(s)$	0.80
Hg^{2+}/Hg_2^{2+}	$2Hg^{2+}(aq.) + 2e^- \longrightarrow Hg_2^{2+}(aq.)$	0.92
$NO_3^-/NO, Pt$	$NO_3^- + 4H(aq.) + 3e^- \longrightarrow NO(g) + 2H_2O(\ell)$	0.97
$Pt, Br_2/Br^-$	$Br_2(\ell) + 2e^- \longrightarrow 2Br^-(aq.)$	1.09
MnO_2/Mn^{2+}	$MnO_2(s) + 4H^+(aq.) + 2e^- \longrightarrow Mn^{2+}(aq.) + 2H_2O(\ell)$	1.23
$H^+/O_2/Pt$	$O_2(g) + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(\ell)$	1.23
$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \longrightarrow 2Cr^{3+}(aq.) + 7H_2O(\ell)$	1.33
Cl_2/Cl^-	$1/2Cl_2(g) + e^- \longrightarrow Cl^-(aq.)$	1.36
Au^{3+}/Au	$Au^{3+}(aq.) + 3e^- \longrightarrow Au(s)$	1.40
$MnO_4^-/Mn^{2+}, H^+/Pt$	$MnO_4^-(aq.) + 8H^+(aq.) + 5e \longrightarrow Mn^{2+}(aq.) + 4H_2O(\ell)$	1.51
$Ce^{4+}/Ce^{3+}, Pt$	$Ce^{4+} + e^- \longrightarrow Ce^{3+}(aq.)$	1.72
H_2O_2/H_2O	$H_2O_2(\ell) + 2H^+(aq.) + 2e^- \longrightarrow 2H_2O(\ell)$	1.78
$Co^{3+}/Co^{2+}, Pt$	$Co^{3+}(aq.) + e^- \longrightarrow Co^{2+}(aq.)$	1.81
O_3/O_2	$O_3(g) + 2H^+(aq.) + 2e^- \longrightarrow O_2(g) + H_2O(\ell)$	2.07
$Pt, F_2/F$	$F_2(g) + 2e^- \longrightarrow 2F^-(aq.)$	2.87

Characteristics of Electrochemical Series

Metals with greater negative E^o (reduction) are strongly electropositive and have more reactivity. It means a lower placed element or metal is in the given series is less reactive is replaced by upper placed or higher element while higher element can be coated by lower metal.

Example, (i) $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Here Cu is replaced by Zn due to more oxidation potential or reactivity of Zn, while Zn is coated by Cu. Zn- Cu couple is also coated by Cu. Here, the solution turns from blue to colorless and the rod becomes Reddish-brown from Gray white.

(ii) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

Here solution becomes colorless to blue and the rod becomes reddish-brown to white.

- Metals above H_2 can easily replace H_2, from acid, bases, etc. due to their more positive E^o_{op} or reactivity.

  For example,
  $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$
  E°_{op} of Mg $> E^\circ_{OP}$ of H_2
  $R - OH + Na \rightarrow R - ONa + H^+$
- Lower placed metals (Cu Hg Ag Pt Au) to H_2 can not do that as E^o_{op} of H_2 is more than their E^o_{op}.
  $Cu + H_2SO_4 \rightarrow$ no reaction
- Oxides of lower metals (Cu, Hg, Ag, Pt, Au) are easily reduced by H_2 or carbon. As they are thermally more unstable due to positive $E_{rp,}$ they also decomposed on heating.
- More E^o_{OP} means more ease or tendency to get oxidize that is, the act as better reducing agents while more E^o_{RP} means more ease to reduced that is, they act as better oxidizing agents. It means metal above hydrogen having positive E_{op} are reducing agents.

  Reducing property $\propto E^\circ_{OP}$

  For example, Li is the strongest reducing agent due to maximum E^o_{OP}
- Metals placed lower in reactivity series (Cu Hg Ag Pt Au) having high E^o_{RP} are oxidizing agents and they have tendency to be reduced.

  For example, Oxidizing power $\propto E_{RP}$
  $F_2 > Cl_2 > Br_2 > I_2$

  Reducing power decreases
  As E°_{op} of $I^- > Br^- > Cl^- > F^-$
- Elements with more positive E^o_{RP} will be discharged first at cathode i.e., discharging order increases as reduction potential increases.

  Increasing ease of deposition of some cations

  $Li^+, K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$
- In case of negative ions, anion with stronger reducing nature is discharged first at anode.

  Increasing ease of discharge of some anion
  $SO_4^{-2} < NO_3^- < OH^- < Cl^- < Br^-$
- Hydroxides of upper metals are strongly basic and their salts do not undergo hydrolysis while hydroxides of lower metals are weakly acidic and their salts undergo hydrolysis.

5.Faraday's Laws of Electrolysis

Faraday's First Law-

According to the Faraday's first law, "The amount of substance or quantity of chemical reaction at electrode is directly proportional to the quantity of electricity passed into the cell".

$$\mathrm{W \text{ or } m \propto q}$$

$$\mathrm{W \propto it}$$

$$\mathrm{W = Zit}$$

$$\mathrm{Z = \frac{M}{nf} = \frac{Eq.wt}{96500}}$$

$$\mathrm{Z = Electrochemical\ equivalent}$$

$$\mathrm{M = Molar\ Mass}$$

$$\mathrm{F = 96500C}$$

$$\mathrm{n = Number\ of\ electrons\ transfered}$$

$$\mathrm{q = amount\ of\ charge\ utilized}$$

Electrochemical equivalent is the amount of the substance deposited or liberated by one-ampere current passing for one second (that is, one coulomb of charge.)
One gram equivalent of any substance is liberated by one faraday.

$$\mathrm{Eq.\ Wt. = Z \times 96500}$$

$$\mathrm{\frac{W}{E} = \frac{q}{96500}}$$

$$\mathrm{w = \frac{E.q}{96500}}$$

$$\mathrm{W = \frac{Eit}{96500}}$$

As w = a x l x d that is, area x length x density
Here a = area of the object to be electroplated
d = density of metal to be deposited
l = thickness of layer deposited
Hence from here, we can predict charge, current strength, time, thickness of deposited layer etc.

NOTE: One faraday is the quantity of charge carried by one mole of electrons.

$$\begin{aligned} &\mathrm{1F = 1.6 \times 10^{-19} \times 6.023 \times 10^{23}} \\ &\mathrm{\simeq 96500\ Coulombs} \end{aligned}$$

Faraday's Second Law-

According to Faraday's second law, "When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights".

$$\mathrm{As\ \frac{W}{E} = \frac{q}{96500} = No\ of\ equivalents\ constant}$$

So

$$\mathrm{\frac{E_1}{E_2} = \frac{M_1}{M_2} or \frac{W_1}{W_2} = \frac{Z_1}{Z_2}}$$

$$\mathrm{E_1 = equivalent\ weight}$$

$$\mathrm{E_2 = equivalent\ weight}$$

$$\mathrm{W\ or\ M = mass\ deposited}$$

From this law, it is clear that 96500 coulomb of electricity gives one equivalent of any substance.

Application of Faraday's Laws

- It is used in the electroplating of metals.
- It is used in the extraction of several metals in pure form.
- It is used in the separation of metals from non-metals.

- It is used in the preparation of compounds

NOTE:
Current Efficiency: It is the ratio of the mass of the products actually liberated at the electrode to the theoretical mass that could be obtained

$$\text{C.E.} = \frac{\text{Actual mass of species liberated}}{\text{Theoretical mass of species liberated}} \times 100\%$$

6. Galvanic Cells

Galvanic Cells-

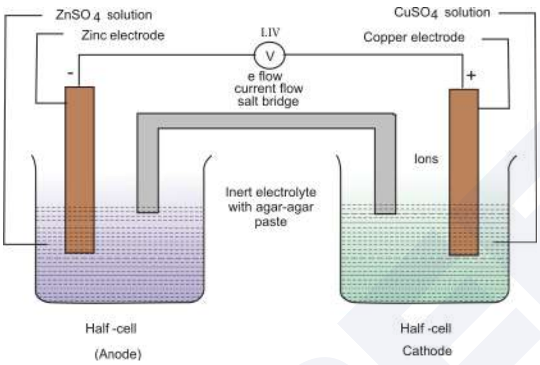
It is the device in which the decrease of free energy during the indirect redox reaction is made to convert chemical energy into electrical energy. Luigi Galvani and Alessandro Volta developed such devices therefore these cells are also known as Galvanic cells or Voltaic cell or Redox cells.

Species having a greater tendency of getting oxidised (greater oxidation potential value) is selected as the anode while species having a greater tendency of getting reduced (greater reduction potential value) is selected as cathode.

It is, however, conventional to deal in terms of the reduction potentials by default so, species with greater reduction potential is selected as Cathode and the one with lesser reduction potential is selected as cathode.

Feature	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Galvanic Cell



- The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.
- The Daniel cell can be conventionally represented as
  $\mathrm{Zn(s)}\,|\mathrm{ZnSO_4(aq)}||\,\mathrm{CuSO_4(aq)}|\,\mathrm{Cu(s)}$
  $\qquad\qquad\text{Saltbridge}$
- The Daniel cell reaction is represented as:
  $\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)}$
- In Daniel's cell, electrons flow from zinc electrode to copper electrode through the external circuit while metal ions flow form one-half cell to the other through a salt bridge.
- Here current flows from the copper electrode to zinc electrode that is, cathode to anode in an external circuit.
- Daniel cell is a reversible cell while a voltaic cell may be reversible or irreversible depending upon the e.g. if one of the products is gaseous and escapes, then the cell is not reversible.

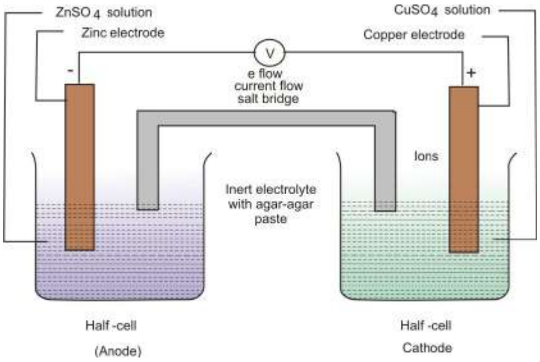
Electrochemical Cell	Electrolytic Cell
It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
The anode is negative, the cathode is positive	The anode is positive, the cathode is negative
Electrons move from anode to cathode in the external circuit.	Electrons enter through cathode and leave through the anode.
It converts chemical energy into electrical energy, produced as a result of a redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
The cell reaction is spontaneous.	Cell reaction is non-spontaneous.
Salt bridge is required.	No salt bridge is required.

Problem in Galvanic Cells and Salt Bridge-

- On anode side in galvanic cell, the electrons move towards the cathode side and Zn^{2+} ions go to the electrolytic solution. Due to this after some time, the large amount of Zn^{2+} ions accumulates near the negatively charged electrode and thus prevents the flow of the electrons.
- Similarly, on the cathode side, Cu^{2+} ions get the electrons and convert to Cu. Due to this, after some time, a large amount of SO_4^{2-} ions accumulate near the positively charged electrode. Since SO_4^{2-} ions are negatively charged, thus they repel the incoming electrons towards the positively charged electrode.

Thus because of this hindrance to the movement of electrons, the current will stop to flow and the cell will not work anymore. Thus to remove this problem in a galvanic cells, we use the salt bridge.

Salt Bridge
Salt bridge is an inverted U-Tube glass vessel. In salt bridge, there is an inert electrolyte like KCl, K_2SO_4, KNO_3, NH_4Cl, etc. This inert electrolyte is mixed with agar-agar solution and gel-like substance is prepared to make the movement of ions easier.
Now this inverted U-Tube vessel in place in the cell and then Cl^- starts to move towards the anode side or positively charged solution and neutralize it. Similarly, K^+ ions start to move towards the cathode side or negatively charged solution and neutralize it. Thus after the neutralization of both solutions, electrons will flow and the cell will start working.



7. Function of Salt Bridge and Condition

It maintains electrical neutrality in two compartments by allowing the movement of anions towards the anodic compartment and cations towards the cathodic compartment.

- It is a glass tube having KCl, KNO_3, and ammonium nitrate in a gelatin gel or agar-agar paste.
- The gelatin gel allows ionic movement through it but prevents any kind of mixing.
- In the case of KCl or ammonium nitrate, the ionic mobility of cation and anion are the same.

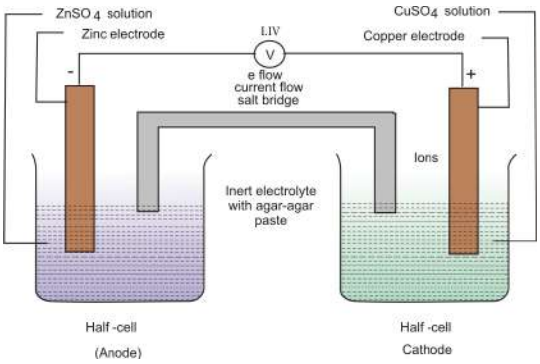
The function of a Salt Bridge

- A salt bridge acts as an electrical contact between the two half-cells.
- It prevents the mechanical flow of the solution but it provides a free path for the migration of ions to maintain an electric current through the electrolyte solution. It prevents the accumulation of excess charges.
- A salt bridge helps maintain the charge balance in the two half-cells.
- A salt bridge minimizes/eliminates the liquid junction potential.
  Liquid Junction Potential: The unequal rates of migration of the cations and anions across a liquid-liquid junction give rise to a potential difference across the junction. This potential difference across the liquid-liquid junction is called liquid junction potential.

NOTE: If the salt bridge is removed the emf of the cell drops to zero.

- Sometimes, both the electrodes are dipped into the same electrolytic solution. in such a case, there is no requirement for a salt bridge.

Cell Representation of Galvanic Cells-



- The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.

- The Daniel cell can be conventionally represented as

$$\underset{\text{Saltbridge}}{\mathrm{Zn(s)\,|ZnSO_4(aq)|\,|CuSO_4(aq)|\,Cu(s)}}$$

- The Daniel cell reaction is represented as

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

- In Daniel cell, electrons flow from zinc electrode to copper electrode through external circuit while metal ions flow form one half cell to the other through salt bridge.
- Here current flows from copper electrode to zinc electrode that is, cathode to anode in external circuit.
- Daniel cell is a reversible cell while a voltaic cell may be reversible or irreversible.
  A voltaic cell is reversible only when it satisfies following conditions:
- The emf of external source is more than that of voltaic cell so that current may flow from external source into the voltaic cell and cell reaction can be reversed.
- If emf of voltaic cell is more than that of external source current flows from voltaic cell into external source.

8. EMF of a Cell

It is the potential difference between the two terminals of the cell when no current is drawn from it. It is measured with the help of potentiometer or vacuum tube voltmeter.

Calculation of the EMF of the Cell
Mathematically, it may be expressed as

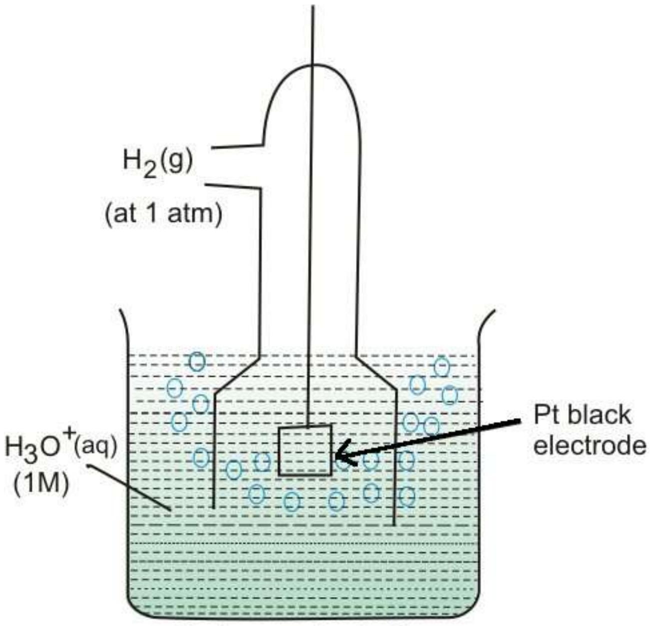
$$\mathrm{E_{cell}\ \text{ or } EMF = [E_{red}\ (\text{ cathode }) - E_{red}\ (\text{ anode })]}$$
$$\mathrm{E^\circ_{cell}\ \text{ or } EMF^\circ}$$
$$\mathrm{= [E^\circ_{red}\ (\text{ cathode }) - E^\circ_{red}\ (\text{ anode })]}$$

- Characteristics of cell and cell potential.
- For cell reaction to occur the E_{cell} should be positive. This can happen only if E_{red} (cathode) > E_{red}(anode).
- E^o cell must be positive for a spontaneous reaction.
- It measures free energy change for maximum convertibility of heat into useful work.
- It causes the flow of current from the electrode of the higher E^o value to the lower E^o value.

Difference between EMF and Cell Potential

EMF	Cell Potential
It is measured by a potentiometer.	It is measured by a voltmeter.
It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the potential difference between two electrodes when a current is flowing through the circuit.
It is maximum voltage obtained from cell.	It is less than maximum voltage.
It corresponds to the maximum useful work obtained from the galvanic cells.	It does not correspond to maintain useful work obtained from Galvanic Cell

9. Standard Hydrogen Electrode



Hydrogen electrode

A hydrogen electrode in which the pressure of hydrogen gas is maintained at 1 atm and the concentration of H^+ ions in the solution is 1M, is called a standard hydrogen electrode (SHE).

SHE half reaction	Electrode potential
$H_2 \rightarrow 2H^+ + 2e^-$	$0.0V(Anode)$
$2H^+ + 2e^- \rightarrow H_2$	$0.0V(Cathode)$

- The emf of a standard hydrogen electrode is taken as 0.00 V at all temperatures.
- It is a reversible electrode.
- It is used as a primary reference electrode.
- The potential of other species can be calculated by conducting a cell with SHE as one of the electrodes and then calculating the potential difference by various methods.

10. Feasibility and Gibbs Free Energy of Reaction

Let n faraday charge be involved in a cell generating an emf E, then the magnitude of the work done by the cell will be calculated as:
|Work| = Charge × Potential = $(nF) \times (E)$

Now, the maximum work that can be extracted from the cell is equal to the decrease in Gibb's free energy.

So, it can be said that

$$-\Delta G = nFE$$

The negative sign is incorporated to include the spontaneity relation between E and Gibb's Free Energy

Similarly, the maximum obtainable work from the cell at standard conditions will be:

$$W_{max} = nFE^0_{cell} \quad \text{where } E^0_{cell} = \text{ standard emf of standard cell potential}$$

$$-\Delta G^\circ = nFE^0_{cell}$$

Thus, for a spontaneous cell reaction,

E > 0 and $\Delta G < 0$

11. Nernst Equation

Nernst Equation-

This equation gives the relationship between electrode potential and the concentration of ions in the solution. In other words, it shows the dependency of electrode potential on the concentration of the ions with which the electrode is reversible.

For a single electrode involving the reduction process,

$$M^{n+} + ne^- \rightarrow M(s)$$

The reaction quotient Q is defined as $\frac{a_M}{[M^+]}$

Now, we learned in thermodynamics that

$\Delta G = \Delta G^o + RT \ln Q$ ..**(1)**

Where $\Delta G = -nFE$

and $\Delta G^o = -nFE^o$

So, substituting these values is (1),

$-nFE = -nFE^o + RT \ln Q$

$\Rightarrow E = E^o - \frac{RT}{nF} \ln Q$

$\Rightarrow E = E^o - \frac{2.303RT}{nF} \log Q$

This is the Nernst equation which helps us to calculate the non-standard EMF of any Half cell. It can be extended to full of any half cell. It can be extended to full cell which we will be learning later.

Now, at 25°C or 298K

$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log_{10} \frac{[M]}{[M^{n+}]}$

$E = E^\circ - \frac{0.059}{n} \log_{10} \frac{[M]}{[M^{n+}]}$

Here R = Gas constant

T = Absolute temperature

E° = Standard Emf of the cell

E = Electrode potential of cell

F = Faraday number

n = number of electrons transferred

- If the electrode is solid its activity mass is taken as one.
- For an electrochemical cell having net reaction:
  $xA + yB \xrightarrow{ne^-} mC + nD$
  The emf can be calculated as
  $E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[C]^m[D]^n}{[A]^x[B]^y}$

In using the above equation, the following facts should be kept in mind.

- The activity of aq. ions are expressed in terms of their concentration.
- Activity of gases is expressed in terms of their partial pressures.
- The activity of solids is taken to be unity.
- n, the number of electrons transferred should be calculated from the balanced net cell reaction.

Nernst Equation for Full Cell-

$E^o_{M^{x+}|M} = Q$ and $E^o_{N^{x+}|N} = P$

In the full cell both the oxidation and reduction reactions occur simultaneously. Thus, the full cell can be represented as follows:

$M \mid M^{x+} \mid N^{x+} \mid N$

The electrode potential values for oxidation and reduction are as follows:

$E^o_{M^{x+}|M} = Q$ and $E^o_{N^{x+}|N} = P$

At Anode:

$M(s) \rightarrow M^{+x}(aq) + xe^-$

At Cathode:

$N^{x+}(aq) + xe^- \rightarrow N(s)$

Thus the complete cell reaction is the addition of both anode and cathode reaction. It given as below:

$$\mathrm{M(s)\ +\ N^{x+}(aq)\ \rightarrow\ M^{x+}(aq)\ +\ N(s)}$$

Thus the reaction quotient(Q) can be given as follows:

$$\mathrm{Q\ =\ \frac{[M^{x+}]}{[N^{x+}]}\ =\ \frac{c_1}{c_2}}$$

where c_1 and c_2 are the concentrations of M^{x+} and N^{x+} respectively.

The standard potential of cell is given as:

$$\mathrm{E^o_{cell}\ =\ [E^o_{cathode}\ -\ E^o_{anode}]}$$

$$= \mathrm{P - Q}$$

At T = 298K, Nernst equation is given as follows:

$$\mathrm{E_{cell}\ =\ E^o_{cell}\ -\ \frac{0.059}{n}log_{10}Q}$$

where n is the number of electrons exchanged.

Thus the Nernst equation for the full cell is given as follows:

$$\mathrm{E_{cell}\ =\ (P - Q) -\ \frac{0.059}{x}log_{10}\frac{c_1}{c_2}}$$

Equilibrium Constant Through Nernst Equation-

If the circuit in Daniell cell is closed then we note that the reaction

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time, the voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, the voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation, the Nernst equation may be written as:

$$\mathrm{E_{(cell)}\ = 0 = E^{\ominus}_{(cell\ )}\ -\ \frac{2.303RT}{2F}\log\frac{[Zn^{2}]}{[Cu^{2+}]}}$$

$$\mathrm{or\ E^0_{(cell\ )}\ =\ \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

But at equilibrium,

$$\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]} = \mathrm{K_c} \text{ for the above reaction}$$

and at $T = 298K$ the above equation can be written as

$$\mathrm{E^{\ominus}_{(cell\ )} = \frac{0.059V}{2}\log K_C = 1.1V \quad (E^{\ominus}_{cell}\ = 1.1V)}$$

$$\mathrm{\log K_C = \frac{(1.1V \times 2)}{0.059V} = 37.288 \simeq 37.3}$$

$$\mathrm{K_C = 2 \times 10^{37}\ at\ 298K}$$

In general,

$$\mathrm{E^{\ominus}_{(cell\ )}\ = \frac{2.303RT}{nF}\log K_C}$$

Alternatively

$$\Delta G = \Delta G^o + RT\ln Q$$

At equilibrium, $\Delta G = 0$ and $Q = K$, so.

$$0 = \Delta G^o + RT\ln K$$

$$\Delta G^o = -RT\ln K$$

$$\Delta E^o = \frac{2.303RT}{nF}\ln K$$

$$\ln K = \frac{nE^o}{0.059}$$

Thus, the above equation gives a relationship between the equilibrium constant of the reaction and the standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding E^o value of the cell.

12. Concentration Cells

Concentration Cells-

The device in which both the half cells contain the same electrode but differ in the concentration (or activity) of the species involved. Oxidation and reduction occur at respective electrodes until the concentration becomes equal in both the half cells. In other words, the concentration cell is one in which emf arises as a result of different concentrations of the same electrolyte in the component half-cells.

- The two solutions are connected by a salt bridge and the electrodes are joined by a piece of metallic wire.
- A concentration cell dilutes the concentrated solution and concentrates the more dilute solution and generate potential till the cell reaches an equilibrium.
- The potential is generated due to a decrease in Gibb's energy of cell till the attainment of equilibrium.
- E^o of a concentration cell is equal to zero where the E_{cell} depends upon the concentration (on acting of species involves).

Let us consider the given concentration cell,

$$\underset{}{Cu(s)} \;|\; \underset{C_1M}{Cu^{2+}} \;||\; \underset{C_2M}{Cu^{2+}(aq.)} \;|\; Cu(s)$$

For the above cell to be working, $E_{cell} > 0$

Therefore, From Nernst Equation:

$$\mathrm{E_{cell}} = \mathrm{E^o_{cell}} - \frac{0.059}{2}\log\frac{c_1}{c_2}$$
$$\mathrm{E_{cell}} = \mathrm{E^o_{cell}} - \frac{0.059}{2}\log\frac{c_1}{c_2}$$
$$\mathrm{E_{cell}} = 0 + \frac{0.059}{2}\log\frac{c_2}{c_1} > 0$$

$$\Rightarrow c_2 > c_1$$

Concentration Cell With Respect to S.H.E-

The cell representation of the concentration cell with respect to hydrogen is given as follows:

$$Pt| \;\underset{P_1}{H_2(g)} \;|\; \underset{C_1}{H^+(aq)} \;||\; \underset{C_2}{H^+(aq)} \;|\; \underset{P_2}{H_2(g)} \;|Pt$$

At anode:

$$\frac{1}{2}\mathrm{H_2} \rightarrow \mathrm{H^+} + 1\mathrm{e^-}$$

At cathode:

$$\mathrm{H^+} + 1\mathrm{e^-} \longrightarrow \frac{1}{2}\mathrm{H_2}$$

The complete cell reaction is the addition of both of these reactions and is given as follows:

$$\frac{1}{2}\mathrm{H_2(g)} \;+\; \mathrm{H^+(aq)} \rightarrow \mathrm{H^+(aq)} \;+\; \frac{1}{2}\mathrm{H_2(g)}$$

Thus, the reaction quotient is given as follows:

$$\mathrm{Q} \;=\; \frac{[\mathrm{H^+}][\mathrm{P_{H2}}]^{1/2}}{[\mathrm{H^+}][\mathrm{P_{H2}}]^{1/2}} \;=\; \frac{\mathrm{c_1(P_2)^{1/2}}}{\mathrm{c_2(P_1)^{1/2}}}$$

where P_1 and P_2 are the pressures of hydrogen gas at anode and cathode, respectively.

Now, we have:

$$\mathrm{E^o_{cell}} \;=\; 0$$
$$\mathrm{n} \;=\; 1$$

Thus, at T = 298K, the cell equation can be given as follows:

$$E_{cell} = -\frac{0.059}{n}\log_{10}Q$$

$$E_{cell} = \frac{0.059}{1}\log_{10}\frac{c_1}{c_2} x \left(\frac{P_2}{P_1}\right)^{1/2}$$

$$E_{cell} = -\frac{0.059}{1}\left[\log_{10}[H^+]_A - \log_{10}[H^+]_c + \log_{10}\left(\frac{P_2}{P_1}\right)^{1/2}\right]$$

$$E_{cell} = 0.059\left[-\log_{10}[H^+]_A - (-\log_{10}[H^+]_c) - \log_{10}\left(\frac{P_2}{P_1}\right)^{1/2}\right]$$

$$E_{cell} = 0.059\left[pH_{(anode)} - pH_{(cathode)} - \frac{1}{2}\log_{10}\left(\frac{P_2}{P_1}\right)\right]$$

$$E_{cell} = 0.059\left[pH_{(anode)} - pH_{(cathode)} + \frac{1}{2}\log_{10}\left(\frac{P_1}{P_2}\right)\right]$$

This is the final equation for the value of E_{cell} for concentration cell with respect to standard hydrogen electrode.

Conductance of Electrolytic Solutions-

It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol 'R' and it is measured in ohm (Ω). It can be measured with the help of a Wheatstone bridge with which you are familiar with your study of physics. The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross-section, A. That is,

$$R \propto \frac{l}{A} \text{ or } R = \rho\frac{l}{A}$$

The constant of proportionality, ρ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm meter (Ω m) and quite often its submultiple, ohm centimeter (Ω cm) is also used.

The inverse of resistance, R, is called conductance, G, and we have the relation:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are $S\ m^{-1}$ but quite often, κ is expressed in $S\ cm^{-1}$. The conductivity of a material in $S\ m^{-1}$ is its conductance when it is 1 m long and its area of cross-section is 1 m^2. It may be noted that 1 $S\ cm^{-1}$ = 100 $S\ m^{-1}$.

The quantity l/A is called cell constant and is denoted by the symbol G*. It depends upon the distance between electrodes and the area of cross-section. On the basis of their definition, the conductance(G), Conductivity(κ) and cell constant (G*) are related as:

$$\kappa = G \times G^* = G \times \frac{l}{A}$$

Now, when l=1 cm^2 then v=1 cm^3 = 1 ml.

So, κ can also be represented as the conductance of 1 ml of the electrolytic solution in the consistent set of units.

It has been observed that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators, and semiconductors depending on the magnitude of their conductivity.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on:
(i) the nature and structure of the metal
(ii) the number of valence electrons per atom
(iii) temperature (it decreases with the increase in temperature).

The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:
(i) the nature of the electrolyte added
(ii) size of the ions produced and their solvation
(iii) the nature of the solvent and its viscosity
(iv) the concentration of the electrolyte
(v) temperature (it increases with the increase in temperature).
Passage of direct current through an ionic solution over a prolonged period can lead to a change in its composition due to electrochemical reactions and hence alternating current is used for the measurement of conductance.

13. Molar Conductivity

Molar Conductance
The molar conductance is defined as the conductance of all the ions produced by the ionisation of 1 mole of an electrolyte when present in V ml of solution. It is denoted by Λ_m.

$$\text{Molar conductance } (\wedge_{\mathrm{m}}) = \kappa \times \mathrm{V}$$

where V is the volume in ml containing 1 gm mole of the electrolyte.
If c is the concentration of the solution in mole per litre, then:

$$\wedge_{\mathrm{m}} = \kappa \times \frac{1000}{\mathrm{c}}$$

where c is the concentration of the solution in M. The units of Λ_m are ohm^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1} When the units of κ is S cm^{-1}.

It is to be noted that changing the units of the quantities involved will lead to a change in the formula. For the sake of homogeneity, $\Lambda_m = \frac{\kappa}{C}$ when all the quantities are expressed in their SI unit.

Also, if A_xB_y is an electrolyte dissociating as:

$$\mathrm{A_xB_y} \rightleftharpoons \mathrm{xA^{y+}} + \mathrm{yB^{x-}}$$

$$\text{Thus, } \wedge_{\mathrm{m}} \mathrm{A}_x\mathrm{B_y} = x \cdot \wedge_{\mathrm{m}}\left(\mathrm{A}^{y+}\right) + \mathrm{y} \cdot \wedge_{\mathrm{m}}\left(\mathrm{B}^{x-}\right)$$

Equivalent Conductance
One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductance.
It is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by Λ_{eq}.

$$\wedge_{\mathrm{eq}} = \frac{1000 \times \kappa}{\mathrm{N}}$$

If 'V' is the volume in ml containing 1 gm equivalent of the electrolyte, the above equation can be written as:

$$\wedge_{\mathrm{eq}} = \kappa \times \mathrm{V}$$

Its units are ohm^{-1} cm^2 equiv^{-1} or S cm^2 equiv^{-1}. A similar constraint of units exists in the formula as that in molar conductance.
Equivalent conductance is also given as follows:

$$\text{Equivalent conductance } = \frac{\text{Molar conductance}}{x},$$

$$\text{where } x = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \mathrm{n}-\text{factor}$$

Effect of Dilution on Conductance, Λ_m , Λ_{eq} and Conductivity-

Effect on conductance

- The conductance of a solution increases with an increase in the number of solute molecules/ions and decreases with decrease in the number of solute molecules/ions.
- Conductance of a solution increases with dilution as the interactions between the molecules/ions decreases due to increase in the average distance between the molecules/ions.

Effect on degree of dissociation

- **Strong electrolytes:** There is almost no change in the degree of dissociation (as it is already close to unity).
- **Weak electrolytes:** With dilution, degree of dissociation increases rapidly and thus, the number of molecules increases.

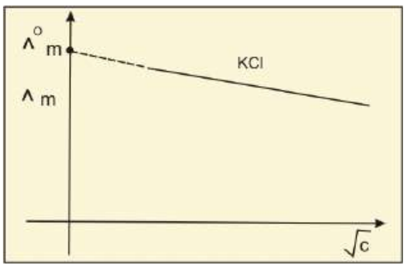
Effect on Molar and Equivalent conductance
Both Λ_m and Λ_{eq} increases with dilution as conductance increases with dilution.
For strong electrolytes, the increase in Λ_m and Λ_{eq} is relatively small as increase in the number of molecules/ions is very small.
For weak electrolytes, the increase in Λ_m and Λ_{eq} is large and rapid as α (degree of dissociation) increases with dilution.

Effect on Conductivity
On dilution, the number of molecules/ions per ml of the solution decreases. Since conductivity is defined as the conductance of one ml of the solution, conductivity decreases with dilution (due to a decrease in the conductance).

Molar Conductance at Infinite Dilution-

When the addition of water doesn't bring about any further change in the conductance of a solution, this situation is referred to as Infinite Dilution.

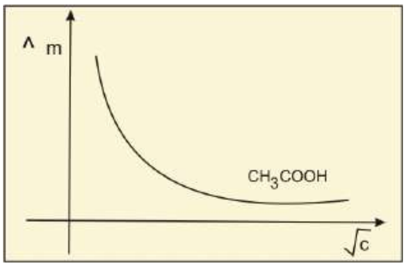
- **Strong Electrolytes:** When infinite dilution is approached, the conductance of a solution of strong electrolyte approaches a limiting value and can be obtained by extrapolating the curve between Λ_m and c$^{1/2}$ as shown in the figure given below:



The molar conductivity of strong electrolytes is found to vary with concentration as:
$\Lambda_m = \lambda_m^0 - B\sqrt{c}$
where B is a constant depending upon the type of electrolyte, the nature of the solvent, and the temperature. This equation is known as the Debye Huckel-Onsage equation and is found to hold good at low concentrations.

All electrolytes having same formula type have the same value of B e.g. (KCl, NaCl) and ($CaCl_2$, $MgCl_2$)

- **Weak Electrolytes:** When infinite dilution is approached, the conductance of a solution of the weak electrolyte increases very rapidly and thus, cannot be obtained through extrapolation. Also, the variation between Λ_m and $c^{1/2}$ is not linear at low concentrations.



14. Kohlrausch's Law

Kohlrausch's Law-

Kohlrausch examined Λ^o or Λ^∞ values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ^o of the electrolytes NaX and KX for any X in nearly constant.
On the basis of these observations he introduced Kohlrausch law of Independent Migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte that is, at infinite dilution, the contribution of any ion towards equivalent conductance is constant; it does not depend upon presence of any ion.

For any electrolyte:

$$P_XQ_Y \rightarrow XP^{+Y} + YQ^{-X}$$

$$\Lambda^\circ(P_XQ_Y) = X\lambda^\circ_{P+Y} + Y\lambda^\circ_{Q-X}$$

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

$$\Lambda_m^\infty(CH_3COOH) = (\lambda_{H^+}^\infty + \lambda_{Cl^-}^\infty) + \left(\lambda_{CH_3COO^-}^\infty + \lambda_{Na^+}^\infty\right) - (\lambda_{Na^+}^\infty - \lambda_{Cl^-}^\infty)$$

$$= \Lambda_{HCl}^\infty + \Lambda_{CH_3COONa}^\infty - \Lambda_{NaCl}^\infty$$

Application of Kohlrausch's Law

- **Determination of Λ_M^o of a weak electrolyte:**
  In the case of weak electrolytes, the degree of ionization increases which increases the value of Λ_m. However, it cannot be obtained by extrapolating the graph. The limiting value, Λm^∞, for weak electrolytes can be obtained by Kohlrausch law.

- To determine the degree of dissociation and equilibrium constant of weak electrolyte:

$CH_3COOH \rightleftharpoons$	$CH_3COO^- +$	H^+
C	0	0
C-Cα	Cα	Cα

Here C = Initial concentration

α = Degree of dissociation

$$\alpha = \frac{\Lambda_M}{\Lambda_M^o}$$

Here Λ° or Λ^∞ = Molar conductance at infinite dilution or zero concentration.

Λ_M = Molar conductance at given conc. C

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$K=\frac{C\alpha^2}{1-\alpha}=\frac{C\cdot\left(\Lambda/\Lambda_M^o\right)^2}{\left(1-\Lambda/\Lambda_M^o\right)^2}=\frac{C\Lambda_M^2}{\Lambda^o(\Lambda^o-\Lambda_m)}$$

These are Ostwald's relations.

- To determine solubility of salt and K_{sp}:

$$AgCl(s)\rightleftharpoons Ag^++Cl^-$$

If the solubility of AgCl be M and the K and Λ^o have values in $S\ cm^{-1}$ and $S\ cm^2mol^{-1}$, then

$$\Lambda^\circ=\frac{1000K}{M}$$

$$\Lambda^\circ=\lambda^\circ Ag^++\lambda^\circ Cl^-$$

$$M=\frac{1000K}{\Lambda^\circ}$$

- Here $M=$ Solubility of AgCl

Solubility product:

$$Ksp=\left[Ag^+\right]\left[Cl^{-1}\right]$$

$$\text{As }\left[Ag^+\right]=\left[Cl^-\right]$$

$$Ksp=\frac{1000K}{\Lambda^\circ}\times\frac{1000K}{\Lambda^\circ}$$

$$Ksp=(1000K/\Lambda^\circ)^2$$

15. Types Of Battery - Primary cell & Secondary cell

Batteries-

Primary Cells
In such cells, redox reaction occurs only once so cells can not be recharged again. The cell becomes dead after some time as electrode reactions cannot be reversed. For example, dry cells and mercury cells.

- **Dry Cell**
  - It is a compact form of the Lechlanche cell.
  - It has anode of Zn-container and cathode of graphite rod surrounded by MnO_2 + carbon.
  - Here a paste of NH_4Cl and $ZnCl_2$ is filled in between the electrodes.

    Cell Reactions
    At anode:
    $Zn(s)\rightarrow Zn^{+2}(aq)+2e^-$
    At cathode:
    $2MnO_2(s)+2NH_4^+(aq)+2e^-\rightarrow Mn_2O_3(s)+2NH_3(g)+H_2O$
  - Zn^{+2} combines with NH_3 to form diammine Zn(II) cation.
  - Dry cell has short life as NH_4Cl (acidic) corrodes the Zn-container even if the cell is not in use.
  - The cell potential is 1.25 to 1.5 volt

- **Mercury Cell**
  - In commonly used mercury cell the reducing agent is zinc and the oxidizing agent is mercury(II) oxide.

    Cell Reactions
    At anode:
    $Zn(Hg)+2OH^-\rightarrow ZnO(s)+H_2O+2e^-$

    At cathode:
    $HgO+H_2O+2e^-\rightarrow Hg(l)+2OH^-$

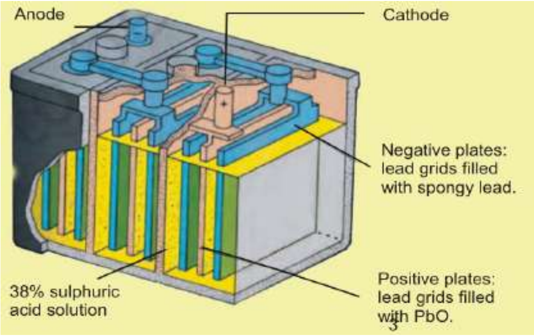
    The overall reaction is:
    $Zn(Hg)+HgO(s)\rightarrow ZnO(s)+Hg(l)$
  - The cell potential is approximately 1.35 V and remains constant throughout its life as the overall reaction does not involve any ion, whose concentration can change during its lifetime. It is used in hearing aids, watches etc.

Secondary Batteries-

It can be recharged by passing current to use again as electrode reactions are reversible. Examples, lead storage battery, Ni-Cd storage cell. Electrochemical cell used as battery. The voltage provided by the battery is the sum of the individual voltage of cells.

Types of Batteries: Batteries are of the following types:

- **Lead Storage Batteries:** Six cells are connected in series, each cell is provided 2V so the total volt provided by the battery is 12V. The anode, a series of lead grids packed with spongy lead and the cathode, a series of grids packed with lead dioxide 38% by weight H_2SO_4 act as an electrolyte.

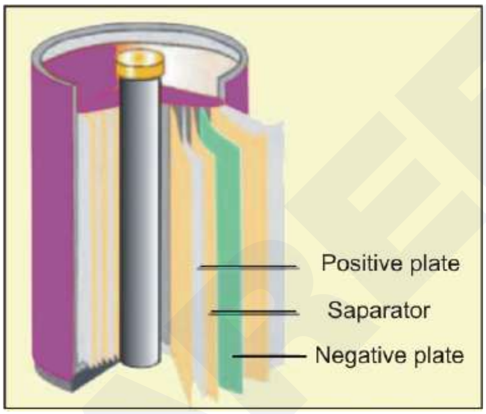


Cell reaction
At anode:
$\mathrm{Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + 2H^+ + 2e^-}$
$\mathrm{E^\circ = 0.296V}$

At cathode:
$\mathrm{PbO_2(g) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow 2PbSO_4(s) + 2H_2O(l)}$
$\mathrm{E^\circ = 1.628V}$

Net Reaction
$\mathrm{Pb(s) + PbO_2(s) + 2H^+ + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(s)}$
$\mathrm{E^\circ = 1.924V}$

- **Nickel-Cadmium Cell:**
A rechargeable nickel-cadmium cell is a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.



The overall cell reaction during the discharge is

$\mathrm{Cd(s) + 2Ni(OH)_2(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)}$

Solutions

Important Formulae

1. Types of Solutions

The solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits. A solution that contains only two components is called a binary solution. The component which has the same physical state as the solution is the solvent. In case both the components have the same physical state, then the component which is present in a larger amount is called the solvent and the other present in a smaller amount is called the solute.

The solutions may be gaseous, liquids, and solids. The most common type of solution is the liquid solution (gas in liquid, liquid in liquid, solid in liquid). In all, we can divide solutions into nine different classes as follows:

Types of solutions	Solute	Solvent	Examples
Gaseous Solutions	Gas	Gas	Air, mixture of gases
	Liquid	Gas	Water in air, Bromine in Chlorine
	Solid	Gas	Iodine in air, Camphor in air
Liquid Solutions	Gas	Liquid	HCl in water
	Liquid	Liquid	Alcohols in water, Bromine in CS_2
	Solid	Liquid	Sugar solution in water, Salt in water
Solid Solutions	Gas	Solid	Hydrogen in Palladium
	Liquid	Solid	Mercury in Zinc
	Solid	Solid	Gold in Silver, All Alloys

2. Concentration Terms

The concentration of a solution gives us an idea about the relative amount of solute and solvent present in the solution. The concentration can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in reality, the qualitative description can cause confusion, and hence there is a need for a quantitative description of the solution.

There are several ways by which we can describe the concentration of the solution quantitatively.

(1) Mass percentage (w/w):

It is the mass of any component present in 100 g of solution.

Mathematically, it can be defined as:

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

For example, a solution described by 20% by mass of glucose in water, it means that 20 g of glucose is dissolved in 80 g of water resulting in a 100 g solution.

The mass % can also be expressed in terms of the mass fraction by simply removing the 100 from the above given formula

Concentration described by mass percentage is commonly used in industrial chemical applications.

(2) Volume percentage (V/V):

It is the volume of any solute present in 100 ml of the solution. Mathematically it is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$

For example, a 20% Methanol solution in water means that 20 mL of Methanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit.

(3) Mass by volume percentage (w/V):

It is the mass of solute dissolved in 100 mL of the solution. Mathematically, it is defined as:

$$\text{Mass by Volume \% of a component} = \frac{\text{Mass of the component}}{\text{Total volume of solution}} \times 100$$

For example, a 20% weight by volume solution of Glucose in water means that 20 g of Glucose was dissolved in water to obtain a 100ml solution.

This concentration term is commonly used in medicine and pharmacy.

(4) Parts per million (ppm):

When a solute is present in trace quantities, it is convenient to express concentration in parts per million (ppm) and is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume, and mass to volume.

This is generally used in expressing the hardness of water and in expressing the concentration of dissolved oxygen in water etc.

For example, if the hardness of a hard water sample is 100pm in $CaCO_3$, it means that 100 g of $CaCO_3$ is present in 10^6 g of the water sample.

(5) Mole fraction:

It is the ratio of the moles of any component present in solution to the total moles present in solution. A commonly used symbol for mole fraction is X and the subscript used on the right-hand side of X denotes the component.

It is defined as:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

For example, in a binary mixture, if the number of moles of A and B is n_A and n_B respectively, the mole fraction of A will be:

$$x_i = \frac{n_1}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i}$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \ldots\ldots\ldots\ldots\ldots + x_i = 1$$

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution, and quite useful in describing the calculations involving gas mixtures.

(6) Molality(m):

It is defined as the number of moles of the solute present per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

For example, 1 molal solution of NaOH means that 1 mol (40 g) of NaOH is dissolved in 1 kg of water.

(7) Molarity (M):

It is defined as the number of moles of solute dissolved in one litre of solution

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

For example, 0.5 mol L^{-1} (or 0.5 M) solution of NaOH means that there is 0.5 mol of NaOH dissolved in water to obtain one litre of solution.

Each method of expressing the concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction, and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and mass does not.

3. Vapour Pressure of solutions

It is the pressure exerted by vapours of a pure liquid over its surface when they are in equilibrium with the liquid at a given temperature. For example, if we take the case of water, then the equilibrium constant of the following physical process will represent the Vapor Pressure of Water (Also sometimes called Aqueous Tension).

$$H_2O(l)) \rightleftharpoons H_2O(g), K_p = P^o$$

At equilibrium, the rate of vaporisation = the rate of condensation and the equilibrium constant of the above vapour-liquid equilibrium represents the vapour pressure of the liquid.

It depends upon the nature of the liquid and temperature. Pure liquid has always a vapour pressure greater than its solution.
The vapour pressure of a liquid helps us to have an idea of forces of attraction amongst the molecules of liquid that is, the more the force of attraction, the lower the vapour pressure and vice versa.
The vapour pressure of a liquid increases with an increase in temperature due to an increase in the kinetic energy of solvent molecules that is, an increase in evaporation however it is independent of the nature of the vessel.

Vapour Pressure of a Solution
When a miscible solute is added to a pure solvent, it results in the formation of a solution. As some molecules of solute will replace the molecules of the solvent from the surface, therefore, escaping tendency of solvent molecules decreases. This causes a lowering of vapour pressure.

- The vapour pressure of a solution is less than that of the pure solvent.
- If the vapour pressure of the solvent is P and that of the solution is Ps then lowering of V.P = P - Ps.
- The vapour pressure of the solution decreases as the surface area occupied by the solvent molecule decreases and density increases.

Factors on which Vapour Pressure depends

1. Temperature: As Temperature increases, the Kinetic Energy of the molecules in the liquid phase increases and as a result, more molecules are able to escape to the gaseous phase and hence the vapour Pressure increases.

The Clausius Clapeyron Equation relates the vapour pressure of the liquid to the temperature and is given as

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where ΔH is the heat of vaporisation of the liquid and P_1 and P_2 are the vapour pressure at temperature T_1 and T_2 respectively.

2. Vapour pressure depends on the nature of the liquid. The greater the force of attraction between the liquid molecules, the lesser the vapour pressure

3. vapour pressure does not depend on the shape or the size of the container and has a fixed value at a particular temperature.

Significance of vapour pressure:

1. Vapour pressure gives us an idea of intermolecular forces of attraction in the liquid. The greater the force of attraction, lower is the vapour pressure and vice versa.
2. Vapour pressure gives us an idea of the volatility (vapour forming tendency of the liquid). Greater the vapour pressure, greater is the volatility of the liquid.
3. Vapour pressure also gives an idea of the boiling point of the liquid. The greater the vapour pressure, lesser is the boiling point of the liquid.

Vapour Pressure of Solution Containing Two Volatile Liquids-

Raoult's law:

Let us consider a binary solution obtained upon mixing two volatile liquids A and B. When the solution is taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between the vapour phase and the liquid phase. The vapor pressure over this solution would depend on the volatility of each of the liquids as well as the relative amount of the liquids present in the solution. French Chemist Raoult gave this quantitative relationship between these parameters.

Statement of Raoult's law:

For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction in the solution.

Let us represent solvent as "A" and solute as "B".

Before mixing, the vapour pressure of A is $\mathrm{P_A^o}$ and vapour pressure of B is $\mathrm{P_B^o}$.

Now, after mixing of solute and solvent, let the partial pressures of solvent A and solute B be P_A and P_B respectively

Now according to Raoult's law, vapour pressure of liquid A is proportional to the mole fraction of liquid A.

Thus,

$$\mathrm{P_A = K_A P_A^o \quad and \quad P_B = K_B P_B^o}$$

Now, to find the value of K_A and K_B, when we have only liquid A, then the partial pressure of A is equal to $\mathrm{P_A^o}$

Thus, $\mathrm{K_A = P_A^o}$ And similarly, it can be shown that $\mathrm{K_B = P_B^o}$.

Thus, we can write:

$$\mathrm{P_A = P_A^o X_A \quad and \quad P_B = P_B^o X_B}$$

Now according to Dalton's law of partial pressure, we have:

Total pressure $(P_T) = P_A + P_B$

Thus, the total pressure exerted by the vapours of the solutions can be represented as

$$\mathrm{(P_T) = P_A^o X_A + P_B^o X_B}$$

Using these equations, the mole fraction of A and B represented as Y_A and Y_B in the vapour phase can be calculated as given by the equations:

$$\mathrm{Y_A = \frac{P_A}{P_T} \text{ and } Y_B = \frac{P_B}{P_T}}$$

Vapour Pressure of Solution Containing Non-Volatile Solute-

A solution is obtained by mixing a non-volatile solid solute in the liquid solvent.

Let's name the solvent "A" and solute "B". Let the vapour pressure of the pure solvent be represented as $P_A{}^0$. Now when the solute is dissolved in the solvent, then the vapour pressure of the solution decreases and is represented as P_s.

According to Raoult's law, we know:

$$\mathrm{P_s = P_A{}^0 X_A \quad ....(1)}$$

Now, the sum of mole fraction of solvent X_A and solute X_B is equal to 1.

Thus $X_A + X_B = 1$

On putting the value of X_A in equation (i), we get:

$$\mathrm{P_S = P_A{}^o\,[1 - X_B]}$$

$$\mathrm{P_S = P_A{}^o - P_A{}^o X_B}$$

Therefore, $\mathrm{P_A{}^o X_B = P_A{}^o - P_S}$

Thus, it can be said that,

$$\mathrm{\frac{P_A^o - P_S}{P_A^o} = X_B}$$

The RHS in the above expression gives us the 'Relative lowering of vapour pressure and is equal to the mole fraction of the solute.

4. Ideal Solution

The solutions which obey Raoult's law for the entire range of composition are called Ideal solutions.

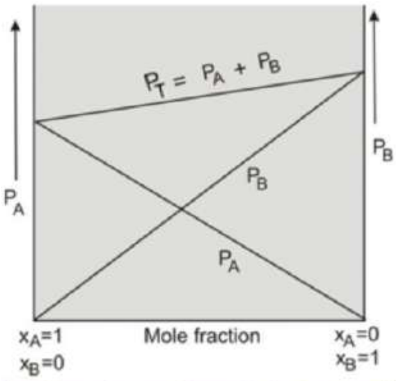
In these solutions, the solute-solute and solvent-solvent interactions are almost similar to solute-solvent interactions (A-B = A-A or B-B interactions). Since the existing forces and the newly formed forces are almost identical, there is no enthalpy change in the mixing of these solutions i.e $\Delta H_{mix} = 0$.

There is no change in the volume during the mixing process i.e. $\Delta V_{mix} = 0$. For example if 1 litre solutions each of liquid A and B are mixed to form an ideal solution, then the solution obtained has a volume equal to 2 litres.

The entropy of mixing is positive as new interactions are introduced into the solution which increases the randomness of the system and hence $\Delta S_{mix} > 0$. The mixing process is spontaneous and hence $\Delta G_{mix} < 0$.

These solutions have vapor pressure as predicted by Raoult's law.
For example:

$$P_A = P_A^o X_A$$
$$P_B = P_B^o X_B$$
$$P_T = P_A + P_B$$



Vapour Pressure Diagram for ideal solution

Examples of Ideal solutions-

For the solutions to follow the ideal solution at all ranges of concentrations and temperatures then the molecular size of the liquids should be nearly the same.

- **CH_3OH + C_2H_5OH:** Both these liquids are polar and have nearly the same size. Thus, this solution is an ideal solution.
- **$C_2H_5Br_2$ + $C_2H_5Cl_2$:** Both these liquids are polar and have nearly the same size. Thus, this solution is an ideal solution.
- **C_2H_5Cl + C_2H_5Br:** Both these liquids are polar and have nearly the same size. Thus, this solution is an ideal solution.
- **C_6H_6 + $C_6H_5CH_3$:** Both these liquids are non-polar and have nearly the same size. Thus, this solution is an ideal solution.
- **C_2H_5Cl + C_2H_5I:** Both these liquids are polar but the size difference between the molecules is large. Thus, this solution is not an ideal solution.

5. Raoult's Law

Non-Ideal Solution Showing Negative Deviation from Raoult's Law-

These solutions have vapour pressure less than that predicted by Raoult's law for the entire range of composition.

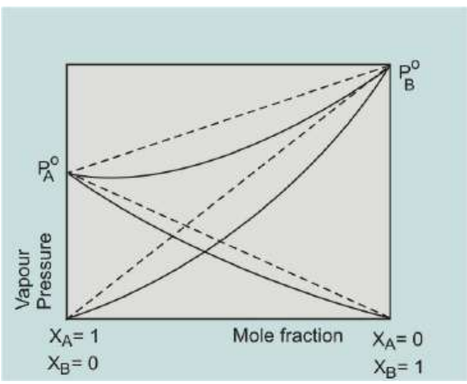
This happens when the new solute-solvent interactions are stronger than the interactions in the pure components. Since the newly formed forces are stronger than the existing forces, heat is liberated. Hence, the enthalpy change in the mixing of these solutions is negative i.e $\Delta H_{mix} < 0$.

The change in the volume during the mixing process is positive i.e. $\Delta V_{mix} < 0$.. For example, if 1 litre solutions each of liquid A and B are mixed, then the solution obtained has a volume lesser than 2 litres.

The entropy of mixing is positive as new interactions are introduced into the solution which increases the randomness of the system and hence, The mixing process is spontaneous and hence $\Delta G_{mix} > 0$.

These solutions have vapour pressure greater than that predicted by Raoult's law.

$$P_A < P_A^o X_A$$
$$P_B < P_B^o X_B$$
$$P_T = P_A + P_B < P_A^o X_A + P_B^o X_B$$



Examples of solutions showing negative deviation:

1. Acetone + Chloroform
2. Nitric acid HNO_3 + water
3. Acetic acid + pyridine
4. Phenol + Aniline

Non-Ideal Solution Showing Positive Deviation from Raoult's Law-

Solutions showing positive deviation from Raoult's law

These solutions have vapour pressure greater than that predicted by Raoult's law for the entire range of composition.

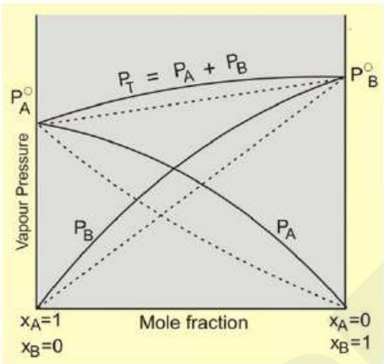
This happens when the new interactions are weaker than the interactions in the pure component **(A-B < A-A or B-B interactions)**. Since the newly formed forces are weaker than the existing forces, heat has to be supplied to break old bonds and form new ones. Hence, the enthalpy change in the mixing of these solutions is positive i.e $\Delta H_{mix} > 0$.

The change in the volume during the mixing process is positive i.e.$\Delta V_{mix} > 0$. For example if 1 litre solutions each of liquid A and B are mixed, then the solution obtained has a volume greater than 2 litres.

The entropy of mixing is positive as new interactions are introduced into the solution which increases the randomness of the system and hence $\Delta S_{mix} > 0$.. The mixing process is spontaneous and hence $\Delta G_{mix} < 0$.

These solutions have vapour pressure greater than that predicted by Raoult's law.

$$P_A > P_A{}^o X_A$$
$$P_B > P_B{}^o X_B$$
$$P_T = P_A + P_B > P_A{}^o X_A + P_B{}^o X_B$$



Examples:

1. C_2H_5OH + cyclohexane
2. Acetone + carbon disulphide
3. Acetone + benzene
4. Acetone + Ethyl alcohol
5. Carbon tetrachloride + chloroform or Toluene
6. Methyl alcohol + water
7. Water + Ethyl alcohol

6. Azeotropic Mixture

Azeotropic Mixture-

An azeotropic mixture is a solution of two liquids having a certain composition in which both the gas phase and the liquid phase composition are the same i.e. $X_A = Y_A$ and $X_B = Y_B$. These solutions distil over without changes in composition and hence, these cannot be separated by distillation. These solutions are formed by non-ideal solutions which show a large deviation from ideality.

These solutions boil at one particular temperature like a pure liquid and distil over in the same composition and hence are also referred to as constant boiling mixtures.

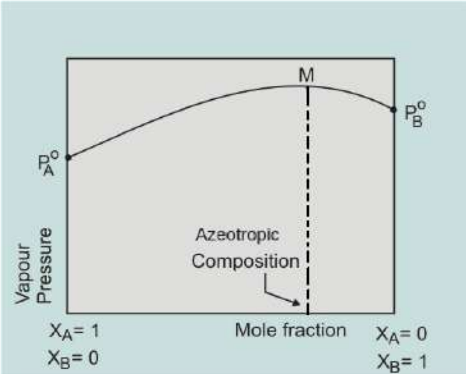
Types of Azeotropic Mixtures

It is of the following types:

1. **Minimum Boiling Azeotropes**

   Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at a temperature lower than the boiling point of either of the components 'A' or 'B'.

In the figure given below, point M represents the azeotropic composition. At this point, vapour pressure is maximum and therefore the solution has the lowest boiling point.

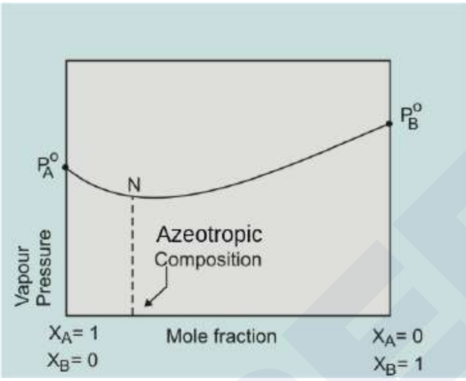


e.g., Ethanol water mixture on fractional distillation gives a solution containing approximately 95 % by volume of ethanol. Once this composition is achieved, no further separation occurs.

2. **Maximum Boiling Azeotropes**

Non-ideal solutions showing large negative deviations from Raoult's law form maximum boiling azeotropes which boil at a temperature higher than the boiling point of either of the components 'A' or 'B'.

In the figure given below, the point B represents the azeotropic composition. At this point, vapour pressure is minimal and therefore the solution has the lowest boiling point.



e.g. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass

Relation Between Raoult's Law and Dalton's Law-

We have two liquids A and B and their vapour pressures are represented as P_A and P_B.

According to Raoult's law, we know:

$$P_A = P_A^o X_A \qquad \text{............(i)}$$

$$P_B = P_B^o X_B \qquad \text{............(ii)}$$

Now, according to Dalton's law of partial pressure, we have:

$$P_A = P_T Y_A \qquad \text{............(iii)}$$

$$P_B = P_T Y_B \qquad \text{............(iv)}$$

Thus, on combining equations (i) with (iii) and (ii) with (iv), we get:

$$P_A^0 X_A = P_T Y_A$$

$$P_B^0 X_B = P_T Y_B$$

$$\text{Thus, } Y_A = \frac{P_A^o X_A}{P_T}$$

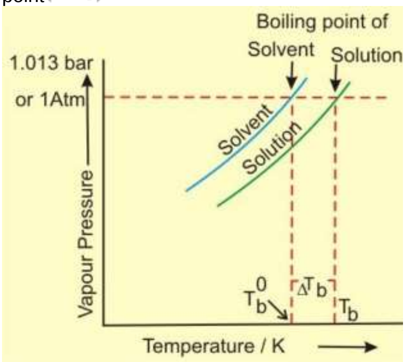
$$\text{And, } Y_B = \frac{P_B^o X_B}{P_T}$$

7. Elevation in Boiling Point

Elevation in Boiling Point:

Boiling Point: It is the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure.

Now, the lowering of the vapour pressure of the solution occurs when the addition of non-volatile solute in solvent happens. In order to boil the solution, it is necessary to increase the temperature of the solution above the boiling point of the pure solvent. It means the boiling point of the solution is always higher than the boiling point of the pure solvent. This increase in the boiling point of the solution is called elevation in boiling point(ΔT_b)



- It is also termed as Ebullioscopy.
- Suppose $\mathrm{T_b^o}$ and $\mathrm{T_b}$ are the B.P. of pure solvent and solution respectively, then elevation in B.P $(\Delta \mathrm{T_b})$ is given as $\Delta \mathrm{T_b} = \mathrm{T_b} - \mathrm{T_b^o}$

$\Delta \mathrm{T_b}$ is directly proportional to the molality of the solution

$$\Delta \mathrm{T_b} \propto \mathrm{m}$$
$$\Delta \mathrm{T_b} = \mathrm{K_b m}$$

- If the molality of the solution is one, then

  $$\Delta \mathrm{T_b} = \mathrm{K_b}$$

- The elevation in B.P. is also given as

  $$\Delta \mathrm{T_b} = \mathrm{K_b} \times \frac{\mathrm{w}}{\mathrm{M}} \times \frac{1000}{\mathrm{W}}$$

- The molecular weight of solute can be found out as follows

  $$\mathrm{M} = \frac{\mathrm{K_b} \times \mathrm{w} \times 1000}{\Delta \mathrm{T_b} \times \mathrm{W}}$$

Here w = weight of solute

W = weight of solvent
K_b= molal elevation constant or ebullioscopic constant.
M = molar mass of solute

M_1 = molar mass of solvent

The value of K_b or Ebullioscopic constant is a property of the solvent only and does not depend on the type of solute. The value of K_b can be calculated as:

$$\mathrm{K_b} = \frac{\mathrm{RM_1 T^2}}{1000\ \mathrm{Lv\ or\ \Delta Hv}}$$

Here L_v or $\Delta \mathrm{T_b} = \mathrm{K_b} \times \frac{\mathrm{w}}{\mathrm{M}} \times \frac{1000}{\mathrm{W}}$ = latent heat of vaporization.

8. Depression in Freezing Point

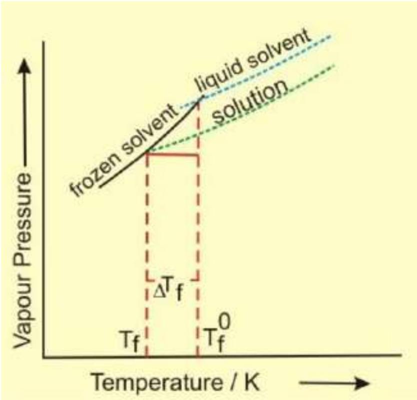
Depression in Freezing Point:

Freezing Point: It is the temperature at which the liquid and the solid form of the same substance are in equilibrium and have the same vapour pressure. A solution freezes when its vapour pressure is equal to the vapour pressure of a pure solid solvent. Due to the lower vapour pressure of the solution, the solid form of a solution separates out at a lower temperature.

On adding a non-volatile solute to the solvent, the vapour pressure of the solution is lesser than the solvent and the vapour pressure of the solution becomes equal to the vapour pressure of solid solvent at a lower temperature when compared to the pure solvent hence the freezing point of decreases.

Suppose $\mathrm{T_f^0}$ and $\mathrm{T_f}$ are the freezing points of pure solvent and solution respectively. The decrease in freezing point ΔT_f is given as:

$$\Delta \mathrm{T_f} = \mathrm{T_f^0} - \mathrm{T_f}$$



- This is also termed cryoscopy and depression of freezing point (ΔT_f)
- For a dilute solution, ΔT_f is directly proportional to the molality (m) of the solution.

Hence $\Delta T_f \propto m$
$\Delta T_f = K_f m$
If the molality of the solution is one, then
$\Delta T_f = K_f$
ΔT_f and M can be found by using these relations.

$$\Delta T_f = K_f \times \frac{w}{M} \times \frac{1000}{W}$$
$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Here w = weight of solute
W = weight of solvent
K_f = molal depression constant or cryoscopic constant.
M = molar mass of solute

M_1 = molar mass of solvent

The value of K_f or Cryoscopic constant is a property of the solvent only and does not depend on the type of solute. The value of K_f can be calculated as:

$$K_f = \frac{M_1 R T^2}{1000 L_f \text{ or } \Delta H_{fusion}}$$

Here, L_f or ΔH_f = latent heat of fusion

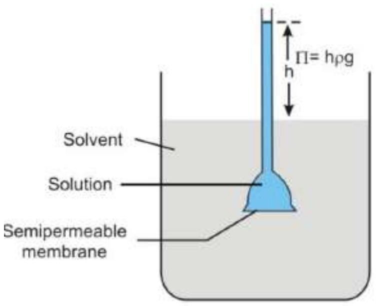
9. Osmosis and Osmotic Pressure

Osmosis: It is the flow of solvent molecules from a solution of low concentration to a solution of higher concentration when they are separated by a semi-permeable membrane(SPM), the concentration obviously being defined with respect to the solute.

Semi-permeable membrane consists of a network of submicroscopic pores or holes. The pore size is such that the smaller solvent molecules can move across the membrane while the movement of larger solute molecules is hindered by the smaller pores of the SPM.

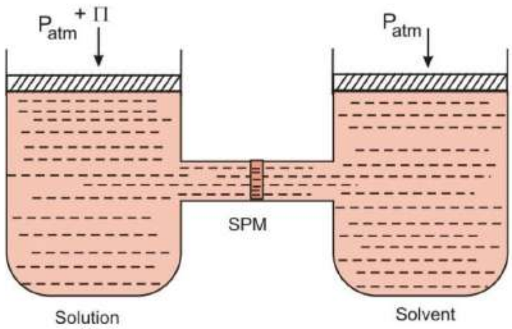
There are many phenomena which include the process of osmosis that we observe in daily lives. For example, raw mangoes shrivel when pickled in brine (saltwater); wilted flowers revive when placed in freshwater, blood cells collapse when suspended in saline water, etc.

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in figure given below, the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called osmosis.



The flow will continue till the equilibrium is attained. This flow of the solvent molecules to the solution side across a semipermeable membrane can be stopped if some extra pressure is applied to the solution. This pressure that just stops the flow of solvent is called the osmotic pressure of the solution. The osmotic pressure is represented by the letter Π (Pi).

This is illustrated in the Figure given below. The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution.



Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus:

$$\Pi = CRT$$

Here Π is the osmotic pressure and R is the gas constant. The above equation can also be written as

$$\Pi = \left(\frac{n_2}{V}\right) RT$$

Here V is the volume of a solution in litres containing n_2 moles of solute.

If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2/M_2$ we can write,

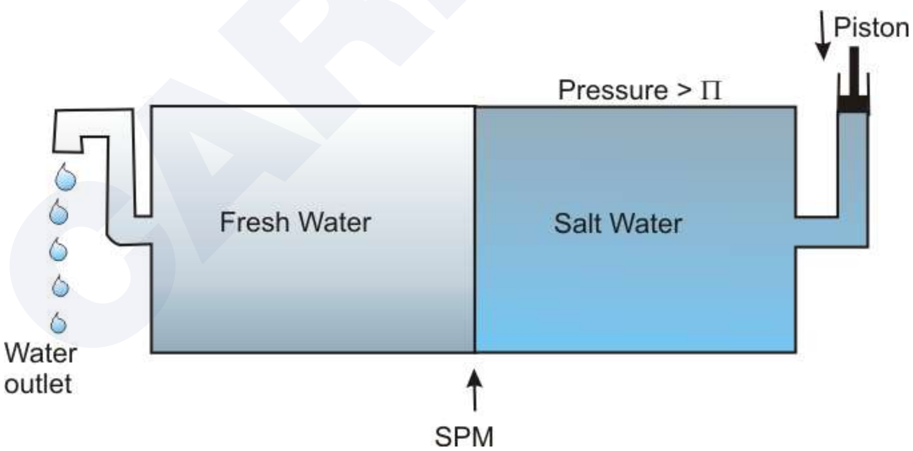
$$\Pi V = \frac{W_2 RT}{M_2}$$

Thus $M_2 = \frac{W_2 RT}{\Pi V}$

Thus, knowing the quantities w_2, T, Π and V we can calculate the molar mass of the solute.

10. Reverse Osmosis

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi-permeable membrane. This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in the desalination of seawater. A schematic setup for the process is shown in the Figure given below. When pressure more than the osmotic pressure is applied, pure water is squeezed out of the seawater through the membrane. A variety of polymer membranes are available for this purpose.



The pressure required for reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in seawater. These days many countries use desalination plants to meet their potable water requirements.

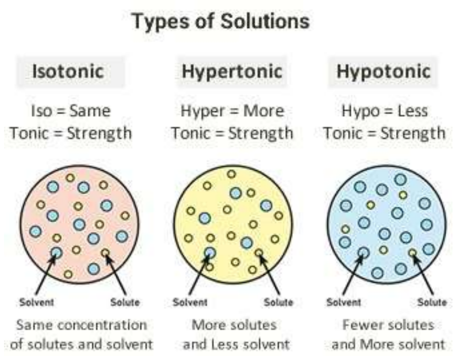
11. Isotonic, Hypertonic, Hypotonic Solution

Isotonic Solution-
Two solutions having the same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously.

Hypertonic Solution-
The solution which has higher osmotic pressure is called a hypertonic solution. For example, if we place the cells in a solution containing more

than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they will shrink. Such a solution is called hypertonic. It is a concentrated solution.

Hypotonic Solution-
The solution which has lower osmotic pressure is called a hypotonic solution. For example, if the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell. It is a diluted solution.



12. Van't Hoff Factor and Abnormal Molar Mass

van't Hoff factor(i) or Abnormal Colligative Property-

If a solute gets associated or dissociated in a solution, the actual number of particles are different from expected or theoretical consideration.

We know, that:

$$\text{Colligative property} \propto \text{number of particles}$$

Thus, we can say that:

$$\mathrm{i} = \frac{\text{Observed number of solute particles}}{\text{Number of particles initially taken}}$$

$$\mathrm{i} = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}}$$

Again, we have:

$$\text{Colligative property} \propto \frac{1}{\text{molecular mass of solute}}$$

Thus;

$$\mathrm{i} = \frac{\text{Theoretical molecular mass of solute}}{\text{Observed molecular mass of solute}}$$

Calculation of Extent of Dissociation in an Electrolytic Solution-

van't Hoff Factor for dissociation of solute

Suppose we have the solute A which dissociates into n moles of A. Then the dissociation occurs as follows:

$$A_n \rightarrow nA$$

At time t = 0 $\quad$ 1 $\quad$ 0

At time t = t $\quad$ $1 - \alpha$ $\quad$ $n\alpha$

At time t = 0, initial number of solute particles = 1

And, At time t =t, observed number of solute particles = $1 - \alpha + n\alpha$

$= 1 + (n-1)\alpha$

Thus, we know that:

$$\mathrm{i} = \frac{\text{observed number of solute particles}}{\text{initial number of solute particles}}$$

$$\mathrm{i} = \frac{1 + (n-1)\alpha}{1}$$

where n = number of solute particles

α = Degree of dissociation

For strong electrolytes, the degree of dissociation is taken to be unity.

Calculation of Extent of Association in an Electrolytic Solution-

Suppose we have a solute A and it associates into $(A)_n$. Then the association occurs as follows:

$$nA \rightarrow (A)_n$$

At time t = 0 1 0

At time t = t 1 - β β/n

Now, the initial number of solute particles = 1

And, the observed number of solute particles = $1-\beta+\frac{\beta}{n}$

$$=1+\beta\left[\frac{1}{n}-1\right]$$

Thus, van't Hoff factor is given as:

$$i=1+\beta\left[\frac{1}{n}-1\right]$$

where, β is the degree of association

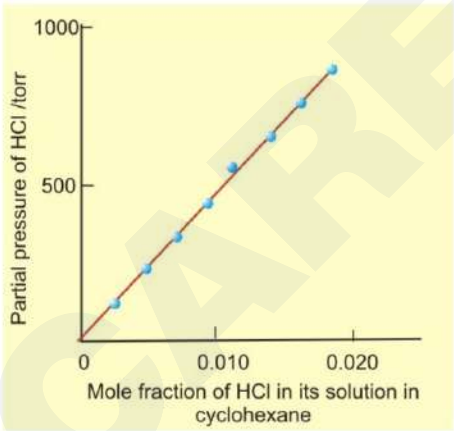
13. Solubility and Henry's Law

Henry's Law:

Henry was the first to give a quantitative relation between the pressure and solubility of a gas in a solvent. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of the liquid or solution. If the solubility of gas is expressed in terms of its mole fraction in the solution, then it can be said that the mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution. Alternatively, the most commonly used form of Henry's law states that "the partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (x) in the solution" and is expressed as:

$$\mathrm{P}=\mathrm{K_H x}$$

Here K_H is the Henry's law constant and has the same units as the units of pressure used in the equation. It can be clearly seen that the plot between the partial pressure of the gas versus the mole fraction of the gas in solution will be a straight-line plot as shown in the figure given below.



Factors governing the value of K_H:

Different gases have different K_H values at the same temperature. Also, the same gas has different values of K_H at different temperatures which is shown in the table given below. The factors governing the value of Henry's constant is given below

1. Nature of gas-solvent interaction

   As gas-solvent interactions become stronger, the solubility will increase keeping the pressure constant and thus the value of K_H will decrease. For example, HCl has a lower value of Henry's constant as compared to O_2

2. Temperature:

   As the temperature increases, the solubility of the gas decreases and hence keeping the pressure constant for the same gas, the value of KH will increase.

Gas	Temperature(K)	K_H/kbar
Helium	293	144.97

Hydrogen	293	69.16
Nitrogen	293	76.48
Nitrogen	303	88.84
Oxygen	293	34.86
Oxygen	303	46.82
Argon	298	40.3
Carbon dioxide	298	1.67
Formaldehyde	298	1.83×10^5
Methane	298	0.413
Vinyl chloride	298	0.611

Applications of Henry's law:

(1) Soda bottle fizzes when opened: When the soda bottle is opened, the pressure decreases in the bottle. Now, due to this decrease in pressure, the solubility of gas decreases. Now if we leave this bottle open for some time, then all fizz goes out and we do not feel the drinking.

(2) Anoxia at higher altitudes: This is the condition of tiredness and mental confusion at higher altitudes. At higher altitudes, pressure decreases and thus the solubility of oxygen gas in the body decreases which causes anoxia.

(3) Avoiding Bends in Scuba divers: When scuba divers go deep into the ocean, then pressure increases. Now due to this increase in pressure, the solubility of gases in the blood increases. Further, when these divers come up at the sea level, then pressure decreases, and the solubility of gases in the blood decreases. Due to this decrease in solubility, the gases come out of the capillaries in the form of bubbles which causes a serious medical condition called as bends. To avoid bends, Helium is used in the diving tanks.

Chemical kinetics

Important Formulae

1. Rate of Reaction

Type of Reaction in terms of their rate:

(1) Very fast reactions:

Some reactions such as ionic reactions occur very fast and it is difficult to calculate the rate of these reactions

e.g. Precipitation of $AgCl$ upon mixing aqeuous solutions of $AgNO_3$ and $NaCl$.

(2) Moderate reactions:

These reactions occur at moderate rates and it becomes easier to calculate the rate due to the moderate pace.

e.g. Hydrolysis of esters, inversion of cane sugar etc.

(3) Very slow reactions :

These reactions occur at very slow rates and it becomes very difficult to perceive these changes.

e.g. Rusting of iron, and conversion of diamond to graphite.

Rate of reaction-

The rate of reaction can be defined in terms of change in concentration of reactant or product in unit time.

To be more specific it can be expressed in terms of

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

There are two types of rates which are generally measured for a chemical reaction

(1) Average Rate

(2) Instantaneous Rate

Average Rate of Reaction:

It is defined as "The rate of change of concentration of a reactant or a product per unit time"

$$\text{Rate of reaction (r)} = \frac{C_2 - C_1}{t_2 - t_1}$$

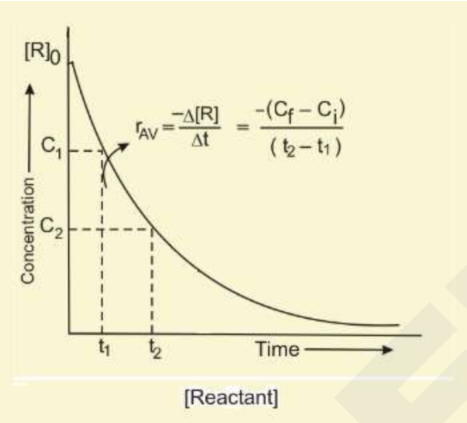
As the rate of reaction varies greatly with time, so generally, average reaction rates and instantaneous reaction rates are used.

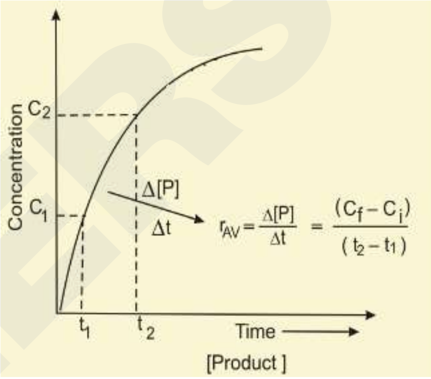
For a reaction $A \rightarrow P$

$$\text{Rate of disappearance of A} = -\frac{\Delta[A]}{\Delta T}$$

$$\text{Rate of appearance of P} = \frac{\Delta[P]}{\Delta T}$$

It is to be noted that the rate of reaction is always a positive quantity and hence, there is a negative sign that has to be included in the expression for rate.



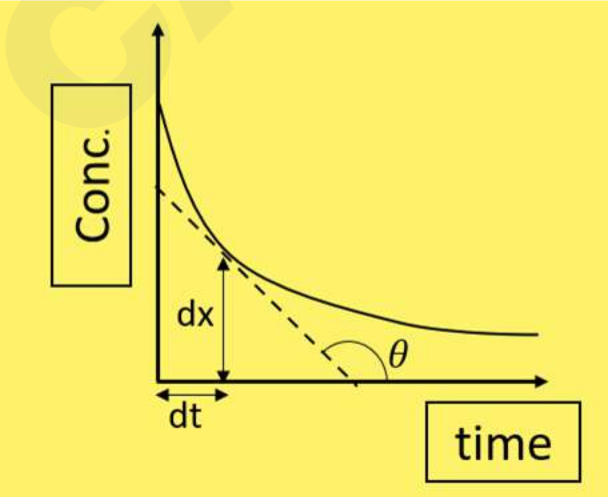


$$\text{Unit of average velocity} = \frac{\text{Unit of concentration}}{\text{Unit of time}} = \frac{\text{mole}}{\text{litre second}} = \text{mole litre}^{-1}\ \text{second}^{-1}$$

Instantaneous Rate of Reaction-

As the average reaction rate fails to predict the rate at a particular moment of time so we use the instantaneous rate which is equal to a small change in concentration (dx) during a small interval of time (dt). It is given as dx/dt.

$$\lim_{\Delta t \to 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$



$$\text{Rate of reaction} = \text{slope of curve} = \frac{dx}{dt}$$

It can be written for any of the reactants or the product in terms of stoichiometric coefficients V_j which is negative for reactants and positive for products as follows:

$$\frac{dx}{dt} = \frac{1}{V_j}\frac{d(J)}{dt}$$

For example, if we have the reaction

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate w.r.t. } [A] = -\frac{d[A]}{dt} \times \frac{1}{a}$$

$$\text{Rate w.r.t. } [B] = -\frac{d[B]}{dt} \times \frac{1}{b}$$

$$\text{Rate w.r.t. } [C] = -\frac{d[C]}{dt} \times \frac{1}{c}$$

$$\text{Rate w.r.t. } [D] = -\frac{d[D]}{dt} \times \frac{1}{d}$$

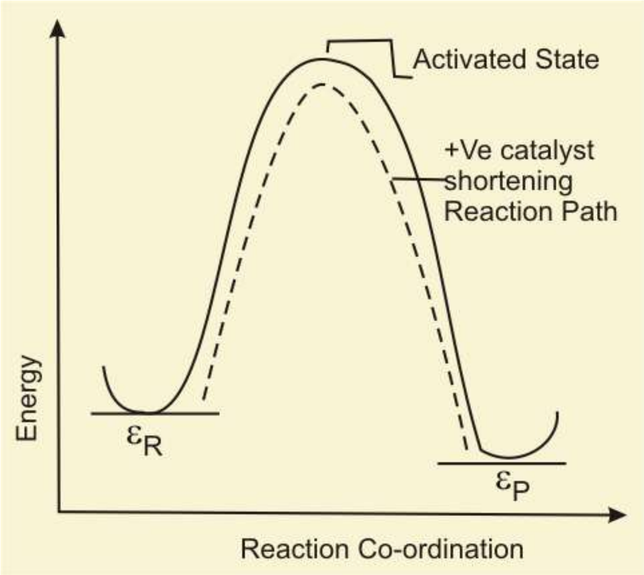
- For the reactants, the negative sign indicates a decrease of concentration and for products positive sign indicates an increase in concentration.
- For a reversible reaction at dynamic equilibrium, the net reaction rate is always zero as:
$$\left(\frac{dx}{dt}\right)_{\text{forward}} = \left(\frac{dx}{dt}\right)_{\text{backward}}$$

Factors Affecting Rate of Reaction-

There are various factors on which the rate of reaction depends:

- **Nature of reactant and product:**
    - For ionic reactants reaction rate is fast as activation energy is zero for them. For example:
    $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
    - Molecules have slow reaction rate due to need of more activation energy. For example:
    $2CO + O_2 \rightarrow 2CO_2$
- **Physical state of reactants:** Rate also changes with physical state.
Gaseous states > Liquid states > Solid states
- **Pressure:** For gaseous reactants rate varies with pressure just like concentration.
$$\frac{dx}{dt} \propto \text{Pressure (as } P \propto C)$$
- **Surface Area:** Greater the surface area, faster is the rate of reaction due to more number of active sites.
$\text{Rate } (dx/dt) \propto \text{Surface area}$
- **Temperature:** Rate of reaction increases with the increase of temperature as it increases the number of effective collisions. It is observed that for every $10^{o}C$ rise in temperature -dx/dt or rates become nearly double.
$$\text{Temp. Coefficient } (\mu) = \frac{K \text{ at } t^\circ C + 10^\circ C}{K \text{ at } t^\circ C}$$
The value of the temperature coefficient lies in between 2-3. In case we increase the temperature by more than $10^{o}C$ the above relation can be given as:
$$\frac{K_{T_2}}{K_{T_1}} = (\mu)^{\Delta T/10}$$
$[\text{Here } \Delta T = T_2 - T_1]$
$$\log_{10}\frac{K_{T_2}}{K_{T_1}} = \frac{\Delta T}{10}\log_{10}\mu$$
$$\frac{K_{T_2}}{K_{T_1}} = \text{Antilog}\left[\frac{\Delta T}{10}\log_{10}\mu\right]$$
- **Catalyst:** It increases the rate of a reaction by decreasing the activation energy by accepting a new alternative smaller path for the reaction. It is reverse in case of negative catalyst to that of positive catalyst. Catalysts are more effective in 'Solid powdered form' due to larger surface

area, that is, more active sites.



- **Intensity of light:** Rate of photochemical reactions depends upon intensity of light radiations.
  $\frac{dx}{dt} \propto$ Intensity of radiation
- **Concentration of reactants:** Rate increases with the increase of concentration as due to more number of reactants there are more collisions.
  Rate of reaction $(dx/dt) \propto$ Concentration

2. Rate Law

Rate Law-

The rate of any reaction depends upon the concentration of the reactants in the rate law equation that is rate law and the rate of reaction depend upon the order of the reaction.
Let us consider this reaction:
$xA + yB \rightarrow$ Product
The rate law equation for the reaction can be given as:

$$R \propto [A]^p[B]^q$$

$$R = K[A]^p[B]^q$$

Order of reaction $= p + q$
Here p, q are experimental quantities which may or may not be equal to the respective stoichiometric coefficients (x, y).

Unit of Rate Constant-

The differential rate expression for n^{th} order reaction is as follows:

$$-\frac{dx}{dt} = k(a-x)^n$$

or $$k = \frac{dx}{(a-x)^n dt} = \frac{(\text{ concentration })}{(\text{ concentration })^n \text{ time}} = (\text{ conc. })^{1-n} \text{ time }^{-1}$$

If concentration is expressed in mole L^{-1} and time in minutes, then
$k = (\text{ mole } L^{-1})^{1-n} \min^{-1}$
For zero order reaction, $n = 0$ and hence, $k = \text{moleL}^{-1}\min^{-1}$
For first order reaction, $n = 1$ and hence,
$k = (\text{ mole } L^{-1})^0 \min^{-1} = \min^{-1}$
For second order reaction, $n = 2$ and hence,
$k = (\text{ mole } L^{-1})^{-1} \min^{-1} = \text{ mole }^{-1} L \min^{-1}$

3. Order of Reaction

Important Points About Order of Reaction-

Order of reaction is defined as the number of reactants which determine the rate of reaction. In other words, it is the sum of exponents raised on active masses of reactants in a rate law equation.
The rate law equation for the reaction can be given as:

$$R \propto [A]^p[B]^q$$

$$R = K[A]^p[B]^q$$

Order of reaction $= p + q$

The rate constant and order for various reacting species is an experimental finding and cannot be predicted directly from the stoichiometry of the balanced reaction.

1. It is an experimental value.
2. It may be zero, negative or in fraction.
3. Order of reaction depends upon temperature, pressure and concentration etc.
4. It determines rate of reaction.
5. Order of reaction is determined by the slowest step of the reaction.
6. High order reactions are rare due to less chance of effective collisions between molecules.
7. Anything in excess is not counted in order of the reaction. Example, in hydrolysis of ester and sugar water is in excess so it is neglected for order.

Simple/Elementary Single-Step Reaction-

- In a complex reactions, there are many steps. Among those only one step is the rate-determining step as it is a slow reaction.
- The order of the reaction can be found out using the stoichiometric coefficients of the rate-determining step or the slowest step.
- In a simple reaction, the reaction completes in one single step and that is the rate-determining step. For simple reactions, Gulberg and Waage law of mass action is valid.
  For example:
  $\mathrm{H_2 + I_2 \rightarrow 2HI}$
  Since it is a simple reaction, thus the rate of reaction is given as:
  $\mathrm{Rate} = \mathrm{K[H_2]^1[I_2]^1}$

Initial Rate Method to Determine Correct Rate Law and Order of Reaction-

Consider the reaction:

$\mathrm{2A + B \rightarrow P}$

The rate law for this reaction is given as follows:

$\mathrm{Rate} = \mathrm{K[a]^x[B]^y}$

Now, x and y are the coefficients that are determined experimentally.

K = Rate constant
x,y = Order of reaction with respect to A and B.

4. Zero Order Reaction

Zero order Reactions

In such reactions rate of reaction is independent of the concentration of the reactants.

$$\mathrm{Rate} \propto [\mathrm{concentration}]^0$$

For example, suppose we have a reaction

$\mathrm{A} \longrightarrow \mathrm{B}$

then, the rate of reaction can be written as

$$\mathrm{Rate} = -\frac{\mathrm{dA}}{\mathrm{dt}} = \mathrm{k[A]^0}$$

From the above equation it is evident that for a Zero order reaction,

(1) The rate of reaction is equal to the rate constant

(2) The rate of reaction is constant and independent of time

(3) The unit of rate constant is $\mathrm{molL^{-1}time^{-1}}$

(4) The rate of reaction cannot be changed by changing the concentration of reactant.

Integrated Rate law for a Zero Order Reaction

Zero-order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$\mathrm{A \rightarrow P}$

$$\mathrm{Rate} = -\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k[A]^0}$$

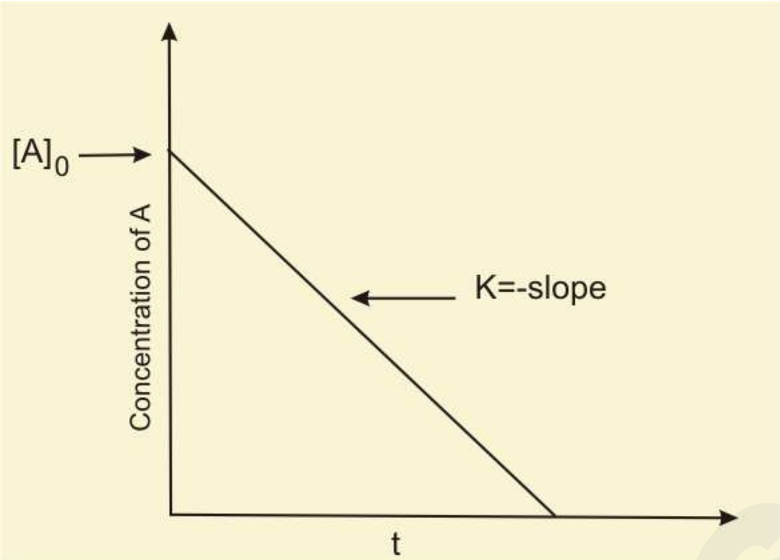
$$\Rightarrow \mathrm{Rate} = -\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k}$$

$$\Rightarrow \mathrm{d[A]} = -\mathrm{kdt}$$

$$\Rightarrow \int_{[A_0]}^{[A_t]} d[A] = -k \int_0^t dt$$

Thus, by integrating both sides, we get:

$$[A_t] = [A]_0 - kt$$



Comparing the above equation with the equation of a straight line, y = mx + c, if we plot [A] against t, we get a straight line as shown in the above figure with slope = –k and intercept equal to $[A]_0$.

The half-life of reaction:

The half-life of a reaction is the time in which the concentration of a reactant is reduced to half of its initial concentration. It is represented as $t_{1/2}$.
For a zero-order reaction, the rate constant is given as follows:

$$A_t = A_0 - kt$$

$$\text{When } t = t_{\frac{1}{2}}, [A]_t = \frac{[A]_0}{2}$$

Putting these values in the integrated rate expression,

$$\frac{[A]_0}{2} = [A]_0 - kt_{\frac{1}{2}}$$

Upon solving the above expression we have,

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

Thus, it is clear that the half-life for a zero-order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

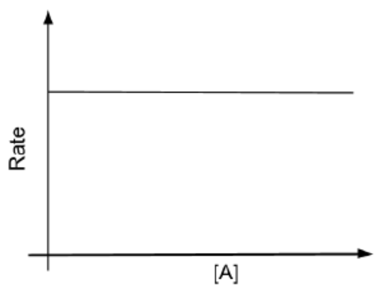
Life time of Reaction: It is time in which 100% of the reaction completes. It is represented as t_{LF}.
Thus, at $t = t_{LF}$, A = 0
Now, from integrated rate equation for zero order, we know:

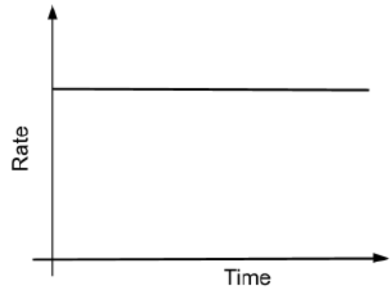
$$A = A_o - kt$$

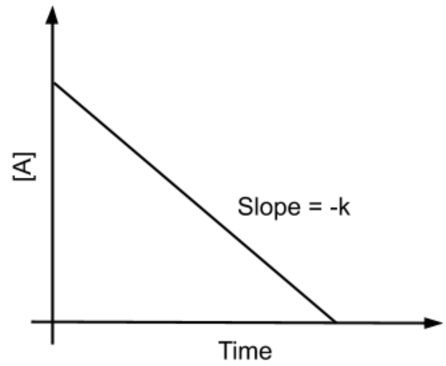
$$0 = A_o - kt_{LF}$$

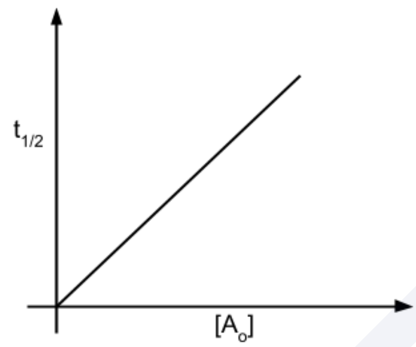
$$\text{Thus, } t_{LF} = \frac{A_o}{k}$$

Graphs for Zero-Order Reaction-









Special Zero Order Reaction-

Example:
The reaction occurs as follows:
$3A \rightarrow P$
The initial concentration of A is given as and the rate of the reaction(r) is given as $k[A]^o$. Find the concentration of A after time 't' and also determine the half-life of A.

Solution:
For zero-order reaction, the rate equation is given as follows:

$$A = A_o - kt$$

According to question, we have given:

$$r = k[A]^0 = -\frac{1}{3}\frac{dA}{dt}$$

$$-\frac{1}{3}\frac{dA}{dt} = k \qquad (\text{Since } [A]^0 = 1)$$

Now, integrating both sides we get:

$$[A]_{A_o}^{A} = -3k(t)_o^t$$

$$A - A_o = -3kt$$

$$\mathbf{A = A_o - 3kt}$$
This is the concentration of A after time 't'.

Now, for zero-order reaction, the half-life of a reaction is given as below:

$$t_{1/2} = \frac{A_o}{2k} = \frac{A_o}{2(3k)}$$

Thus, $\mathbf{t_{1/2}} = \dfrac{\mathbf{A_o}}{\mathbf{6k}}$

This is the half-life of A for this reaction.

5. First Order Reaction

First Order Reactions-

The rate of the reaction is proportional to the first power of the concentration of the reactant

Let us consider a chemical reaction which occurs as follows:

$$A \longrightarrow B$$

We have,

$$\text{rate}(r) = K[A]^1$$

$$\frac{-d[A]}{dt} = K[A]$$

$$\Rightarrow \frac{d[A]}{[A]} = -kdt$$

Integrating both sides and putting limits

$$\Rightarrow \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$\Rightarrow \ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

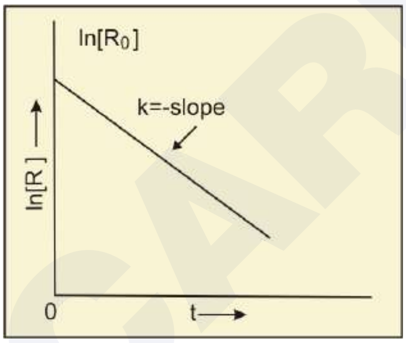
Simplifying the above expression we have,

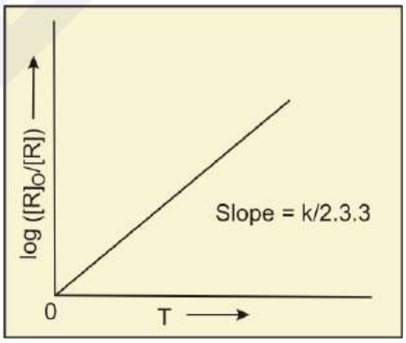
$$\Rightarrow \ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

In case we are dealing in terms of a and x (where a is the initial concentration of A and x is the amount of A dissociated at any time t)

$$\Rightarrow k = \frac{1}{t} \ln\left(\frac{[A]_0}{[A]_t}\right) = \frac{1}{t} \ln\left(\frac{a}{a-x}\right)$$

Graphical Representation of first-order reaction





Units of $k = \text{time}^{-1}$

Other Forms of Rate Law-

We know that the first-order equation is given as follows:

$$\log_{10}A = \log_{10}A_o - \frac{kt}{2.303}$$

But there are other forms of rate law also available that we use for different purposes. These forms are mentioned below:

- **Use to solve numerical:**

$$\log_{10}A = \log_{10}A_o - \frac{kt}{2.303}$$

$$\Rightarrow \log_{10}\left[\frac{A_o}{A}\right] = \frac{kt}{2.303}$$

$$\text{Thus, } t = \frac{2.303}{k}\log_{10}\left[\frac{A_o}{A}\right]$$

- **Exponential form:**

$$\log_e A = \log_e A_o - kt$$
$$\Rightarrow \log\frac{A}{A_o} = -kt$$
$$\Rightarrow \frac{A}{A_o} = e^{-kt}$$
$$\text{Thus, } A = A_o e^{-kt}$$

This equation is also known as the exponential form.

Half-Life of First Order Reaction-

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one-half of its initial concentration. It is represented as $t_{1/2}$.

For a zero-order reaction, the rate constant is given as:

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes:

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero-order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first-order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2}$$

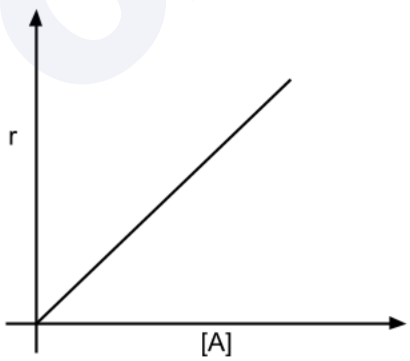
So, the above equation becomes

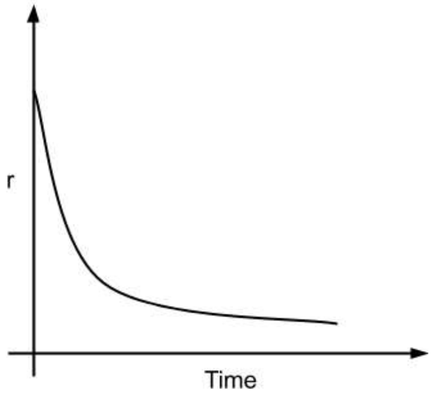
$$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}$$

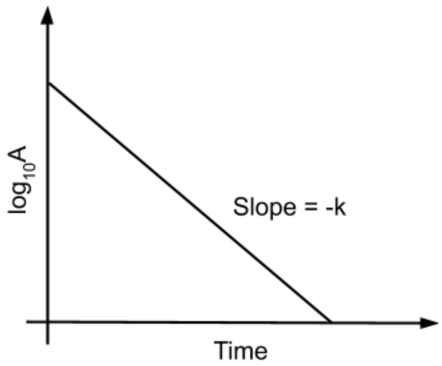
$$\text{or} \quad t_{1/2} = \frac{2.303}{k}\log 2$$

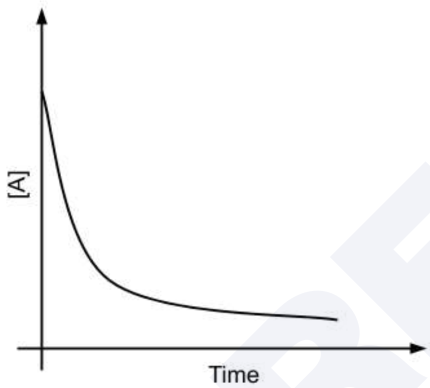
$$t_{1/2} = \frac{0.693}{k}$$

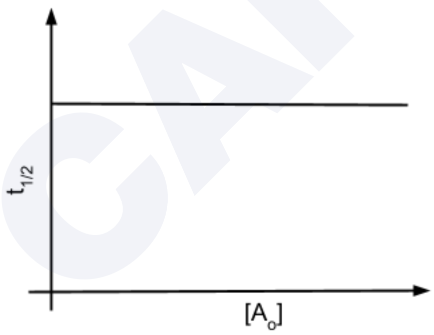
Graphs of First Order Kinetics-











6. Second Order Reaction

Consider the reaction

$A \rightarrow P$

For a second-order reaction, the rate law is given as follows:

$$\text{Rate} = k[A]^2 = -\frac{dA}{dt}$$

- **Integrated Rate Law:** Since it is a second-order reaction, thus:
  $$\frac{-dA}{dt} = k[A]^2$$
  Integrating both sides, we get:
  $$\int_{A_o}^{A} \frac{dA}{A^2} = -\int_0^t kdt$$
  where A_o is the initial concentration of A at time t = 0
  A is the remaining concentration of A after time 't'
  $$\Rightarrow \left[\frac{-1}{A}\right]_{A_o}^{A} = -k(t)_0^t$$
  $$\Rightarrow \left[\frac{1}{A}\right]_{A_o}^{A} = kt$$
  $$\Rightarrow \frac{1}{A} - \frac{1}{A_o} = kt \qquad \text{...............(i)}$$
  $$\text{Thus, } \mathbf{\frac{1}{[A]} = kt + \frac{1}{[A_o]}}$$
- **Half-life($t_{1/2}$):** We know that the half-life for a reaction is the time when the concentration of the reactant(A) is half of its initial value.
  Thus, at time t = $t_{1/2}$, A = $A_o/2$
  From equation (i) we have:
  $$t = \frac{1}{k}\left[\frac{1}{A} - \frac{1}{A_o}\right]$$
  $$\Rightarrow t_{1/2} = \frac{1}{k}\left[\frac{1}{A_o/2} - \frac{1}{A_o}\right]$$
  $$\text{Thus, } \mathbf{t_{1/2} = \frac{1}{kA_o}}$$
  This is the half-life for the second-order reaction.

7. nth Order Reaction

n^{th} order kinetics-

The rates of the reaction is proportional to nth power of reactant

$$\frac{d[A]}{dt} = -k[A]^n$$

$$\Rightarrow \frac{d[A]}{[A]^n} = -k\ dt$$

$$\Rightarrow \int_{A_0}^{[A]_t} \frac{d[A]}{[A]^n} = -k \int_0^t dt$$

$$\Rightarrow \left[\frac{[A]^{1-n}}{1-n}\right]_{[A]_0}^{[A]_t} = -k[t]_0^t$$

$$\Rightarrow \frac{1}{(n-1)}\left[\frac{1}{[A]_t^{(n-1)}} - \frac{1}{[A]_0^{(n-1)}}\right] = k(t)$$

Half life for any n^{th} order reaction

$$t_{\frac{1}{2}} = \frac{1}{(k)(n-1)([A]_0^{n-1})}[2^{n-1} - 1]$$

Thus for any general nth order reaction it is evident that,

$$t_{\frac{1}{2}} \propto [A]_0^{1-n}$$

It is to be noted that the above formula is applicable for any general nth-order reaction except n=1.

8. Methods of Determining Reaction Order

How to Determine Order of Reaction: Half-Life Method-

It is used when the rate law involves only one concentration term.

$t_{1/2} \propto (a)^{1-n}$
or
$t_{1/2} \propto 1/a^{n-1}$

For two different concentrations, we have:

$$\frac{(t^{1/2})_1}{(t^{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

On taking logarithms on both sides, we get:

$$\log_{10} \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \log_{10}(a_2/a_1)$$

Hence,

$$n = 1 + \frac{\log(t^{1/2})_1 - \log(t^{1/2})_2}{\log a_2 - \log a_1}$$

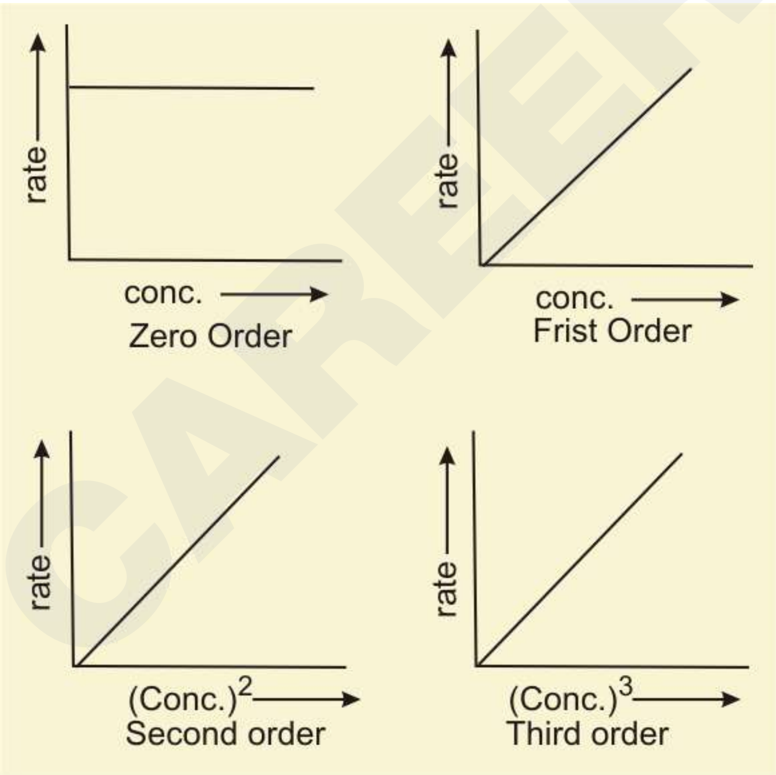
Here, n is the order of the reaction.

How to Determine Order of Reaction: Graphical Method-

Here graphs are plotted between rate and concentration to find the order of the reaction.

$[\text{Rate} \ = k(\text{concentration})^n]$

Plots of Rate vs Concentration



How to Determine Order of Reaction - Integrated Rate Law Method-

If the data for time(t) and [A] is given then this method is applicable. Thus follow the steps given below to find the order of reaction by using the integrated rate law method.

- **Check for First Order:**
  1. Use the formula given below to find out the two values of k as k_1 and k_2.
  $$k = \frac{2.303}{t} \log_{10}\left[\frac{A_o}{A}\right]$$
  2. If these two values k_1 and k_2 are same, then this given reaction is of first-order. But if $k_1 \neq k_2$, then check for zero-order.

- **Check for Zero-Order:**
  1. Use the formula given below to find out the two values of k as k_1 and k_2.
  $$k = \frac{A_o - A}{t}$$
  2. Again, if these two values k_1 and k_2 are same, then this given reaction is of zero-order. But if $k_1 \neq k_2$, then check for second-order.
- **Check for Third-Order:**
  1. Use the formula given below to find out the two values of k as k_1 and k_2.
  $$k = \frac{1}{t}\left[\frac{1}{A} - \frac{1}{A_o}\right]$$
  2. Further, if these two values k_1 and k_2 are same, then this given reaction is of second-order. But if $k_1 \neq k_2$, then check for third-order and so on.

9. Molecularity of reaction

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is Molecularity.

Description:

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ (unimolecular)

$H_2 + I_2 \rightarrow 2HI$ (bimolecular)

$2NO + O_2 \rightarrow 2NO_2$ (trimolecular)

Molecularity is the theoretical concept. It cannot be zero/non-integer.

10. Pseudo First Order Reaction

If one reactant is present in large excess a 2^{nd} order reaction is converted to 1^{st} order reaction. This is called a pseudo-first-order reaction.

acid catalysed hydrolysis of ester

$$C_3H_6O_2 + H_2O \rightarrow CH_3COOH + CH_3OH$$

This reaction is first order with respect to ester. The 2nd order reaction with respect to that reactant which has been taken in more amount. For example:

$$r = k[CH_3CO_2CH_3][H_2O] = k^{'}[CH_3CO_2CH_3]$$

$$k[H_2O] = k^{'}$$

11. Complex Reaction

Complex Reaction -

Complex reactions are those reactions when a sequence of elementary reactions or single-step reactions gives us the products. Since complex reactions occur in multiple steps, the molecularity of such reactions cannot be determined. It can only be determined for elementary reactions.
For example:

$$NO_2 + CO \rightarrow NO + CO_2$$

The rate of the reaction is given experimentally as follows:

$$\text{rate} = k[NO_2]^2$$

Now, clearly, the order of this reaction is 2 but since it is a complex reaction, thus the molecularity of this reaction cannot be determined.

NOTE: For any complex or elementary reaction, it has been found that:

$$\text{Molecularity} \leq 3$$

Because the probability of simultaneous and effective collision of three molecules is very low. Thus, termolecular or higher molecularity reaction is rarely observed.

Order of Reaction vs Molecularity-

Difference between Order of Reaction and Molecularity

Order of Reaction	Molecularity
Experimentally determined	Theoretically determined
Defined for elementary as well as complex	Defined only for elementary reactions
Can be zero, positive or fractional	Always a positive integer
The order of reaction can vary according to the conditions	Molecularity is fixed for any elementary reaction

12. Arrhenius Equation

Effect of Temperature on Rate of Reaction: Temperature Coefficient-

We know that on increasing the temperature, the rate of the reaction or rate constant increases.
The rate equation is given as follows:

$$\mathrm{Rate} = \mathrm{k[conc]^n}$$

Here k is the rate constant

Now, we will see the relation between k and T or also known as the 'approximate dependency of k on T'.

Generally on 10^{o}C rise in temperature, the rate constant nearly doubles.

Temperature Coefficient: It is the ratio of two rate constants. Thus, mathematically it is given as:

$$\mathrm{T_{coeff}} = \frac{\mathrm{k_{(t+10)^{\circ}C}}}{\mathrm{k_{t^{\circ}C}}}$$

Thus, the temperature coefficient shows the dependency of the rate constant(k) on temperature(T).

NOTE: The standard value of the temperature coefficient is given at t = 25^{o}C and (t+10) = 35^{o}C.

Effect of Temperature on Rate of Reaction: Accurate Dependency of K on T-

The temperature dependence of the rate of a chemical reaction can be accurately explained by the Arrhenius equation. It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$\mathrm{k = Ae^{-Ea/RT}}$$

where A is the Arrhenius factor or the frequency factor. It is also called the pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole(J mol^{-1}).

Ratio of Two Rate Constants at Two Different Temperatures-

We have the rate constant K_1 at temperature T_1 and the rate constant K_2 at temperature T_2.

We know that the Arrhenius equation is given as follows:

$$\log_{10}\mathrm{K_1} = \log_{10}\mathrm{A} - \frac{\mathrm{E_a}}{2.303\mathrm{RT_1}} \quad \text{............(i)}$$

$$\log_{10}\mathrm{K_2} = \log_{10}\mathrm{A} - \frac{\mathrm{E_a}}{2.303\mathrm{RT_2}} \quad \text{............(ii)}$$

On subtracting equation (i) from (ii), we get:

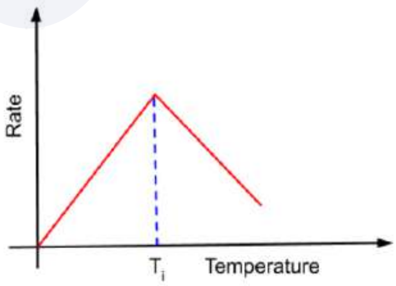
$$\log_{10}\mathrm{K_2} - \log_{10}\mathrm{K_1} = \frac{\mathrm{E_a}}{2.303\mathrm{RT_1}} - \frac{\mathrm{E_a}}{2.303\mathrm{RT_2}}$$

$$\textbf{Thus}, \log\frac{\mathrm{K_2}}{\mathrm{K_1}} = \frac{\mathrm{Ea}}{2.303\mathrm{R}}\left[\frac{1}{\mathrm{T_1}} - \frac{1}{\mathrm{T_2}}\right]$$

Exception(Arrhenius Theory)-

Although the Arrhenius equation explains the exact relationship between the rate of reaction and the temperature but there are still some exceptions in this theory. Actually, on increasing the temperature rate may decrease sometimes and may not follow Arrhenius equation. Following examples will illustrate these exceptions.

- **Bacterial decomposition**



From the graph, it is clear that first on increasing the temperature the rate also increases but at T_i (also known as inversion temperature) rate starts to decrease on further increasing the temperature.

13. Complex Reaction - Mechanism of Reaction

On the basis of mechanism, we have two types of reactions:

- Simple or elementary reaction
- Complex or multi-step reaction

Simple or Elementary reaction

- The reactions, which occur in a single step, are called simple or elementary reactions. For example:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

- An elementary reaction is an individual molecular event that involves the breaking or making of chemical bonds. The overall reaction describes the stoichiometry of the overall process but provides no information on how the reaction occurs.

Complex Reaction

- A complex reaction takes place in a sequence of a number of elementary steps.
- Molecularity of complex reaction is not defined. The molecularity of each step can be defined but not for overall.
- Overall rate of reaction is given by the slowest step of the complex reaction.
  For example, a combination of NO_2 and CO occurs in a sequence of elementary steps.

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g) \qquad \text{(elementary step I)}$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \qquad \text{(elementary step II)}$$

Important Facts:

- The number of reactant molecules taking part in an elementary step or in an elementary reaction is expressed as the molecularity of that step of the molecularity of that reaction respectively.
- For elementary reactions usually, the order of reaction and molecularity are the same. Thus, it can be said that if the order of a reaction for a change is fractional it cannot be an elementary reaction.

14 . Complex Reaction (When Intermediate is Incorporated)

This example will illustrate how to determine the rate law when the intermediate is involved in the rate-determining step.

$$2O_3 \rightarrow 3O_2$$

Mechanism

$$O_3 \rightleftharpoons O_2 + O \qquad \text{K}_1 \text{ and } \text{K}_2 \text{ are the forward and backward reaction constants respectively}$$

$$O + O_3 \rightarrow 2O_2 \qquad \text{K}_3 \text{ is the rate constant}$$

In this case, step 1 is fast and step 2 is slow.

The rate law is given as follows:

$$\text{rate} = K_3[O]^1[O_3]^1$$

We know from equilibrium theory that:

$$K_{eq} = \frac{K_1}{K_2} = \frac{[O_2][O]}{[O_3]}$$

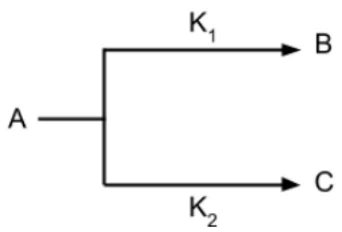
$$[O] = \frac{K_1[O_3]}{K_2[O_2]}$$

$$\text{Thus, rate} = \frac{K_3.K_1}{K_2}\frac{[O_3][O_3]}{[O_2]} = \frac{K_3.K_1}{K_2}\frac{[O_3]^2}{[O_2]}$$

$$\text{Thus, Order} = 2 - 1 = 1$$

$$\text{rate constant} = \frac{K_3.K_1}{K_2}$$

15 . Parallel First Order Kinetics



In this situation, B and C both are forming. These types of reactions are known as parallel reactions. Both these reactions are first-order reactions with rate constants K_1 and K_2 respectively and half-lives as $t_{(1/2)1}$ and $t_{(1/2)2}$.

For these parallel reactions, we need to find:

- Effective order
- Effective rate constant
- Effective $t_{1/2}$
- Effective Activation energy
- [A], [B], [C] with time (t) variation
- % of [B] and % of [C]

We know that the rate equations are given as follows:

$$r_1 = \frac{-dA}{dt} = K_1[A]$$

$$r_2 = \frac{-dA}{dt} = K_2[A]$$

Thus, overall rate of reaction is :

$$\frac{-dA}{dt} = K_1[A] + K_2[A] = (K_1 + K_2)[A]$$

Thus, rate $= (K_1 + K_2)[A]^1$

$\textbf{Effective Rate Constant}(\mathbf{K_{eff}}) = (K_1 + K_2)$

$\textbf{Effective order of reaction} = 1$

$$\text{Now, effective half-life}(t_{1/2}) = \frac{0.693}{K_{eff}} = \frac{0.693}{K_1 + K_2}$$

$$\Rightarrow \frac{0.693}{\frac{0.693}{(t_{1/2})_1} + \frac{0.693}{(t_{1/2})_2}}$$

Thus, effective half life is given as :

$$\frac{1}{(t_{1/2})_{eff}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

NOTE: Effective activation energy, [A], [B], [C] with time (t) variation and % of [B] and % of [C] will be discussed in later concepts.

16 . Effective Activation Energy

We know that the Arrhenius equation is given as:

$$K = A.e^{-Ea/RT}$$

$$K_{eff} = K_1 + K_2$$

$$\text{Thus, } A_{eff}.e^{-Ea_{eff}/RT} = A_1.e^{-Ea_1/RT} + A_2.e^{-Ea_2/RT}$$

Differentiate this equation with respect to temperature 'T'

Thus, we have :

$$A_{eff}.e^{-Ea_{eff}/RT}\left(\frac{+Ea_{eff}}{RT^2}\right) = A_1.e^{-Ea_1/RT}\left(\frac{+Ea_1}{RT^2}\right) + A_2.e^{-Ea_2/RT}\left(\frac{+Ea_2}{RT^2}\right)$$

$$K_{eff}\,E_{eff} = K_1Ea_1 + K_2Ea_2$$

$$E_{eff} = (K_1Ea_1 + K_2Ea_2)/K_{eff}$$

p- Block Elements

Important Formulae

1. Physical Properties of Boron Family

Physical Properties of Group 13-

Electronic configuration

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas cores, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*-electrons plus 10 *d*-electron cores. Thus, the electronic structures of these elements are more complex than the *s*-block elements. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

Atomic radii

On moving down the group, for each successive member, one extra shell of electrons is added and, therefore, the atomic radius is expected to increase. However, a deviation can be seen. The atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of an additional 10 *d*-electrons offers only a poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in the atomic size of the elements.

Density

Density increases from boron to thallium. However, boron and aluminium have comparatively low values. This is due to their lower atomic masses as compared to gallium, indium and thallium.

Melting and boiling points

The elements of this group do not show a regular change in their melting points with an increase in atomic number. The melting point decreases from B to Ga and then increases. The high melting point of boron is due to the fact that it exists as a giant covalent polymer in both solid and liquid states. The elements Al, In and Tl all have close-packed metal structures. Gallium has an unusual structure. It consists of only Ga_2 molecules. It has thus low melting point. It exists as liquid up to 2000^oC and is hence used in high-temperature thermometry.

Ionization enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with an increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to the inability of *d*- and *f*-electrons, which have low screening effect, to compensate for the increase in nuclear charge. The order of ionisation enthalpies, as expected, is $\Delta H_1 < \Delta H_2 < \Delta H_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. The effect of this will be apparent when you study their chemical properties.

Oxidation states

It is in group 13 that we first encounter elements possessing more than one oxidation state. As s^2p^1 grouping is present in the outermost energy shell of the elements of the group IIIA, the expected oxidation states are +3 and +1. Boron shows a +3 oxidation state in all its compounds. Other members show +3 and +1 oxidation states. The stability of the +1 oxidation state increases from aluminium to thallium and the stability of +3 is a more important oxidation state for Al, Ga and In whereas the +1 oxidation state is more important for Tl.

Electropositive character

The elements of group 13 are less electropositive as compared to the elements of groups 1 and 2. This is due to their size and high ionisation energy. The electropositive character increases from boron to aluminium and then decreases from aluminium to thallium. Boron having very high ionisation energy is considered to be as a semimetal. It is closer to non-metals. Aluminium is a metal and is most electropositive. The increase in electropositive nature from B to Al is due to increases in atomic size. The remaining three elements Ga, In and Tl are less electropositive and less metallic than aluminium and there is a decrease from Ga and Tl.

Complex formation

Group IIIA elements form complexes much more readily than the *s*-block elements, because of their smaller size, increased charge and availability of vacant orbitals.

Nature of compounds

- The tendency of the formation of ionic compounds increases from B to Tl.

- Boron forms only covalent compounds.
- Aluminium forms both ionic as well as covalent compounds.
- Gallium forms mainly ionic compounds except anhydrous $GaCl_3$ which is covalent in nature.

2. Anomalous Behaviour of Boron

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in an aqueous medium.
The monomeric trihalides, being electron-deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$F_3B + : NH_3 \rightarrow F_3B \leftarrow NH_3$$

It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (e.g., $AlCl_3$) are dimerised through halogen bridging (e.g., Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

3. Diagonal Relationship of B and Si

Boron exhibits resemblance with its diagonal element silicon of group 14:

- Both boron and silicon are non-metals.
- Both are semiconductors.
- Both form covalent hydrides i.e, boranes and silanes.
- Both form solid oxides which get dissolve in alkalies forming borates and silicates respectively.

4. Chemical Properties of Boron Family

Chemical Properties of Group 13-

Reaction towards air
Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at a high temperature, they form nitrides.

$$2E(s) + 3O_2(g) \longrightarrow 2E_2O_3(s)$$
$$2E(s) + N_2(g) \longrightarrow 2EN(s)$$
Where E is an element

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

Reactivity towards acids and alkalies
Boron does not react with acids and alkalies even at moderate temperatures, but aluminium dissolves in mineral acids and aqueous alkalies and thus shows an amphoteric character. Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.
Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$$

Reactivity towards halogens
These elements react with halogens to form trihalides (except TlI_3).

5. Group 14 Elements (Carbon Family)

Group 14(Carbon Family) - Physical Properties-

Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members.

Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general, the ionisation enthalpy decreases down the group. The small decrease in $\Delta_i H$ from Si to Ge to Sn and a slight increase in $\Delta_i H$ from Sn to Pb is the consequence of the poor shielding effect of intervening *d* and *f* orbitals and the increase in the size of the atom.

Electronegativity

Due to the small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Allotropy

The ability of an element to exist in more than one physical form is called allotropy. All the elements of this group except Pb exhibit allotropy. Carbon has three allotropes i.e, diamond, graphite and fullerene

Valency

All the elements of this group show tetravalency as they have 4 electrons in their valence shell.

Atomic and Ionic radii

As we move down the group, the radius of these elements increases.

Multiple Bonding

Carbon forms $p\pi$-$p\pi$ bonding with itself and with S, N and O. While the other elements of this group form $p\pi$-$d\pi$ bonding as they have a vacant *d*-orbital while carbon does not have.

Group 14 (Carbon Family): Chemical Properties-

Hydrides

- All the members of this group form covalent hydrides.
- Hydrides of carbon are called hydrocarbons.
- Hydrides of Si and Ge are known as silanes and germanes.
- The thermal stability of hydrides decreases down the group.
- Reducing character increases down the group.

Halides

These elements can form halides of the formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except for carbon, all other members react directly with halogen under a suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because the Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to a higher orbital to have four unpaired electrons around the lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. The stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more stable than PbX_4. Except for CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from the oxygen atom of a water molecule in the *d* orbital.

Oxides-

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperatures. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

6. Group 15 Elements (Nitrogen Family)

Group 15 - Physical and Chemical Properties-

Electronic configuration

The valence shell electronic configuration of these elements is ns^2np^3. The s orbital in these elements is completely filled and the p orbitals are half-filled, making their electronic configuration extra stable.

Atomic and Ionic Radii
Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

Ionisation Enthalpy
Ionisation enthalpy decreases down the group due to a gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is .

Electronegativity
The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced. $\Delta H_1 < \Delta H_2 < \Delta H_3$

Reactivity towards hydrogen
All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. The hydrides show a regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. Due to high electronegativity and the small size of nitrogen, NH_3 exhibits hydrogen bonding in the solid as well as the liquid state. Because of this, it has higher melting and boiling points than that of PH_3.

Reactivity towards oxygen
All these elements form two types of oxides: E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of the lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and that of bismuth predominantly basic.

Reactivity towards halogens
These elements react to form two series of halides: EX_3 and EX_5. Nitrogen does not form pentahalide due to the non-availability of the d orbitals in its valence shell. Pentahalides are more covalent than trihalides. This is due to the fact that in pentahalides +5 oxidation state exists while in the case of trihalides +3 oxidation state exists. Since elements in the +5 oxidation state will have more polarising power than in the +3 oxidation state, the covalent character of bonds is more in pentahalides. All the trihalides of these elements except those of nitrogen are stable. In the case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

Reactivity towards metals
All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Anomalous properties of nitrogen
Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals. Nitrogen has the unique ability to form pπ-pπ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group seldom form pπ-pπ bonds as their atomic orbitals are so large and diffused that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one sigma and two pi) between the two atoms.

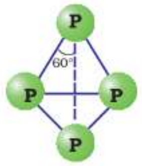
Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high.

On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in the elemental state. However, the single N–N bond is weaker than the single P–P bond because of the high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result, the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form a dπ –pπ bond as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphorus and arsenic can form dπ – dπ bonds also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

7. Phosphorus

Phosphorus is found in many allotropic forms, the important ones being white, red and black.
White phosphorus is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in the dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

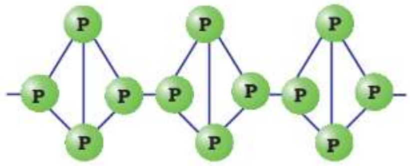
$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$



White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°. It readily catches fire in the air to give dense white fumes of P_4O_{10}.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

Red phosphorus is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses an iron-grey lustre. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.



It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner shown in the figure given above.

Black phosphorus has two forms α-black phosphorus and β-black phosphorus. α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in the air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air up to 673 K.

8. Group 16 Elements (Oxygen Family)

Group 16: Oxyen Family - Physical Properties-

Some of the physical properties of Group 16 elements are given in Table 7.6. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short-lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as a diatomic molecule (O_2) whereas sulphur exists as a polyatomic molecule (S_8).

Details of some atomic and physical properties of Group 16 elements can be found below:

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol^{-1}	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$
Covalent radius/(pm)[a]	66	104	117	137	146
Ionic radius, E^{2-}/pm	140	184	198	221	230[b]
Electron gain enthalpy, $/\Delta_{eg}H$ kJ mol^{-1}	–141	–200	–195	–190	–174
Ionisation enthalpy (Δ_iH_1) /kJ mol^{-1}	1314	1000	941	869	813
Electronegativity	3.50	2.44	2.48	2.01	1.76
Density /g cm^{-3} (298 K)	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	55	393[f]	490	725	520
Boiling point/K	90	718	958	1260	1235
Oxidation states*	–2,–1,1,2	–2,2,4,6	–2,2,4,6	–2,2,4,6	2,4

[a]Single bond; [b]Approximate value; [c]At the melting point; [d] Rhombic sulphur; [e]Hexagonal grey; [f]Monoclinic form, 673 K.
* *Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF_2 and O_2F_2 respectively.*

Group 16: Oxyen Family - Chemical Properties-

Oxidation states and trends in chemical reactivity
The elements of Group 16 exhibit a number of oxidation states. The stability of the -2 oxidation state decreases down the group. Polonium hardly shows a –2 oxidation state. Since the electronegativity of oxygen is very high, it shows only a negative oxidation state as –2 except in the case of OF_2 where its oxidation state is +2. Other elements of the group exhibit +2, +4, +6 oxidation states but +4 and +6 are more common. Sulphur, selenium and tellurium usually show a + 4 oxidation state in their compounds with oxygen and +6 with fluorine. The stability of the +6 oxidation state decreases down the group and the stability of the +4 oxidation state increases (inert pair effect). Bonding in +4 and +6 oxidation states is primarily covalent.

- **Reactivity with hydrogen:** All the elements of Group 16 form hydrides of the type H_2E (E=O, S, Se, Te, Po). Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of a decrease in bond enthalpy for the dissociation of the H–E bond down the group. Owing to the decrease in enthalpy for the dissociation of the H–E bond down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing properties and this character increases from H_2S to H_2Te.
- **Reactivity with oxygen:** All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. The reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature
- **Reactivity towards the halogens:** Elements of Group 16 form a large number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have an octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

9 Group 17 Elements (Halogen Family)

Group 17 Elements: General Characteristics and Group Trends

The trends of some of the atomic, physical and chemical properties are discussed below.

Electronic Configuration

All these elements have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

Atomic and Ionic Radii
The halogens have the smallest atomic radii in their respective periods due to the maximum effective nuclear charge. The atomic radius of fluorine like the other elements of the second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to the increasing number of quantum shells.

Ionisation Enthalpy
They have little tendency to lose electrons. Thus they have very high ionisation enthalpy. Due to an increase in atomic size, ionisation enthalpy decreases down the group.

Electron Gain Enthalpy
Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. This is due to the small size of the fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity
They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

Oxidation states
All the halogens exhibit a –1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms, e.g., in interhalogens, oxides and oxoacids. The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no *d* orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

10 Group 18 Elements (Noble Gases)

Group 18 Elements: General Characteristics

Electronic Configuration:- All noble gases have a general electronic configuration ns^2np^6 except helium which has $1s^2$. Many of the properties of noble gases including their inactive nature are ascribed to their fully filled orbital configuration.

Ionisation Enthalpy:- Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.

Atomic Radii:- Atomic radii increase down the group with an increase in atomic number.

Electron Gain Enthalpy:- Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Solubility:- Noble gases are slightly soluble in water and their solubility increases down the group from He to Rn with an increase in atomic size.

Electrical conductivity:- These gases have fairly high electrical conductivity. They produce characteristic coloured lights when an electrical discharge is passed through them at low pressure.

Some atomic and physical properties of Noble gases are tabulated below:

Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	[He]$2s^22p^6$	[Ne] $3s^23p^6$	[Ar]$3d^{10}4s^24p^6$	[Kr]$4d^{10}5s^25p^6$	[Xe]$4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionisation enthalpy /$kJmol^{-1}$	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /$kJmol^{-1}$	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

* *radioactive*

Group 18 Elements: Chemical Properties

In general, noble gases are the least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2 ,np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Xe and Kr show some chemical activity under certain conditions.

Reaction with fluorides:-Xe react with fluorides and make different fluorides at different condition.

$$Xe + F_2 \xrightarrow[673K]{Ni\,tube} XeF_2$$

$$Xe + 2F_2 \xrightarrow[5-6\,atm]{Ni\,tube} XeF_4$$

Oxides:- Xenon fluorides compound reacts with water and gives oxides of xenon.

$$2XeF_4 + 3H_2O \rightarrow Xe + XeO_3 + 6HF + F_2$$

$$XeF_6 + 3H_2O \rightarrow +XeO_3 + 6HF$$

Oxyfluorides:-

$$XeF_4 + H_2O \rightarrow +XeOF_2 + 2HF$$
$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

d - and f - BLOCK ELEMENTS

Important Formulae

1. Transition Elements

Transition Elements Introduction-

In the extended form of the periodic table, the elements have been grouped into four blocks namely *s*, *p*, *d* and *f*-blocks. The elements belonging to groups 3 to 12 are called *d*-block or transition elements. In these elements, the last electron enters (n-1) *d*-subshell. The configuration of these elements is $(n-1)d^{1-10}ns^{1-2}$. These are present between *s*-block and *p*-block elements. The properties of these elements are intermediate between the properties of *s*-block and *p*-block elements, i.e., *d*-block elements represent change or transition in properties from most electropositive *s*-block elements to least electropositive *p*-block elements. Therefore, these elements are called transition elements.
Earlier, the transition elements were regarded as those elements which possessed partially filled penultimate *d*-subshells in their ground state or in one of their commonly occurring oxidation states. This definition included coinage metals(Cu, Ag and Au) in the transition elements as their ions have partially filled (n-1)*d*-subshells although their atoms have filled(n-1) *d*-subshells in the ground state.
However, the above definition does not cover the elements of group 12, i.e. Zn, Cd and Hg as these elements do not have partially filled (n-1) *d*-subshells either in the ground state or in ions.
However, zinc metals showing similarities in some of the chemical properties with transition metals are also included in this block. These are considered as end members of the transition series in order to maintain a rational classification of elements.
Certain *d*-block elements are particularly important in living organisms. Iron, the transition element, is present in the largest quantity in the human body. The best-known biological iron-containing compound is the protein haemoglobin, the red component of blood that is responsible for the transport of oxygen. Cobalt is the crucial element in vitamin B12, a compound that acts as a catalyst in the metabolism of carbohydrates, fats and proteins. Molybdenum and iron together with sulphur form the reactive portion of nitrogenase, a biological catalyst used by nitrogen-fixing organisms to convert atmospheric nitrogen into ammonia. Copper and zinc are important in other biological catalysts. Iron, zinc, copper, cobalt, nickel, manganese and molybdenum are known to be essential components of enzymes. Vanadium and chromium are also essential for life. Some harmful elements are also present in this block. For example, mercury is toxic and is a threat to the environment.

Screening Effect and Lanthanoid Contraction-

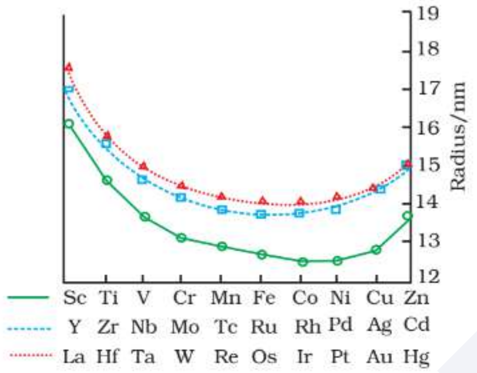
The Lanthanide Contraction describes the atomic radius trend that the lanthanide series exhibits. The Lanthanide Contraction refers to the fact that the *5s* and *5p* orbitals penetrate the *4f* sub-shell so the *4f* orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease. This decrease in size continues throughout the series.

The Lanthanide Contraction is the result of a poor shielding effect of the *4f* electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not affected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The *s* orbital has the greatest shielding while *f* has the least and *p* and *d* are in between the two with *p* being greater than *d*.

The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d block elements. Pd and Pt are such elements. Pd has *4d* electrons while Pt has *5d* and *4f* electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the *4f* electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller-than-expected radius.

Atomic Size/Radii-

In general, ions of the same charge in a given series show a progressive decrease in radius with increasing atomic number. This is because the new electron enters a d orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. An interesting point emerges when the atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves in the figure below, show an increase from the first (*3d*) to the second (*4d*) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanide contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of the usual family relationship.



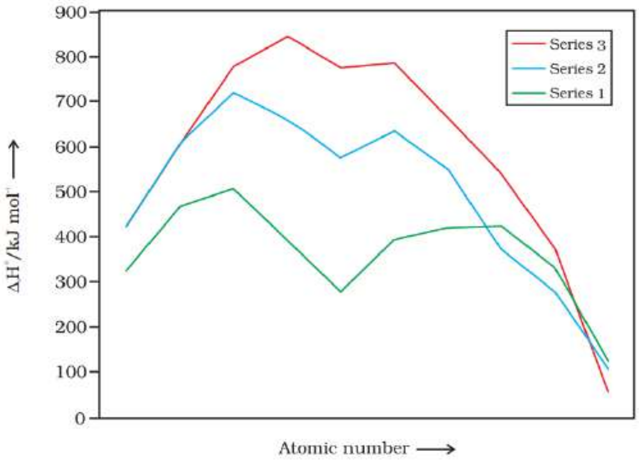
The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to a similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one 4f electron by another is less than that of one d electron by another, and as the nuclear charge increases along the series, there is a fairly regular decrease in the size of the entire 4f orbitals.
The decrease in metallic radius coupled with an increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (Z = 22) to copper (Z = 29) a significant increase in the density may be noted.

Metallic Character and Enthalpy of Atomization-

Metallic character-

- All the transition elements or *d*-block elements are metals since the number of electrons in the outermost shell is very small, i.e., either 1 or 2. They possess metallic properties such as:
    - High melting and boiling points.
    - Good conductors of heat and electricity.
    - Hard, malleable and ductile. Hg is an exception which is liquid and soft.
    - High density, metallic lustre and high enthalpies of atomization.
- They exhibit all three types of structures, i.e., fcc, hcp and bcc.
- Both metallic and covalent bonding exist in transition metals. The metallic bonding is due to the possession of one or two electrons in the outermost energy shell. They have low ionisation energies.

Enthalpy of atomisation
They have high enthalpies of atomisation which are shown in the figure given below. The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favourable for strong interatomic interaction. In general, the greater the number of valence electrons, the stronger the resultant bonding. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions (see later for electrode potentials).
Another generalisation that may be drawn from the given figure is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal–metal bonding in compounds of the heavy transition metals.



Ionisation Energy-

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner d orbitals. The variation in ionisation enthalpy along a series of transition elements is much less in comparison to the variation along a period of non-transition elements. The first ionisation enthalpy, in general, increases, but the magnitude of the increase in the second and third ionisation enthalpies for the successive elements is much higher along a series.
The irregular trend in the first ionisation enthalpy of the metals of the 3d series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. You have learnt that when d-block elements form ions, ns electrons are lost before (n – 1) d electrons. As we move along the period in the 3d series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of the inner subshell, i.e., 3d orbitals. These 3d electrons shield the 4s electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the 3d series. The doubly or more highly charged ions have d^n configurations with no 4s electrons. A general trend of increasing values of second ionisation enthalpy is expected as the effective nuclear charge increases because one d electron does not shield another electron from the influence of nuclear charge because d-orbitals differ in direction. However, the trend of a steady increase in second and third ionisation enthalpy breaks for the formation of Mn^{2+} and Fe^{3+} respectively. In both cases, ions have a d^5 configuration. Similar breaks occur at corresponding elements in the later transition series.
The three terms responsible for the value of ionisation enthalpy are the attraction of each electron towards the nucleus, repulsion between the electrons and the exchange energy. Exchange energy is responsible for the stabilisation of the energy state. Exchange energy is approximately proportional to the total number of possible pairs of parallel spins in the degenerate orbitals. When several electrons occupy a set of degenerate orbitals, the lowest energy state corresponds to the maximum possible extent of a single occupation of orbital and parallel spins (Hund's rule). The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult. There is no loss of exchange energy at the d^6 configuration. Mn^+ has a $3d^54s^1$ configuration and the configuration of Cr^+ is d^5, therefore, the ionisation enthalpy of Mn^+ is lower than Cr^+. In the same way, Fe^{2+} has a d^6 configuration and Mn^{2+} has a $3d^5$ configuration. Hence, the ionisation enthalpy of Fe^{2+} is lower than the Mn^{2+}. In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn.

Oxidation State-

One of the notable features of transition elements is the great variety of oxidation states these may show in their compounds.
The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons up to manganese ($Ti^{IV} O_2$, $V^VO_2^+$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^-$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.
The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III},V^{IV}, V^V. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two.
An interesting feature in the variability of oxidation states of the d–d-block elements is noticed among the groups. Although in the p–block the lower oxidation states are favoured by the heavier members (due to the inert pair effect), the opposite is true in the groups of d-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in an acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.
Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

Magnetic Properties and Character-

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: diamagnetism and paramagnetism. Diamagnetic substances are repelled by the applied field while paramagnetic substances are attracted. Substances which are attracted very strongly are said to be ferromagnetic. In fact, ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.
Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the ‘spin-only’ formula, i.e.,

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM). A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication of the number of unpaired electrons present in the atom, molecule or ion.

2. Colour Of Transition Elements

When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions are observed.

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+}Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

3. Properties Of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$,$TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows:
(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamonds in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

4. $KMnO_4$ - Potassium Permanganate

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ + O_2 \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4 + 10SO_4^{2-} + 16H^+$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.
The manganate and permanganate ions are tetrahedral; the π-bonding takes place by the overlap of the p orbitals of oxygen with the d orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.

A few important oxidising reactions of $KMnO_4$ are given below:
(1) In acidic solutions:

- Iodine is liberated from potassium iodide:
  $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$
- Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):
  $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(2) In neutral or faintly alkaline solutions:

- A notable reaction is the oxidation of iodide to iodate:
$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$
- Thiosulphate is oxidised almost quantitatively to sulphate:
$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

5. Potassium Dichromate - $K_2Cr_2O_7$

Potassium dichromate is a very important chemical used in the leather industry and as an oxidant for the preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access to air. The reaction with sodium carbonate occurs as follows:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is, therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in an aqueous solution depending upon the pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

The structures of the chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°. Sodium and potassium dichromates are strong oxidising agents; sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$$6I \rightarrow 3I_2 + 6e^- \qquad 3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$$
$$3H_2S \rightarrow 6H^+ + 3S + 6e^- \qquad 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent,

for example,

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

6. F Block Elements

Physical Properties of F-block-

Electronic Configurations
It may be noted that atoms of these elements have an electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

Atomic and Ionic Sizes
The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of lanthanoids. It has far-reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite as regular as it is regular in M^{3+} ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is a fairly regular decrease in the sizes with increasing atomic number.

Oxidation States
In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E^o value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly, Yb^{2+} which has an f^{14} configuration is a reductant. Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

General Characteristics
All the lanthanides are metals. They are soft, malleable and ductile in nature. They are not good conductors of heat and electricity. They are highly dense metals and their densities are in the range of 6.77 to 9.74 gcm^{-3}. The densities and atomic volumes, in general, increase with the increase in atomic number. But a regular trend is not observed. They have fairly high melting points. However, no definite trend is observed.

Colour
Many of the lanthanide ions are coloured in solid-state as well as in solution. The colour is due to partially filled *f*-orbitals which allow *f-f* transitions. M^{3+} ions having $4f^0$, $4f^7$ or $4f^{14}$ configurations are colourless.

Magnetic Properties
Ions having unpaired electrons are paramagnetic while those having all the orbitals paired are diamagnetic. The lanthanide ions(M^{3+}) except La^{3+} ($4f^0$) and Lu^{3+}($4f^{14}$) are paramagnetic since they contain 1,2,....7 unpaired electrons.

Chemical Properties of Lanthanoids-

- The metals combine with hydrogen when gently heated in the gas.
- The carbides Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.
- They liberate H_2 from dilute acids and burn in the presence of halogens to form halides.
- They form oxides M_2O_3 and hydroxides $M(OH)_3$.

Properties of Actinoids -

The actinoids include the fourteen elements from Th to Lr. The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

Electronic Configurations
All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are $[Rn]5f^7 7s^2$ and $[Rn]5f^7 6d^1 7s^2$. Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

Ionic Sizes
The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Oxidation States
The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in the +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Coordination Compounds

Important Formulae

1. Coordination Compounds

Addition Compounds or Molecular Compounds
These are those compounds which are formed by the combination or simple addition of two or more simple salts. These compounds are of two types, i.e., Double salts and Coordination compounds.

The difference between a double salt and a coordination compound
Both double salts, as well as complexes, are formed by the combination of two or more stable compounds in a stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ do not dissociate into Fe^{2+} and CN^- ions.

Terminologies Related to Coordination Compounds-

Coordination entity
A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$

Central atom/ion
In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ions are also referred to as Lewis acids.

Coordination sphere
The central atom/ion and the ligands attached to it are enclosed in the square bracket and are collectively termed the coordination sphere. The

ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+

Coordination polyhedron
The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar.

Homoleptic and heteroleptic complexes
Complexes in which a metal is bound to only one kind of donor group, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor group, e.g., $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

Types of Ligands-

Mono or Unidentate ligands
They have one donor atom, i.e., they supply only one electron pair to a central metal atom or ion. F^-, Cl^-, Br^-, H_2O, NH_3, CN^-, etc. are examples of monodentate ligands.

Bidentate ligands
Ligands which have two donor atoms and have the ability to link with the central metal ions at two positions are called bidentate ligands. Some examples include ethylenediamine(en), oxalate(ox), etc.

Tridentate ligands
The ligands having three donor atoms are called tridentate ligands. Some examples include diethylenetriamine(dien), and 2.2,2-terpyridine (terpy).

Tetradentate ligands
These ligands possess four donor atoms. Some examples include nitriloacetate, and triethylenetetramine(trien).

Pentadentate ligands
They have five donor atoms. Some examples include ethylenediamine triacetate ion.

Hexadentate ligands
They have six donor atoms. The most important example is ethylenediaminetetraacetate ion.

Ambidentate ligands
These are those ligands which can bind to the central metal atom through two different sites. For example CN^-, NCS^-, etc.

Flexidentate ligands
These are the polydentate ligands having many donor sites but according to the availability they change their number of donor sites

Chelating ligands
Some polydentate ligands form coordinate bonds with central metal atoms through their donor sides forming a closed ring-like structure, these ligands are known as chelating ligands and the complex so formed is known as chelating complex.

- The stability of these ligands can be explained on the basis of entropy change.
- When a chelating ligand bonds to a central metal atom it displaces some number of monodentate ligands equal to its denticity which leads to an increase in the entropy of the system.
- 5 or 6-membered rings are more stable because angle strain is not there.

Oxidation Number-

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, the oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

Coordination Number -

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and$[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and$[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.
It is important to note here that the coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

Effective Atomic Number(EAN)-

Ligands are attached to the central metal ion through donor atoms. Each donor atom donates one electron pair to the central metal ion, i.e., the central metal atom or ion gains electrons from the donor atoms. In order to explain the stability of the complex, Sidgwick proposed an effective atomic number denoted as EAN, which is defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands. The effective atomic number (EAN) generally coincides with the atomic number of the next noble gas in some cases. EAN is calculated by the given relation:

EAN = Atomic number of the metal - number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands.

The EAN values of various metals in their respective complexes are tabulated below:

Complex	Metal(Oxidation State)	At. No. of Metal	Co-ordination	Effective atomic

			number	number
$K_4[Fe(CN)_6]$	+2	26	6	(26-2) + (6x2) = 36[Kr]
$[C0(NH_3)_6]Cl_3$	+3	27	6	(27-3) + (6x2) = 36[Kr]
$Ni(CO)_4$	0	28	4	(28-0) + (4x2) = 36[Kr]
$K_2[PtCl_6]$	+4	78	6	(78-4) + (6x2) = 86[Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	(47-2) + (2x2) = 50

Just as the octet is helpful in formulating the bonding in compounds of the light elements, an EAN provides a rough guide for bonding in coordination compounds. Almost all the metals achieve the EAN of a noble gas through coordination. The EAN concept has been particularly successful for complexes of low-valent metals.

Writing the Formula of a Complex or Coordination Compound-

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:
(i) The central atom is listed first.
(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
(iii) Polydentate ligands are also listed alphabetically. In the case of an abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in alphabetical order.
(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
(v) There should be no space between the ligands and the metal within a coordination sphere.
(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.
(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

IUPAC Nomenclature of Coordination or Complex Compound

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:
(i) The cation is named first in both positively and negatively charged coordination entities.
(ii) The ligands are named in alphabetical order before the name of the central atom/ion. (This procedure is reversed from the writing formula).
(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).
(iv) Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, and tetrakis are used, and the ligand to which they refer is placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).
(v) The Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by a Roman numeral in parenthesis.
(vi) If the complex ion is a cation, the metal is named the same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $[Co(SCN)_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.
(vii) The neutral complex molecule is named similar to that of the complex cation.

Naming of Complex Ions/Molecules

In the naming of complex ions, the names of ligands are written in alphabetical order followed by the name of a central metal atom with its oxidation number in Roman numerals. If the complex part contains two or more same type of ligands then di, tri, tetra, etc. are used.

For example, $[Co(NH_3)_3Cl_3]$ is written as Triamminetrichloridocobalt(III).

Naming of Complex Ions/Molecules

- The naming of the metal is replaced by placing the suffix - "ate".
- Some special names are given to some metals.

Metals	Cationic	Anionic
Ag	Silver	Argentate
Fe	Iron	Ferrate
Cu	Copper	Cuprate
Au	Gold	Aurate
Pb	Lead	Plumbate
Sn	Tin	Stannate

- For example, $[Ag(NH_3)_2]Cl$ is named as diamminesilver(I)chloride.

Naming of Complex Anion and Complex Cation

The IUPAC of $[PtCl_2(NH_3)_4]^{+2}[PtCl_4]^{-2}$ is written as Tetraamminedichloridoplatinum(IV)tetrachloroplatinate(II).

Naming of Complex Anion and Complex Cation

1. Use prefix -μ for ligands present in bridging.
2. If the charge on the complex is odd, then distribute this charge to the metal atoms and if the charge is even, then divide this charge equally to the central metal atoms.
3. Now, the naming can be written according to the rules discussed earlier.

2. Bonding in Coordination Compounds(Werner's Theory)

The main postulates are:

- In coordination compounds, metals show two types of linkages (valences)-primary and secondary.
- The primary valences are normally ionisable and are satisfied by negative ions.
- The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^{+}$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

3. Valence Bond Theory of Coordination Compounds

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands can use its **(n-1)d** or **nd** orbitals along with its **ns** and **np** for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. The different types of hybridisation and their respective shapes are given below

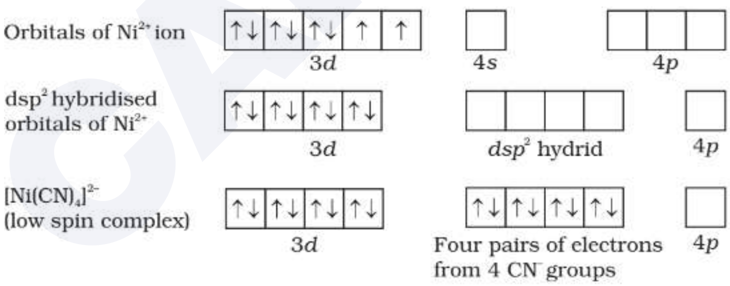
Coordination Number	Type of Hybridisation	Shape
4	sp^3	Tetrahedral
4	dsp^2	Square Planar
5	sp^3d	Trigonal Bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Analysis of Complex Compound on the Basis of VBT

Let us consider the case of $[Ni(CN)_4]^{2-}$ and try to predict the hybridisation of this complex

Here nickel is in a +2 oxidation state and the ion has a valence electronic configuration $3d^8 4s^0$.

In the presence of Cyanide ions, the electrons will be paired up and the hybridisation of Ni in the complex will be dsp^2 as shown below

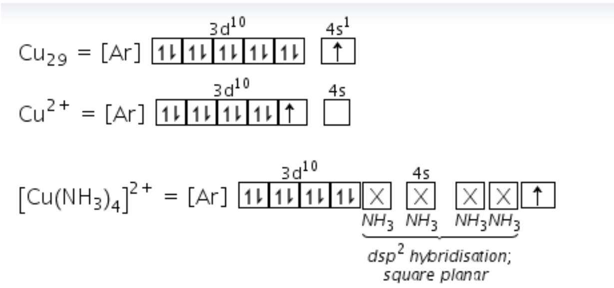


Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electrons.

Exceptional Case of Hybridisation(VBT)

$[Cu(NH_3)_4]^{2+}$ is an exception for determining the hybridisation. On the experimental basis, it has been found that its geometry is square planar, thus at least one *d* orbital is compulsory.

The electronic configuration of $[Cu(NH_3)_4]^{2+}$ is as follows:



But in this case, the last electron can easily be removed and Cu^{2+} will become Cu^{3+}, which does not exist in reality.

Thus to explain its square planar geometry, Huggins proposed sp^2d hybridisation that this last unpaired electron remains in the 3*d* orbital and the hybridisation is done by 4*s* orbital, 2 4*p* orbitals and 1 4*d* orbital. The third 4*p* orbital does not participate in hybridisation. Thus, in this way, its hybridisation is sp^2d and the geometry is square planar.

Magnetic Moment(On the Basis of VBT)

The magnetic moment of coordination compounds can be measured by magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes.
A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with up to three electrons in the d orbitals, like Ti^{3+} (d^1); V^{3+}(d^2); Cr^{3+}(d^3); two vacant d orbitals are available for octahedral hybridisation with 4s and 4p orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, the required pair of 3d orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4(Cr^{2+}, Mn^{3+}), d^5(Mn^{2+}, Fe^{3+}), d^6(Fe^{2+}, Co^{3+}) cases, a vacant pair of d orbitals results only by pairing of 3d electrons which leaves two, one and zero unpaired electrons, respectively.
The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions, there are complications. $[Mn(CN)_6]^{3-}$ has a magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has a magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of the formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Limitations of VBT

While the Valence Bond theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it has some shortcomings which are listed below:
(i) It involves a number of assumptions.
(ii) It does not give a quantitative interpretation of magnetic data.
(iii) It does not explain the colour exhibited by coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

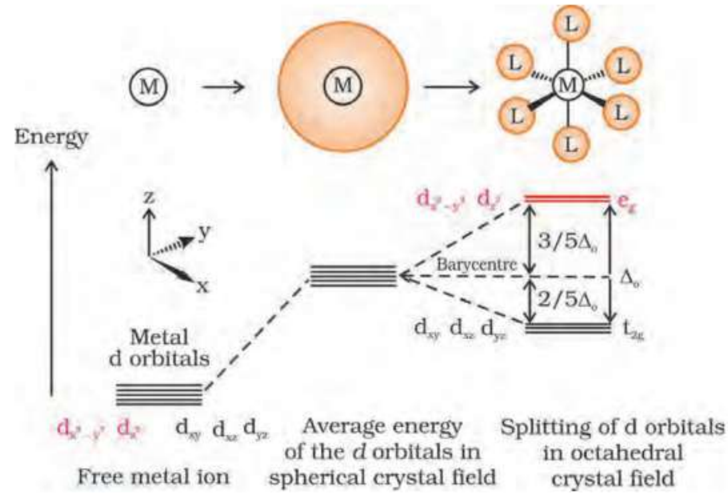
4. Crystal Field Theory (CFT)

Main Postulates of Crystal Field Theory-

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in the case of anions or point dipoles in the case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have the same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in the splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

Crystal Field Splitting in Octahedral Field

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which are oriented towards the axes along the direction of approach of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{zx} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0. Thus, the energy of the two e_g orbitals will increase by $\frac{3}{5}\Delta_0$ and that of the three t_{2g} will decrease by $\frac{2}{5}\Delta_0$.



The crystal field splitting, Δ_0, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

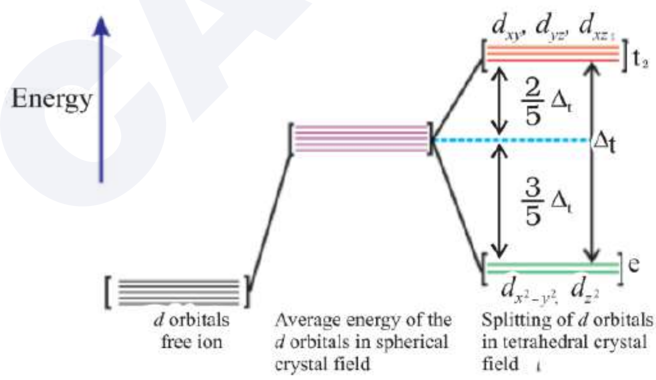
Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the *d* orbitals of metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the *d* electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

- If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which Δ_o < P are known as weak field ligands and form high spin complexes.
- If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

Crystal Field Splitting in Tetrahedral Field

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = \frac{4}{9}\Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed. The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.



Factors Affecting CFSE

1. **Nature of central metal atom:** As we move down the group, the CFSE increases. From 3d to 4d, there is a 30% increase in CFSE and from 4d to 5d, there is a 50% increase in CFSE.
2. **The oxidation state of the central metal atom: The oxidation** state is directly proportional to CFSE.
   The CFSE of $[Fe(CN)_6]^{3-}$ is greater than $[Fe(CN)_6]^{4-}$.
3. **Nature of ligand:** In the case of a strong field ligand, the magnitude of CFSE is high. In the case of a weak field ligand, the magnitude of CFSE is low.

4. **Nature of complex:** In an octahedral complex, 6 ligands approach the central metal atom and thus repulsion is higher, due to which the CFSE is higher. But, in a tetrahedral complex, 4 ligands approach the central metal atom and thus repulsion is lower and thus the CFSE is lower.

Applications of CFT-

These are the various applications of crystal field theory.

- **Configuration of metal ion:** In weak field ligand, the crystal field splitting energy difference is very low. Thus, the pairing of electrons is done by Hund's rule. But for strong field ligands, the splitting energy difference is high due to which the pairing of electrons is not done by Hund's rule.
- **Magnetic nature of complex:** On the basis of magnetism, all the complexes can be divided into two categories, paramagnetic and diamagnetic. Paramagnetic complexes are weakly attracted by the magnetic field and have unpaired electrons, while diamagnetic complexes are weakly repelled by the magnetic field and these molecules have no unpaired electrons.
- **Colour in coordination compounds:** The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of the blue-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level i.e the configuration changes from $t_{2g}^1 e_g^0$ to $t_{2g}^0 e_g^1$. Consequently, the complex appears violet in colour. This phenomenon is called d-d transition and the crystal field theory attributes the colour of the coordination compounds to this d-d transition of the electron.

Limitations of CFT

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

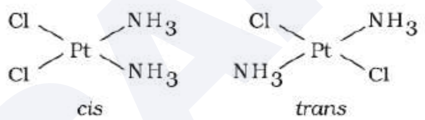
5. Factors Affecting the Stability of Complexes

- The stability of complex compounds increases as the oxidation state of the central metal atom increases.
- The stability of complex compounds increases as the charge on the central metal atom increases.
- The stability of complex compounds increases as the charge density on the central metal atom increases.
- The stability of complex compounds increases as the electronegativity of the central metal atom increases.
- The stability of complex compounds increases as the strength of the ligand increases.
- Chelating ligands which form 5-6 membered ring complex compounds are far more stable than any other complex compound.

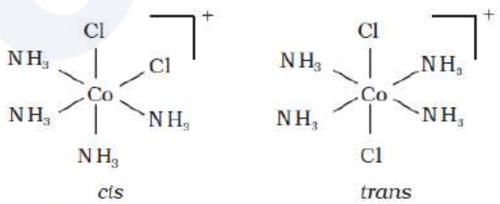
6. Isomerism in Coordination Complexes

Stereoisomerism-

Geometrical Isomerism
This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis-trans isomerism. When two same ligands are at the right angle(90^o), the form is cis- form and when they are present diagonally at 180^o to each other, the form is termed as trans- from. Geometrical isomerism is very common in coordination number 4 and 6 complexes.

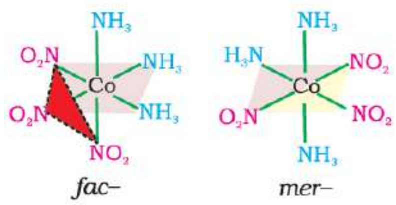


Geometrical isomers (cis and trans) of Pt(NH$_3$)$_2$Cl$_2$)



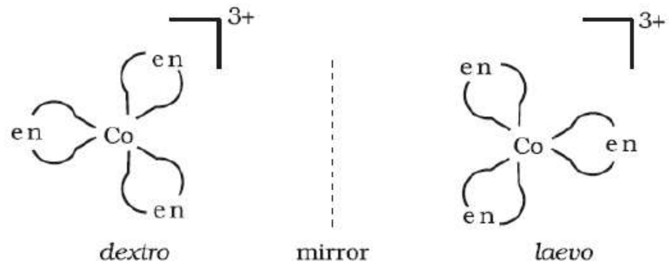
Geometrical isomers (cis and trans) of [Co(NH$_3$)$_4$Cl$_2$]$^+$

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like [$[Co(NH_3)_3(NO_2)_3]$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



Optical Isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.



Structural Isomerism-

Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-NO_2$).

Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

Solvate Isomerism

This form of isomerism is known as 'hydrate isomerism' in cases where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

Stability of Complexes-

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant (stability or formation) for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + nL \rightleftharpoons ML_n$$

then the larger the stability constant, the higher the proportion of ML_n that exists in the solution. Free metal ions rarely exist in the solution so M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write the respective stability constants as follows:

$$M + L \rightleftharpoons ML \quad K_1 = [ML]/[M][L]$$

$$ML + L \rightleftharpoons ML_2 \quad K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \rightleftharpoons ML_3 \quad K_3 = [ML_3]/[ML_2][L]$$

$$ML_{(n-1)} + L \rightleftharpoons ML_n \quad K_4 = [ML_n]/\left[ML_{(n-1)}\right][L]$$

where K_1, K_2, ...K_n, etc., are stepwise stability constants. The overall stability constant (β) of the formation of species ML_n from M and L can be given as:

$$M + nL \rightleftharpoons ML_n \quad \beta = [ML_n]/[M][L]^n$$

The stepwise and overall stability constant are therefore related as follows:

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots. K_n$$

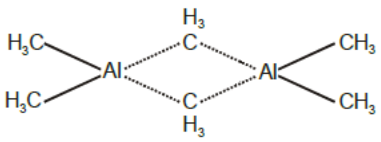
7. Organometallic Compounds

Compounds that contain at least one carbon-metal bond are called organometallic compounds. Zeise, in 1830, prepared the first organometallic compound by the action of ethylene on a solution of potassium chloroplatinate(II). In the last four decades, enormous work has been done in this field and many fascinating compounds have been synthesized and investigated. Grignard reagent, RMgX is a familiar example of organometallic compounds where R is an alkyl group. Diethyl zinc $[Zn(C_2H_5)_2]$, lead tetraethyl $[Pb(C_2H_5)_4]$, ferrocene $[Fe(C_5H_5)_2]$, dibenzene chromium$[Cr(C_6H_6)_2]$, metal carbonyls are other examples of organometallic compounds. The compounds of metalloids such as germanium and antimony and non-metallic elements such as boron and silicon are also included under this classification.

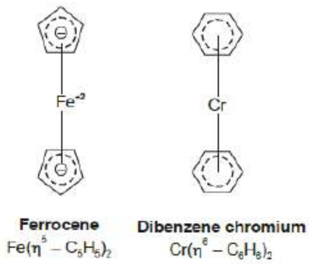
Organometallic compounds may be classified in three classes:

Sigma(σ) bonded complexes: These complexes contain a metal and carbon atom attached with a sigma bond e.g. Tetramethyl Tin, Trimethyl aluminium etc.

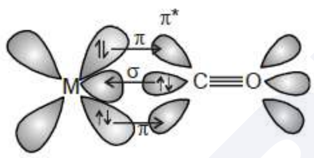
Bonding in Trimethyl aluminium is shown below



Pi(π) bonded complexes: These complexes contain a metal and carbon atom attached with a Pi bond. e.g. Ferrocene, Dibenzene Chromium etc. Bonding in Ferrocene and Dibenzene Chromium is shown below:

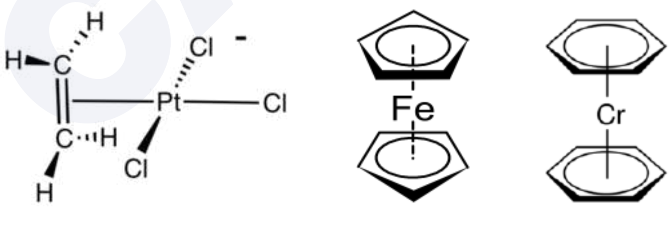


Complexes containing both σ and π bonding characteristics: These complexes contain both σ as well as π bonding characteristics. e.g. Metal Carbonyls. The $M-C$ σ bond is formed by the donation of the lone pair of electrons of carbonyl group into the vacant d orbital of metal while the $M-C$ π bond is formed by back donation of lone pair of electrons from the metal into vacant antibonding π^* molecular orbital of CO. This synergic bonding leads to the formation of stronger bonds and stable metal carbonyl complexes. The bonding in metal carbonyls is shown below:



8. Pi - Complex

These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown in the figure below:



Zeise' salt Ferrocene Dibenzene chromium

The number of carbon atoms bound to the metal in these compounds is indicated by the Greek letter 'η' with a number. The prefixes η^2, η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are involved in the formation of the bond with the metal atom/ion in the compound.

Some Basic Principles of Organic Chemistry

Important Formulae

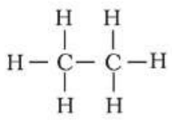
1. Organic Compounds - Classification Of Organic Compounds

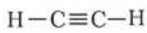
Characteristics Features of π-bonds

In a π (pi) bond formation, parallel orientation of the two *p* orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in an $H_2C{=}CH_2$ molecule, all the atoms must be in the same plane. The *p* orbitals are mutually parallel and both the *p* orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to another interferes with maximum overlap of p orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.

Complete, Condensed and Bond-line Structural Formulas

Complete structural formula
Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, the double dash is used for a double bond and a triple dash represents a triple bond. Lone pairs of electrons on heteroatoms (e.g., oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C2H6), ethene (C2H4), ethyne (C2H2) and methanol (CH3OH) can be represented by the structural formulas as shown below. Such structural representations are called complete structural formulas.

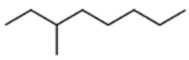

Ethane


Ethyne

Condensed structural formula
These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula. Thus, ethane, ethene and ethyne can be written as:

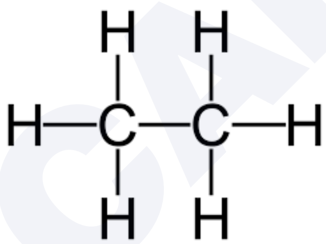
CH_3CH_3	$H_2C{=}CH_2$	$HC{\equiv}CH$
Ethane	*Ethene*	*Ethyne*

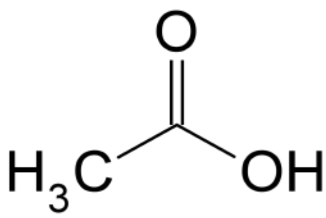
Bond-line structural formula
In this bond-line structural representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl (–CH3) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to an appropriate number of hydrogens required to satisfy the valency of the carbon atoms. For example, 3-methyloctane is represented as follows:



Classification of Organic Compounds-

Acyclic or Open-chain compounds-
These are the compounds in which the carbon atoms are linked to each other in such a manner that the molecule has an open-chain structure. The chain of the carbon atoms may be straight or branched. These compounds are also called aliphatic compounds. The term aliphatic has been derived from the Greek word *aleiphatos* meaning fats since the earliest compounds to be studied were fatty acids or compounds found in fats. Some examples include:

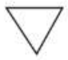

Ethane


Acetic acid

Cyclic or Closed-chain compounds-
These are the compounds in which carbon atoms are linked to each other or to the atoms of other elements in such a manner that the molecule has a closed-chain or cyclic or ring structure. One or more close chains or rings may be present in the molecule. The compounds with only one ring of atoms in the molecule are known as monocyclic but those with more than one ring of atoms are termed as polycyclic. These are divided into two categories:

(a) Homocyclic compounds: These are the compounds having a ring or rings of carbon atoms only in the molecule. The carbocyclic or homocyclic compounds may again be divided into two types, i.e.,

- **Alicyclic compounds:** These are the compounds that contain rings of three or more carbon atoms. These resemble aliphatic compounds than aromatic compounds in many respects. That is why these are named alicyclic, i.e., aliphatic cyclic. Some examples include,

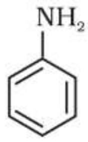

Cyclopropane


Cyclohexane

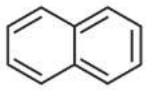

Cyclohexene

- **Aromatic compounds:** These compounds consist of at least one benzene ring, i.e., a six-membered carbocyclic ring having alternate single and double bonds. Generally, these compounds have some fragrant odour and hence, are named aromatic.


Benzene



Aniline


Naphthalene

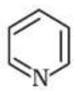
The above compounds are also known as benzenoid aromatics as their molecules consist of benzene rings or rings. However, there are aromatic compounds, which have structural units different from the benzenoid type and are known as non-benzenoid aromatics.

Tropone

(b) Heterocyclic compounds: These are cyclic compounds having rings or rings built up of more than one kind of atoms. The most common other atoms besides carbon are O, N and S. Some examples include,

Furan

Thiophene



Pyridine

2. Functional Groups

The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. Some examples are the hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

Refer to the table below containing a list of functional group

RX : Alkyl Halide

ROH : Alcohol

ROR$'$: Ether

RCHO : Aldehyde

RCOR$'$: Ketone

RCOOH : Carboxylic Acid

RCOOR$'$: Ester

$RCONH_2$: Amide

RCOX : Carbonyl Halide

RSO_3H : Sulphonic Acid

RCN : Cyanide

RNH_2 : Amine

3. Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $–CH_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.
It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

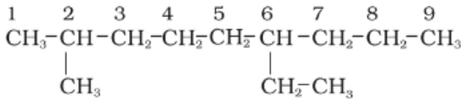
4. IUPAC Nomenclature of Organic Chemistry

Nomenclature of straight-chain hydrocarbons
The names of such compounds are based on their chain structure, end with the suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight-chain saturated hydrocarbons are given in the Table below. The alkanes in this Table differ from each other by merely the number of -CH_2 groups in the chain. They are homologues of the alkane series.

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Nomenclature of branched-chain alkanes:
The rules for naming branched-chain alkanes are as follows:

1. First of all, the longest carbon chain in the molecule is identified. In the example given below, the longest chain has nine carbons and it is considered as the parent or root chain.

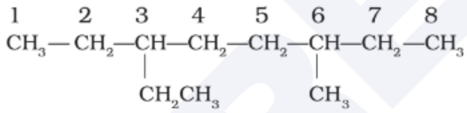


2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6).

3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and the position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, the name for the compound shown above is 6-ethyl-2-methylnonane.

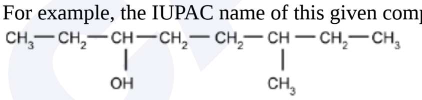
4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered.

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



Organic compounds having Functional Groups
The longest chain of carbon atoms containing the functional groups is numbered in such a way that the functional group attached to the carbon atom gets the lowest number in the chain.
When there are more functional groups then a priority order is followed:
-COOH, –SO_3H, -COOR (R=alkyl group), COCl, -$CONH_2$, -CN,-HC=O, >C=O, -OH, -NH_2, >C=C<, -C≡C-

For example, the IUPAC name of this given compound is written as:



- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at the 6^{th} carbon.

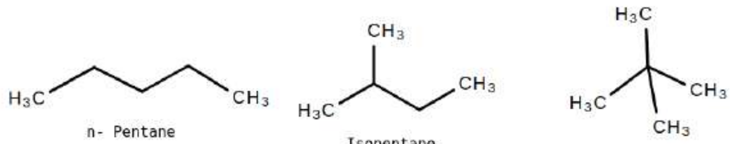
Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

5. Isomerism

Structural and Geometrical Isomerism-

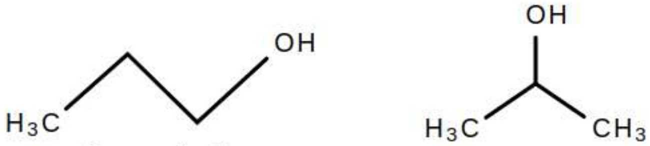
Structural isomerism
Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

- **Chain isomerism:** When two or more compounds have similar molecular formulas but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed chain isomerism. For example, C_5H_{12} represents three compounds as follows:



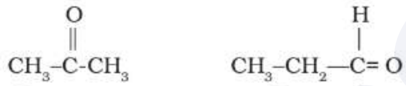
n- Pentane, Isopentane, Neopentane

- **Position isomerism:** When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:



Propan-1-ol, Propan-2-ol

- **Functional group isomerism:** Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone as follows:



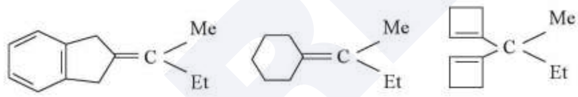
Propanone, Propanal

- **Metamerism:** It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

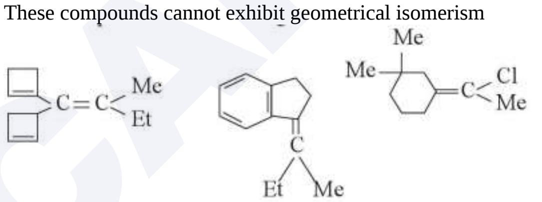
It is the type of isomerism in which the compounds possessing the same molecular formula differ in their properties due to the difference in their geometry that is, due to the difference in the direction of attachment of the same atoms or groups in their molecule. It is not shown by single bonded compounds like(C-C) due to free rotation.
Geometrical isomerism is shown by [>C=C<], [>C=N-], [-N=N-] and cyclo alkanes.

Geometrical isomerism in Alkenes and Cyclo Alkanes

- **Case I**
  These compounds cannot exhibit geometrical isomerism



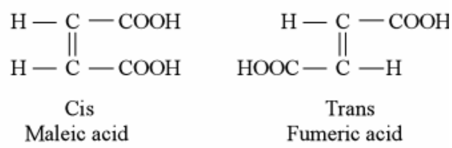
These compounds cannot exhibit geometrical isomerism



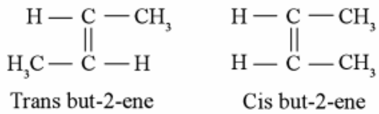
- **Case II**

cis, trans

For example, $C_4H_4O_4$



For example, But-2-ene



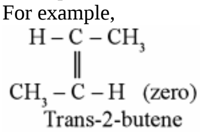
Difference between Cis and Trans Forms

Cis

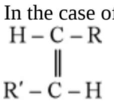
- Cis is a more reactive, but less stable form as the same species are on the same side, so steric repulsion increases reactivity and decreases stability.
- The dipole moment of cis is more.
- It has less melting point as the same groups are on the same side.
- The boiling point of cis is more.
- The solubility, viscosity, and refractive index of cis is more. Trans

Trans

- It is a more stable, but less reactive form as the same species are on opposite sides.
- The dipole moment is mostly zero due to symmetry in the case of symmetrical alkenes.
  For example,

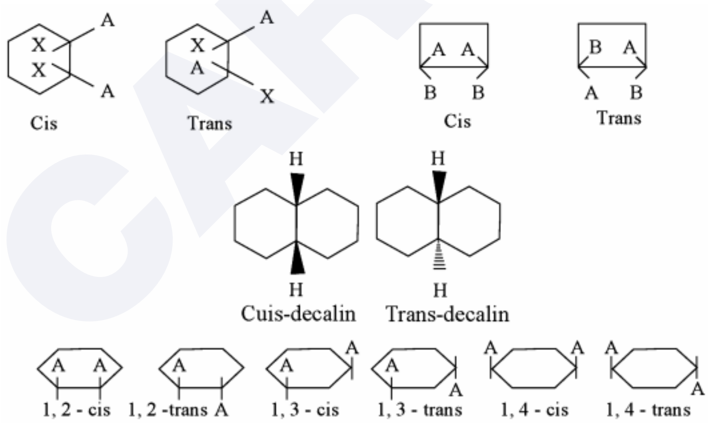


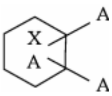
- In the case of unsymmetrical alkenes, due to little unsymmetric, there may be some dipole moment value as well



  For example, trans-2-pentene has some dipole moment value but is lesser than cis form.
- It has more melting points than cis.
- The boiling point of the transform is less.
- The solubility, viscosity, and refractive index are less than cis form.

Geometrical isomerism in cycloalkanes

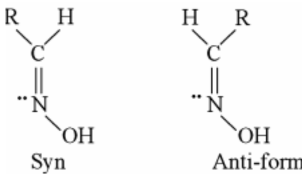




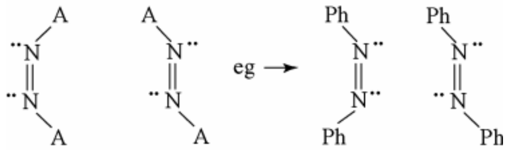
A It cannot show geometrical isomerism as one carbon atom has two similar species 'A'.

Geometrical isomerism in Oximes and Azo compounds

- **In oximes**



- **In azo compounds**



Here, the attached groups may also differ, that is, A and B.

- When Ends are Different Number of geometrical isomers = 2^n
  Here, n = number of double bonds
  For example, CH_3-CH=CH-CH=CH-Cl
  Here, n=2
  Number of geometrical isomers = $2^n = 2^2 = 4$
- **When Ends Are Same**
  (i) When n is an even number
  Number of Geometric Isomers = $2^{n-1} + 2^{n/2-1}$
  For example, X-CH=CH-CH-CH=CH-CH=CH-CH=CH-X
  n=4
  Number of geometric isomers = $2^{4-1} + 2^{4/2-1}$
  $= 2^3 + 2^1 = 10$

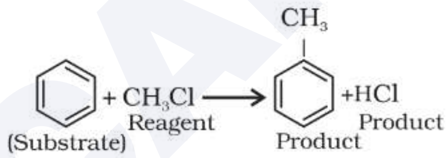
  (ii) When n is an odd number
  Number of geometric isomers = $2^{n-1} + 2^{\{(n+1)/2\}-1}$
  For example, CH_3-CH=CH-CH=CH-CH=CH-CH_3
  Here, n=3
  Number of geometric isomers = $2^{3-1} + 2^{\{(3+1)/2\}-1}$
  $= 2^2 + 2^1 = 6$

6. Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and another as reagent. In general, a molecule whose carbon is involved in new bond formation is called a substrate and the other one is called a reagent. When a carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on the molecule under observation. Some examples include:

(i) $\underset{\text{Substrate}}{CH_2=CH_2} + \underset{\text{Reagent}}{Br_2} \longrightarrow \underset{\text{Product}}{CH_2Br-CH_2Br}$

(ii)



7. Homolytic and Heterolytic Cleavage

A covalent bond can get cleaved either by:

- Heterolytic cleavage
- Homolytic cleavage

Heterolytic cleavage
In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments. After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give CH3$^+$ and Br$^-$ as shown below.

$$H_3C-Br \longrightarrow H_3C^+ + Br^-$$

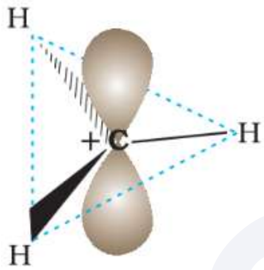
Homolytic cleavage
In homolytic cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by a 'half-headed' curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals. A homolytic cleavage can be shown as below:

$$R-X \xrightarrow{\text{Heat or Light}} \dot{R} + \dot{X}$$

Alkyl free radical

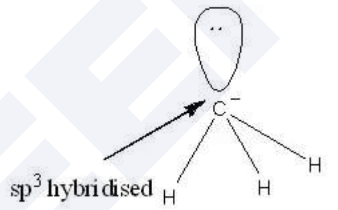
8. Carbocations

A species having a carbon atom possessing a sextet (6 in a group) of electrons and a positive charge is called a carbocation (earlier called carbonium ion). The $^+CH_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects. The observed order of carbocation stability is $^+CH3 < CH_3C^+H_2 < (CH_3)_2C^+H < (CH_3)_3C^+$. These carbocations have a trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $^+CH_3$ may be considered as being derived from the overlap of three equivalent $C(sp^2)$ hybridised orbitals with 1*s* orbital of each of the three hydrogen atoms. Each bond may be represented as $C(sp^2)–H(1s)$ sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. The shape of methyl carbocation is given below:



9. Carbanions

The carbon species carrying a negative charge on carbon atoms is called carbanion. Carbon in carbanion is generally sp^3 hybridised and its structure is a distorted tetrahedron as shown in the figure given below. Carbanions are also unstable and reactive species.

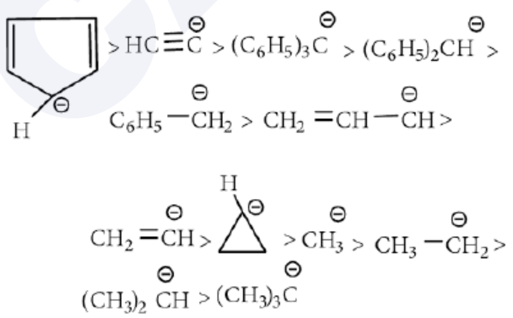


Orbital structure of carbanion

The stability order of carbanions:-

1. The stability of carbanions is influenced by resonance, inductive effect and s-character of orbitals. The group having +I effect decreases the stability while groups having -I effect increase the stability of carbanions.

2. The groups like $-NO_2$, -CN, $-COOC_2H_5$, halogens and C_6H_5-(electron attracting) increase the stability of carbanions.



10. Alkyl Free Radicals

This is the case when the movement of a single electron takes place instead of an electron pair. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals. Like carbocations and carbanions, free radicals are also very reactive. Alkyl radicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary:

$$\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 < \dot{C}(CH_3)_3$$

Methyl free radical	Ethyl free radical	Isopropyl free radical	Tert-butyl free radical

11. Nucleophiles and Electrophiles

A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:) i.e., nucleus seeking and the reaction is then called nucleophilic.

A reagent that takes away an electron pair from the reactive site is called electrophile (E+) i.e., electron seeking and the reaction is called electrophilic.

During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at the nucleophilic centre, which is the electron-rich centre of the substrate. Thus, the electrophiles receive an electron pair from the substrate when the two undergo a bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile.

Some examples of nucleophiles are negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3C:^-$). Neutral molecules such as H_2O, R_3N, R_2NH, etc., can also act as nucleophiles due to the presence of lone pair of electrons.

Examples of electrophiles include carbocations ($^+CH_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R_3C-X, where X is a halogen atom). The carbon atom in carbocations has a sextet configuration; hence, it is electron-deficient and can receive a pair of electrons from the nucleophiles.

In neutral molecules such as alkyl halides, due to the polarity of the C-X bond, a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

12. Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider chloroethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that carbon-1 gains some positive charge (δ^+) and the chlorine has some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by the symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.

$$\underset{2}{\overset{\delta\delta^+}{CH_3}}\underset{1}{\overset{\delta^+}{CH_2}}\overset{\delta^-}{Cl}$$

In turn, carbon-1, which has developed a partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises a relatively smaller positive charge as compared to that on carbon – 1.

In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarization of σ- bond caused by the polarisation of adjacent σ-bond is referred to as the inductive effect. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds.

The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substituents can be classified as electron-withdrawing or electron-donating groups relative to hydrogen.

(1) Electron Withdrawing Groups: Halogens and many other groups such as nitro ($-NO_2$), cyano (-CN), carboxy (-COOH), ester (COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups.

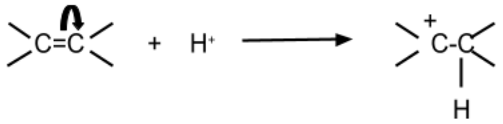
(2) Electron Donating Groups: Alkyl groups like methyl ($-CH_3$) and ethyl($-CH_2-CH_3$) are electron-donating groups.

13. Electromeric Effect

It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.

The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E.

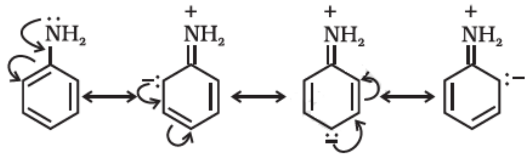
In this effect, the π−electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example:



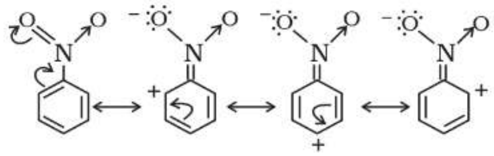
14. Mesomeric or Resonance Effect

The resonance effect is defined as ‘the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom’. The effect is transmitted through the chain. There are two types of resonance or mesomeric effects designated as R or M effects.

- **Positive Resonance Effect (+R effect):** In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as:



- **Negative Resonance Effect (- R effect):** This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example, in nitrobenzene this electron displacement can be depicted as:



The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

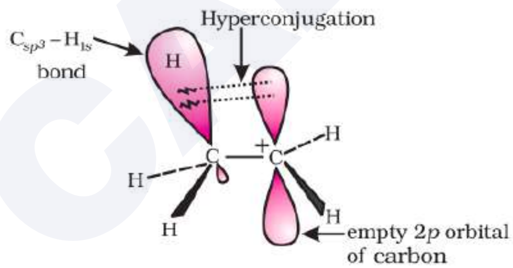
- **+R effect:** $-\ddot{X}, -\ddot{O}H, -\ddot{O}R, -\ddot{O}COR, -\ddot{H}_2, -\ddot{N}HR, -\ddot{N}R_2, -\ddot{N}HCOR$
- **– R effect:** $-COOH, -CHO, > C = O, -CN, -NO_2, -SO_3H$

The presence of alternate single and double bonds in an open-chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.

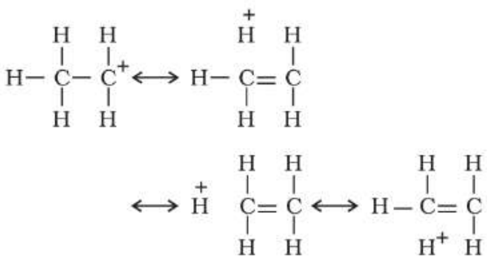
15. Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves the delocalisation of σ electrons of the C—H bond of an alkyl group directly attached to an atom of an unsaturated system or to an atom with an unshared p orbital. The σ electrons of the C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect.

To understand the hyperconjugation effect, let us take an example of $CH_3CH_2^+$(ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as shown in the figure given below:



This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.



In general, the greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations:

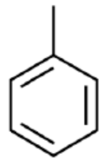
$$CH_3-\overset{+}{\underset{CH_3}{\overset{CH_3}{C}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Hyperconjugation is also possible in free radicals, alkenes and alkylarenes.

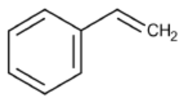
In general, the greater the number of hyperconjugative structures, the greater the stability.

16. Nomenclature of Compounds(Arenes) -

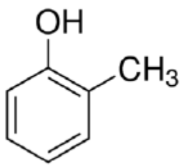
The IUPAC names and common names of some of the compounds are given below:



IUPAC name - Methylbenzene
Common name - Toluene



IUPAC name - Ethenylbenzene
Common name - Styrene



IUPAC name - 2-Methylphenol
Common name - *o*-Cresol

17. Application of Electrophile and Nucleophile

Electrophiles: These are those species that accept electrons. Usually, they are positively charged species.

$\text{Neutral electrophiles : } BF_3, R, CR_2, AlCl_3, FeCl_3$

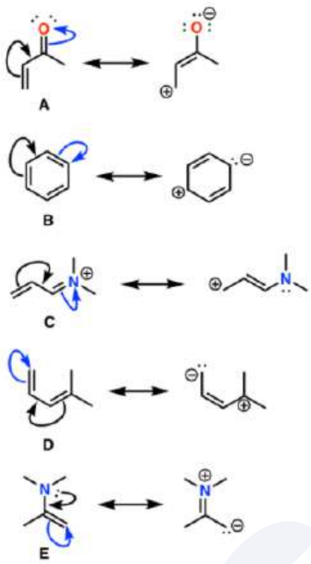
$\text{Positive electrophiles : } H^+, H_3O^+, Cl^+, Br^+, I^+, N^+O_2,\ N^+O, R^+$

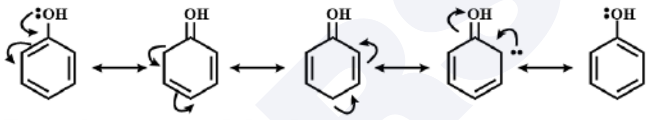
Nucleophiles: These are those species which has a tendency to donate electron pairs or react at electron-poor sites.

Carbanions	$\overset{\ominus}{C}H_3$, R–CH=CH$^{\ominus}$, R–C≡C$^{\ominus}$
Thiols	R-S$^{\ominus}$ R-SH
Hydroxide ion	$\overset{\ominus}{O}H$
Alkoxides	R-O$^{\ominus}$
Amines	NH_3, R-NH_2, R_2NH
Iodide	$I^{\ominus}$
Nitrile ion	$\overset{\ominus}{C}N$
Azide ion	$\overset{\ominus}{N}_3$

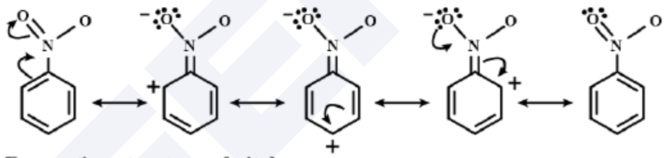
18. Rules for Writing Resonance Structure

1. For various resonating structures, the difference should be in the position of electrons but not in the relative position of atoms or nuclei.
2. In the case of resonating structures, it is mandatory that all the resonating structures should have the same number of unpaired electrons.
3. In the case of atoms of the second period in the periodic table, the resonating structure which violates the octet rule must not be considered.
4. All resonating structures must have the same energy. The greater the number of resonating structures, the more stable the compound.





Resonating structure of phenol



Resonating structure of nitrbenzene

19. Tautomerism

Tautomers are isomers of a compound which differ only in the position of H^+ and electrons. The carbon skeleton of the compound is unchanged. A reaction which involves simple proton transfer in an intramolecular fashion is called tautomerism.

In the above molecule, the $\alpha - \mathrm{H}$ has changed its position from carbon to oxygen atom with the rearrangement of the double bond. This can be visualised in the following manner hypothetically:

(1) Breaking of C-H bond and generation of Carbanion at $\alpha - \mathrm{C}$

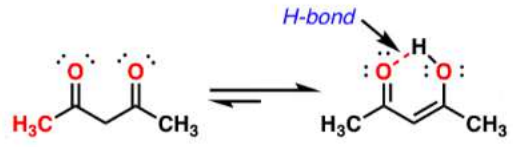
(2) Resonance of the carbanion with the conjugated keto group

(3) Attachment of the proton at the O atom carrying a negative charge

Can you write the above steps in a diagrammatic fashion in order to get a better understanding?

It is to be noted that the keto form is preferred over the enol form in most of the cases. This is because of the high bond energy of the C=O. However, the enol form is more stable under cases where the product is aromatic (Phenol) or in the case of 1,3- dicarbonyl compounds which are stabilised due to intramolecular H-Bonding.

: Aromaticity



: Intramolecular H Bonding

Some other cases where Tautomerism is seen

- Enamine -Imine

$$\mathrm{NH_2 - CH = CH_2 \rightleftharpoons NH = CH - CH_3}$$

- Nitroso - oxime

$$\mathrm{CH_3 - N = O \rightleftharpoons CH_2 = N - O - H}$$

20. Application of Inductive Effect

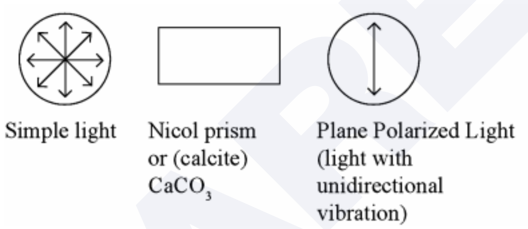
The decreasing -I effect or increasing +I effect order is as follows:
$–NH_3^+$ > $–NO_2$ > $–SO_2R$ > –CN > $–SO_3H$ > –CHO > –CO > –COOH > -F > –COCl > $-CONH_2$ > –Cl > –Br > –I > –OR > -OH > $-NR_2$ > $–NH_2$ > $–C_6H_5$ > $–CH=CH_2$ > –H

21. Applications of Hyperconjugation

In hyperconjugation, more is the number of α-carbons, more is the number of hyperconjugated structures and thus more is the stability. Thus, stability follows the given order:
3^o carbocation > 2^o carbocation > 1^o carbocation

22. Some mixed concepts

Optical Isomerism
It is the type of isomerism in which the compounds possessing the same molecular formula differ in their direction of bringing the optical rotation or the extent of bringing the optical rotation.
Plane Polarized Light
The light from an ordinary source is composed of waves vibrating in many different planes perpendicular to the plane of its propagation. When such a light is passed through a Nicol prism, the light coming through is found to be vibrating in only one plane. Such a light is called a plane polarized light and here nicol prism is called a Polaroid.



Optical Activity or Optical Rotation
The optically active substances rotate the plane polarized light clockwise or anti-clockwise that is, dextro and laevo rotation, respectively at an angle θ. This rotation is called optical rotation. Here, in both the rotations value of θ is the same but with opposite signs, that is, the same in magnitude but opposite in direction.

Optical rotation is measured by a polarometer in terms of specific rotation.

$$[\alpha]_{\lambda}^{t^o c} = \frac{\alpha(\text{ observed })}{l \times c}$$

Here the α= specific rotation
α (observed) = observed value of rotation
l = length of solution
c = concentration of solution.

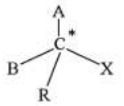
Specific Rotation Depends Upon

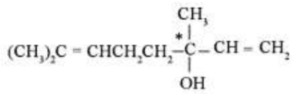
- Nature of solute and solvent.
- Wavelength of light during the experiment.
- Temperature during the experiment.
- Length and concentration of solution.

Reason for Optical Activity or Optical Isomerism

- The compound must be asymmetric or dissymmetric with a non-superimposable mirror image. For example, a hand in the mirror, and an ambulance in the mirror.
- The asymmetric molecule does not have a plane or central or axial axis of symmetry.

Chiral Center or Stereogenic Center

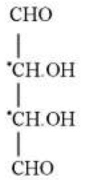


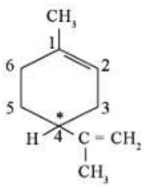


Linalool
(a pleasant smelling oil obtained from orange flowers)

For example, Lactic acid,
$CH_3.{}^*CH.OH.COOH$

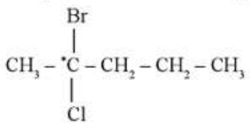
For example,

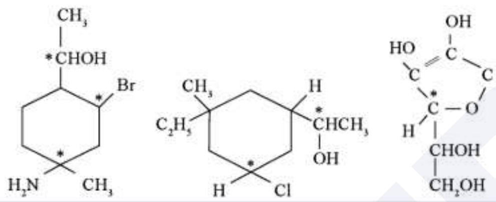




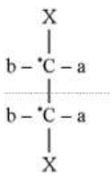
Limonene
(a constituent of lemon oil)

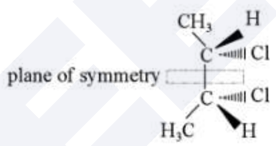
For example, 2-Bromo-2-chloro-pentane





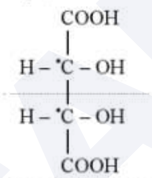
Plane of Symmetry: For it, a minimum of two stereogenic centers are needed. Here, the molecule can be divided into two equal halves.



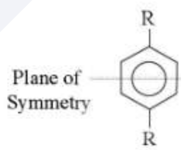


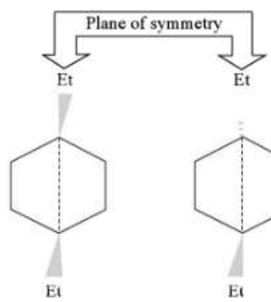
- It is an optically inactive form due to mutual cancellation (or) internal compensation.

For example,

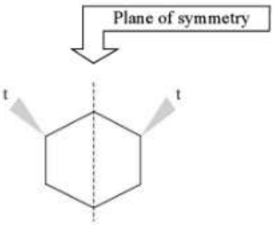


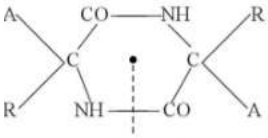
Meso tartaric acid



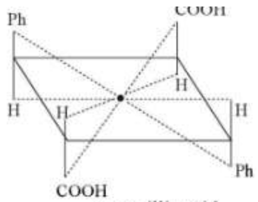


The cis and trans forms of 1,4 -dimethyleyclohexane are diastercomers of each other. Both compounds are achiral.





Centre of symmetry



α-truxillic acid

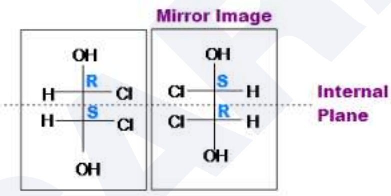
Diastereomers are stereoisomers that are not related to objects and mirror images are not enantiomers. Unlike enantiomers which are mirror images of each other and non-superimposable, diastereomers are not mirror images of each other and non-superimposable. Diastereomers can have different physical properties and reactivity. They have different melting points, boiling points and different densities. They have two or more stereocenters.
It is easy to mistake between diastereomers and enantiomers. For example, we have four stereoisomers of 3 -bromo- 2 -butand. The four possible combinations are SS, RR, SR and RS. One of the molecules is the enantiomer of its mirror image molecule and the diastereomer of each of the other two molecules (SS is an enantiomer of RR and diastereomer of RS and SR). SS's mirror image is RR and they are not superimposable, so they are enantiomers. RS and SR are not the mirror image of SS and are not superimposable to each other, so they are diastereomers.

Meso compounds are achiral compounds that have multiple chiral centres. It is superimposed on its mirror image and is optically **inactive** despite its stereocenters.

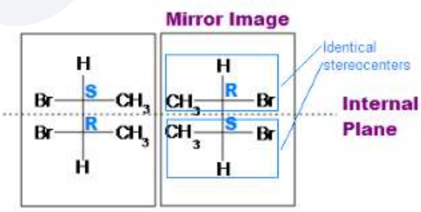
Introduction
In general, a meso compound should contain two or more identical substituted stereocenters. Also, it has an internal symmetry plane that divides the compound in half. These two halves reflect each other by the internal mirror. The stereochemistry of stereocenters should" "cancel out". What it means here is that when we have an internal plane that splits the compound into two symmetrical sides, the stereochemistry of both the left and right sides should be opposite to each other, and therefore, result in optically inactive. cyclic compounds may also be meso.

Identification
If A is a meso compound, it should have two or more stereocenters, and an internal plane, and the stereochemistry should be R and S.

1. Look for an internal plane, or internal mirror, that lies in between the compound.
2. The stereochemistry (e.g. R or S) is very crucial in determining whether it is a meso compound or not. As mentioned above, a meso compound is optically inactive, so its stereochemistry should cancel out. For instance, R cancels S out in a meso compound with two stereocenters.



trans-1,2-dichloro-1,2-ethanediol



(meso)-2,3-dibromobutane

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The method for this is formally known as R/S nomenclature.

Introduction

The method of unambiguously assigning the handedness of molecules was originated by three chemists: R.S. Cahn, C. Ingold, and V. Prelog and, as such, is also often called the Cahn-Ingold-Prelog rules. In addition to the Cahn-Ingold system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

1. X-ray diffraction analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

However, for non-laboratory purposes, it is beneficial to focus on the R/S system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule, at the same temperature, **cannot** be used to establish the absolute configuration of an enantiomer; this is because the sign of optical rotation for a particular enantiomer may change when the temperature changes.

Stereocenters are labelled R or S

The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labelled as R or S.

Consider the first picture: a curved arrow is drawn from the highest priority (*1*) substituent to the lowest priority (4) substituent. If the arrow points in a counterclockwise direction (**left** when leaving the 12 o'clock position), the configuration at the stereocenter is considered ***S*** ("Sinister" → Latin= "left"). If, however, the arrow points clockwise,(**Right** when leaving the 12 o'clock position) then the stereocenter is labelled ***R*** ("Rectus" → Latin= "right"). The ***R or S*** is then added as a prefix, in parenthesis, to the name of the enantiomer of interest.

Hydrocarbons

Important Formulae

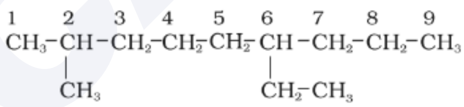
1. IUPAC Nomenclature of Alkanes

Nomenclature of straight-chain hydrocarbons
The names of such compounds are based on their chain structure, and end with the suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight-chain saturated hydrocarbons are given in the Table below. The alkanes in this Table differ from each other by merely the number of -CH_2 groups in the chain. They are homologues of the alkane series.

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Nomenclature of branched-chain alkanes:
The rules for naming branched-chain alkanes are as follows:

1. First of all, the longest carbon chain in the molecule is identified. In the example given below, the longest chain has nine carbons and it is considered as the parent or root chain.

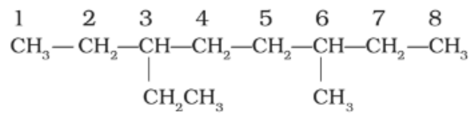


2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6).

3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and the position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, the name for the compound shown above is 6-ethyl-2-methylnonane.

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered.

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.

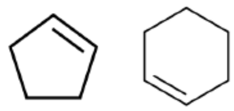


2. Adsorption and Degree of Unsaturation

Adsorption
The phenomenon of the deposition of particles on the surface of the adsorbent is called adsorption.

$$\text{Adsorption } \alpha \ \frac{1}{\text{size}}$$
$$\text{Adsorption } \alpha \ \frac{1}{\text{crowding}}$$
$$\text{Adsorption } \alpha \ \frac{1}{\text{stability}}$$

For example, the rate of adsorption among the following molecules is higher for cyclopentene.



Cyclopentene **Cyclohexene**

Since the size of cyclopentene is smaller than cyclohexene, the rate of adsorption is higher for cyclopentene than cyclohexene.

Occlusion
The adsorption of hydrogen on the surface of the noble metals is known as occlusion. These noble metals can be Platinum or Palladium.

Degree of Unsaturation
It is the calculation to analyse the total number of double bonds and rings in the organic compound. It is also known as the index of hydrogen deficiency or unsaturation index.

- The degree of unsaturation for simple compounds like benzene is given as:
  Degree of unsaturation = Number of pi bonds + Number of rings
  Thus, Degree of unsaturation = 3 + 1 = 4 (Since there are 3 double bonds in the benzene ring and 1 ring is only present)
- For complex compounds like $C_{10}H_6N_4$, the degree of unsaturation is given as follows:
  These complex compounds can be represented as $C_xH_yN_zO_pX_q$. Now, the degree of unsaturation for complex compounds is given using the following formula:
  $$\text{Degree of Unsaturation} = (C+1) - \frac{(H-N+X)}{2}$$

  Where C is the number of Carbon atoms, H is the number of Hydrogen atoms, N is the number of Nitrogen atoms and X is the number of Halogen atoms. It is to be noted that the Oxygen atoms have no bearing on the degree of unsaturation

  Now for the compound $C_{10}H_6N_4$ we have, x = 10, y = 6 and z = 4
  Thus, degree of unsaturation = (10 + 1) - (6 + 0 - 4)/2
  Degree of unsaturation = 10

3. Preparation of Alkanes

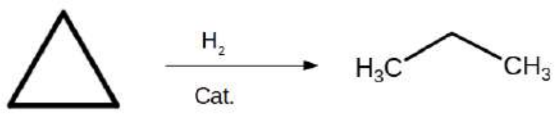
Preparation of Alkanes(Reduction of Alkenes/Alkynes)-

Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called hydrogenation. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen–hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

$$\underset{\text{Propyne}}{CH_3 - C \equiv C - H} + 2H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3 - CH_2 - CH_3}$$

It is to be noted that the highly strained ring of cyclopropane under ring opening upon catalytic hydrogenation to form propane.



Preparation of Alkanes(Hydroboration Reaction)-

Diborane(B_2H_6) adds to an olefinic bond-forming trialkyl borane which on treatment with acetic acid or propionic acid yields the corresponding alkane.

$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow{B_2H_6} (R-CH_2-CH_2-)_3B \xrightarrow[(H^+)]{CH_3COOH} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

It is an important method for preparing alkane from an alkene. Methane cannot be prepared by this method.

It is to be noted that the B atom attaches to the less hindered carbon atom in the first step while the H atom attaches to the adjacent C atom containing the double bond.

In the next step, the BH_2 group is replaced by the H of the acid (CH_3COOH or H_2SO_4)

The mechanism of this reaction is beyond the scope of the syllabus

Preparation of Alkanes(Grignard Reagent)-

Alkyl magnesium halides(RMgX) are called Grignard reagents. These undergo double decomposition reactions with water or ammonia or alcohol or amine having active H atom(attached to strongly electronegative O, N, S or F and triple bond, etc.) to give alkane corresponding to an alkyl group of Grignard reagent. The reaction occurs as follows:

$$CH_3MgBr + C_2H_5OH \longrightarrow CH_4 + (C_2H_5O)MgBr$$

A similar reaction occurs with other sources of acidic hydrogen or acids

$$CH_3MgBr + H_2O \longrightarrow CH_4 + (OH)MgBr$$

$$CH_3MgBr + NH_3 \longrightarrow CH_4 + (NH_2)MgBr$$

$$CH_3MgBr + RNH_2 \longrightarrow CH_4 + (RNH)MgBr$$

$$CH_3MgBr + R-C\equiv C-H \longrightarrow CH_4 + (R-C\equiv C)MgBr$$

$$CH_3MgBr + CH_3COOH \longrightarrow CH_4 + (CH_3COO)MgBr$$

It is to be noted that Grignard reagents are not stable in Protic Solvents like Water or Ethanol and require aprotic solvents like Ether or Tetrahydrofuran (THF) for their synthesis and reactions.

Preparation of Alkanes(Corey House Reaction, Reduction of Alkyl Halides by LiAlH4, Wurtz Reaction)-

Corey House Synthesis
It is suitable for the preparation of alkanes with an odd number of carbon atoms by the following S_N2 mechanism.

$$R-X \xrightarrow[\text{Ether}]{Li} R-Li \xrightarrow{CuI} R_2CuLi \xrightarrow[S_N2]{R'-X} R-R' + R-Cu + LiX$$

For example:
$$CH_3I + (CH_3CH_2)_2CuLi \longrightarrow CH_3CH_2CH_3 + CH_3CH_2Cu + LiI$$

It is to be noted that in this method of preparation, tertiary halides should be avoided as they may lead to the formation of Alkenes via the elimination mechanism

Reduction by $LiAlH_4$
In this reaction, alkyl halides are reacted with $LiAlH_4$ (a strong reducing reagent) to reduce to alkanes. The reaction occurs as follows:

$$R-X + LiAlH_4 \rightarrow R-H$$

It is to be noted that in this method of preparation, tertiary halides should be avoided as they may lead to the formation of Alkenes via the elimination mechanism

Wurtz reaction
Alkyl halides on treatment with sodium metal in a dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as the Wurtz reaction and is used for the preparation of higher alkanes containing an even number of carbon atoms.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaBr$$

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5$$

Wurtz Fittig Reaction

A modification of the Wurtz reaction is the Wurtz Fitting reaction in which an Alkyl halide and an Aryl halide on treatment with sodium metal in dry ether give substituted aromatic compounds. This reaction involves the coupling of an alkyl halide and an aryl halide.

$$PhBr + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} Ph-CH_3 + 2NaBr$$

$$PhBr + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} Ph-C_2H_5 + 2NaBr$$

Frankland reaction

Alkyl halides on treatment with Zinc metal give higher alkanes. This reaction is known as the Frankland reaction and is used for the preparation of higher alkanes containing an even number of carbon atoms.

$$CH_3Br + Zn + BrCH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + ZnBr_2$$

$$C_2H_5Br + Zn + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5 - C_2H_5 + ZnBr_2$$

Preparation of Alkanes(Decarboxylation and Kolbe's electrolysis)-

Decarboxylation of Fatty acids
When anhydrous sodium salt of fatty acid is fused with soda lime (NaOH +CaO) a paraffin dry ether having one carbon atom less than the fatty acid is acid. The reaction occurs as follows:

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

For example:
$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Kolbe's Electrolysis
Sodium or potassium salts of carboxylic acids on electrolytic hydrolysis give alkanes at anode as follows:

$$2R - COONa \xrightarrow{\text{electrolytic hydrolysis}} R - R + 2CO_2 + 2NaOH + H_2 \uparrow$$

For example:
$$2CH_3 - COONa \xrightarrow{\text{electrolytic hydrolysis}} CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2 \uparrow$$

4. Physical Properties of Alkanes

The various important physical properties of alkanes are discussed below:

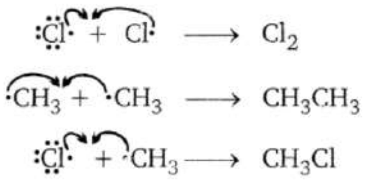
- **State:** Due to weak forces, the alkanes up to four carbon atoms, i.e., methane, ethane, propane and butane are colourless, odourless gases but the next thirteen members are colourless, odourless liquids. Alkanes from C_{18} onwards are colourless and odourless solids.
- **Density:** The density of alkanes increases very slowly with the rise of molecular mass until it becomes constant at about 0.8. Thus, all alkanes are lighter than water.
- **Solubility:** They are generally insoluble in polar solvents such as water but soluble in non-polar solvents like ether, carbon tetrachloride, benzene, etc. The solubility decreases with an increase in molecular mass.
- **Boiling point:** The boiling points of straight-chain or *n*-alkanes increase regularly with the increasing number of carbon atoms. Among the isomeric alkanes, the normal isomer has a higher boiling point than the branched-chain isomers. The greater the branching of the chain, the lower will be the boiling point.
- **Melting point:** The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. Alkanes with an even number of carbon atoms have a higher melting point than the next lower and next higher alkanes having an odd number of carbon atoms.

5. Chemical Properties of Alkanes

Chemical Properties(Free Radical Reaction, Chlorination, Nitration and sulphonation)-

Halogenation
When alkanes are treated with halogens in the presence of light or at elevated temperatures, the hydrogen atoms of alkanes are successively replaced by halogen atoms. This process is known as halogenation. The rate of reaction of alkanes with halogen follows the following order:
$F_2 > Cl_2 > Br_2 > I_2$
This reaction is carried out with chlorine as fluorine is too violent to be controlled and iodine is too slow and reversible.
The mechanism of this reaction occurs by a free radical mechanism and it is done in three successive steps as follows:

1. **Chain initiation step:** The reaction is initiated by homolysis of chlorine molecules in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break.
$$:\ddot{\underset{..}{Cl}} - \ddot{\underset{..}{Cl}}: \xrightarrow[\text{or } h\nu]{\Delta} 2:\ddot{\underset{..}{Cl}}\cdot$$
2. **Chain propagation step:** Chlorine-free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.
$$:\ddot{\underset{..}{Cl}}\cdot + H - CH_3 \longrightarrow HCl: + \underset{\text{a methyl radical}}{\cdot CH_3}$$
$$\cdot CH_3 + :\ddot{\underset{..}{Cl}} - \ddot{\underset{..}{Cl}}: \longrightarrow CH_3Cl + :\ddot{\underset{..}{Cl}}\cdot$$
3. **Chain termination step:** The reaction stops after some time due to the consumption of reactants and/or due to the following side reactions. The possible chain-terminating steps are:



The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during the chlorination of methane.

Nitration

Nitration is a substitution reaction in which a hydrogen atom of alkane is replaced by a nitro(-NO_2) group. The reaction occurs as follows:

$$R-H + HONO_2 \xrightarrow[\text{Temperature}]{\text{High}} R-NO_2 + H_2O$$

Lower members do not react with concentrated nitric acid at ordinary temperatures but long-chain members on heating with fuming nitric acid yield nitroalkanes. However, when a mixture of vapours of alkane and nitric acid is heated at 673-773K, nitroalkane is formed readily. This is known as vapour phase nitration. By this process, lower, as well as higher alkanes, can be converted into nitroalkanes.

$$CH_3 + HONO_2 \overset{723K}{\rightarrow} CH_3 - NO_2 + H_2O$$

Sulphonation

The replacement of hydrogen atoms by sulphonic cid group(-SO_3H) is known as sulphonation. Lower alkanes do not undergo sulphonation but higher members (from hexane onwards) are sulphonated slowly when treated with fuming sulphuric acid. at about 673K. The reaction occurs as follows:

$$R-H + HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} R-SO_3H + H_2O$$

For example:

$$C_6H_{13} + HOSO_3H \overset{SO_3}{\longrightarrow} C_6H_{12}SO_3H + H_2O$$

However, lower members such as propane, butane, pentane, etc. react with SO_3 in the vapour phase to form sulphonic acids.

Chemical Properties (Combustion, Catalytic Oxidation, Isomerisation, Aromatisation and Pyrolysis)-

Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amounts of heat.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1), \Delta_cH^o = -890kJ/mol$$

Due to the production of large amounts of heat, alkanes are used as fuels.

Catalytic oxidation

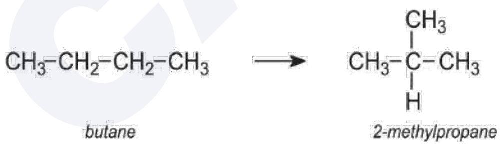
Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products. The reactions occur as follows:

$$2CH_4 + O_2 \overset{Cu,\ 523K}{\longrightarrow} 2CH_3OH$$

$$2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

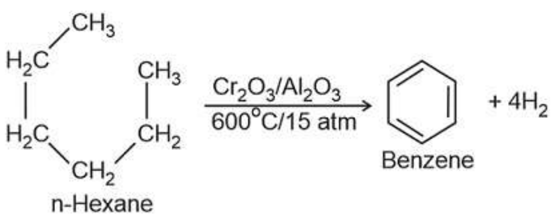
Isomerisation

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched-chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.



Aromatization

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



Pyrolysis
The higher alkanes split into lower alkanes when heated strongly at a high temperature in the absence of air. During pyrolysis, C-C bond breaks rather than C-H bonds as bond energy of C-H > C-C. Here product formation depends upon the structure of alkane, the extent of temperature and pressure and the presence/absence of catalysts like SiO_2-Al_2O_3 etc. Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example:

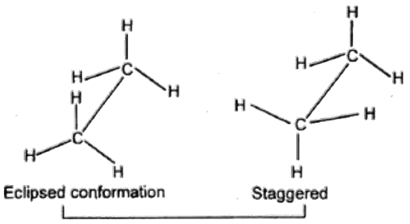
$$C_{12}H_{26} \xrightarrow[973K]{Pt/Pd/Ni} C_7H_{16} + C_5H_{10} + \text{other products}$$

Dodecane Heptane Pentene

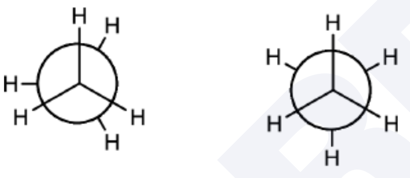
6. Conformation, Sawhorse and Newman Projections

Conformations-
Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results in different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers. Alkanes can thus have an infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol^{-1} due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain.

Sawhorse projections
In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. The upper end of the line is slightly tilted towards the right or left-hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are shown in the figure.



Newman projections
In this projection, the molecule is viewed at the C–C bond head-on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. Newman's projections for ethane are shown in the figure.



Eclipsed Staggered

7. Nomenclature and Isomerism of Alkenes

Nomenclature of Alkenes
The general rules and principles of the IUPAC nomenclature are already discussed in the earlier chapter. Here we will discuss some common examples of naming them.

IUPAC name: Octa-1,3,5,7-tetraene

IUPAC name: 2-n-propylpent-1-ene

Isomerism
Alkenes show two kinds of isomerism i.e., stereoisomerism and geometrical isomerism

- **Stereoisomerism:** Ethene (C2H4) and propene (C3H6) can have only one structure but alkenes higher than propene have different structures. For example, But-1-ene can have three different structures as follows:

$CH_2=CH-CH_2-CH_3$ But-1-ene

$CH_3-CH=CH-CH_3$ But-2-ene

$CH_2=C(CH_3)-CH_3$ 2-Methyprop-1-ene

- **Geometrical isomerism:** When the groups attached to doubly bonded carbon atoms are different, they can be represented with different geometries. This type of isomerism is known as geometrical isomerism. The two structures or isomers are known as *cis* and *trans* isomers.

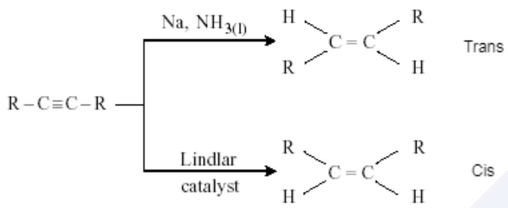
cis-2-butene *trans*-2-butene

NOTE: The *trans* isomer has stronger close packing than the *cis* isomer, thus the melting point of the *trans* isomer is higher than the *cis* isomer. Further, the molecules of the *cis* isomer are loosely held thus they are more soluble in the particular solvent than the *trans* isomer.

8. Preparation of Alkenes

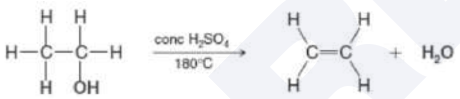
Reduction of Alkynes to Alkenes-

Alkynes on partial reduction with the calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkenes thus obtained have cis geometry. However, alkynes on reduction with sodium in liquid ammonia form trans alkenes.

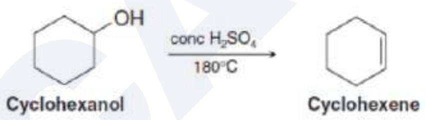


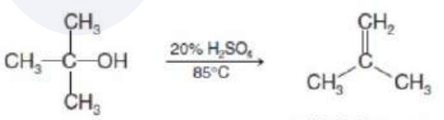
Dehydration of Alcohol by Conc. H_2SO_4

Dehydration of Alcohols:
Alcohols undergo dehydration when allowed to react with concentrated acids in the presence of heat.



This reaction can be used to dehydrate all three types of alcohol viz. Primary, secondary and tertiary alcohols. Some examples are given below:



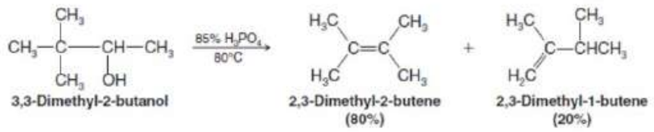


2-Methylpropene

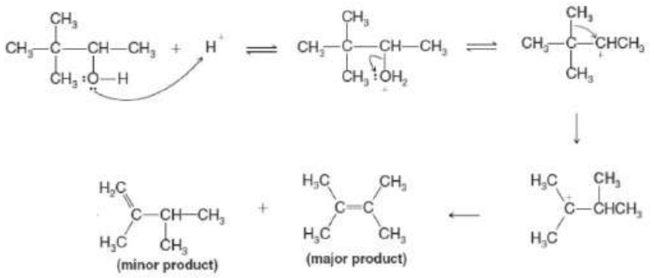
It is to be noted that the dehydration usually occurs via the Unimolecular elimination reaction (E_1) and involves a carbocation intermediate which can undergo rearrangement via hydride or alkyl shift and also undergo ring expansion for suitable substrates where the ring strain can be released. A drawback of this reaction is that a mixture of alkenes can be obtained due to the involvement of carbocation intermediates. Saytzeff's alkene which is the more stable alkene is usually obtained as a major product.

Consider the examples given below in which the carbon skeleton changes due to carbocation rearrangement and ring expansion respectively.

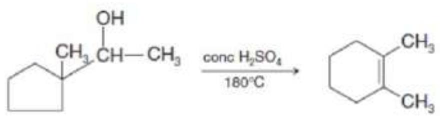
Case of Methyl shift



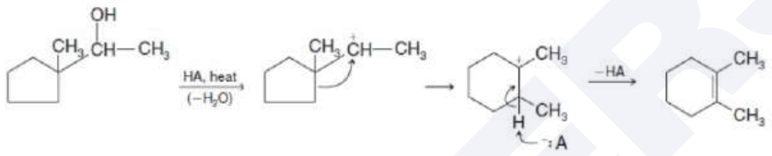
The mechanism of the reaction is given below:



Case of Ring expansion



The mechanism of the reaction is given below



Saytzeff's and Hoffmann's Rule, Dehydration by Al_2O_3 and ThO_2

Saytzeff's rule
This rule states that in dehydrohalogenation reactions, the preferred product is always that alkene which is most stable or in other words which has more number of α-hydrogen atoms.

Hoffmann's rule
This rule states that the alkene formed would be the least stable as the major product or in other words that alkene would be formed which has the least number of α-hydrogen atoms.

Dehydration by Al_2O_3
Since the reagent used is Al_2O_3, thus the Saytzeff's rule will be applied and E_2 elimination will take place and no carbocation will form. When ethanol is passed over heated aluminium oxide then ethene is formed as the final product. The reaction occurs as follows:

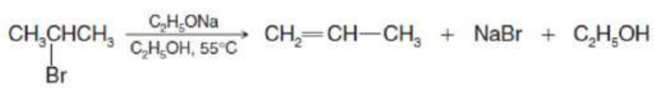
$$CH_3 - CH_2 - OH \xrightarrow{Al_2O_3} CH_2 = CH_2 + H_2O$$

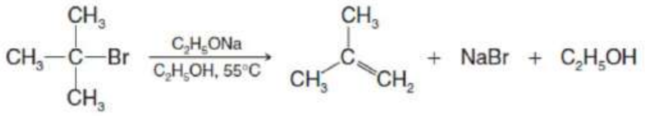
Dehydration by ThO_2
Since the reagent used is ThO_2, thus the Hoffmann's rule will be applied and E_2 elimination will take place and no carbocation will form. The reaction occurs as follows:

$$CH_3 - CH_2 - CH - OH - CH_3 \xrightarrow{ThO_2} CH_3 - CH_2 - CH = CH_2$$

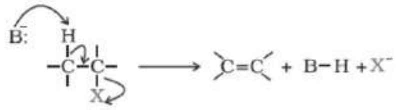
Dehydrohalogenation of Alkyl Halides-

Dehydrohalogenation of Haloalkanes with Strong Bases
Secondary and tertiary alkyl halides undergo dehydrohalogenation on reaction with a strong base to form Alkenes. The reaction is an elimination reaction. It is to be noted that primary haloalkanes form ether by Williamson’s synthesis of Ethers. Some examples of the reaction are given below



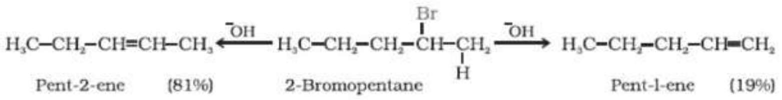


This reaction is an example of β elimination in which a $\beta - hydrogen$ is eliminated along with a halogen at the α carbon. The reaction occurs in a concerted mechanism and anti elimination takes place as shown below.

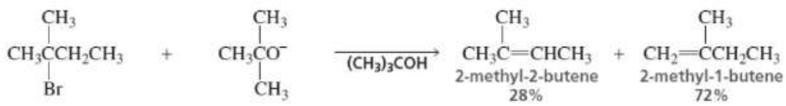


B=Base ; X=Leaving group

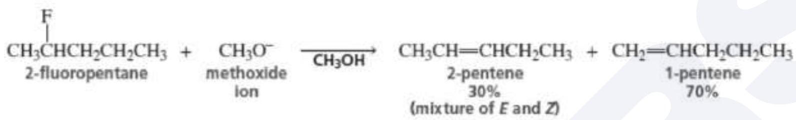
If there are different types of β - hydrogen present in the substrate then usually the Saytzeff's alkene is obtained as a major product. Please recall that Saytzeff's alkene is the more substituted alkene having a greater number of α hydrogens or greater alkylation around the double bond.



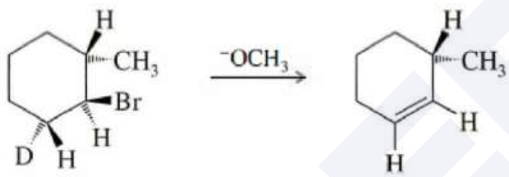
However, in cases where bulky bases are used, the reaction usually takes place by the extraction of the least hindered hydrogen atom and often less substituted alkenes are obtained as a major product. Steric hindrance thus plays an important role in the reaction.



There is an anomaly shown in the reaction when Fluorine is present as the leaving group in the haloalkane and usually less substituted alkene is produced as a major product. This is explained by the poor leaving group ability of Fluorine and the reaction proceeds by a significant anionic character in the transition state.

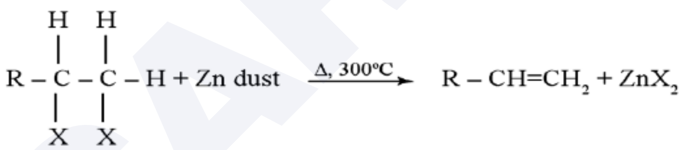


The dehydrohalogenation occurs in an anti periplanar fashion and the hydrogen and the halogen should be in an anti orientation.

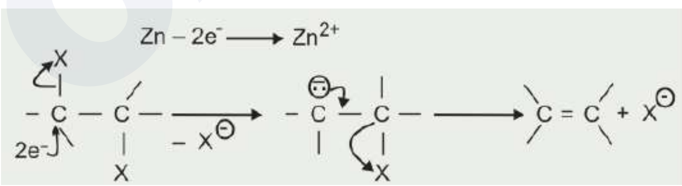


Dehalogenation of Vicinal Halides

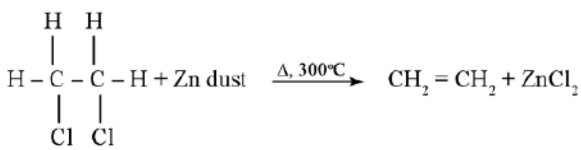
When vicinal dihalides are heated with Zn dust or NaI/Acetone, an alkene having the same number of carbon is obtained. This reaction is known as dehalogenation. The reaction occurs as follows:



Mechanism



For example:



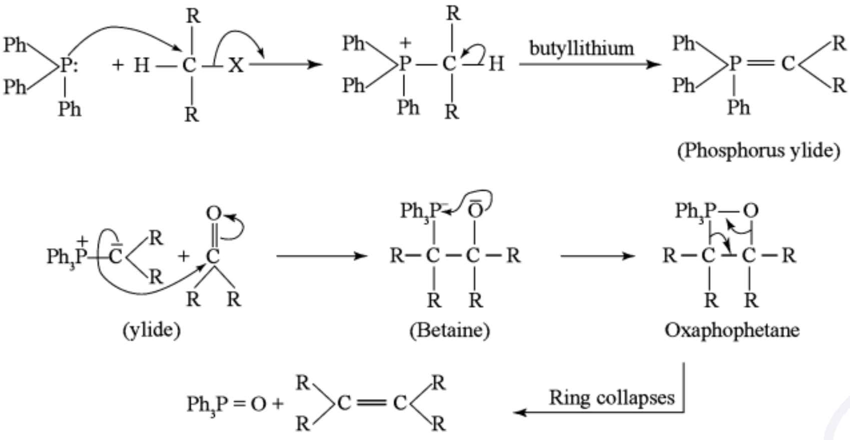
Wittig's Reaction-

In this reaction, methylene triphenyl phosphorane or phosphorous ylide is treated with a carbonyl compound to prepare an alkene. There are two important components of this reaction:

- A carbonyl compound
- A species known as "ylide". The "ylide" is a species with opposite charges on adjacent atoms.

This reaction is named after George Wittig who was awarded the Nobel prize for this work in 1979. A principal advantage of alkene synthesis by the Wittig reaction is that the location of the double bond is absolutely fixed, in contrast to the mixtures often produced by alcohol dehydration.

Mechanism



For example:

$$CH_3-CO-CH_3 + (Ph)_3P = CH_2 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + (Ph)_3PO$$

Acetone — Iso butene

Pyrolysis of Quaternary Ammonium Salts-

Pyrolysis of quaternary ammonium salts follows the Hoffmann elimination. This means the less stable alkene will form. In this reaction, an amine reacts with 3 moles of methyl iodide and forms quaternary ammonium salt. Now heating this salt with moist Ag_2O or AgOH will form alkene.

The reaction occurs as follows:

$$R-CH_2-CH_2-NH_2 \xrightarrow{CH_3I} R-CH_2-CH_2-NH-CH_3 + HI \xrightarrow{CH_3I} R-CH_2-CH_2-N-(CH_3)_2 + HI$$

$$\xrightarrow{CH_3I} R-CH_2-CH_2-N^+-(CH_3)_3 \xrightarrow[\text{AgOH}]{\text{Moist } Ag_2O \text{ or}} R-CH=CH_2 + N-(CH_3)_3$$

Cope's Reaction, Pyrolysis of Ester-

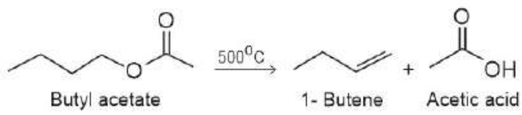
Cope's reaction
When a tertiary amine oxide bearing one or more beta hydrogens is heated, it is converted to an alkene. The reaction is known as Cope elimination or Cope reaction. The net reaction is 1,2-elimination hence the name Cope elimination.

For example:

In Cope's elimination, the least hindered beta H is eliminated and Hoffman alkene is formed

Pyrolysis of Esters
When esters are heated in the presence of liquid N_2 and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester converts into respective acid.

For example:



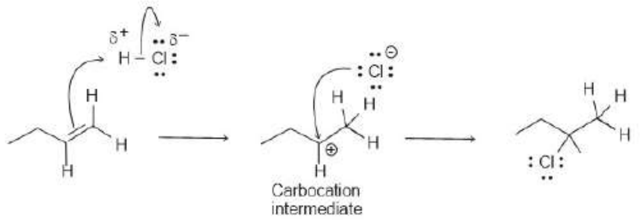
In pyrolysis of esters, the least hindered beta H is eliminated and Hoffman alkene is formed

9. Chemical Properties of Alkenes

Hydrohalogenation of Alkenes-

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond and a halogen atom to another. There is a formation of a carbocation intermediate and rearrangement may occur in cases where there is a possibility of more stability.

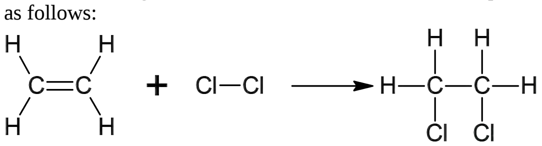
The reaction occurs as follows:



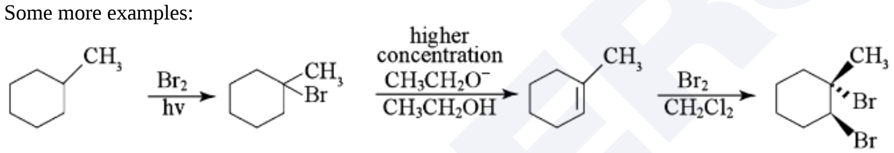
Mechanism
The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both an electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of π electrons, attaching it to the molecule. The resulting molecule will have a single carbon-carbon bond with a positive charge on one of them (carbocation). In case there is a possibility for the carbocation to rearrange, it will rearrange to form a more stable carbocation. The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant.

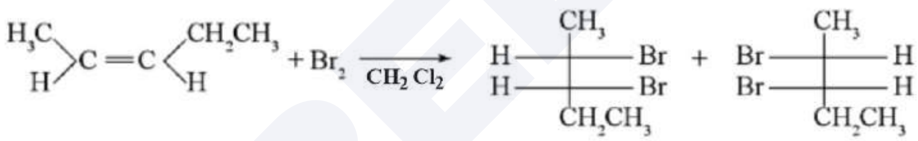
Halogenation of Alkenes-

Alkenes decolourises Bromine water (Br_2 in CCl_4) following the addition of Br_2 across a double bond. This serves as a test of unsaturation. The addition of halogens to an alkene is an anti-addition and provides an illustration for a stereoselective and stereospecific reaction. The reaction occurs as follows:



Some more examples:





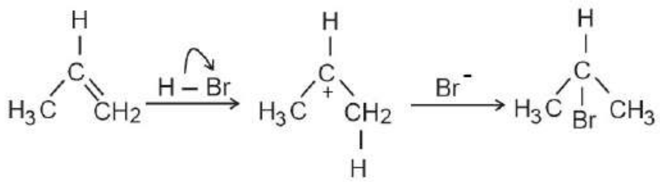
trans-2 pentene

erythro enantiomers
(Fischer projections)

Markonikov and Anti-markonikov Reaction-

Markovnikov's rule
This rule states that the acid hydrogen of the protic acid gets attached to the carbon with more hydrogen substituents and the negative part adds to the atom with less number of hydrogen atoms.

Mechanism
The addition of halogens and halogen acids takes place by electrophilic addition(EA) reaction. +E mechanism is that when electrons of the π-bonds are transferred to that atom of the multiple bonds to which the reagent finally gets attached. First, the electrophile(H^+) adds to the positive C atom and hence this step is slow and the rate-determining step. Afterwards, the negative part of the reagent (Br^-) adds to the positive C atom. Thus, it is known as the (+E) reaction.



Rule 1: In alkene and alkyne, (+E) reaction takes place, first electrophile is added, and then the negative part of the reagent is finally added.

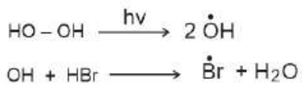
Rule 2: In general, when the inductively electron-withdrawing group(-I) is attached to (C=C) and has a lone pair of electrons then +R effect is operative than -I effect and Markovnikov's addition takes place.

Rule 3: If an inductively electron-withdrawing group(-I) is not attached to (C=C), is one or more C atoms away from (C=C), and has a lone pair of electrons, then the -I effect is operative than +R effect and anti-Markovnikov's addition takes place.

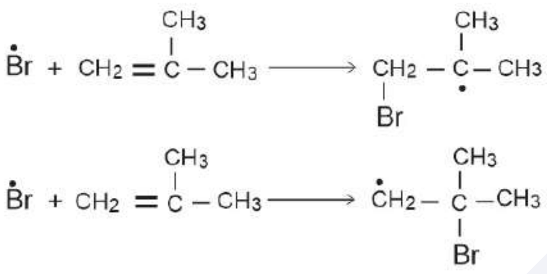
Anti-Markovnikov's rule
In the presence of peroxide, such as benzoyl peroxide and light, the addition of HBr(not HCl and HI) to unsymmetrical alkenes occurs contrary to Markovnikov's rule.

Mechanism
The mechanism of this process occurs in three steps:

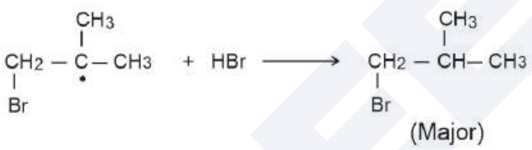
1. **Chain initiation:** Hydrogen Peroxide is an unstable molecule, if we heat it, or shine it with sunlight, two free radicals of OH will be formed. These OH radicals will go on and attack HBr, which will take the Hydrogen and create a Bromine radical. Hydrogen radicals do not form as they tend to be extremely unstable with only one electron, the bromine radical which is more stable will be readily formed.



2. **Chain propagation:** The Bromine Radical will go on and attack the less substituted carbon of the alkene. This is because after the bromine radical attacked the alkene a carbon radical will be formed. A carbon radical is more stable when it is at a more substituted carbon due to induction and hyperconjugation. Thus, the radical will be formed at the more substituted carbon, while the bromine is bonded to the less substituted carbon. After a carbon radical is formed, it will go on and attack the hydrogen of HBr, and thus a bromine radical will be formed again.



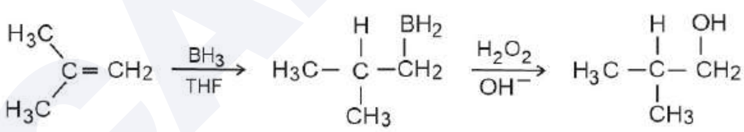
3. **Chain termination:** In the termination step, two bromine radicals combined to give bromine. This radical addition of bromine to alkene by radical addition reaction will go on until all the alkene turns into bromoalkane, and this process will take some time to finish.



10. Hydroboration and Oxidation

Hydroboration and Oxidation-

Hydroboration-oxidation serves as an important method for the synthesis of alcohol(1^o & 2^o). The reaction occurs as follows:



The addition of boron hydride is syn-addition. It is generally carried out by BH_3 (boron hydride) or B_2H_6 (diborane) in THF. In each addition, the boron atom becomes attached to the less substituted carbon atom of the double bond and H is transferred from the boron atom to the other carbon atom of the double bond. Thus it follows Anti-Markonikoff's addition.

In the second step on reaction with H_2O_2, OH^-, the OH group of H_2O_2 replaces the BH_2 from the less substituted carbon initially containing the double bond.

It is to be noted that there is no formation of carbocation during the reaction and hence no rearrangement occurs in the reaction.

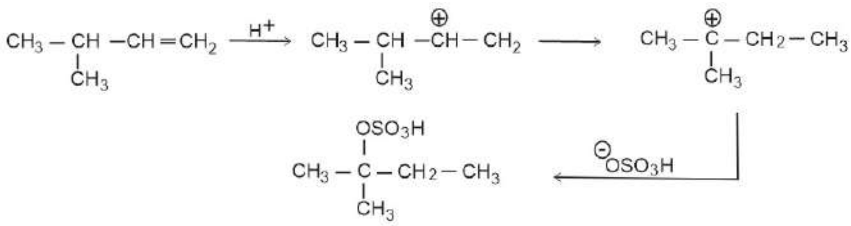
Reaction of Alkene with Dilute H_2SO_4-

Cold-concentrated sulphuric acid is added to alkenes in accordance with the Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.

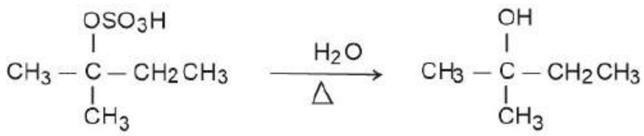
For example:

$CH_2 = CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_2OH$

Mechanism: In this reaction, the carbon-carbon double bond is broken first. Then one of the H^+ is released and combined with one of the carbon. Now, a carbocation is already formed after the breaking of the double bond. Now, if the carbocation has a possibility to achieve more stability, then first it becomes more stable either by hydride shift or methyl shift. Then HSO^{-}_{4} binds with carbocation and forms the final product as given below.



Upon heating the above product with boiling H_2O, OH^- group replaces the HSO_4^- leading to the formation of Alcohol



11. Preparation of Alkynes

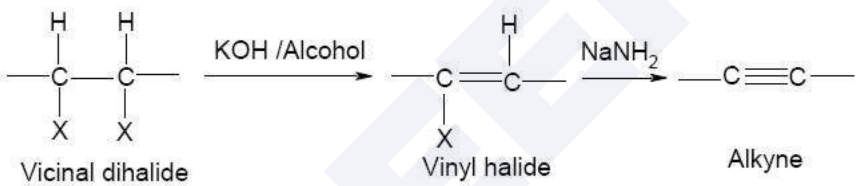
Calcium carbide: Ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CaO + 3C \longrightarrow CaC_2 + CO$

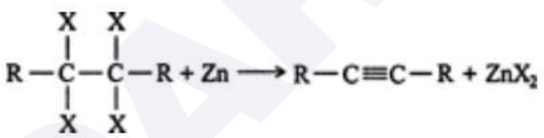
$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

Vicinal dihalides: Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



Using Zinc:

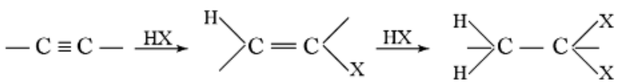
Vicinal tetrahaloalkanes can be dehalogenated with zinc metal in an organometallic reaction to form alkynes.



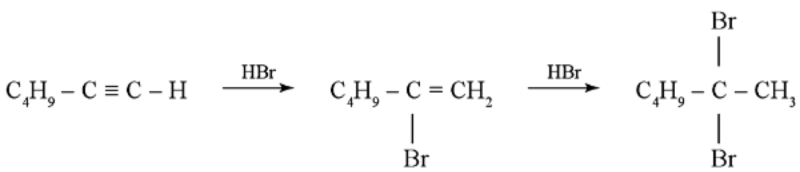
12. Chemical Properties of Alkynes

Hydrohalogenation and Halogenation of Alkynes-

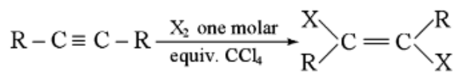
Hydrohalogenation
The addition of one molecule of halogen gives vinyl halide which then adds another molecule of hydrogen halide to form gem-dihalide. This addition follows Markownikoff's rule. The reaction occurs as follows:



For example:



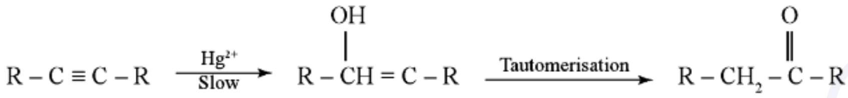
Halogenation
Alkenes combine with gaseous chlorine or bromine in the dark to form di or tetrahalides. Here the addition is Anti Markownikoff's. The reaction occurs as follows:



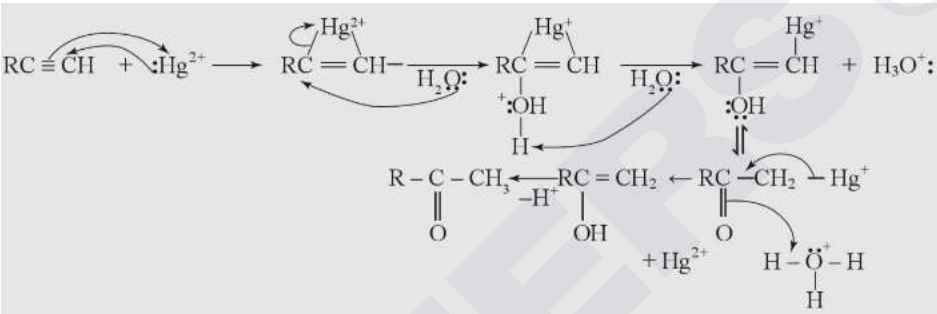
For example:

Hydration, Hydroboration and Oxidation of Alkynes-

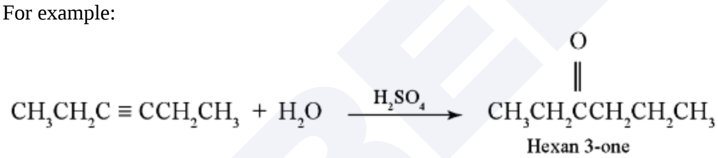
Hydration
Alkynes cannot be hydrated more easily than alkenes because of their low reactivity towards electrophilic addition reactions. The reaction occurs as follows:



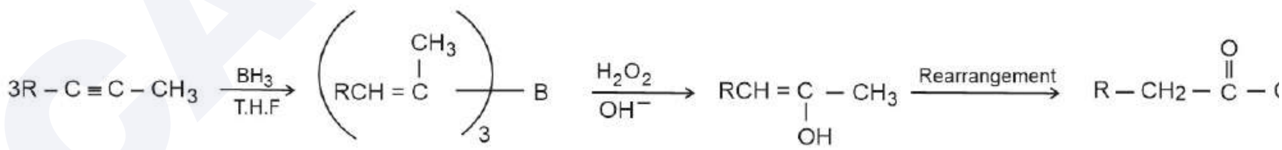
Mechanism



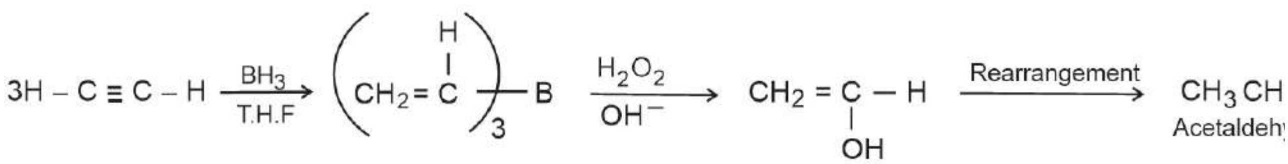
For example:



Hydroboration-Oxidation reaction
Alkynes react with BH_3 (in THF) and are finally converted into carbonyl compounds. This method is useful for preparing aldehyde from terminal alkyne, which is otherwise not possible by hydration. The reaction occurs as follows:



For example:



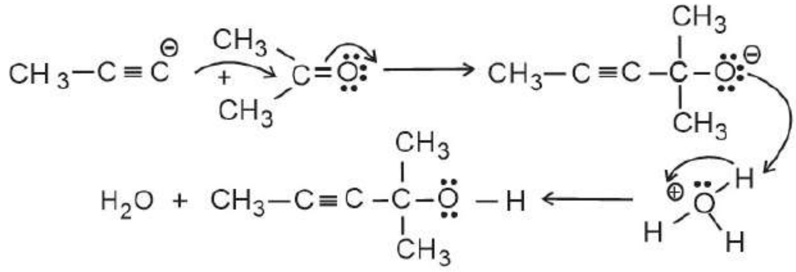
Reaction with Carbonyls and Oxidative Coupling-

Reaction with carbonyls
This reaction is very useful for the preparation of alcohol. In this reaction, a salt like $NaNH_2$ is used which produces a carbanion as follows:

$$CH \equiv CH \xrightarrow{NaNH_2} CH \equiv C^-$$

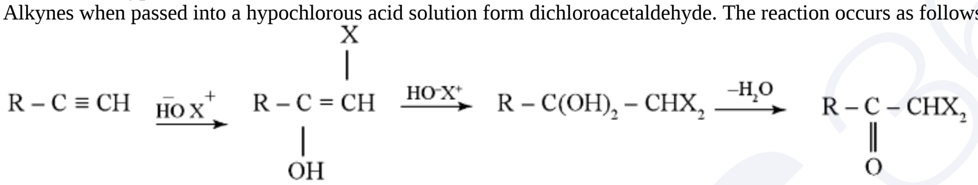
Now this carbanion reacts with the carbonyl group. Here, the carbanion binds with the carbonyl carbon and the carbon-oxygen bond shifts to the oxygen giving it a negative charge. Now we use H_3O^+ to bind with O^- and thus form the OH or alcohol.

The complete mechanism is given below:

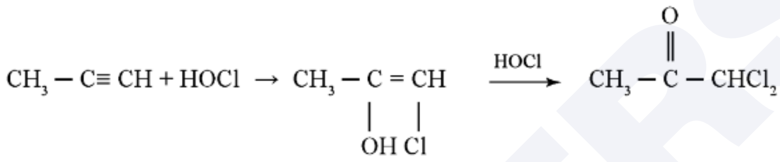


Reaction with HOCl and Polymerisation Reaction-

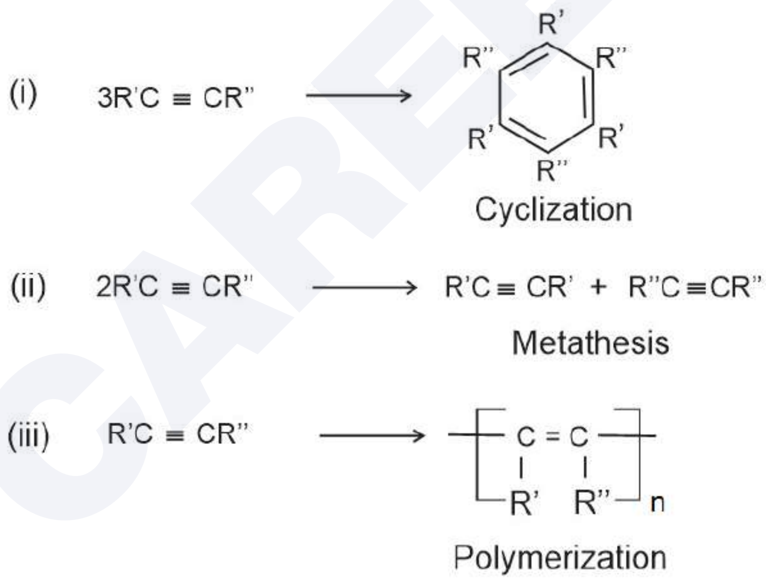
Addition of Hypochlorous acid
Alkynes when passed into a hypochlorous acid solution form dichloroacetaldehyde. The reaction occurs as follows:



For example:



Polymerisation
Alkynes polymerize to give the following compounds. The reactions occur as follows:

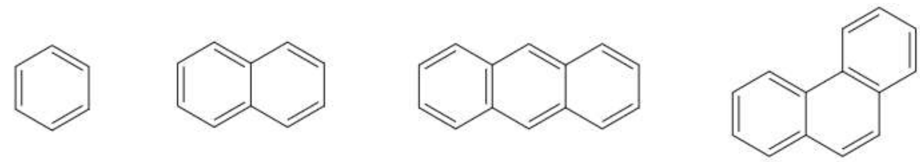


13. Aromaticity

Aromaticity is defined as "An aromatic compound having a cyclic planar structure with $(4n+2)\pi$ electrons and has high resonance energy and stability due to delocalization of π electrons." Any compound is aromatic if the following conditions are fulfilled:

- It has complete delocalization of π electrons.
- Has a high resonance energy.
- Has a conjugate system.
- Has number of π electrons according to 4n +2 or Huckel's rule that is, 2,6,10,14,18. Here, n = 0,1,2 ....
- If number of π electrons 4 "n' i.e., 4, 8, 12, 16, it will be anti-aromatic.
- If any of these conditions is not obeyed it will be non-aromatic.

Some example of aromatic compound include



Benzene Naphthalene Anthracene Phenanthrene

14. Reaction of Aromatic Compounds

Resonance Structures and Mesomeric Effect-

A group which accumulates a positive charge during resonance is said to show a +M effect. A group which accumulates a negative charge during resonance is said to show the -M effect.

We can see that the group showing(+M) effect donates the electron density whereas the group showing (-M) effect withdraws the electron density towards it. For example, the Nitro group is an electron-withdrawing group and hence it takes the electron density towards it. Thus it shows the (-M) effect.

In general, the group exerting the +M effect have a lone pair of electrons on the atom connected to the ring while groups showing the -M effect have an unsaturation at the atom connected to the ring.

Some examples are given below:

$$+M : -\ddot{O}H, -\ddot{N}H_2, -\ddot{S}H, -\ddot{O}R, -\ddot{N}HCOCH_3, -\ddot{F}, -\ddot{Cl}$$

$$-M : -CHO, -COOH, -CN, -SO_3H, -COCl, -NO_2$$

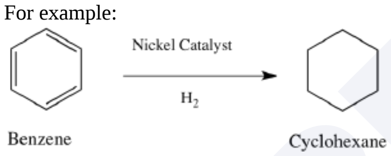
It is to be noted that groups like Benzene and Alkenes can show both +M as well as -M effects depending upon the type of group which is attached to them.

Reduction of Aromatic Compounds and Radical Addition-

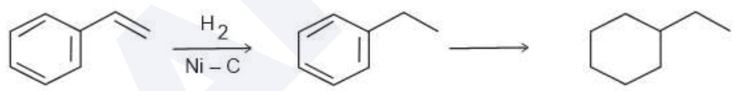
Reduction of Aromatic compounds
Reduction of the aromatic compounds is not easy as they are very stable due to their aromaticity and hence they have high resonance energy. So, we need to supply a greater amount of energy to reduce them.

Benzenes can be reduced by hydrogen in the presence of a Ni catalyst under stronger reaction conditions

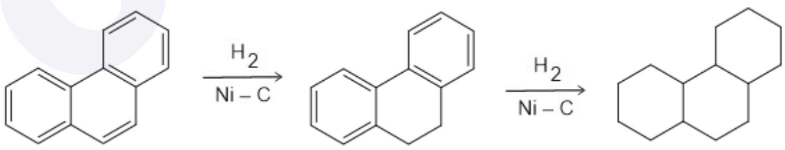
For example:



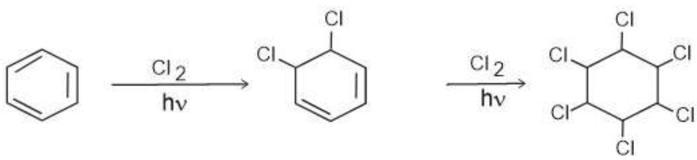
If in case there is unsaturation present in the compound not involved in aromaticity, these unsaturations would be reduced first. Subsequent reduction of the benzene ring would take place only when these have all been reduced.



In the case of Catalytic hydrogenation of Phenanthrene, the middle ring gets reduced first and on subsequent reduction becomes completely saturated.



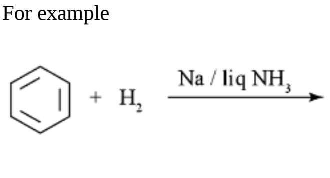
Benzene also shows free radical addition under UV light and adds three molecules of Chlorine to form $C_6H_6Cl_6$ which is also called Benzene Hexachloride or Gammaxane.



Birch Reduction-

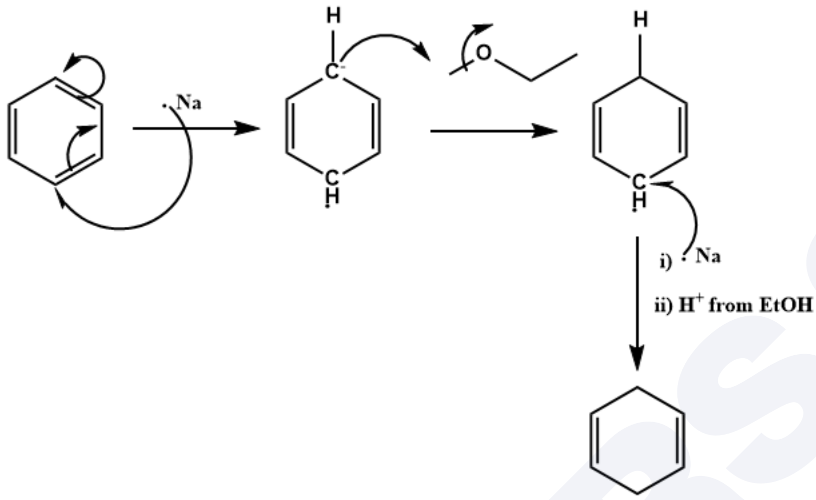
The birch reduction is an organic reaction which is used to convert aromatic compounds into cyclohexadienes. In this reaction, organic reduction of aromatic rings in liquid ammonia with sodium, potassium or lithium and alcohol occurs.

For example

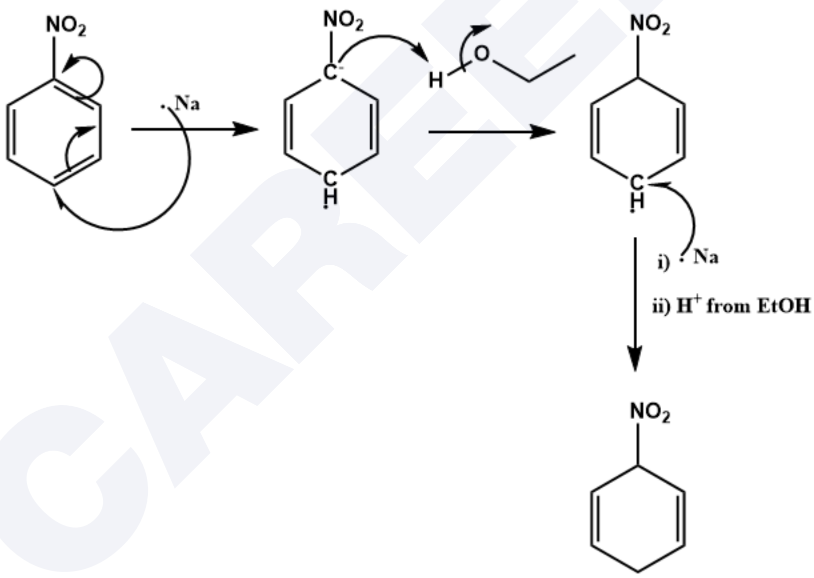


1,4-dihydro benzene

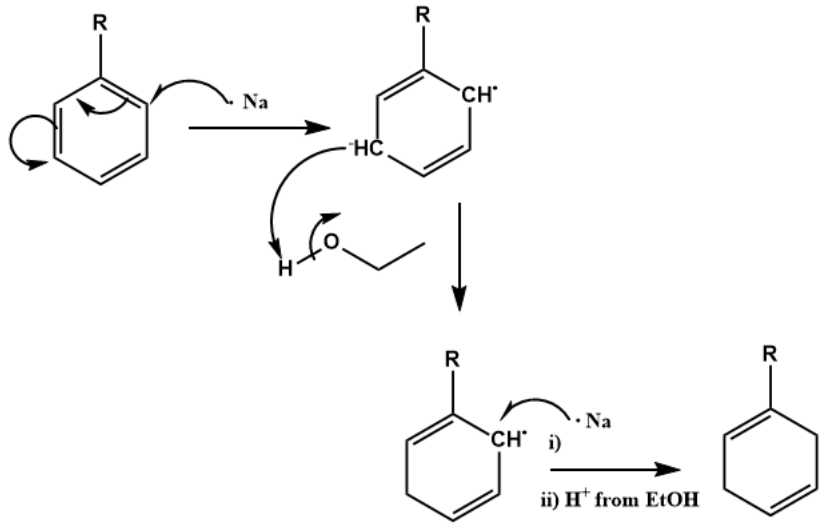
Mechanism



Birch Reduction when an Electron Withdrawing group is present on the Benzene ring



Birch Reduction when an Electron Donating group is present on the Benzene ring

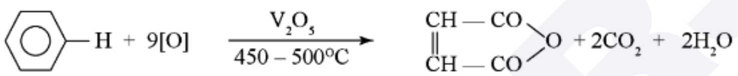


It is important that you remember the products of the Birch Reduction when an Electron donating or a withdrawing group is present on the Benzene Ring

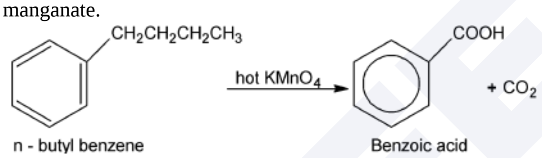
Oxidation of Aromatic Compounds-

Benzene is unreactive towards even strong oxidising agents such as $KMnO_4/K_2Cr_2O_7$. However, in drastic conditions, it can be oxidised slowly to CO_2 and H_2O. It can undergo a combustion reaction to give a luminous and smoky flame.

1. **Controlled oxidation with air:** Benzene on oxidation with air at 773 K in the presence of V_2O_5 as catalyst gives Maleic anhydride.



2. **Oxidation of Alkyl benzene:** Alkyl groups when attached to the benzene ring, they are easily oxidised by an alkaline solution of potassium manganate.



15. Electrophilic Substitution Reaction

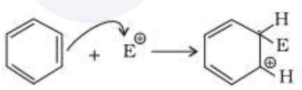
According to experimental evidence, electrophilic substitution reactions are supposed to proceed via the following three steps:

(a) Generation of the electrophile

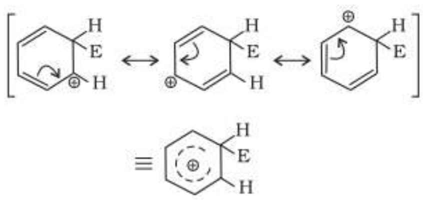
During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in the generation of the electrophile by extracting a lone pair donor and forming the respective electrophile

(b) Formation of carbocation intermediate

The electrophile generated in the first step attacks the Benzene ring and forms the Arenium ion or the σ-complex

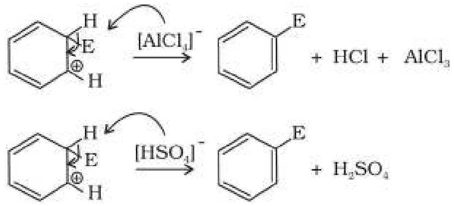


It is to be noted that the formation of Arenium ion leads to a loss of aromaticity. There is resonance stabilisation of the arenium ion



(c) Removal of proton

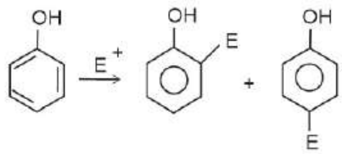
To restore the aromaticity of the Benzene ring, there is a removal of a proton from the Arenium ion by the conjugate base of the Lewis acid



Directive influence of a functional group in monosubstituted benzene

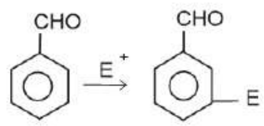
When the substituent is Electron Donating in nature

- The groups like OH, NH_2, CH_3 etc are electron donating and they create a partial negative charge at their ortho and para positions
- The ortho, para positions of these substituted benzenes are electron-rich in nature.
- Electrophile is electron deficient in nature. Thus, it tries to attack the position which is electron-rich.
- Thus, these groups are called as are called ortho-para directing.



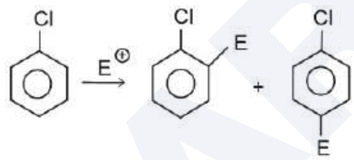
When the substituent is Electron Withdrawing in nature

- The groups like Nitro, acyl, sulpho groups are electron-withdrawing and they create a partial positive charge at their ortho and para positions
- Thus, relatively the meta position is more electron-rich in such cases and the electrophile attacks there
- These groups are hence known as Meta-directing groups because they sent the electrophile to the meta position.



Case of Halogens

- Halogens exert a +M and -I effect and generally the effect of -I dominate
- Halogens are hence deactivating in nature
- However, the +M effect stabilises the Arenium ion which is formed by the attachment of electrophile at the Ortho and para positions
- Halogens are thus deactivating and yet Ortho-Para directing in nature as far as the electrophilic aromatic substitution is concerned

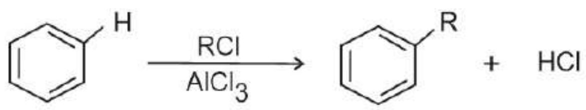


16. Friedel-Crafts Reaction

Friedel craft alkylation-

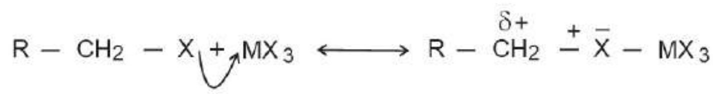
This reaction allowed for the formation of alkyl benzenes from alkyl halides. The reactivity of haloalkanes increases as we move up the periodic table and increase polarity. This means that an RF haloalkane is most reactive followed by RCl than RBr and finally RI. This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend to have similar halogen combinations such as BF_3, $SbCl_5$, $AlCl_3$, $SbCl_5$, and $AlBr_3$, all of which are commonly used in these reactions.

For example:

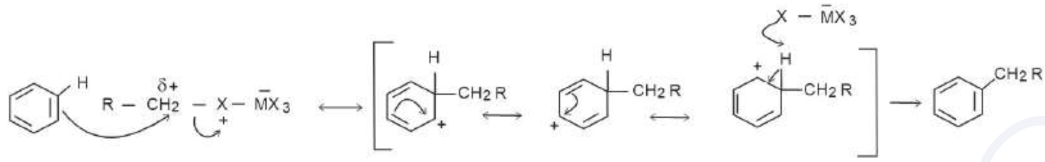


Mechanism

1. In this step, a carbocation is formed that acts as the electrophile in the reaction. This step activates the haloalkane. Secondary and tertiary halides only form the free carbocation in this step.



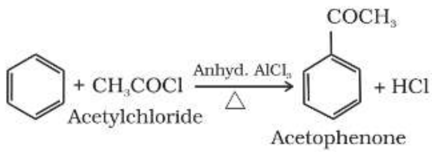
2. In this step, an electrophilic attack on the benzene occurs which results in multiple resonance forms. The halogen reacts with the intermediate and picks up the hydrogen to eliminate the positive charge. The aromaticity is regained by the substrate after this step.



Friedel Craft Acylation-

This electrophilic aromatic substitution allows the synthesis of monoacylated products from the reaction between arenes and acyl chlorides or anhydrides. The products are deactivated and do not undergo a second substitution.

For example:



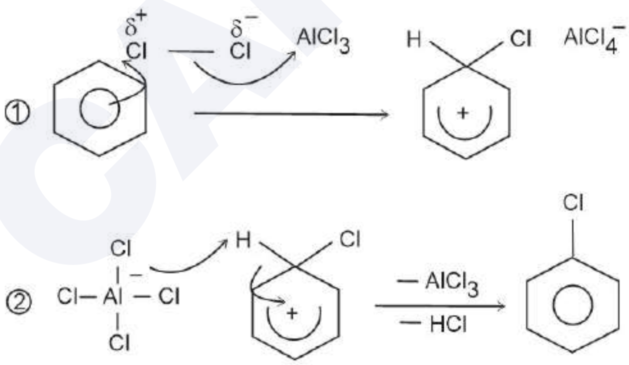
17. Benzene Reactions - Sulfonation, Nitration and Halogenation

Halogenation on ring or alkyl chain-

Benzene undergoes chlorination when it is treated with chlorine in the presence of a Lewis catalyst such as $AlCl_3$ or Fe or $FeCl_3$ and in the absence of light.

For example:

Mechanism
The mechanism of this reaction follows two-step:

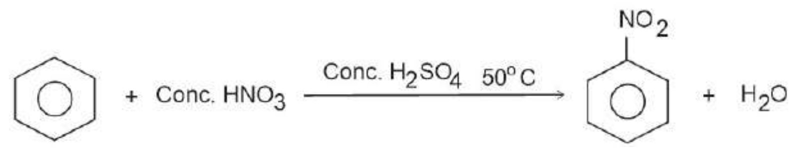


NOTE: The hydrogen is removed by the $AlCl^{-}_4$ ion which was formed in the first stage. The aluminium chloride catalyst is re-generated in this second stage.

Nitration and Sulphonation-

Nitration
Benzene undergoes nitration when treated with concentrated nitric acid in the presence of concentrated sulphuric acid, i.e., nitrobenzene is formed. The reaction is carried out at 313-323 K when one of the H atoms from the benzene ring is replaced by the nitro group.

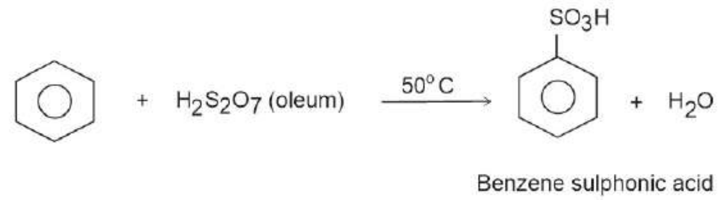
For example:



Sulphonation

Benzene forms benzene sulphonic acid with hot concentrated sulphuric acid or with fuming sulphuric acid (oleum). The attacking electrophile in the reaction is Sulphur trioxide (SO_3)

For example:



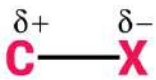
Organic Compounds containing Halogens

Important Formulae

1. Alkyl Halides

Nature of C-X bond and Physical Properties-

Halogen atoms are more electronegative than carbon, therefore, carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge. As we go down the group in the periodic table, the size of halogen atom increases. Fluorine atom is the smallest and iodine atom is the largest. Consequently, the carbon-halogen bond length also increases from $\mathrm{C-F}$ to $\mathrm{C-I}$.



Physical properties of Haloalkanes and Haloarenes:

(1) These are less soluble in H_2O but more soluble in Organic solvents

(2) Their density follows the order:

Iodide > Bromide > Fluoride > Chloride

(3) Their boiling point follows the order:

Iodide > Bromide > Fluoride > Chloride

(4) Boiling point of Isomeric haloalkanes decreases with the increase in branching

(5) Boiling point of isomeric dihalobenzene is nearly the same and follows the order

para > ortho > meta

Huns-dicker Reaction-

The silver(I) salts of carboxylic acids react with halogens to give unstable intermediates which readily decarboxylate thermally to yield alkyl halides. The reaction is believed to involve homolysis of the C-C bond and a radical chain mechanism. In this reaction, ester is formed as a by-product. The reaction occurs as follows:

$$\mathrm{RCOOAg + X_2 \xrightarrow{CCl_4} R-X + CO_2 + AgX}$$

For example:

$$\mathrm{CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3COOBr + AgBr}$$

Mechanism

Chain Initiation

$$\mathrm{CH_3COOBr \xrightarrow{RDS} CH_3COO^{\bullet} + Br^{\bullet}}$$

Chain Propagation

$$CH_3COO^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CO_2$$

$${}^{\bullet}CH_3 + CH_3COOBr \longrightarrow CH_3Br + CH_3COO^{\bullet}$$

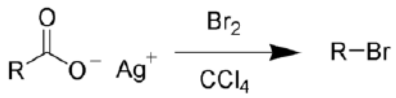
Chain Termination

${}^{\bullet}CH_3 + Br^{\bullet} \longrightarrow CH_3Br$ **(major)**

$CH_3COO^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3COOCH_3$ **(minor)**

$CH_3COO^{\bullet} + Br^{\bullet} \longrightarrow CH_3COOBr$ **(minor)**

For example:



The rate of reaction with changing the alkyl group (R) in the above reaction varies as

$1^{\circ} > 2^{\circ} > 3^{\circ}$

It is to be noted that with I_2, silver salt of carboxylic acid gives ester as the main product instead of alkyl iodide.

$$2RCOOAg + I_2 \xrightarrow{CCl_4} RCOOR + CO_2 + 2AgI$$

Reaction with NaCN, AgCN, $NaNO_2$ and $AgNO_2$-

- **Reaction with NaCN:** NaCN or KCN is ionic in nature i.e, Na^+CN^-. Thus, the nucleophile in this case is CN^-. The reaction occurs as follows:

  $$R - CH_2 - X \xrightarrow{NaCN} R - CH_2 - CN + NaX$$

  For example:

  $$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$$

- **Reaction with AgCN:** AgCN is covalent in nature and as a result, the C atom is covalently bonded to Ag. Thus, the attack of the nucleophile in this case will take place from the Lone pairs over N atom

  $$R - CH_2 - X \xrightarrow{AgCN} R - CH_2 - NC + AgX$$

  For example

  $$CH_3CH_2CH_2Br + AgCN \rightarrow CH_3CH_2CH_2NC + AgBr$$

- **Reaction with $NaNO_2$:** $NaNO_2$ or KNO_2 is ionic in nature and it breaks into Na^+ and NO^-_2. Nitrite ion NO^-_2 with structure O=N-O- is an ambient nucleophile with electron pairs on both N & O. NO^-_2 ion having an excess of electrons on O thus, allows it to act as a nucleophile in preference to N.

  The reaction occurs as follows:

  $$CH_3Br + NaNO_2 \rightarrow CH_3 - O - NO + NaBr$$

- **Reaction with $AgNO_2$:** $AgNO_2$ is covalent in nature and it does breaks into Ag^+ and NO^-_2 ions. The O atom remains bonded to the Ag and hence the attack of the nucleophile takes place by the lone pairs over Nitrogen.

  The reaction occurs as follows

  $$CH_3Br + AgNO_2 \rightarrow CH_3 - NO_2 + NaBr$$

Finkelstein and Swartz Reaction-

Finkelstein Reaction

Finkelstein's reaction is a method of preparation of alkyl iodides from alkyl chlorides or alkyl bromides. In this reaction, alkyl chlorides or bromides are treated with NaI in the presence of acetone to form alkyl iodides. The reaction occurs as follows:

$$R - X + NaI \rightarrow R - I + NaX$$

We use NaI because it is soluble in acetone as it is covalent in nature. All other sodium halides are ionic in nature and thus not soluble.

For example:

$$CH_2 = CH - CH_2 - Cl \xrightarrow{NaI/Acetone} CH_2 = CH - CH_2 - I$$

Swarts Reaction

Halide exchange is also used for the preparation of alkyl fluorides by Swarts Reaction. Alkyl chloride/bromide is heated in presence of AgF, Hg_2F_2, CoF_2 or SbF_3 to give alkyl fluoride.

For example:

$$CH_3 - Br + AgF \longrightarrow CH_3 - F + AgBr$$

Reaction with PCl_5, PCl_3, $SOCl_2$ and HX-

The reaction of alcohols ROH with PCl_5 and PCl_3 yields an alkyl halide RCl. The reactions of alcohols with PCl_5, PCl_3 and $SOCl_2$ occurs as follows:

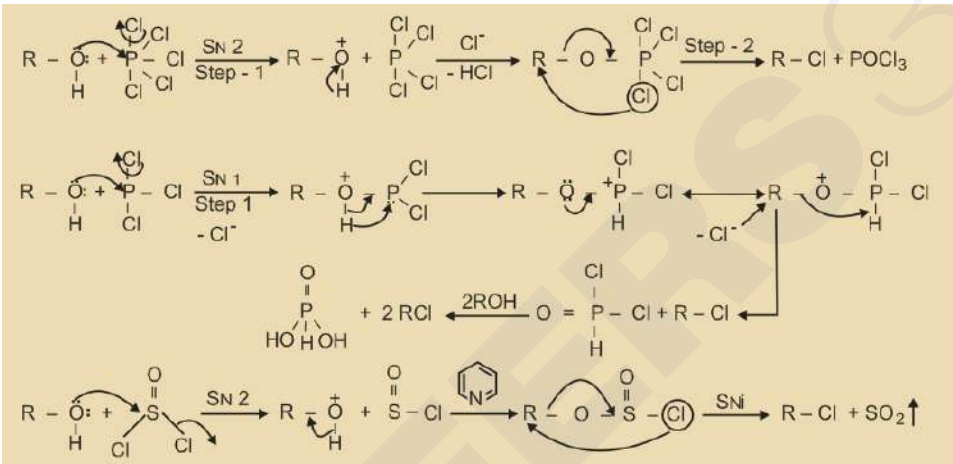
$$PCl_5 \rightarrow POCl_3 + HCl + RCl$$

$$PCl_3 \rightarrow H_3PO_3 + HCl + RCl$$

$$SOCl_2 \rightarrow SO_2 + HCl + RCl$$

$POCl_3$ and H_3PO_3 are generated in liquid phase and hence they are very hard to separate while SO_2 and HCl are gases and thus they are easy to remove. Hence, for chlorination, we always use $SOCl_2$ as the best option among the given reagents.

Mechanism



The reactions occurs as follows:

$$RCOOH + PCl_3/PCl_5/SOCl_2 \rightarrow RCOCl$$

$$R - OH + PCl_3/PCl_5/SOCl_2 \rightarrow R - Cl$$

2. Physical & Chemical Properties of Haloalkanes

Strong and Weak bases-

Most common bases that we have use are alc.KOH and aqueous NaOH. In alc.KOH, we have $EtO^-(CH_3\text{-}CH_2\text{-}O^-)$ as the base while in aqueous NaOH, the base is OH^-. The strength of these two bases are given below:

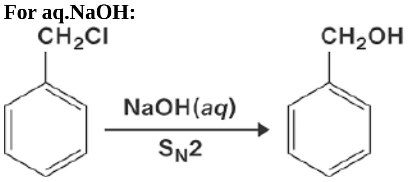
$CH_3\text{-}CH_2\text{-}O^- > OH^-$

Because $CH_3\text{-}CH_2\text{-}$ is the releasing group and hence it unstabilize the O^-, thus it reacts faster and hence it is stronger base. The reactions occurs as follows:

For alc.KOH:

$$CH_3CH_2Br + KOH(alc) \longrightarrow H_2C = CH_2 + KBr + H_2O$$

For aq.NaOH:

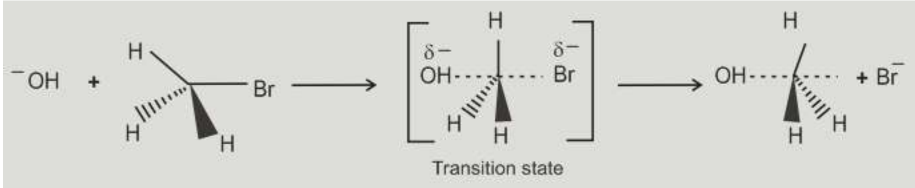


SN2 Reaction-

The general reaction occurs as follows:

$$R - CH_2 - Cl + OH^- \rightarrow R - CH_2 - OH$$

Mechanism



- It is bimolecular nucleophilic substitution (SN_2) reaction.
- Rate of reaction follows second order kinetics and depends upon the concentration of both the nucleophile as well as the substrate.

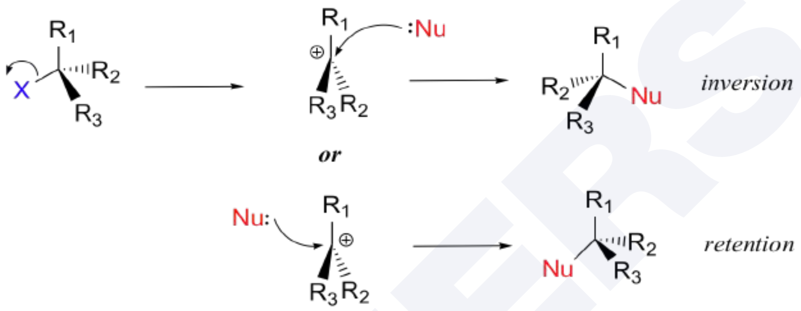
$$\text{Rate} \propto [R-X][Nu^-]$$

- Rate determinig step depends on how fast the transition state is formed and also the stability of the transition state
- Stronger nucleophile is required as it has to attack and make the leaving group leave
- Polar aprotic solvents favour SN_2 reaction as they do not facilitate formation of ions
- The reaction occurs in concerted mechanism and inversion of configuration (Walden Inversion) takes place if the leaving group and the nucleophile have the same priority
- Steric hinderance in the substrate decreases the reactivity of the subtrate towards SN_2 reaction

SN1 Reaction-

The general reaction occurs as follows:
$R-CH_2-Cl + OH^- \rightarrow R-CH_2-OH$

- The mechanism occurs as follows:



- SN_1 reactions are nucleophilic substitution reactions, involving a nucleophile replacing a leaving group.
- SN_1 reactions are unimolecular. The rate of this reaction depends only on the concentration of one reactant and does not depend upon the strength of the nucleophile

$$\text{Rate} \propto [R-X]$$

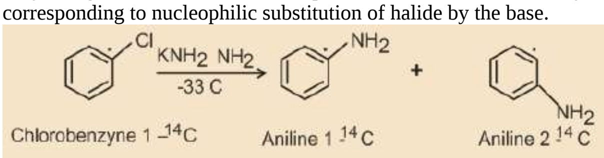
- Rate determinig step depends on the stability of the intermediate carbocation which is obtained during the course of the reaction

$$\text{Rate} \propto \text{stability of carbocation}$$

- Since the mechanism involves the attack of nucleophile on an already formed carbocation, the strength of nucleophile is unimportant for the rate of the reaction
- The rate of formation of intermediate is independent of concentration of nucleophile and depends only on the concentration of reactants.
- Good ionising solvents (polar protic solvents) are required to carry out SN_1 reaction as there has to be formation of ions
- Configuration of the product may be same or inverted and in cases where the leaving group departs from a chiral centre, racemisation occurs.
  - If Nu^- attacks on the same side from where X^- leaves, then it is called 'Retention'.
  - If Nu^- attacks from the opposite side from where X^- leaves, then it is called 'Inversion'.
  - Racemic mixture is obtained when equal amount of retention and inversion products are formed in the reaction.
  - Generally, partial racemisation is seen in the reactions as it both SN_1 and SN_2 are both competing

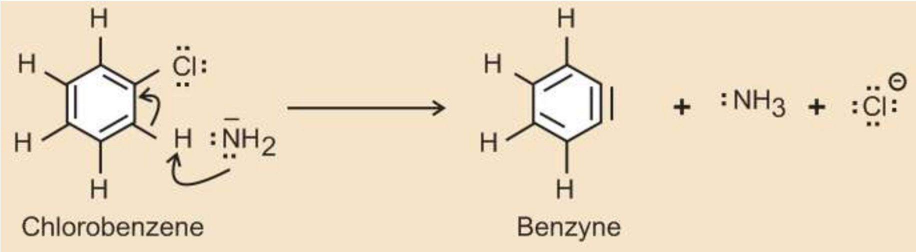
Elimination-Addition Mechanism

Very stong base such as sodium or potassium amide react with aryl halide, even those without electron withdrawing substituents to give products corresponding to nucleophilic substitution of halide by the base.

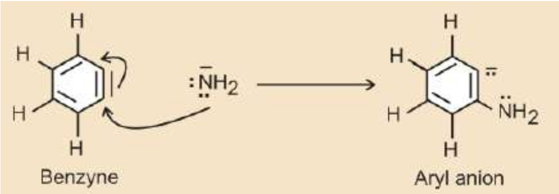


Mechanism

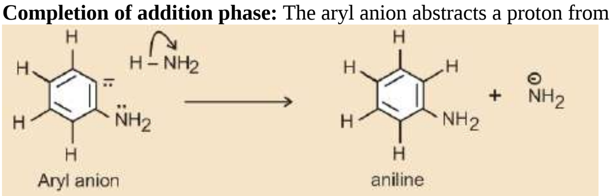
1. **Elimination stage:** Amide ion is a very strong base and brings about the dehydrohalogenation of chlorobenzene by abstracting a proton from the carbon adjacent to the one that bears the leaving group. The product of this step is an unstable intermediate called benzyne.



2. **Beginning of addition phase:** Amide ion acts as a nucleophile and adds to one of the carbons of the triple bond. The product of this step is a carbanion.



3. **Completion of addition phase:** The aryl anion abstracts a proton from the ammonia used as the solvent in the reaction.

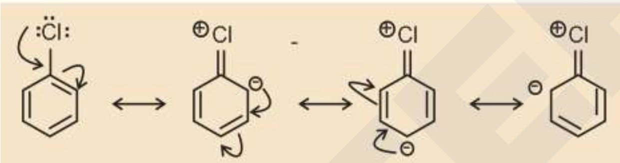


4.

Nucleophilic Substitution-

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

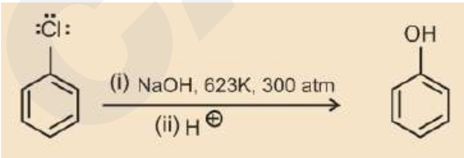
- **Resonance effect:** In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



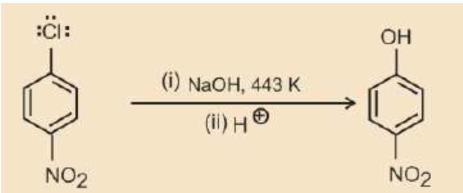
C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

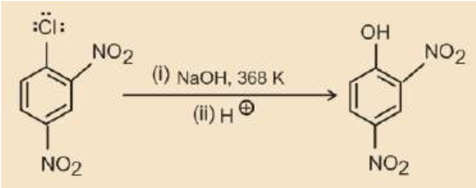
- **Difference in hybridisation of carbon atom in C—X bond:** In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised. The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-chararcter. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.
- **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.
- Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

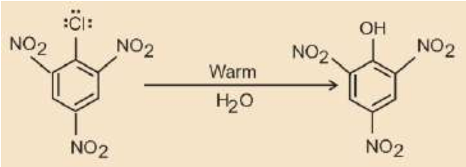
Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.



The presence of an electron withdrawing group (-NO_2) at ortho- and para-positions increases the reactivity of haloarenes.



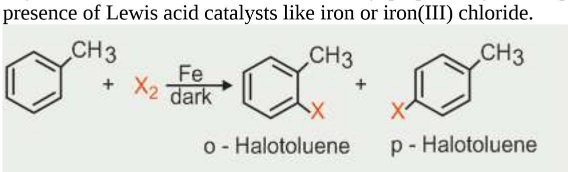




3. Haloarene

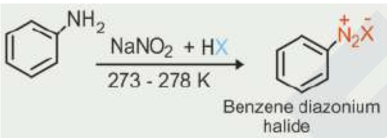
Preparation of Aryl Halides-

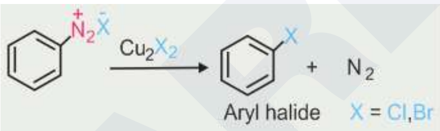
- **From hydrocarbons by electrophilic substitution**
  Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



- The ortho and para isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO3, HIO4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

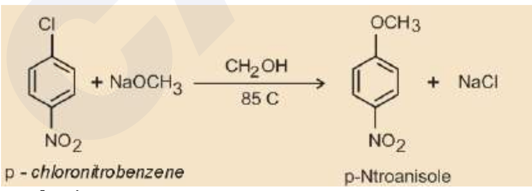
- **From amines by Sandmeyer's reaction**
  When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.





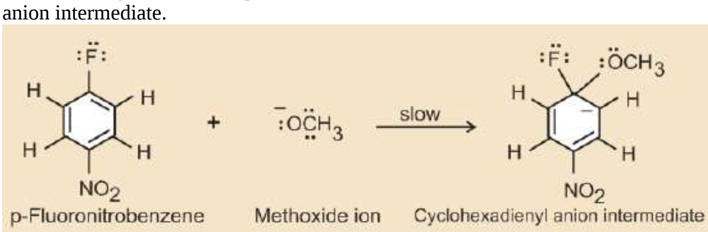
Elimination-Addition Mechanism-

The accepted mechanism for nucleophilic aromatic substitution in nitro-substituted aryl halides is given as follows.

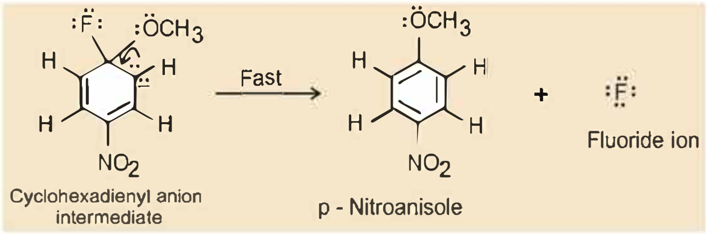


Mechanism

1. **Addition stage:** The nucleophile, in this case methoxide ion, adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



2. **Elimination stage:** Loss of halide form the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.


:F:
:ÖCH3
H
H
H
H
NO2
Cyclohexadienyl anion
intermediate
Fast
:ÖCH3
H
H
H
H
NO2
p - Nitroanisole
+
:F:
Fluoride ion

Organic Compounds containing Oxygen

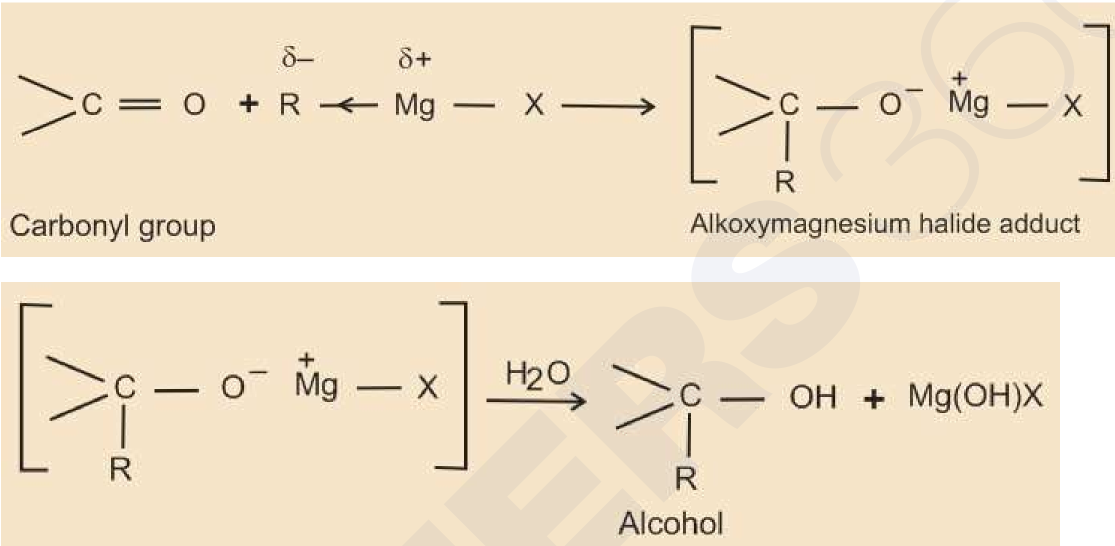
Important Formulae

1. Preparation of Alcohol

Grignard Reagent -

All three types of monohydric alcohols can be prepared by the use of Grignard reagents. Grignard reagents form additional compounds by nucleophile attack with aldehydes and ketones which on hydrolysis with dilute acid yields alcohol.

Mechanism

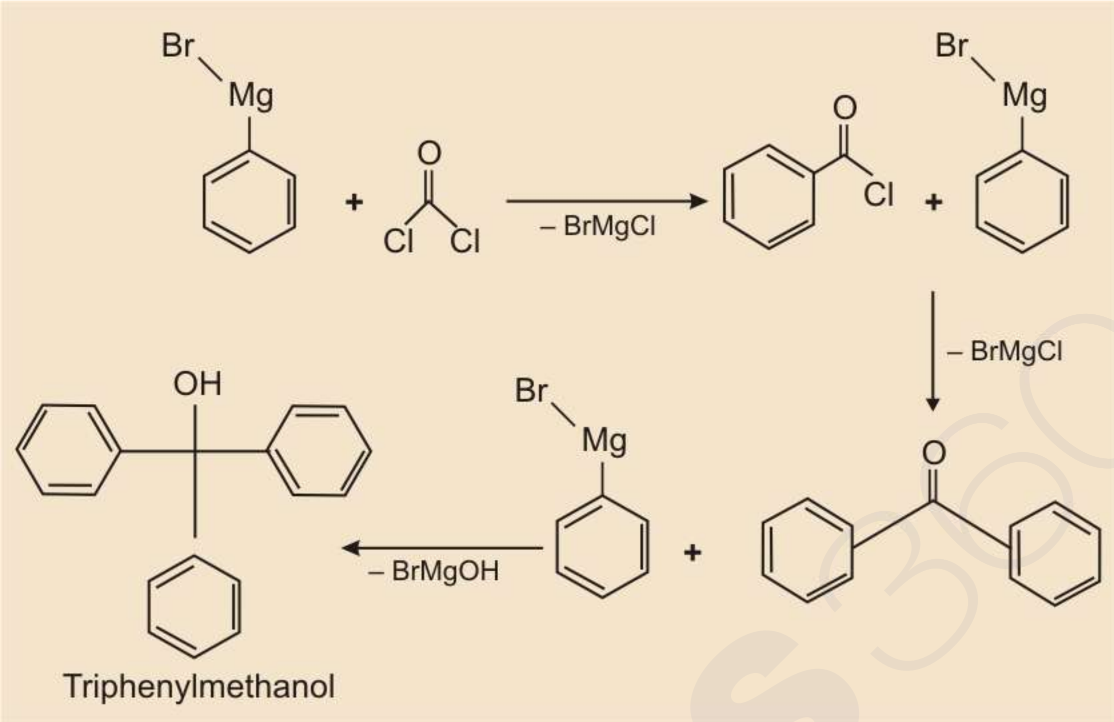


For example:

$$HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones. The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields alcohol.

Mechanism



Reduction of Anhydrides and Esters-

Anhydrides are formed by heating two (-COOH) groups to remove (H_2O) molecules. Aldehydes, ketones, carboxylic acids and derivatives on reduction yield alcohols. A number of reducing agents linked to Zn/HCl, Na/C_2H_5OH, $LiAlH_4$ or $NaBH_4$ can be used for this purpose. These derivatives are reduced by nascent hydrogen into corresponding alcohols.

Some examples include,

$$(CH_3CO)_2O + 4H \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2OH + CH_3COOH$$

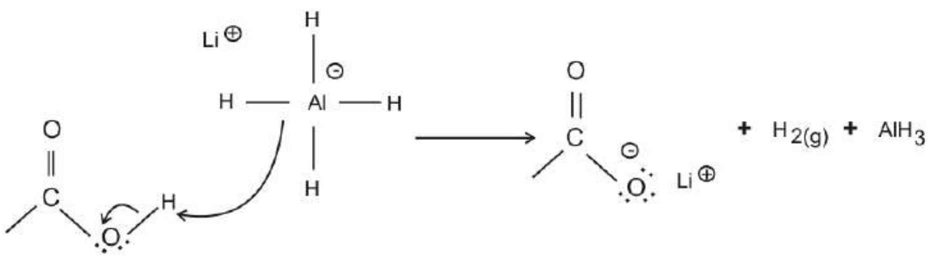
$$CH_3COOC_2H_5 + 4H \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} 2CH_3CH_2OH$$

Reduction by $LiAlH_4$ and $NaBH_4$-

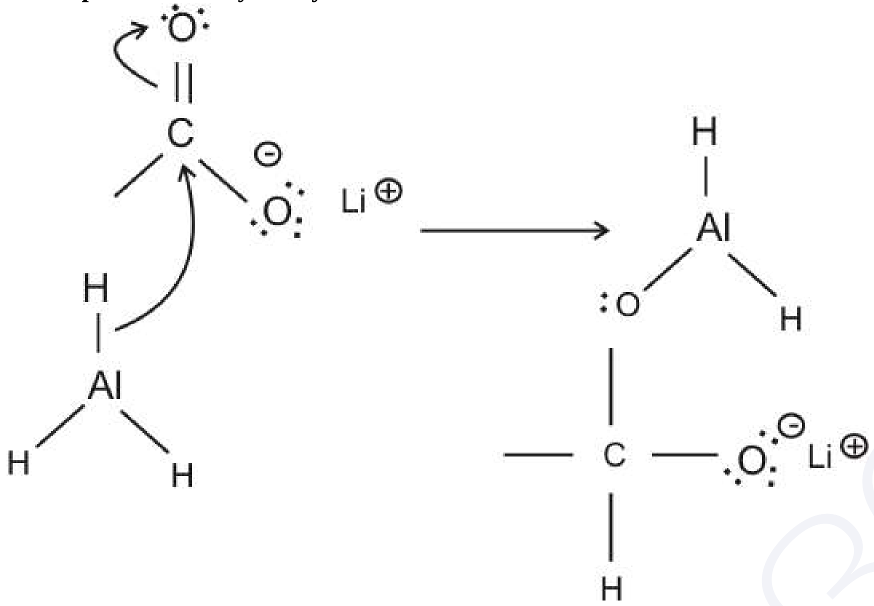
$NaBH_4$ can only reduce keto groups. But $LiAlH_4$ can reduce even anhydrides and esters. $LiAlH_4$ is a very good reducing agent because the (Al) atom present in ir is more covalent than the (B) atom in $NaBH_4$. Therefore, Al has more tendency to gain the electrons, thus, it will try to keep the electrons to itself and hence H^- will go in a particular manner. Thus, $LiAlH_4$ is a better reducing agent than $NaBH_4$.

Mechanism
The mechanism for $LiAlH_4$ occurs in the following steps:

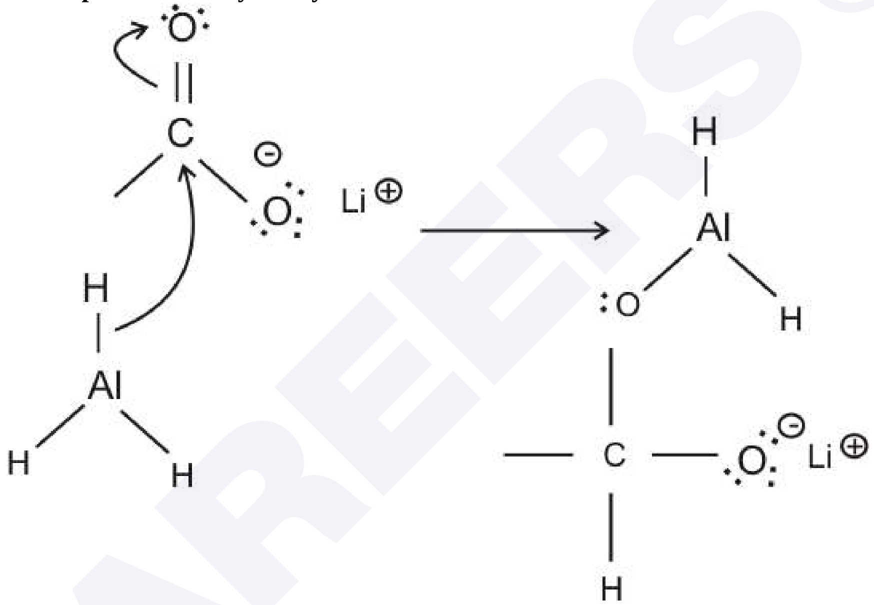
1. **Deprotonation**



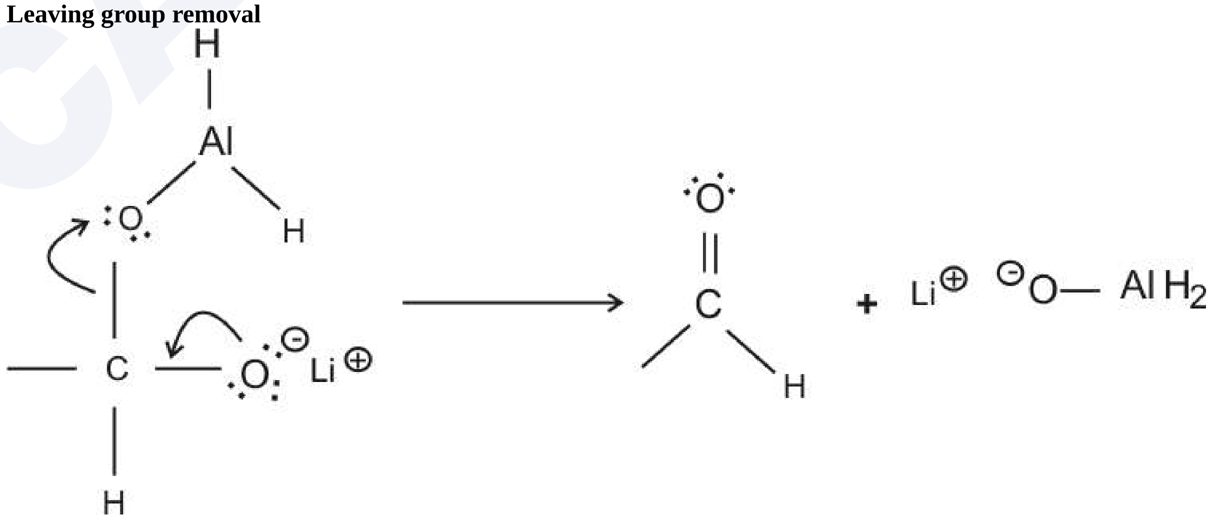
2. **Nucleophilic attack by the hydride ion**



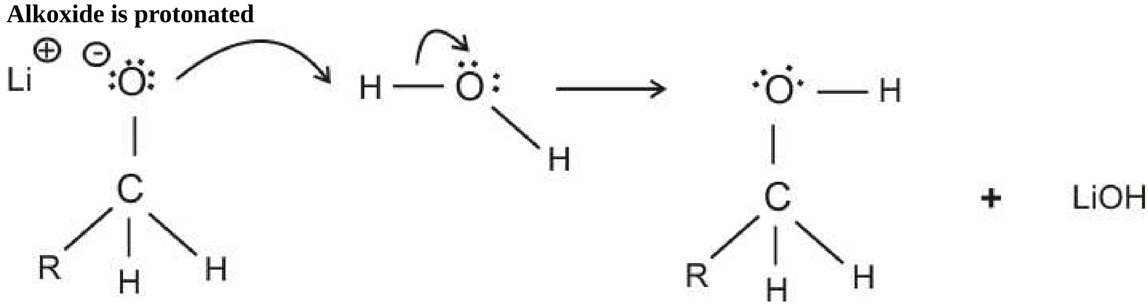
3. **Nucleophilic attack by the hydride ion**



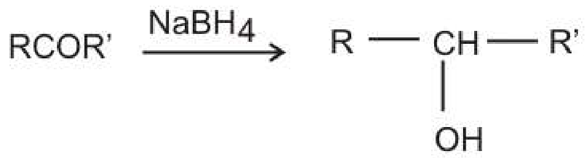
4. **Leaving group removal**



5. **Alkoxide is protonated**



Some examples include:



$$RCOOH \xrightarrow[(2)\ H_2O]{(1)\ LiALH_4} RCH_2OH$$

2. Physical and Chemical Properties of Alcohols

Properties of Alcohols-

- Lower members of alcohols are colourless liquids whereas higher members are colourless solids.
- Alcohols have higher boiling points.
- The boiling point of alcohols increases with an increase in members of the OH group.
- Lower members are highly soluble in water.

Acylation and Oxidation of Alcohols-

Acylation of alcohols
Ethanoyl chloride reacts instantly with cold ethanol. There is a very exothermic reaction in which a steamy acidic gas is given off (i.e. hydrogen chloride) and ethyl ethanoate (an ester) is formed.

For example,

Oxidation of Alcohols
The nature of the oxidation products depends on whether the alcohol is primary, secondary or tertiary. The oxidising agents usually employed are acidified potassium dichromate, acidified or alkaline potassium permanganate or dilute nitric acid. It is a test of different alcohols as primary, secondary and tertiary alcohols give different products during oxidation.

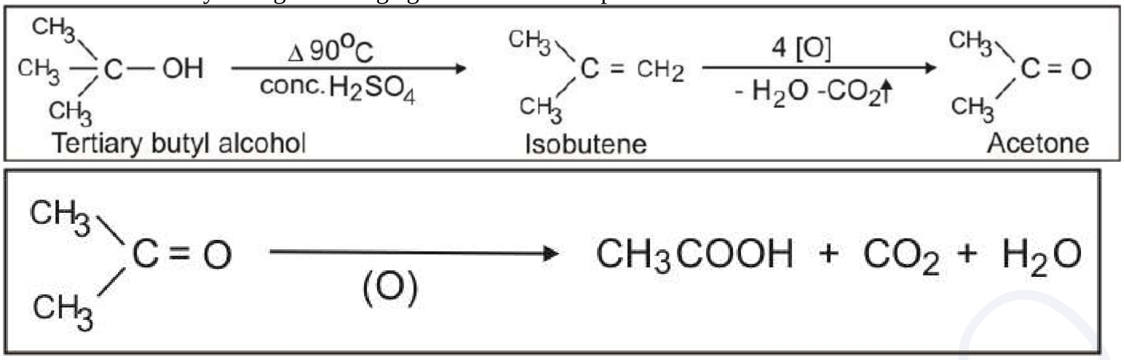
- Primary alcohols give acids having the same number of carbon atoms with acidic $KMnO_4$ or $K_2Cr_2O_7$. For example,

$$CH_3CH_2OH \xrightarrow[-H_2O]{[O]\ \text{acidic}\ KMnO_4} CH_3 - CHO \xrightarrow{[O]\ \text{acidic}\ KMnO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

- Secondary alcohol on oxidation gives ketone which undergoes further oxidation under drastic conditions by strong oxidizing agents like HNO_3 to give acid with one carbon atom less than the alcohol. For example,

$$(CH_3)_2 - CHOH \xrightarrow[K_2Cr_2O_7\ /\ Cr_2O_3]{\text{Gla}\ CH_3COOH\ [O]} CH_3 - CO - CH_3 \longrightarrow CH_3COOH + CO_2 + H_2O$$

- Tertiary alcohol cannot undergo oxidation by mild oxidizing agents as above however it can be oxidized under drastic conditions by strong oxidizing agents and the final product acid will have two carbon atoms less than alcohol.



Haloform Reaction-

Ethyl alcohol when heated with iodine and sodium hydroxide or aqueous sodium carbonate forms a yellow crystalline solid, iodoform. The reaction occurs as follows:

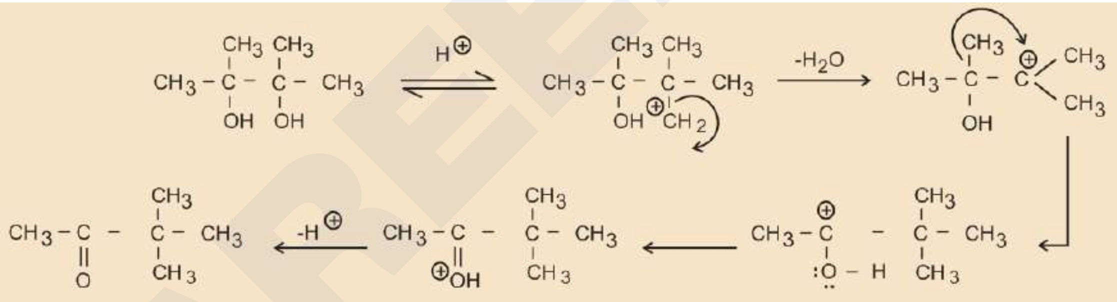
$$C_2H_5OH + 4I_2 + 6NaOH \xrightarrow{\text{Heat}} CHI_3 + 5NaI + HCOONa + 5H_2O$$

Methyl alcohol does not respond to the iodoform test. In place of iodine, bromine or chlorine can be taken when the corresponding compounds bromoform or chloroform are to be formed. The reaction in general is known as haloform reaction.

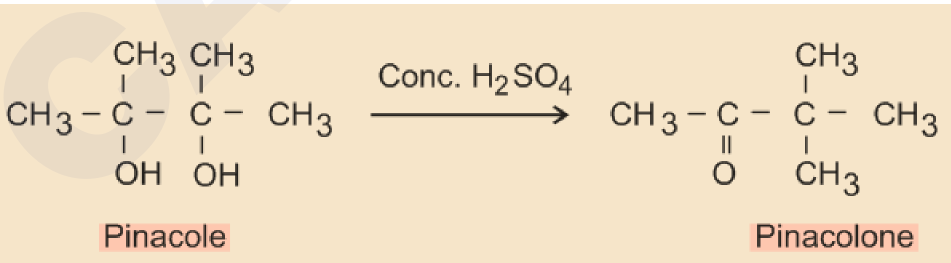
Pinacol Pinacolone Rearrangement-

The pinacol rearrangement is the acid-catalyzed dehydration of glycols, which converts the glycol into an aldehyde or a ketone. When pinacols are treated with mineral acids, acid chlorides, $ZnCl_2$, or another electrophilic reagent, they rearrange to form ketones called pinacolones with the elimination of H_2O.

Mechanism



For example

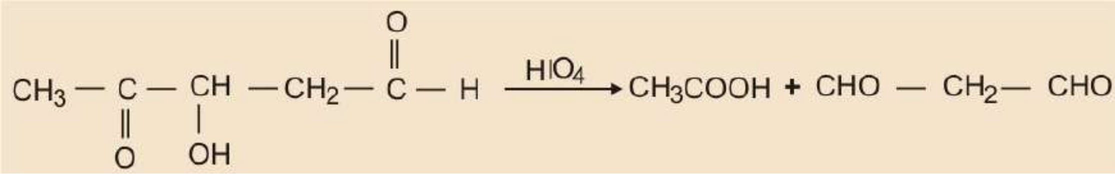


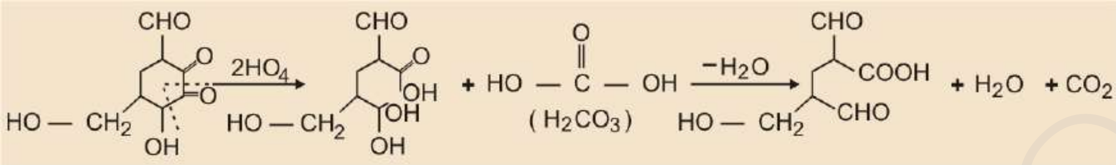
NOTE: With unsymmetrical glycols, the product obtained is determined mainly by the OH that is lost as H_2O to give more stable carbocation and thereafter by the better migrating group.

Oxidative Cleavage with HIO_4-

At least 2-OH or 2 >C=O or 1-OH and 1 >C=O should be at adjacent carbons. HIO_4 works as an oxidising agent here.

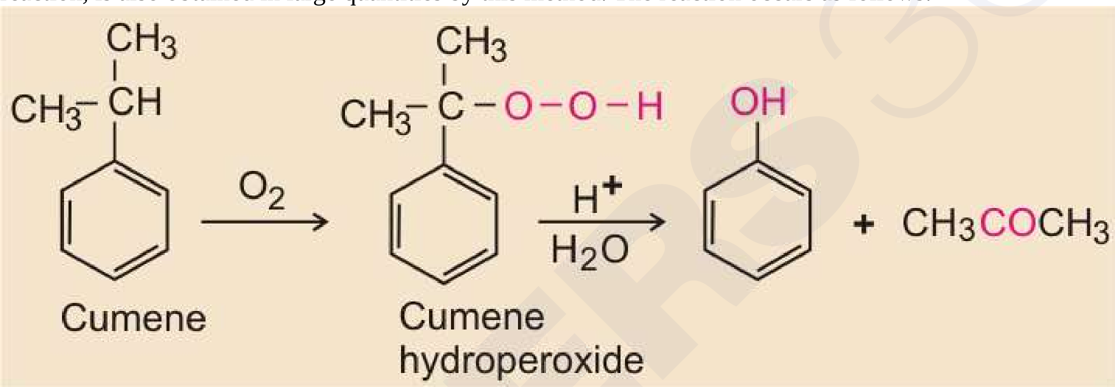
Some examples include,





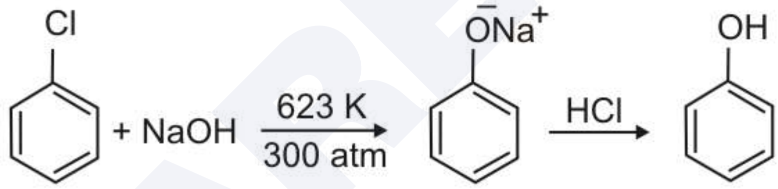
3. Preparation of Phenols

Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method. The reaction occurs as follows:



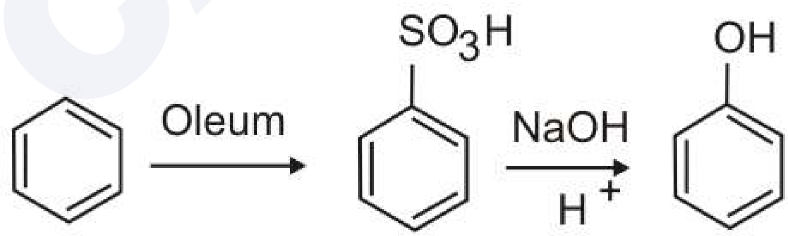
From Haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by the acidification of sodium phenoxide produced. The reaction occurs as follows.



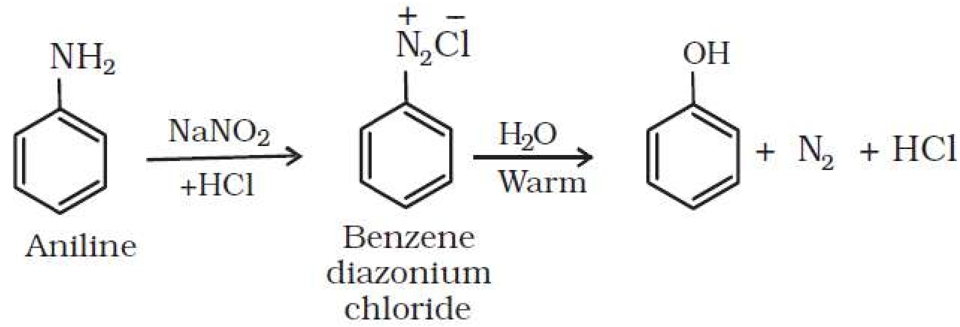
From Benzene sulphonic acid

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol. The reaction occurs as follows:



From Diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids. The reaction occurs as follows.



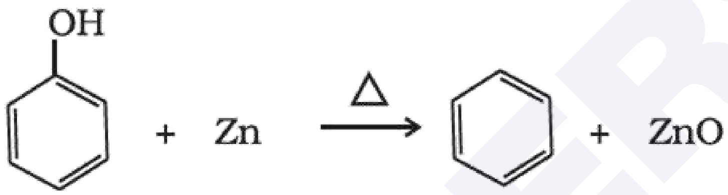
4. Physical and Chemical Properties of Phenols

Properties of Phenols-

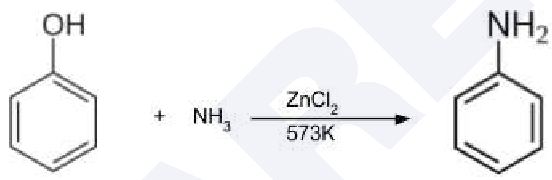
1. Phenols are either colourless liquids or white crystalline solids.
2. Phenols are soluble in hot water.
3. The boiling points of phenols are much higher than the corresponding aromatic hydrocarbons and the haloarenes.
4. Phenols have anti-fungal and anti-bacterial properties. Thus used as disinfectants and antiseptics.
5. Phenols are poisonous in nature but act as antiseptic and disinfectant.

Reactions due to (-OH) group

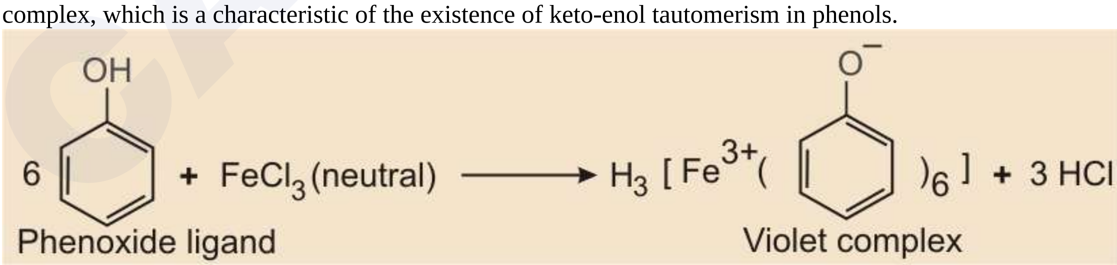
Reaction with zinc dust: When phenol is distilled with zinc dust, benzene is obtained. The reaction occurs as follows:



Reaction with NH_3: Phenol reacts with ammonia in the presence of anhydrous zinc chloride at 573K or $(NH_4)_2SO_3$-NH_3 at 423K to form aniline. This conversion of phenol into aniline is called the Bucherer reaction.



Reaction with $FeCl_3$: Phenol gives violet colouration with ferric chloride solution due to the formation of a coloured iron complex, which is a characteristic of the existence of keto-enol tautomerism in phenols.



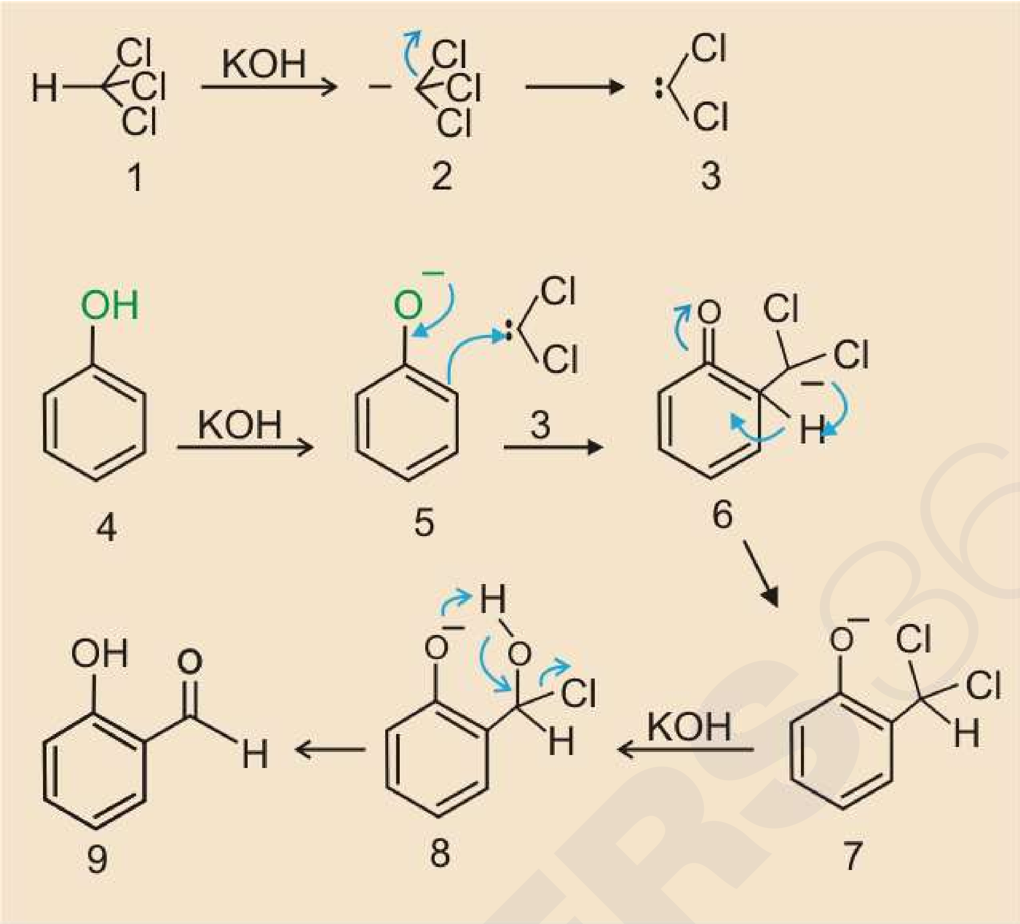
Reimer-Tiemann and Kolbe's Schmidt Reactions-

Riemer-Tiemann Reaction

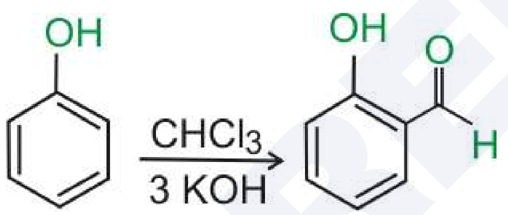
Phenols for aromatic compounds containing EDG when refluxed with $CHCl_3$ and alkali yield *o*- and *p*-hydroxybenzaldehyde. The *ortho* product is the predominant product. It is an electrophilic substitution on PhO^- ion. The electrophile is dichlorocarbene (: CCl_2) which contains a C with only six electrons.

Mechanism

The mechanism of this reaction follows the following steps.

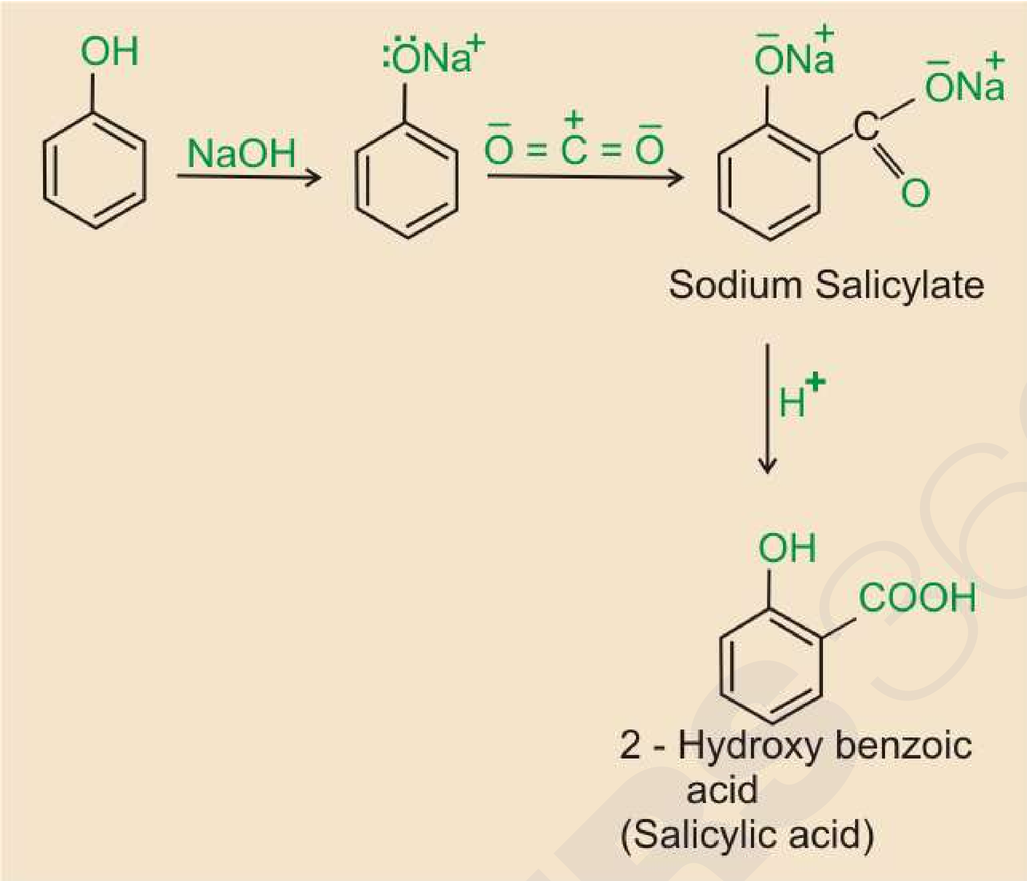


For example,

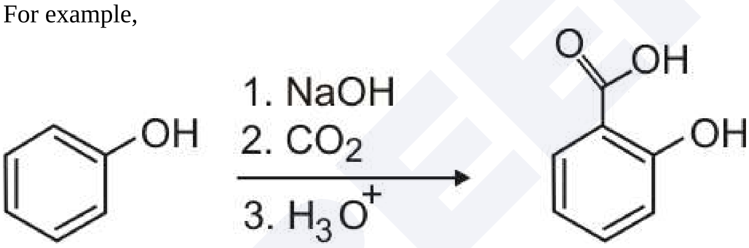


Koble-Schmitt Reaction
Phenol when heated at(390-410K) under pressure with CO_2 and alkali gives salicylic acid after acidification in addition to some amount of *p*-isomer.

Mechanism



For example,



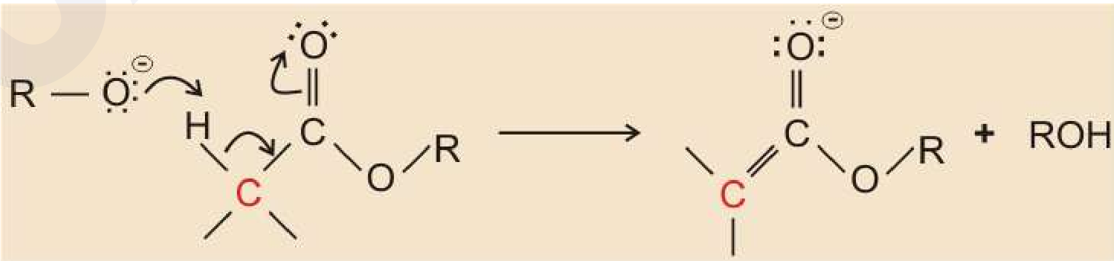
Claisen's Rearrangement-

On heating aryl allyl or alkyl allyl ethers in an inert solvent, the allyl group migrates from the *ortho* position to the ring, preferably at *ortho* position, but *para* if the *ortho* position is blocked.

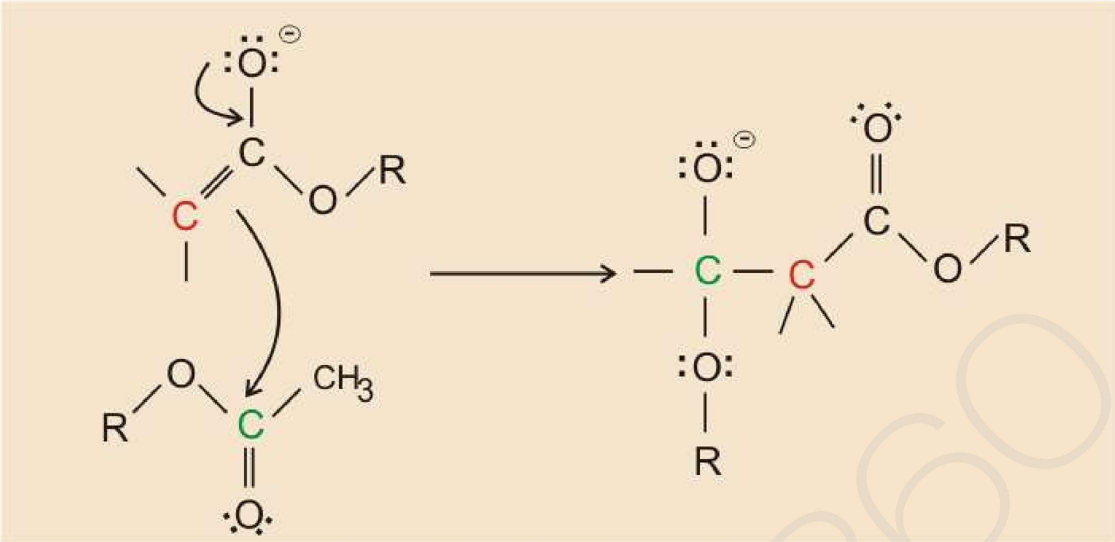
Mechanism

The mechanism of this reaction occurs in three following steps:

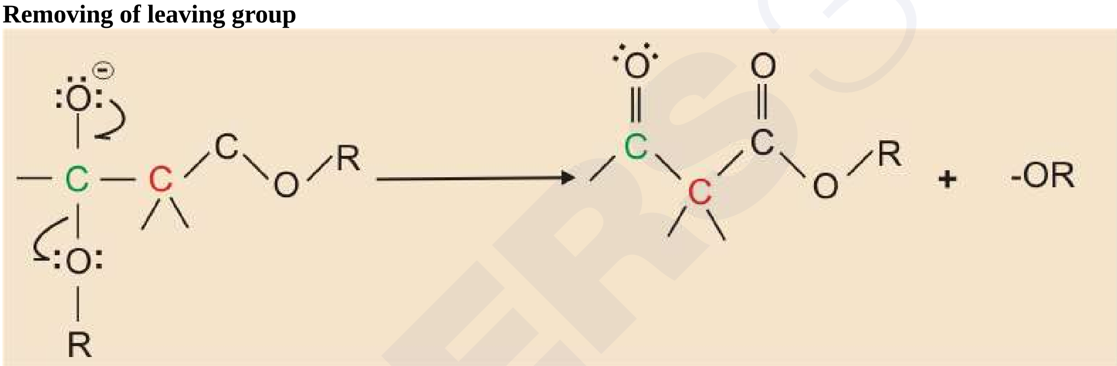
1. **Enolate formation**



2. **Nucleophilic attack**

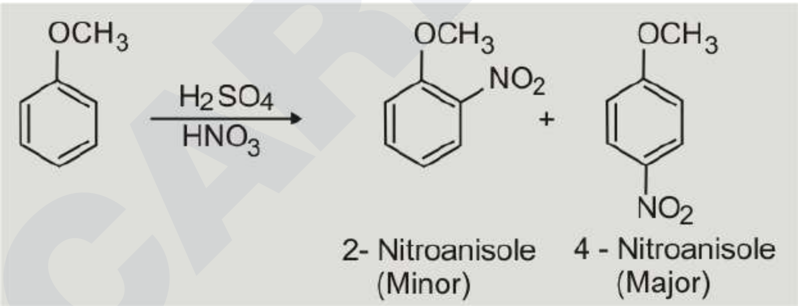


3. **Removing of leaving group**

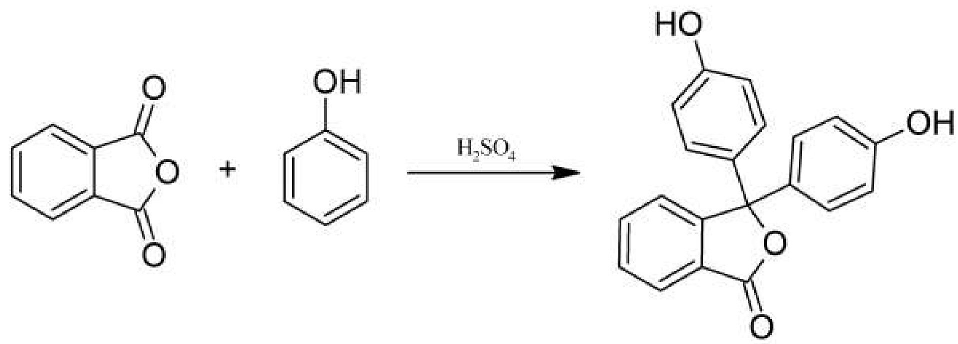


Reaction with Conc. HNO_3, Phthalic Anhydride-

Nitration
Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho* and *para* nitroanisole. The reaction occurs as follows.

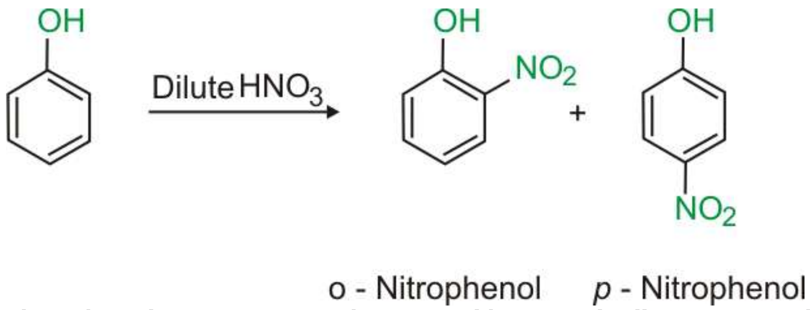


Phthalic Anhydride
Phenol couples with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein which is used as an indicator. The reaction occurs as follows.

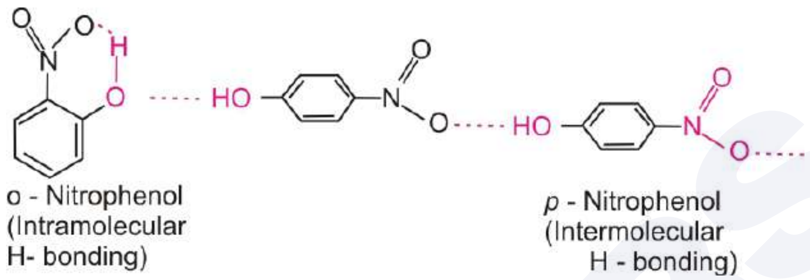


Reaction of Phenols with dil. HNO_3-

With dilute nitric acid at low temperatures (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols. The reaction occurs as follows.

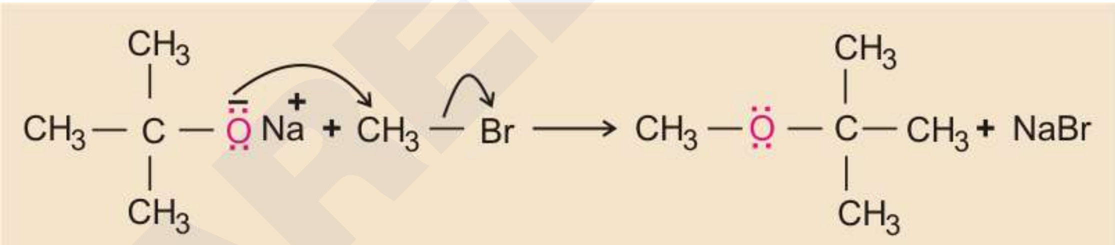


The *ortho* and *para* isomers can be separated by steam distillation. *O-nitrophenol* is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



5. Williamson's Ether Synthesis

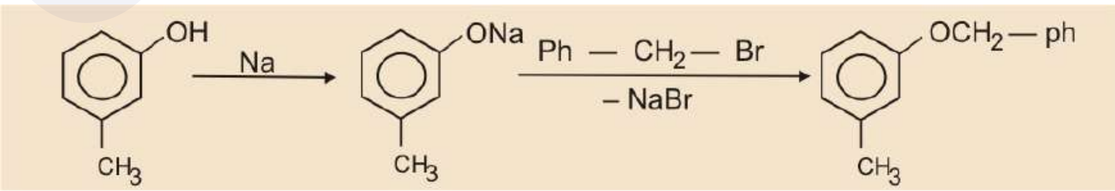
It is the best method to prepare all types of ethers, that is, simple, mixed or aromatic ethers. Here, alkyl halides are treated with sodium alkoxide in the presence of magnesium to give ethers. It involves the S_N2 mechanism during the attack of R-O^- on R-X, that is, the backside attack occurs here. The reaction occurs as follows:



Some examples include:

$$C_2H_5—ONa + C_2H_5Br \xrightarrow{\Delta Mg} C_2H_5—O—C_2H_5 + NaBr$$

Sodium ethoxide — Diethyl ether



6. Methods of Preparation of Aldehydes and Ketones

Preparation of Aldehydes and Ketones-

Oxidation
Oxidation of ROH involves the cleavage of (O-H) and (C-H) bonds to form (C=O) bonds. Such reactions are also called dehydrogenation reactions because H_2 is lost from an alcohol molecule. Strong oxidising agents such as acidic $KMnO_4$ or

acidic $K_2Cr_2O_7$ oxidise 1^o ROH first to an aldehyde and then to carboxylic acids. Further, 2^o alcohols are oxidised to ketones and 3^o alcohols do not undergo oxidation, but under drastic conditions such as strong oxidising agents($KMnO_4$) and at high temperatures cleavage of (C-C) bonds takes place and a mixture of RCOOH containing a lesser number of C atoms is formed. 1^o ROH can be converted up to the aldehyde stage either by the use of CrO_3 in an anhydrous medium or with PCC or with Jones reagent.
Some examples include:

$$CH_3 - CH = CH - CH_2OH \xrightarrow{PCC} CH_3 - CH = CH - CHO$$

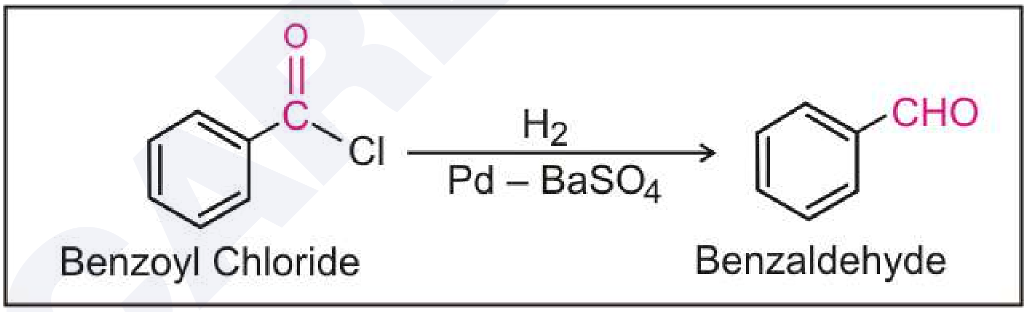
Dehydrogenation
1^o alcohols undergo dehydrogenation to give aldehydes only. 2^o alcohols give ketones and 3^o alcohols give alkenes. Some examples include.

$$RCH_2OH \xrightarrow[573\ K]{Cu} RCHO$$

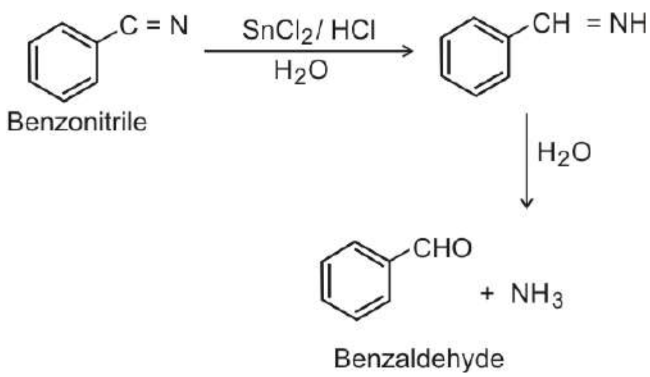
$$R - \underset{\underset{OH}{|}}{CH} - R' \xrightarrow[573\ K]{Cu} R - \underset{\underset{O}{\|}}{C} - R'$$

Preparation of Aldehydes-

Rosenmund Reduction
Partial hydrogenation of benzoyl chloride with finely divided Pd as catalyst in the presence of $BaSO_4$ and S or quinoline in boiling xylene as solvent gives benzaldehyde. This reaction is called Rosenmund reduction. The catalyst under the above condition is called Lindlar's catalyst or poisoned Pd. The Lindlar's catalyst also reduces ($C \equiv C$) to (C=C) in syn-addition.
It is $BaSO_4$ that prevents the aldehyde from being further reduced to alcohol and acts as a poison to the Pd catalyst. The small amount of sulphur and quinoline is very effective in poisoning the catalyst in aldehyde reduction. Moreover, S and quinoline react with a small amount of H_2 to give H_2S gas and hydroquinoline, thereby limiting H_2 for further reduction of aldehyde to alcohol.
The reaction occurs as follows:



Stephen Reduction
Nitriles are partially reduced to corresponding imine with $SnCl_2$ in the presence of HCl, which on hydrolysis gives the corresponding aldehyde. It does not reduce (C=C) or ($C \equiv C$). This reaction is known as Stephen reduction. The reaction occurs as follows.

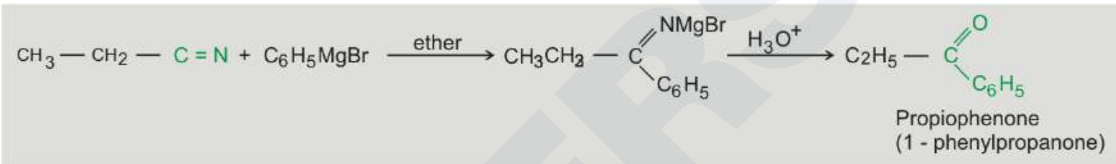


Preparation of Ketones-

From Acyl chlorides
Formyl chloride gives an aldehyde and all other halides five ketones. The reaction occurs as follows.

$$2\,R'-\underset{\underset{O}{\|}}{C}-Cl \;+\; R_2Cd \longrightarrow 2\,R'-\underset{\underset{O}{\|}}{C}-R \;+\; CdCl_2$$

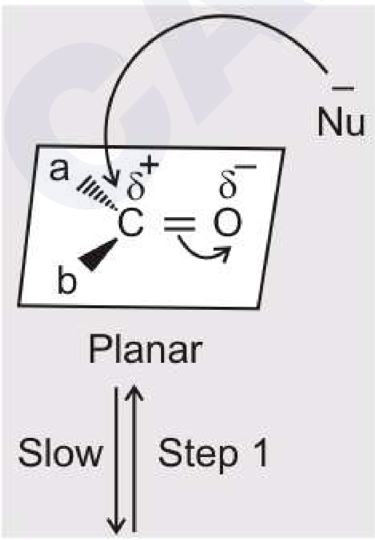
From Nitriles
Grignard reagents give aldehydes with hydrogen cyanide (HCN) and ketones with alkyl cyanides (RCN). The reaction occurs as follows:

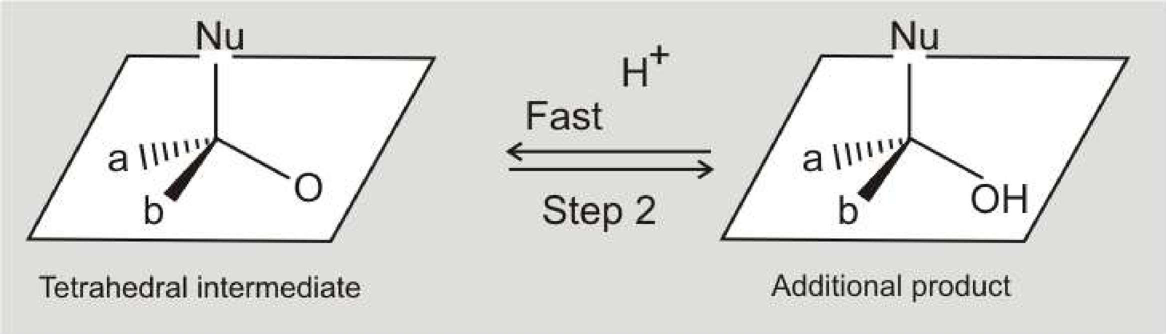


7. Reaction of Aldehydes and Ketones

Nucelophilic Addition Reaction-

(i) Mechanism of nucleophilic addition reactions:
A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is the addition of Nu^- and H^+ across the carbon-oxygen double bond as shown in the figure below.





(ii) Reactivity
Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Reduction and Oxidation Reaction-

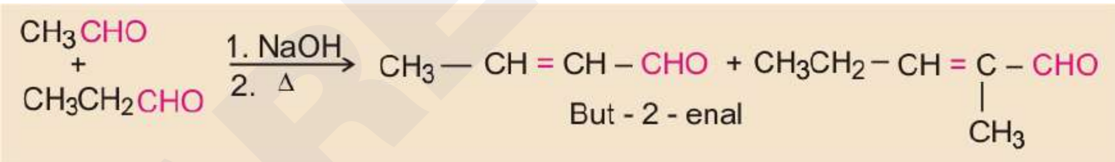
Reduction to hydrocarbons:
The carbonyl group of aldehydes and ketones is reduced to the CH2 group on treatment with zinc amalgam and concentrated hydrochloric acid (Clemmensen reduction) hydrazine hydrazone or with hydrazine followed by heating with sodium or potassium hydroxide in a high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).

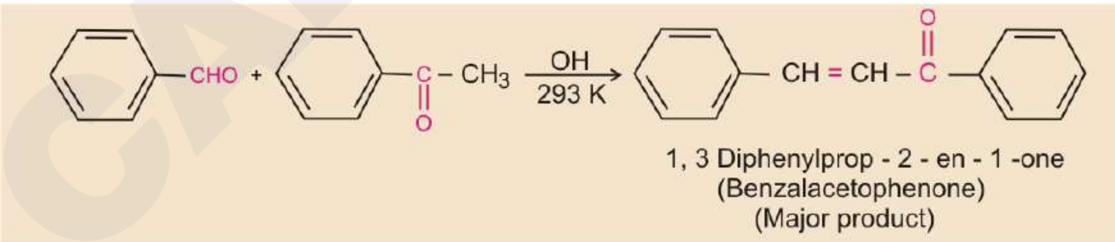
Oxidation
Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.

Intermolecular Aldol Condensation-

It is the condensation taking place when two different aldehydes or two different ketones or one aldehyde and one molecule of ketone both contain α-H atoms. A number of products due to self-condensation and cross-condensation are obtained. The reaction occurs as follows.

For example,

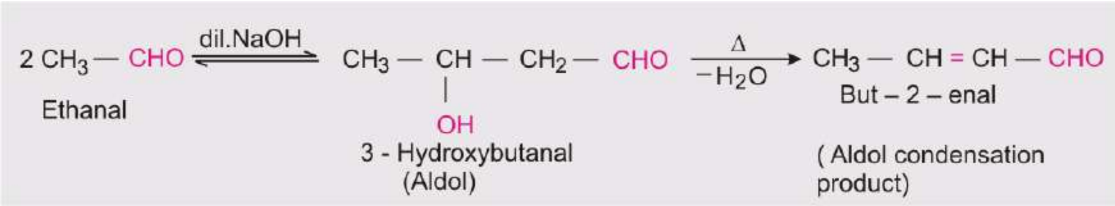


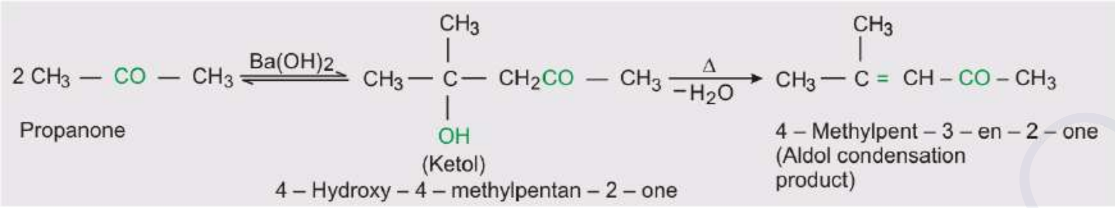


Intramolecular Aldol Condensation-

The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-H, which in turn is due to the strong electron-withdrawing effect of the (C=O) group and resonance stabilisation of the conjugate base. When two molecules of the same aldehyde or ketone containing α-H atom condense together in the presence of dilute alkali, such as NaOH, KOH, K_2CO_3, Na_2CO_3, or at least 2 α-H-atoms to give a molecule of aldol or ketol, it is called aldol condensation. On heating, it loses a molecule of H_2O to give a molecule of α, β-unsaturated aldehyde or ketone.

For example,

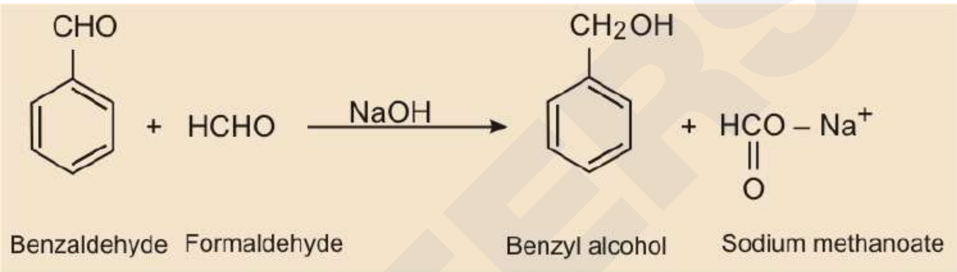




Intermolecular Cannizaro Reaction-

When two different aldehydes lacking α-H atom are reacted in the presence of a strong base, they undergo disproportionation or redox reaction to give a molecule of alcohol and salt of an acid. Alcohol is obtained from the less reactive aldehyde and acid salt is obtained from the more reactive aldehyde. In this reaction, OH^- attacks at the C of the (C=O) group of more reactive aldehyde and gives an adduct anion from which H^- ion is transferred to the less reactive aldehyde. It gives acid ions from more reactive aldehyde and alcohol from less reactive aldehyde.

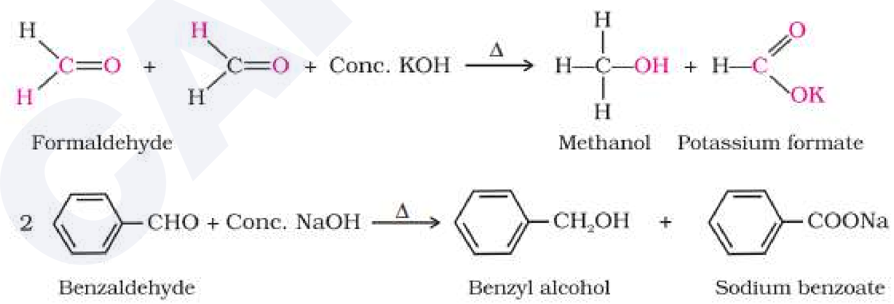
For example,



Intramolecular Cannizaro Reaction-

Two molecules of the same aldehyde lacking α-H atom undergo disproportionation or redox reaction in the presence of a strong base to give a molecule of alcohol and a molecule of the salt of an acid.

For example,

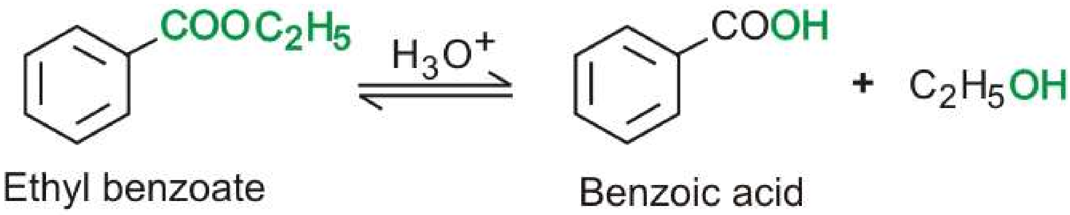


8. Carboxylic Acids

Methods of Preparation of Carboxylic Acids-

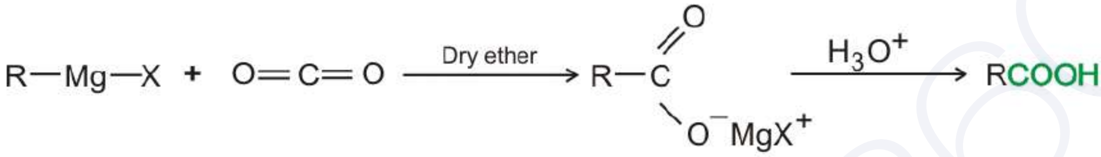
From Esters

Esters on acidic hydrolysis give acids, while on basic hydrolysis give carboxylates, which on acidification give corresponding acids. The reaction occurs as follows:



From Grignard reagents

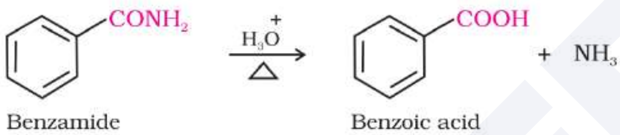
Grignard reagents with dry ice form salts of carboxylic acids which after acidification give corresponding carboxylic acids. The reaction occurs as follows:



From Nitriles and Amides

Nitriles are hydrolysed in an acidic or basic medium first to amides and then to acids. The reaction occurs as follows:

$$CH_3CONH_2 \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$$



Chemical Properties of Carboxylic Acids-

Formation of Anhydride

Carboxylic acid on heating with H_2SO_4 or P_2O_5 gives the corresponding anhydride. The reaction occurs as follows:

Reaction with Ammonia

On heating with NH_3, carboxylic acid gives ammonium salt which on further heating at high temperature gives amides. The reaction occurs as follows:

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3\overset{-}{CO}\overset{+}{O}NH_4} \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$$

Reduction

Carboxylic acids are reduced to 1° alcohol by $LiALH_4$ or better with B_2H_6. B_2H_6 does not easily reduce esters, nitro, and halo groups, and $NaBH_4$ does not reduce the (-COOH) group. The reaction occurs as follows:

$$R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ ether or } B_2H_6} R-CH_2OH$$

Decarboxylation

When sodium salts of carboxylic acids are heated with soda lime (NaOH and CaO in a 3:1 ratio), they form hydrocarbons by losing CO_2. This is known as decarboxylation. The reaction occurs as follows:

$$R-COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R-H + Na_2CO_3$$

Kolbe's electrolysis

The electrolysis of aqueous solution of sodium or potassium salts of carboxylic acid makes the carboxylic acid to undergo decarboxylation to form alkane. The reaction occurs as follows:

$$\underset{\text{Sodium acetate}}{2\,CH_3COONa\,(aq.)} \xrightarrow{\text{Electrolysis}} CH_3-\underbrace{CH_3 + 2CO_2}_{\text{At anode}} + \underbrace{2\,NaOH + H_2}_{\text{At cathode}}$$

Halogenation

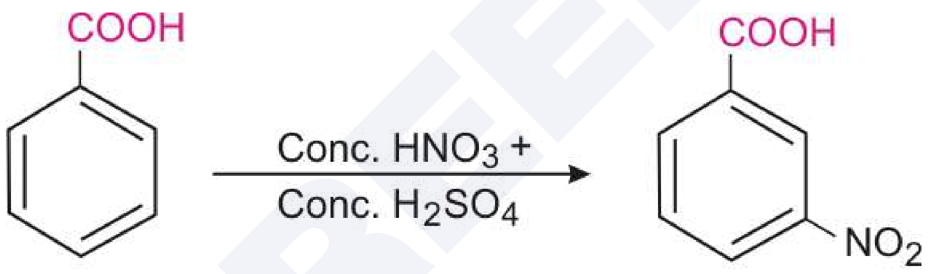
The method of preparing α-chloro or α-bromo acid is by Hell-Volhard-Zelinsky reaction, which is carried out by treating the acid with Cl_2 or Br_2 in the presence of a small amount of red phosphorous. The reaction occurs as follows:

$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{ Red phosphorus}} R-\underset{\substack{|\\X}}{CH}-COOH$$

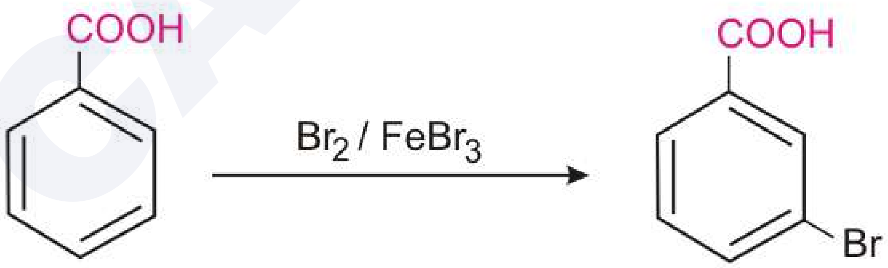
$X = Cl, Br$

Ring substitution

Aromatic carboxylic acid undergoes substitution electrophilic reactions in which the (-COOH) group acts as a deactivating and *meta*-directing group. It does not undergo Friedel-Crafts reaction because the (-COOH) group is deactivating and the catalyst $AlCl_3$ gets bonded to the (COOH) group. The reactions occur as follows:



m - Nitrobenzoic acid



m - Bromobenzoic acid

Acidity in Carboxylic Acids-

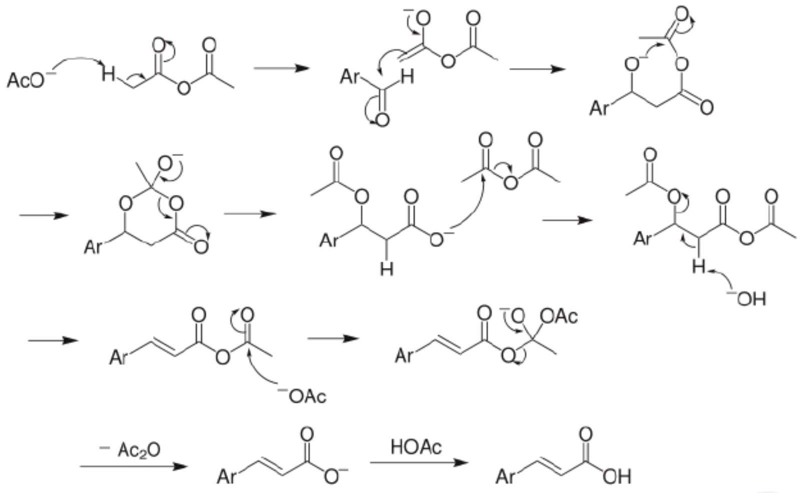
Carboxylic acids are weaker than mineral acids but they are stronger than alcohols, phenols and peroxy acids.

- Phenols are stronger acids than alcohols.
- Carboxylic acids are stronger acids than phenols.
- Carboxylic acids are stronger than peroxy acids.
- Formic acid is stronger is a stronger acid than benzoic acid.

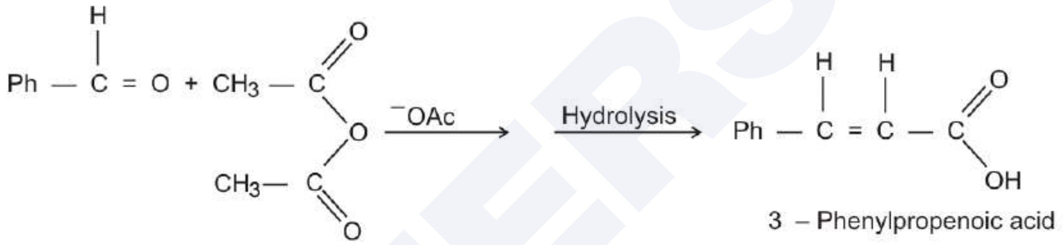
Perkin's Condensation-

Aromatic aldehydes when heated with the anhydride of an aliphatic acid (containing two α-H atoms) in the presence of its sodium or potassium salt result in condensation to form α,β-unsaturated acid.

Mechanism



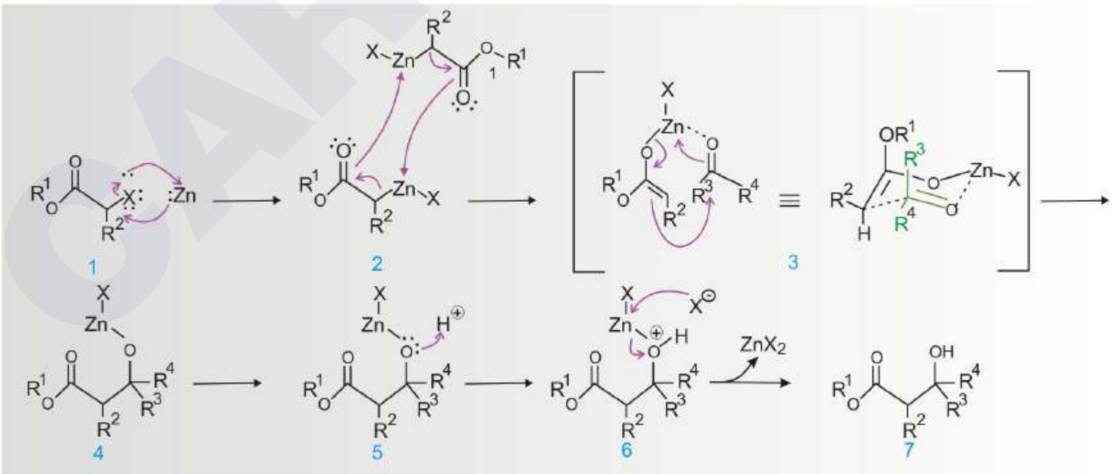
For example,



Reformatsky Reaction-

Ketones and aldehydes react with α-bromoesters(BrCHRCOOEt) and Zn in benzene to form β-hydroxy esters. First, the zinc organometallic BrZnCHRCOOEt is formed and then it adds to the (C=O).

Mechanism



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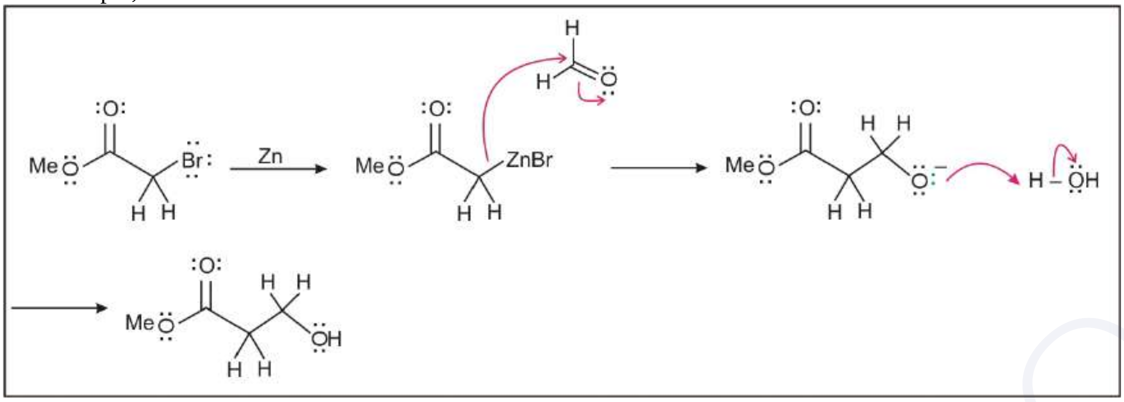
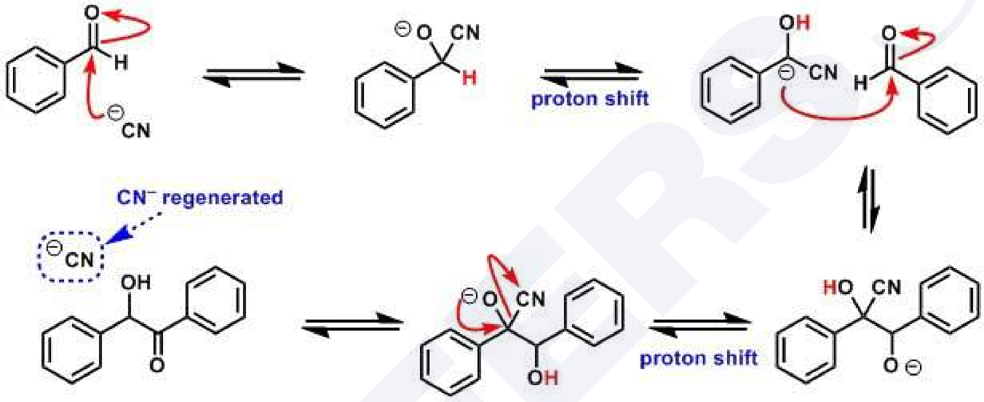


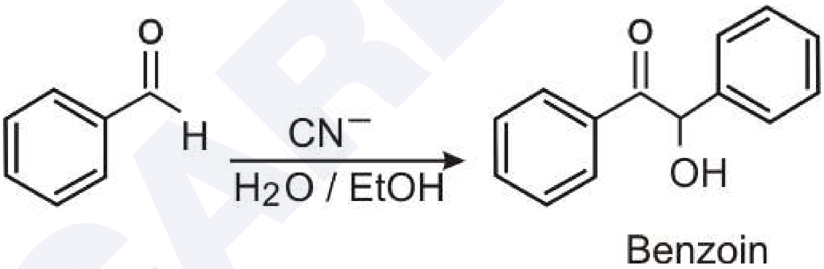
Benzoin Condensation, Benzil-Benzilic Acid Rearrangement-

Benzoin condensation
When benzaldehyde is refluxed with aq. alcoholic KCN solution to give benzoin(α-hydroxy ketone), the process is called benzoin condensation.

Mechanism

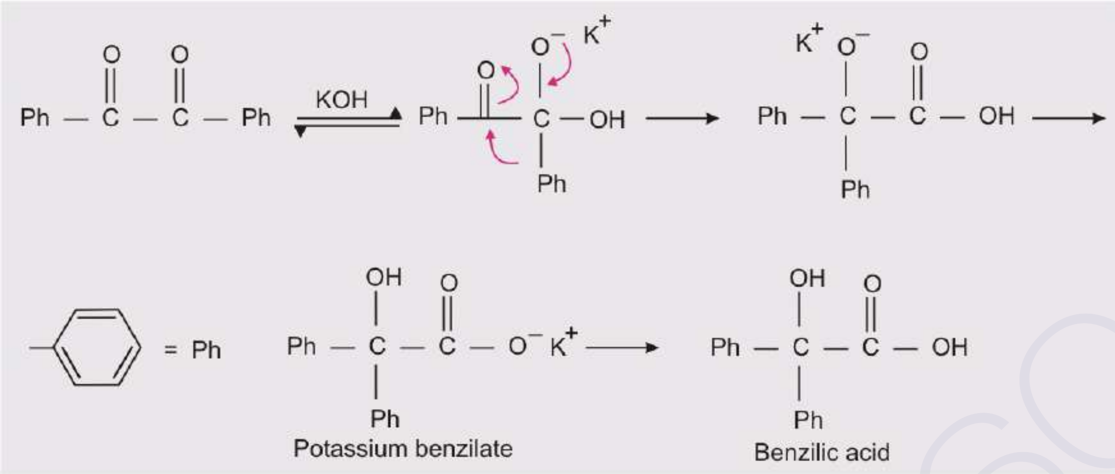


For example,

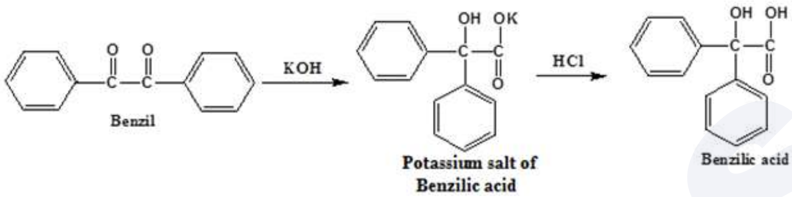


Benzil-Benzilic acid rearrangement
α-Diketones undergo a rearrangement when treated with base (NaOH) to give α-hydroxy acids.

Mechanism



For example,



Organic Compounds Containing Nitrogen

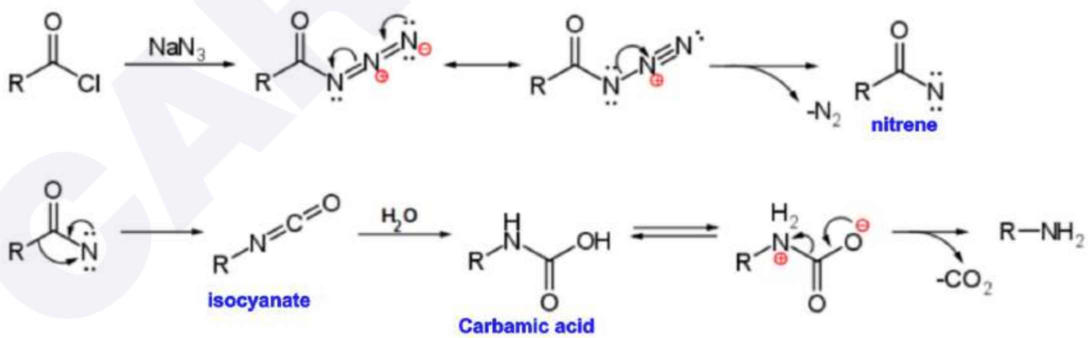
Important Formulae

1. Preparation of Amines

Methods of Preparation of Amines-

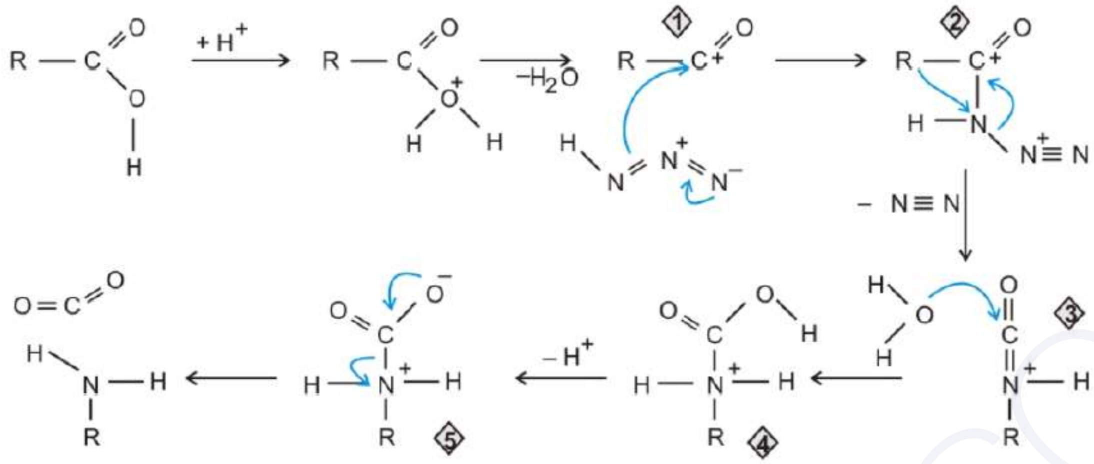
Curtius Reaction

The Acid azides on heating in a non-polar solvent give alkyl isocyanate *via* acylnitrene formation, which on hydrolysis gives 1^o amine. The reaction occurs as follows:



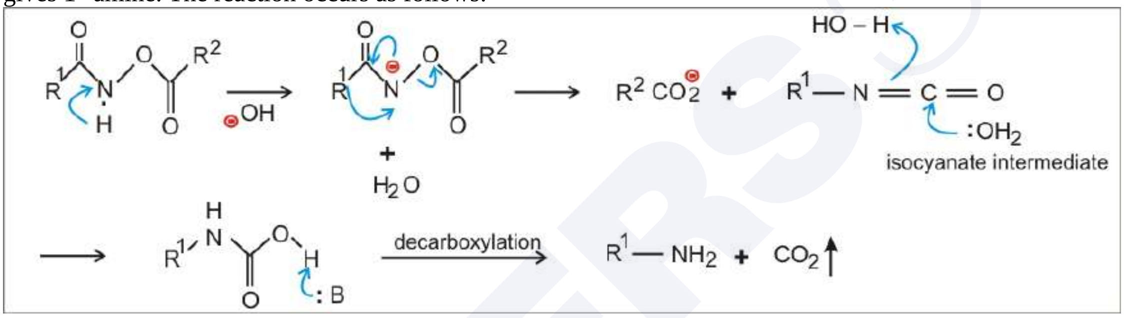
Schmidt Reaction

Carboxylic acid in reaction with hydrazoic acid in the presence of acid(H_2SO_4) gives acid azide which on heating gives alkyl isocyanate followed by hydrolysis to give 1^o amine. The reaction occurs as follows:



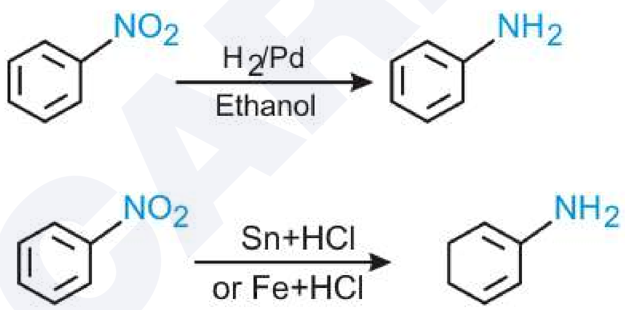
Lossen Reaction

Hydroxamic acid in a basic medium rearranges to give alkyl isocyanate *via* acylnitrene formation, which on hydrolysis gives 1^{o} amine. The reaction occurs as follows:



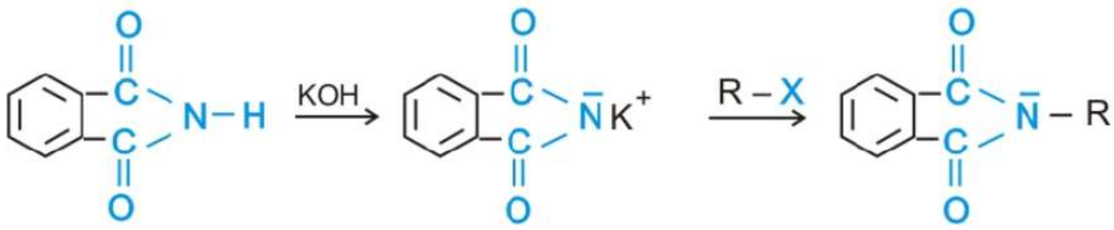
Reduction of Nitroalkanes

Nitro compounds are reduced to amines by reduction with metals(Fe, Sn or Zn) in dil. HCl or $SnCl_2$ in HCl or by passing H_2 gas in the presence of finely divided Ni, Pt, or Pd. Reduction with Fe scrap and HCl is preferred because the $FeCl_2$ formed gets hydrolysed to give HCl during the reaction, and thus only a small amount of HCl is required for the initiation of the reaction. The reactions occur as follows:



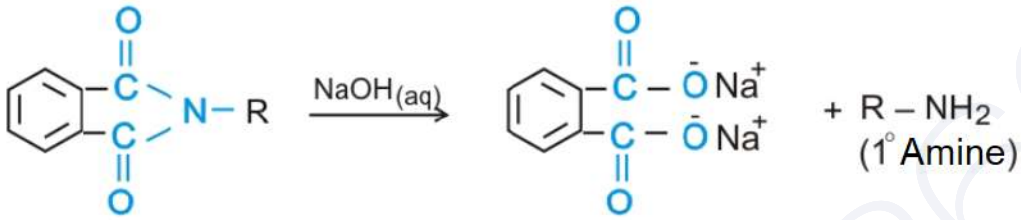
Gabriel Phthalimide Synthesis-

This reaction is used for the preparation of 1^{o} aliphatic amine and 1^{o} aromatic amine. Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with RX followed by either alkaline hydrolysis or hydrazinolysis with hydrazine($H_2N.NH_2$) produces the corresponding 1^{o} amine. 1^{o} aromatic amine cannot be synthesised by this method because ArX does not undergo SN reaction with an anion formed by phthalimide. The reaction occurs as follows:



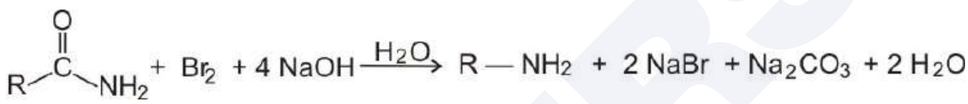
Phthalimide

N - Alkylphthalimide

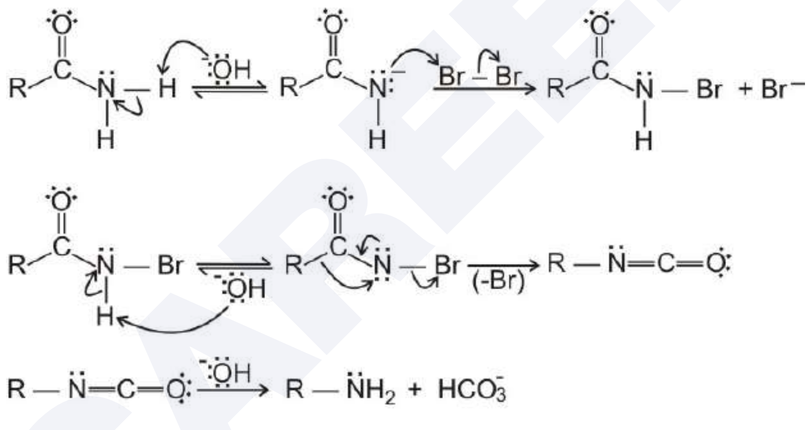


Hoffmann Bromamide Reaction-

Amides on reaction with Br_2 in alkali give 1^o amine with one C atom less than the parent amide. This is known as the Hofmann bromamide rearrangement or degradation reaction. The reaction occurs as follows:



The mechanism of the reaction is given as

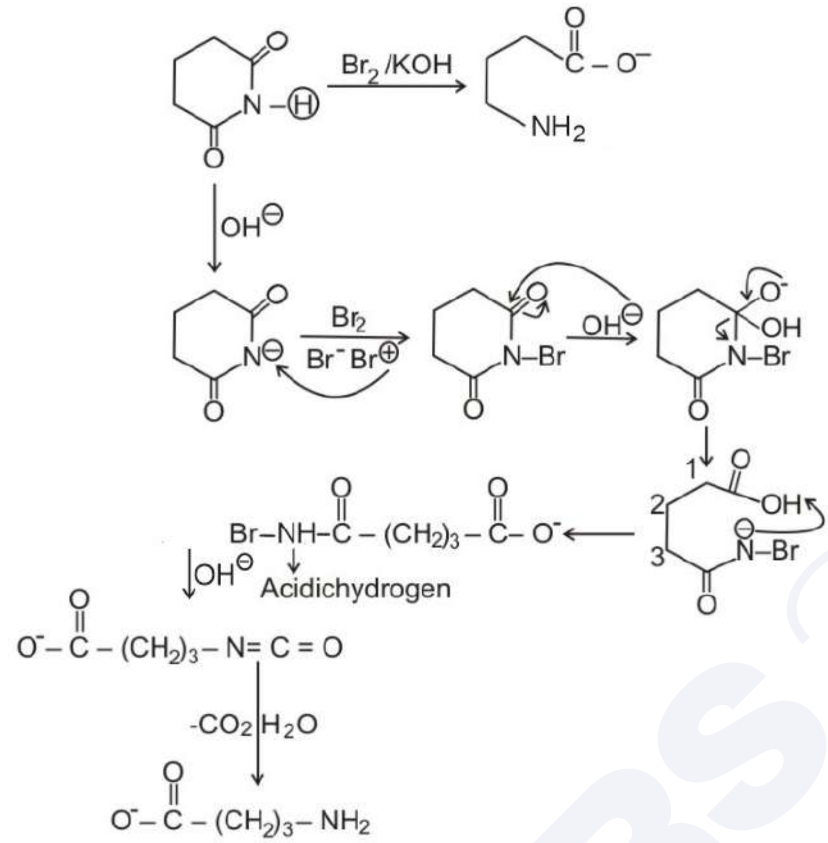


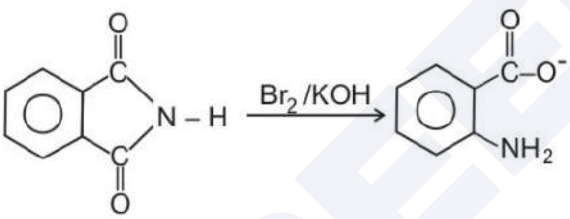
Isocyanate

Amine

Special Case of Hoffmann Bromamide Reaction-

It is only the primary amides that undergo the Hoffmann Bromamide reaction. Secondary amides do not undergo this reaction. However, secondary diamides (also called IMIDES) undergo this reaction to form amino acids. Thus, it is considered a special case of Hoffmann Bromamide reaction. The reaction occurs as follows:





2. Test for Amines

The action of Nitrous Acid:
Nitrous acid can distinguish between primary, secondary and tertiary amines. Primary amines on reaction with nitrous acid form Alcohols with the evolution of dinitrogen gas. Secondary amines form N- Nitrosoamines which have a characteristic yellow oily texture. Tertiary amines do not react with Nitrous acid and there is no visible change in the reaction mixture.

The reaction occurs as follows:

Action of Nitrous Acid

$$R-CH_2-NH_2 \xrightarrow{HNO_2} R\,CH_2\overset{\oplus}{N}_2 \xrightarrow{(-N_2)\uparrow} R\overset{\oplus}{C}H_2 \xrightarrow{H_2O} \underset{\text{(Alcohol)}}{R-CH_2\,OH}$$

$$R-\underset{\underset{H}{|}}{\ddot{N}}-R \xrightarrow{HNO_2} R-\underset{\underset{R}{|}}{N}-N=O$$

Nitroso Amine
(yellow oily liquid)

$$R-\underset{\underset{H}{|}}{\ddot{N}}-R \xrightarrow{HNO_2} \text{No Reaction}$$

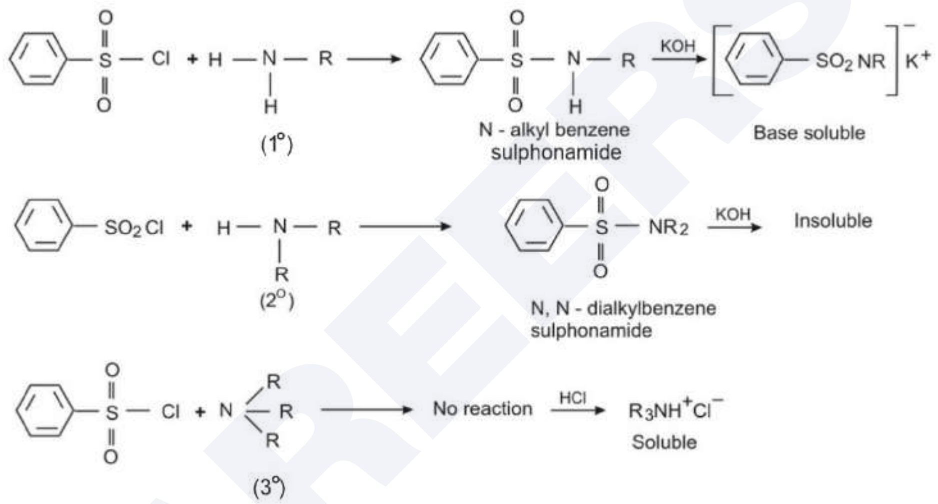
(No Visible change)

Hoffmann's Test
Separation of primary, secondary and tertiary amines by Hoffmann's method. The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide, a secondary amine gives a liquid oxamic ester while a tertiary amine does not react.

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \\ \text{diethyloxalate} \end{array} + 2RNH_2 \longrightarrow \begin{array}{l} CONHR \\ | \\ CONHR \\ \text{dialkyloxamide} \\ \text{(solid)} \end{array} + 2C_2H_5OH$$

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + R_2NH \longrightarrow \begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \\ \text{Oxamic ester} \\ \text{(liquid)} \end{array} + C_2H_5OH$$

Hinsberg's Test
The Hinsberg test which is used to distinguish between primary, secondary, and tertiary amines, is based upon sulfonamide formation. In this test, an amine is reacted with benzene sulfonyl chloride. If a product forms, the amine is either a primary or secondary amine, because tertiary amines do not form stable sulfonamides. If this sulfonamide that formed is dissolved in aqueous sodium hydroxide solution, it is a primary amine. But if it is insoluble in aqueous sodium hydroxide, then it is a secondary amine. The sulfonamide of a primary amine is soluble in an aqueous base because it still possesses an acidic hydrogen on the nitrogen, which can be lost to form a sodium salt.



Hoffmann's Mustard Oil Reaction
When ethylamine is heated with carbon disulphide and mercuric chloride, ethyl isothiocyanate is formed which smells like mustard oil.

$$C_2H_5NH_2 + CS_2 + HgCl_2 \rightarrow C_2H_5NCS + HgS + 2HCl$$

Carbylamine Test-

When any primary amine(aliphatic or aromatic) is heated with chloroform and alcoholic potassium hydroxide solution, isocyanide(carbylamine) is formed which has a very unpleasant smell. This test is called carbylamine test or isocyanide test. The reactions occur as follows:

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

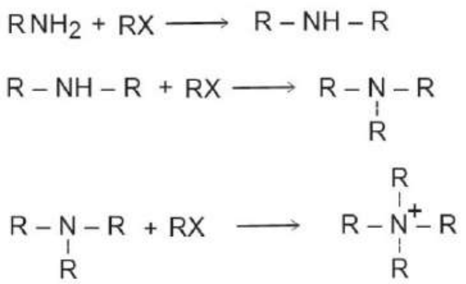
$$C_6H_5NH_2 + CHCl_3 \rightarrow C_6H_5NC + 3KCl + 3H_2O$$

It is to be noted that Aromatic primary amines also respond to this test as shown in the reaction above.

Alkylation and Acylation of Amines-

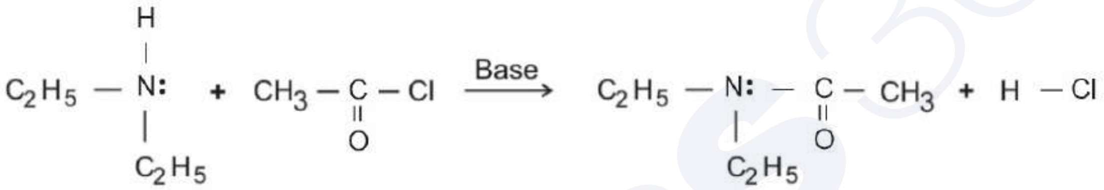
Alkylation
Amines undergo alkylation with RX and undergo complete alkylation and this is called exhaustive alkylation, but with

Me_2SO_4 amines undergo monomethylation. 1° and 2° amines are also methylated by heating HCHO and excess of HCOOH at 100°C. This reaction is known as Eschweiler-Clarke methylation. The reaction occurs as follows:



Acylation

1° and 2° aliphatic and aromatic amines react with acid chlorides (RCOCl), anhydrides and esters by SN^2 reaction is called acylation reaction. The reaction is carried out in the presence of a base stronger than amine, such as pyridine, which removes HCl so formed and shifts the equilibrium to the product side. The reaction occurs as follows:



N-Ethylethanamine N, N-Diethylethanamine

Reaction with $NaNO_2$ + HCl-

Nitrous acid(HNO_2) is obtained *in situ* by the reaction of sodium nitrite ($NaNO_2$) with dil. HCl. The reaction occurs as follows:

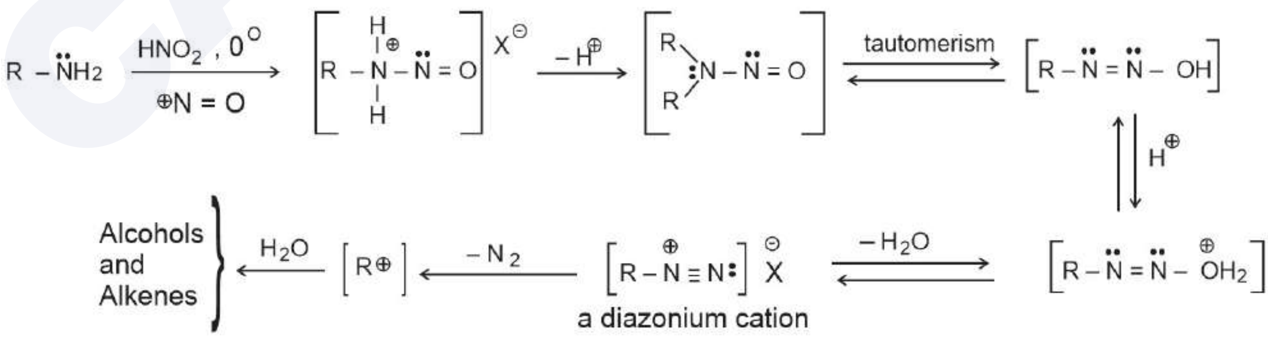
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

1° aliphatic amines react with HNO_2 to form aliphatic diazonium salts, which, being unstable, liberate N_2 gas quantitatively and form alcohols. Quantitative evolution of N_2 is used in the estimation of amino acids and proteins.

The reaction occurs as follows:

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

Mechanism

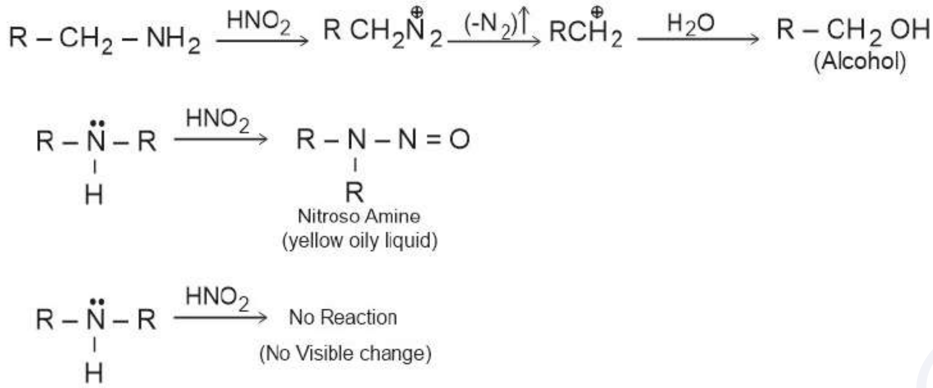


Nitrous acid can distinguish between primary, secondary and tertiary amines. Primary amines on reaction with nitrous acid form Alcohols with the evolution of dinitrogen gas as seen above.

Secondary amines form N- Nitrosoamines which have a characteristic yellow oily texture. Tertiary amines do not react with Nitrous acid and there is no visible change in the reaction mixture.

The reaction occurs as follows:

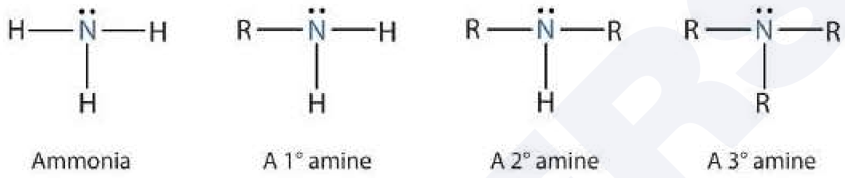
Action of Nitrous Acid



3. Basicity of Amines

Basicity of Aliphatic Amines-

Amines like ammonia are basic in nature. The basic nature is due to the presence of an unshared pair of electrons on a nitrogen atom. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acids.



Amines are weak bases as they combine partially with water to form hydroxyl ions.

$$R - NH_2 + H_2O \rightleftharpoons R - NH_3^+ + OH^-$$

Alkylamines are stronger bases than ammonia. This can be explained in terms of the electron-releasing inductive effect of the alkyl group. As a result, the electron density on the nitrogen atom increases and thus, they can donate the lone pair of electrons more easily than ammonia.

The electron-releasing effect is maximum in tertiary amines and minimum in primary amines. Aromatic amines have lesser electron density as the lone pairs over nitrogen are delocalised with the benzene ring.

$$3^\circ\text{Amine} > 2^\circ\text{Amine} > 1^\circ\text{Amine} > NH_3 > \text{Arylamines}$$

However, to state that the basic nature would follow the electron-releasing effect would be an oversimplification and a number of other factors like solvation and steric factors also have to be taken into account.

Thus, the actual order of basic strength of amines essentially is an experimentally derived order and is usually found to follow the following order:

$2^\circ\text{Amine} > 1^\circ\text{Amine} > 3^\circ\text{Amine} > NH_3$ when $R = CH_3$ and

$2^\circ\text{Amine} > 3^\circ\text{Amine} > 1^\circ\text{Amine} > NH_3$ when $R = C_2H_5$

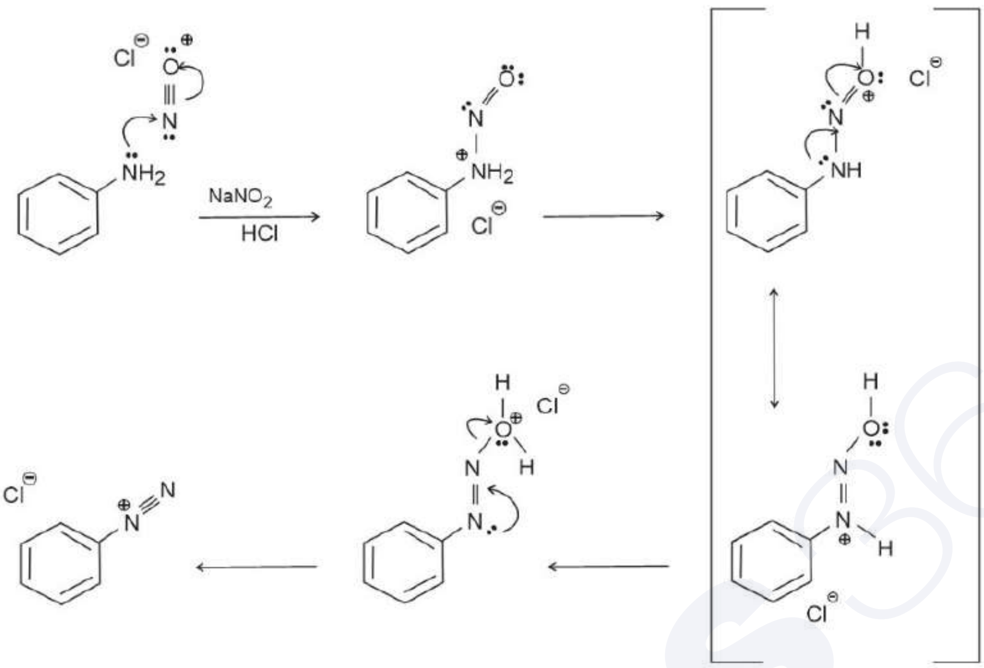
It is also to be noted that the basic strength of Alkyl amines is more than that of Ammonia which is more basic than Aryl amines.

4. Azo-Coupling Reaction

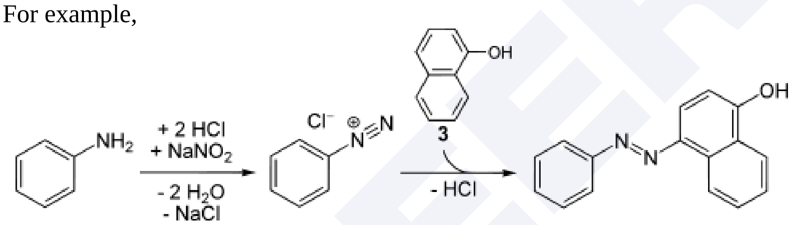
Azo-Coupling Reaction-

Benzene diazonium salts react with highly reactive compounds such as phenols and amines to form brightly coloured azo compounds. This reaction is called a coupling reaction. Coupling with phenols occurs in the basic medium(pH 9-10) and that of amines occurs in a fairly acidic medium(pH 4-5) at 273-298K. It is to be noted that the diazo coupling reaction is an example of an Electrophilic aromatic substitution reaction and happens on activated Benzene rings.

Mechanism of diazotisation



For example,

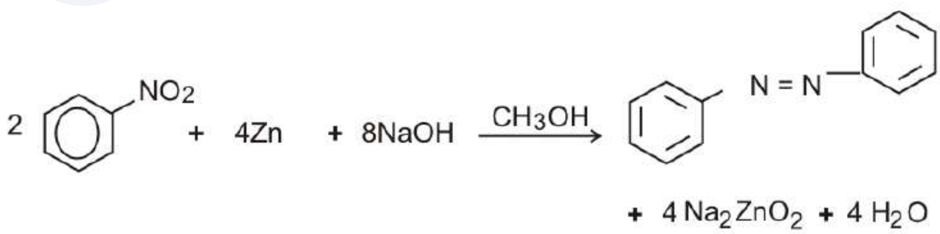


Properties of Nitrocompounds and Mulliken Barker Test-

Reduction in acidic medium
Both aliphatic and aromatic nitro compounds are reduced to corresponding primary amines with Sn/HCl or Fe/HCl by a combination of some active metals like tin, iron or zinc and conc. HCl or catalytic reduction with Ni, Pt or Pd/C. The reaction occurs as follows:

$$C_6H_5NO_2 + 6H \xrightarrow[\text{or Sn/HCl}]{\text{Fe/HCl}} C_6H_5NH_2 + 2H_2O$$

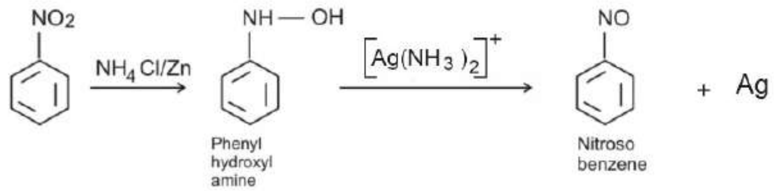
Reduction in basic medium
Both aliphatic and aromatic nitro compounds are reduced to corresponding hydroxylamines in the neutral medium with zinc dust and NH_4Cl or Al-Hg couple.



Reduction in neutral medium
Both aliphatic and aromatic nitro compounds are reduced to corresponding hydroxylamines in the neutral medium with zinc dust and NH_4Cl or Al-Hg couple. The reaction occurs as follows:

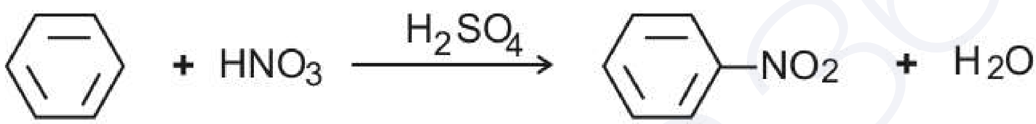
$$CH_3CH_2NO_2 + 4H \xrightarrow[\Delta]{Zn/NH_4Cl, H_2O} CH_3CH_2NHOH + H_2O$$

Mulliken barker test
The test is based on the fact that a neutral agent, -NO_2 is reduced to the NHOH group. The formed hydroxylamine reduces the Tollen's reagent and gets oxidised to a nitroso compound. The reaction occurs as follows:



5. Preparation of Aromatic Nitro compounds

1. By nitration of benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature below 330K. The temperature should not increase otherwise *m*-dinitrobenzene is formed. So, the nitration of benzene depends upon the temperature and nature of the nitrating agent used. The reaction occurs as follows:



2. Nitrobenzene can be prepared by carrying out our diazotization of aniline and then reacting with nitrous acid(HNO_2) in the presence of cuprous oxide. The reaction occurs as follows:
   $C_6H_5N_2Cl + HNO_2 \xrightarrow{Cu_2O} C_6H_5NO_2 + N_2 + HCl$
3. Nitrobenzene can be prepared from the oxidation of aniline by trifluoroacetic acid. The reaction occurs as follows:
   $C_6H_5NH_2 + 3[O] \xrightarrow{CF_3COOH} C_6H_5NO_2 + H_2O$
4. Nitrobenzene can be prepared by the action of acetyl nitrate on benzene.
   $C_6H_5H + CH_3COONO_2 \rightarrow C_6H_5NO_2 + CH_3COOH$

6. Basicity of Aromatic Amines

Aniline and other aromatic amines are far less basic than ammonia and aliphatic amines. Aniline is a weak base as it forms salts with strong mineral acids. The weaker basic nature of aniline as compared to aliphatic amines can be explained on the basis of resonance. In aliphatic amines, the non-bonding electron pair of N is localized and is fully available for coordination with a proton. On the other hand, in aniline or other aromatic amines, the non-bonding electron pair is delocalized into a benzene ring by resonance and the electron-donating capacity of nitrogen for protonation is considerably decreased to that of NH_3 and aliphatic amines.

Lower stability of anilinium ion than aniline
Anilinium ion formed by aniline on accepting a proton is less resonance stabilized than aniline.

Thus, the electron density is less on the N-atom due to which aniline or other aromatic amines are less basic than aliphatic amines.

Biomolecules

Important Formulae

1. Classification of Carbohydrates and its Structure

Carbohydrates-

These are polyhydroxy aldehydes or ketones or substances that form these on hydrolysis and possess at least one chiral atom. The (-OH) group is available in the form of hemiacetals or hemiketals. The carbohydrates are stored in the animal

body as glycogen which is also known as animal starch because its structure is highly branched like amylopectin. It is found in the liver, muscles and brain as well as in fungi and yeast. When the body requires glucose, the enzymes break glycogen into glucose.
Carbohydrates are indispensable for both plant and animal lives. These are utilised as storage molecules in the form of starch in plants and glycogen in animals. The cell wall of bacteria and plants consists of cellulose. Carbohydrates are present in biosystems in combination with several proteins and lipids.

Classification
Carbohydrates can be classified into three categories:

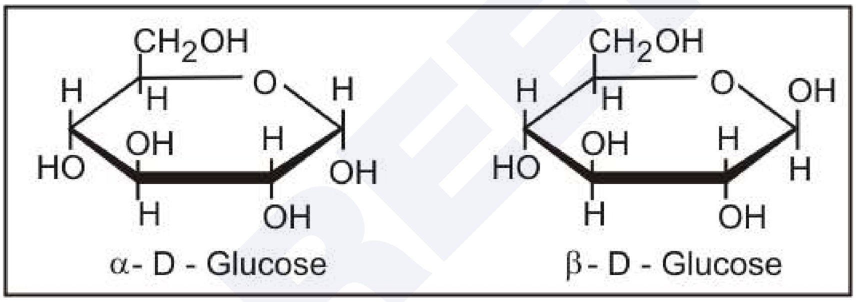
1. **Monosaccharides:** They are the simplest carbohydrates which cannot be hydrolysed into smaller molecules. They are sweet and crystalline and are called sugars.
2. **Oligosaccharides:** These carbohydrates on hydrolysis give two to nine molecules of monosaccharides classified as di-, tri, tetra-saccharides, etc. For example, sucrose, maltose, lactose and raffinose, etc. They are also called sugars.
3. **Polysaccharides:** These carbohydrates, on hydrolysis, give a large number of monosaccharides, e.g., starch, cellulose, etc. They are also called non-sugars.

Reducing and Non-reducing Sugars
Those sugars which reduce Fehling's and Tollens's solutions are called reducing sugars and those which do not reduce these reagents are called non-reducing sugars. All the monosaccharides and disaccharides, except sucrose, are reducing sugars, whereas all the polysaccharides are called non-reducing carbohydrates.

Cyclic Structure of Glucose(Haworth Projection)-

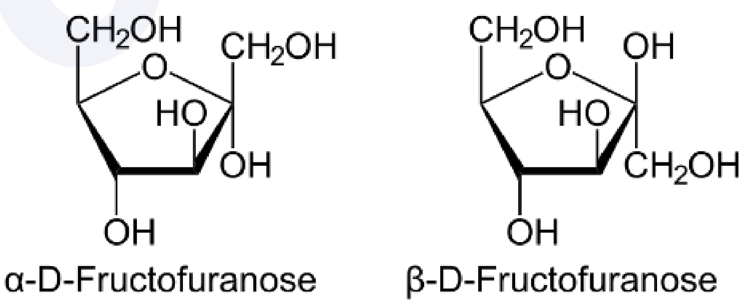
The CHO group of glucose either reacts with the C-5 OH group or the C-4 OH group to give hemiacetalic linkage and forms stable six- and five-membered cyclic rings, respectively. The reaction of the CHO group with the C-6 OH group or with C-3 OH does not occur as the formation of seven-membered or four-membered rings respectively is not favourable due to angle strain theory.

Haworth representation: The cyclic structure of glucose was established by English chemist W.N. Haworth. The cyclic structure of glucose is depicted below.



Cyclic Structure of Fructose(Haworth Projection)-

It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the (C=O) group. The ring, thus formed is a five-membered ring and is named furanose with an analogy to the compound furan. Furan is a five-membered cyclic compound with one oxygen and four carbon atoms. The cyclic structures of two anomers of fructose are represented by Haworth structures as given below.



Anomers, Epimers, Mutarotation

Anomers
Anomers are diastereomers that differ in the configuration at the acetal or hemiacetal C atom of sugar in its cyclic form. In

other words, anomers are epimers whose conformations differ only about C-1. For example, α-D(+) and β-D(+) glucose are anomers.

Epimers
Diastereomers with more than one stereocentre that differ in the configuration about only one stereocentre are called epimers.

1. D-glyceraldehyde and L-glyceraldehyde are epimers
2. D-Erythrose and L-threose are epimers.
3. Epimerisation of glucose at C-2 gives mannose.
4. Epimerisation of glucose at C-3 gives allose.
5. Epimerisation of glucose at C-4 gives galactose.

Mutarotation
The change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called mutarotation, or it is the change in the optical rotation occurring by epimerisation, i.e., the change in the equilibrium between two epimers, when the corresponding stereocentres interconvert. During mutarotaion, the ring opens and then the ring recloses either in the inverted position or in the original position giving a mixture of α and β forms. All reducing carbohydrates, i.e., monosaccharides and disaccharides undergo mutarotation in an aqueous solution. Mutarotation proves the existence of anomers and cyclic structures.

2. Test for Carbohydrates

Molisch's Test
A drop of alcoholic solution of α-Naphthol is added in 2ml of carbohydrate solution and 1ml of conc.H_2SO_4 is added carefully along the side of the tube. The formation of a violet ring at the junction of 2-liquids shows the presence of carbohydrates.

Molisch's test is a general test for all carbohydrates. In this test, carbohydrates when reacted with conc. H_2SO_4 get dehydrated to form furfural and its derivatives. When monosaccharides are treated with conc. H_2SO_4 or conc. HCl, -OH group of sugar are removed in the form of water and furfural is formed from pentose sugar and hydroxymethyl furfural is formed from hexose sugar. These products react with sulphonated α- naphthol to give a purple (violet-red) coloured complex.

3. Properties of Glucose

Evidence for Open Chain Structure of Glucose-

1. Glucose, on complete reduction with HI and red phosphorus, finally *n*-hexane. This indicates that it contains a straight chain of six carbon atoms.
2. It reacts with acetic anhydride and forms penta-acetate derivate. This shows the presence of five hydroxyl groups each linked to a separate carbon atom as the molecule is stable.
3. Glucose combines with one mole of HCN to form a cyanohydrin. These reactions indicate the presence of a carbonyl group, C=O, in the glucose molecule.
4. Mild oxidation of glucose with bromine water gives gluconic acid. Further, glucose also reduces Tollen's reagent and Fehling's solution. These reactions show the presence of an aldehyde group.

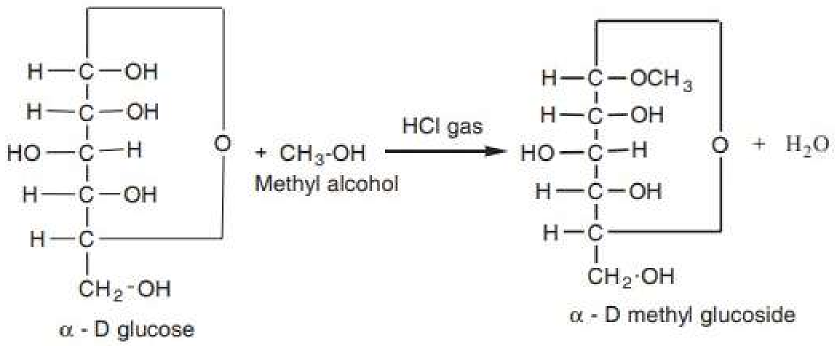
Evidence for Ring Structure of Glucose-

1. Glucose does not react with sodium bisulphite. It confirms the absence of a free -CHO group.
2. Glucose does not give Schiff's test and DNP test. It confirms the absence of a free -CHO group.
3. Glucose pentaacetate does not react with hydroxylamine. It means the absence of a free -CHO group.

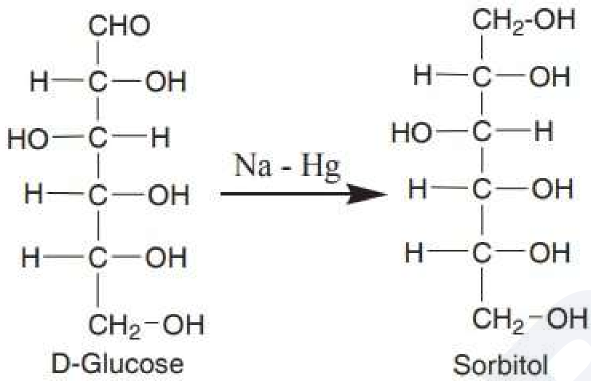
Chemical Properties of Glucose-

1. **Glucoside formation**
   Glucose reacts with methanol in the presence of HCl and gives α and β glucoside. Glucoside formation is due to the

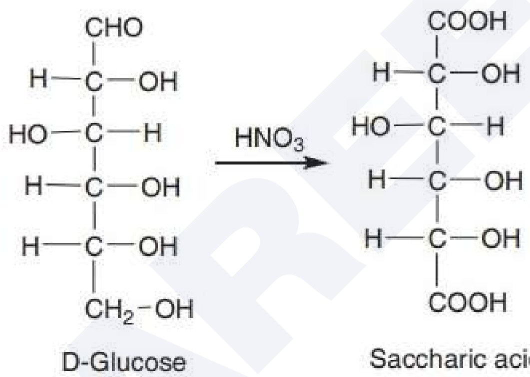
reaction of alcohol with the glucoside -OH group of glucose. β, D glucose forms β, D-methyl glucoside.



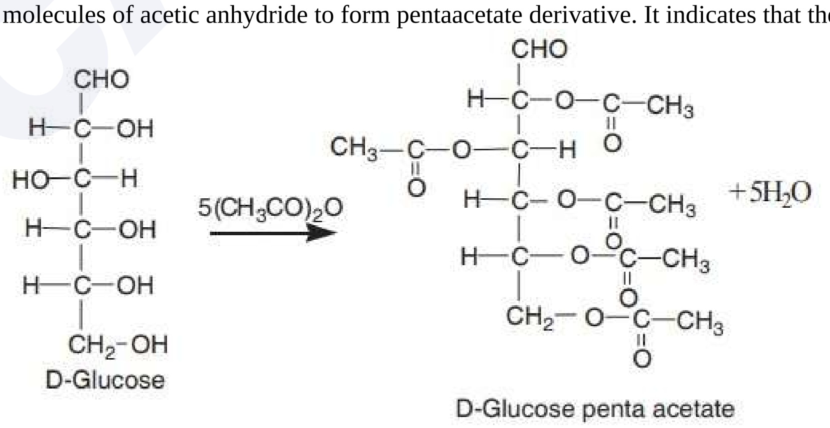
2. **Reduction**
   Monosaccharides can be reduced by various reducing agents such as sodium amalgam or by hydrogen under high pressure in the presence of catalysts.



3. **Reaction with nitric acid**
   When glucose is oxidised with nitric acid, saccharic acid is formed. Saccharic acid is also known as glucaric acid.



4. **Ester formation**
   They can form esters with carboxylic acids due to the presence of OH groups. For eg. glucose reacts with five molecules of acetic anhydride to form pentaacetate derivative. It indicates that the glucose contains five OH groups.



Disaccharides and Polysaccharides-

Disaccharides

The disaccharides consist of two molecules of monosaccharides. When hydrolysed with enzymes or dilute acids, they give two molecules of either the same or varying monosaccharides. Some examples include,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

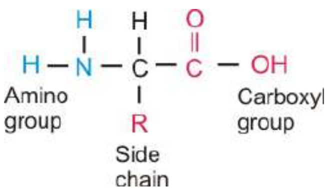
$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

On the basis of the position of linkages between the two monosaccharide units, the disaccharides might be reducing or non-reducing in nature. The resultant disaccharide is non-reducing if the glycosidic linkage involves the carbonyl functions of both monosaccharide units. On the other hand, the resulting disaccharide is the reducing sugar, e.g., maltose and lactose, if one of the carbonyl functions in either of the monosaccharide units is free.

Polysaccharides
Polysaccharides are carbohydrates having hundreds or even thousands of monosaccharide units joined together by glycosidic linkages, e.g., starch, cellulose, glycogen and dextrins. However, starch and cellulose are the most important polysaccharides.

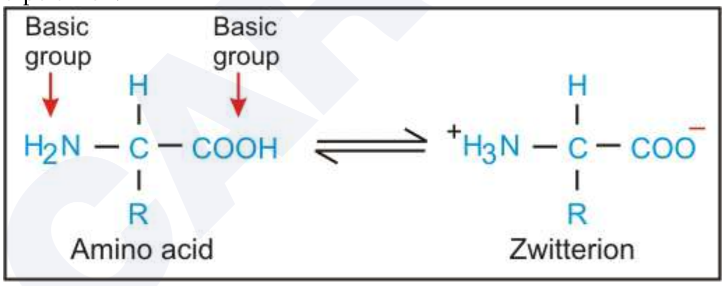
4. Amino Acids

Amino acids have amino $(-NH_2)$ and carboxyl $(-COOH)$ functional groups. Based on the relative position of the two functional groups in the alkyl chain, the amino acids are categorised as α, β, γ, δ and so on. On the hydrolysis of proteins, only α-amino acids are formed. Amino acids may also contain other functional groups.



- Amino acids which can be synthesized in our body are known as non-essential amino acids while those that can not be synthesized in our body are known as essential amino acids.
- They are usually colourless, water-soluble, high melting and crystalline solids.
- Except glycine, all other naturally occurring amino acids are optically active.
- Most naturally occurring amino acids have L-configuration.

Since, the $-NH_2$ group is basic and the -COOH group is acidic, in a neutral solution, it exists in an internal ionic form called a zwitter ion where the proton of -COOH group is transferred to the $-NH_2$ group to form inner salt, also known as dipolar ion.



The zwitter ion is dipolar, charged but overall electrically neutral and contains both a positive and negative charge. Therefore, amino acids are high-melting crystalline solids moderately soluble in water and amphoteric in nature. Depending on the pH of the solution, the amino acid can donate or accept proton. In the acidic medium, COO^- ion acts as the base and accepts a proton to form the cation(II) while in the basic medium, $^+NH_3$ ion loses a proton to form the anion(III). Thus, $^+NH_3$ group acts as the acid while COO^- group acts as the base.
When an ionised form of amino acid is placed in an electric field, it will migrate towards the opposite electrodes. Depending on the pH of the medium, the following three things may happen:

1. In an acidic solution(low pH), the positive ion moves towards the cathode.
2. In the basic solution, the negative ion moves towards the anode.
3. The zwitter ion does not move towards any of the electrodes.

Electrophoresis is a method used for the separation and analysis of amino acids. At an isoelectric point, an amino acid has the least solubility in water. This method is based on pH control and electric charge. The amino acids differ in their isoelectric point.

Amino acids	**Isoelectric point**
(i) Neutral	pH lies between 5 - 6.3
(ii) Acidic	pH lies between 3 - 5.4
(iii) Basic	pH lies between 7.6 - 10.8

Amino acids can undergo esterification and acetylation reactions. However, some important points have to be noted which are listed below:

1. Esterification of amino acid should be carried out in an acidic medium so as to protonate the amino group which would otherwise interfere with the esterification reaction.
2. Acylation should be carried out in a slightly basic medium as the amino acid might get protonated in the acidic medium and will not give the reaction.
3. *p*-Aminobenzoic acid and *o*-Aminobenzoic acid do not exist in the form of zwitter-ion due to the lesser basic strength of aromatic amines.
4. *p*-Aminobenzenesulphonic acid can exist in the form of zwitter-ion.

Test for amino acids and proteins
There are two types of tests, *viz*:

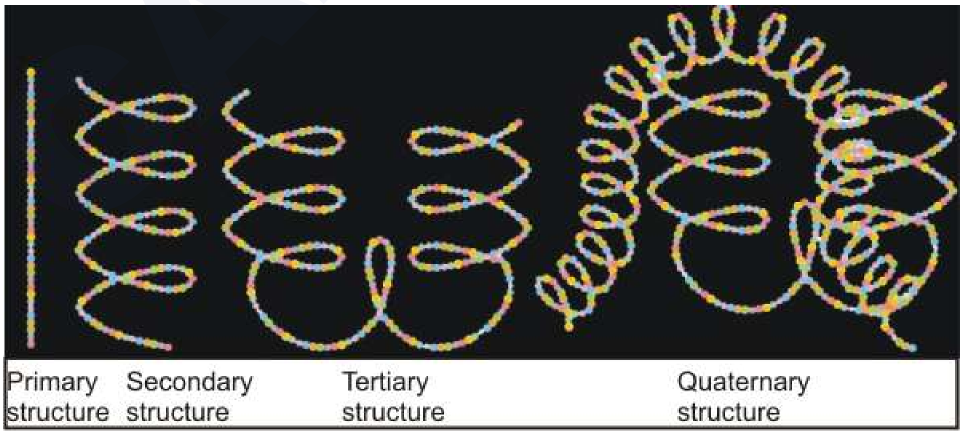
1. **Ninhydrin test:** This test is given by all proteins and amino acids. When a protein is boiled with a dilute solution of ninhydrin, a blue-violet colour is produced.
2. **Biuret test:** On adding a dilute solution of copper sulphate to an alkaline solution of protein, a violet colour is developed. This test is due to the presence of the peptide (-CO-NH-) linkage.

5. Proteins

Proteins are considered biopolymers having a large number of amino acids linked to each other through peptide linkages containing three-dimensional (3D) structures. Protein structure can be studied at four levels, i.e., primary, secondary, tertiary and quaternary structures.

1. **Primary structure:** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.
2. **Secondary structure:** The conformation in which the polypeptide chains assume a shape as a result of H-bonding is called the 2^o structure on protein. Due to the fractional double bond nature of the C-N bond is peptide linkage, the amide part, i.e., -CO-NH- is planar and inflexible, i.e., free rotation about this bond is not possible. The secondary structure is further divided into α-helix and β-pleated sheets.
3. **Tertiary structure:** The 3^o structure of a protein pertains to its entire 3D structure, i.e., the way in which the whole protein molecule folds up in the 3D space to form a particular shape.
4. **Quaternary structure:** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

The diagrammatic representation of all these structures is shown below:



On the basis of molecular structure, proteins are classified as:

1. **Fibrous proteins:** They are linear or thread-like molecules, lying side by side to form fibres. The polypeptide chains are held by H-bonding and some by disulphide bonds and hence have high intermolecular forces of attraction. Thus, they are insoluble in H_2O and are stable to moderate changes in pH and temperature. They are chief structural materials of animal tissues, e.g., keratin in skin, hair, wool, nails; collagen in tendons; fibroin in silk, etc.

2. **Globular proteins:** The folding of polypeptide chains gives a spheroidal shape in which hydrophobic parts are inward and hydrophilic parts are outwards, thus water molecules interact strongly with the polar groups and hence they are water-soluble. They are very sensitive to small changes in pH and temperature. They include all enzymes, many hormones such as insulin from the pancreas, thyroglobulin from the thyroid gland, antibodies, haemoglobin, etc.

6. Enzymes

Enzymes are naturally occurring simple or conjugated proteins which act as biological catalysts in living enzymes. Without enzymes, the living process will be too slow to sustain life. Chemically all enzymes are globular proteins. However, some enzymes are also associated with a non-protein component called prosthetic group or co-factor for their activity.

Properties of Enzymes
Some common properties of enzymes are:

- **Specificity:** They are highly specific in their action. Each enzyme catalyses only one chemical reaction. For example, the enzyme urease hydrolyses urea to NH_3 and CO_2.
- **Efficiency:** Enzymes are very efficient catalysts. They can speed up the rate of a reaction by factors of up to 10^{20}.
- **Optimum temperature and pH:** They are active at moderate temperature and at moderate pH.
- **Small quantity:** Even a small amount of enzymes can be highly efficient.

Applications of Enzymes:
Enzymes are widely used for:

- In the manufacture of beer and wine by the fermentation of carbohydrates.
- In the production of cheese by coagulation of milk.
- In the manufacture of sweet syrup from corn starch.

Some Enzymes, the substrates on which they act and the products are summarised below :

- Diastase acts on Starch and converts it into Maltose.
  - $\text{Starch} \xrightarrow{\text{Diastase}} \text{Maltose}$
- Maltase acts on Maltose and converts it into Glucose.
  - $\text{Maltose} \xrightarrow{\text{Maltase}} \text{Glucose}$
- Zymase acts on Glucose and converts it into Ethyl alcohol and Carbon dioxide.
  - $\text{Glucose} \xrightarrow{\text{Zymase}} C_2H_5OH + CO_2$
- Invertase acts on Sucrose and converts it into Glucose and Sucrose.
  - $\text{Sucrose} \xrightarrow{\text{Invertase}} \text{Glucose} + \text{Fructose}$
- Urease acts on Urea and converts it into Ammonia and Carbon Dioxide
  - $\text{Urea} \xrightarrow{\text{Urease}} NH_3 + CO_2$
- Pepsin acts on Proteins and converts it into Amino Acids
  - $\text{Proteins} \xrightarrow{\text{Pepsin}} \text{Amino Acids}$

7. Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

- They are the chemical substances that are needed in small amounts for the growth of human beings.
- They can't be synthesized in our bodies and therefore need to be taken from outsourced.
- Their deficiency can cause one or other types of diseases.

Vitamins are classified into two groups depending on their solubility
in water or fat.
(i) Fat-soluble vitamins: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.
(ii) Water soluble vitamins: B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in the diet because they are readily excreted in urine and cannot be stored (except vitamin B12) in our body.

The following vitamins with their function and deficiency disease are listed below:

Vitamin	Source	Function
A	Milk, butter, egg yolk, carrot, tomato, green vegetables	- night vision, -healthy skin
B	Yeast, eggs, liver	- Releases energy from carbohydrates - Healthy nervous system - Healthy skin - Formation of red blood cells
C	Fresh fruits and vegetables	- healing of wounds - resistance to disease
D	Butter, fish oils, eggs	- strong bones and teeth
E	Cereals, green vegetables	- May be needed for reproduction - Helps to fight against diseases
K	Milk, butter, egg yolk, carrot, tomato, green vegetables	- clotting of blood

The diseases caused by them with their symptoms:

Vitamin/ Mineral	Deficiency disease/disorder	Symptoms
Vitamin A	Loss of vision	Poor vision, loss of vision in darkness (night), sometimes complete loss of vision
Vitamin B1	Beriberi	Weak muscles and very little energy to work
Vitamin C	Scurvy	Bleeding gums, wounds take longer time to heal
Vitamin D	Rickets	Bones become soft and bent
Calcium	Bone and tooth decay	Weak bones, tooth decay
Iodine	Goiter	Glands in the neck appear swollen, mental disability in children
Iron	Anaemia	Weakness

Purification and Characterisation of Organic Compounds

Important Formulae

1. Purification of Organic Compounds

Sublimation and Crystallisation-

Sublimation is the transition of a substance directly from the solid phase to the gas phase without passing through the intermediate liquid phase. This method of purification is used for those sublimable substances which are associated with non-volatile impurities. On heating the impure compound, the volatile compound gets sublimed and its vapours are collected whereas, the non-volatile impurity remains as such. e.g., camphor, naphthalene, anthracene, benzoic acid, iodine, etc.

Crystallisation is the process of formation of solid crystals from solution, melt or by deposition directly from a gas phase. In this process, a saturated solution of sparingly soluble compounds is prepared at high temperatures and filtered. The clear solution thus obtained is set undisturbed to get cooled so that the pure solid organic substance is separated out in the form of fine crystals which can be filtered out and dried. For example, Benzoic acid mixed with naphthalene can be separated using hot water.

Note: Sometimes the process of crystallisation takes a long time. In such cases, crystallisation is initiated by adding a small crystal of some substance. This process is called seeding and the small crystal is known as the seed which acts as a nuclei for crystallisation.

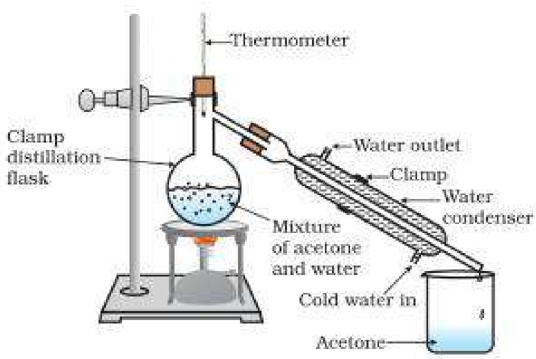
Distillation and fractional distillation-

Simple distillation is a procedure by which two liquids with different boiling points can be separated. Simple distillation can be used effectively to separate liquids that have some major degree difference in their boiling points. As the liquid being distilled is heated, the vapours that form will be richest in the component of the mixture that boils at the lowest temperature. Purified compounds will boil, and thus turn into vapours, over a relatively small temperature range (2 or 3°C) by carefully watching the temperature in the distillation flask, it is possible to affect a reasonably good separation.

As distillation progresses, the concentration of the lowest boiling component will steadily decrease. Eventually, the temperature within the apparatus will begin to change; a pure compound is no longer being distilled.

Steps to be followed in the simple distillation process:

(i) Take a mixture(Acetone and water) in the distillation flask and fit it with the thermometer.
(ii) Arrange the apparatus as shown in the given figure.
(iii) Heat the mixture slowly keeping a close watch on a thermometer.
(iv) Since acetone has a lower boiling point, it starts to vaporise and condense in the condenser which is finally collected in the beaker.



Note: Simple distillation is effective only when separating a volatile liquid from a nonvolatile substance. If the liquids comprising the mixture that is being distilled have boiling points that are closer than 50 degrees to one another, the distillate collected will be richer in the more volatile compound but not to the degree necessary for the complete separation of the individual compounds.

Fractional distillation is used for the mixture of two liquids which differ in their boiling point by 10-15 K. It is a type of distillation which involves the separation of miscible liquids. The process involves repeated distillations and condensations and the mixture is usually separated into component parts. In this method, a fractionating column is used to increase the cooling surface area so that the ascending vapour phase becomes richer in the more volatile component and the descending liquid phase becomes richer in the less volatile component.

The basic principle of this type of distillation is that different liquids boil and evaporate at different temperatures. So when the mixture is heated, the substance with a lower boiling point starts to boil first and convert into vapours.

Fractional distillation is used for the separation of

(i) Acetone (b.pt. 329 K) from methyl alcohol (b.pt. 338 K)

(ii) Crude oil into various useful fractions such as gasoline, kerosene oil, lubricating oil, etc.

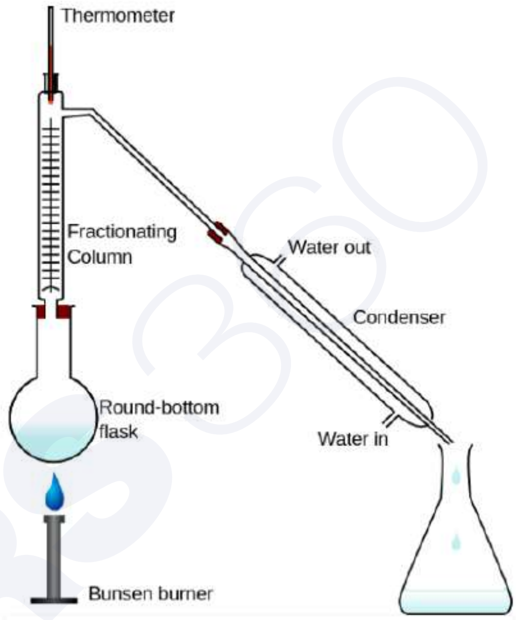
Steps to be followed in the fractional distillation process:

1. After setting up the apparatus, a mixture of two miscible liquids A and B is taken where A has more volatility than substance B.

2. The solution is added to the distilling flask while the fractionating column is connected at the tip of the flask. Heat is applied which increases the temperature slowly. The mixture then starts to boil and vapours start rising in the flask.

3. The vapours are from the volatile component A. The vapours then start moving through the fractionating column into the condenser where it is cooled down to form a liquid which is collected in the receiver.

Throughout the process, vaporization and condensation take place repeatedly until the two mixtures are separated completely.

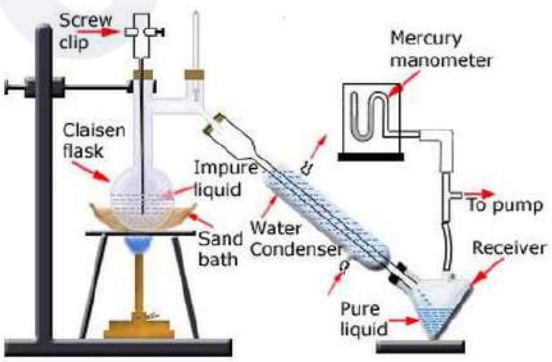


Distillation under reduced pressure and Steam distillation

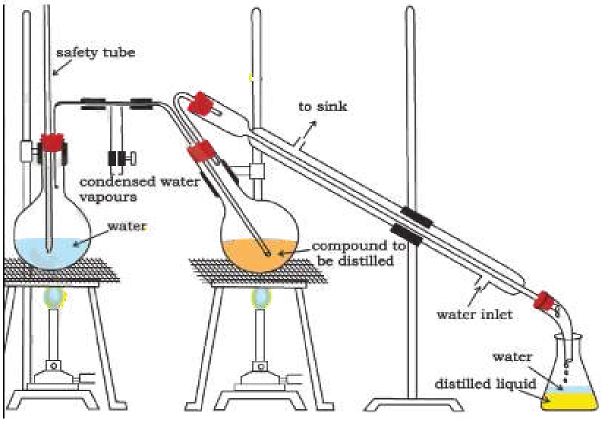
Distillation under reduced pressure or vacuum distillation is a type of distillation process that is used for the purification of high-boiling liquids and liquids which decompose at or below their normal boiling point.

If the pressure on the surface of the liquid is reduced by a suction pump or vacuum pump, the liquid boils at a lower temperature without decomposition. e.g., glycerol (b.pt. 563 K) can be distilled at 453 K under 12 mm Hg pressure without decomposition.

Raw juice in sugar factories is generally concentrated by vacuum distillation.



The steam distillation process is used for the separation and purification of organic compounds (solid or liquid) which are volatile in steam, immiscible with water, possess a high vapour pressure of about 10-15 mm Hg at 373 K and contain non-volatile impurities.



In this process, steam is passed through the organic mixture to be distilled so that the distilling mixture consists of steam and volatile organic compound, which follows that

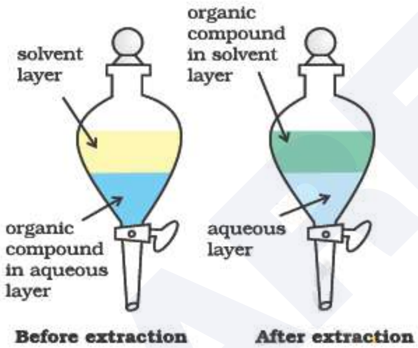
Atmospheric pressure = vapour pressure of organic substance + vapour pressure of steam.

From the above relation, it can be interpreted that organic compounds distil below their normal boiling point without decomposition. For example,
(1) Aniline can be distilled at 371.5 K against its normal boiling point of 457 K.
(2) o-Nitrophenol can be separated from p-Nitrophenol, since o-Nitrophenol is volatile in steam.

Differential extraction-

Differential extraction also means extraction with solvent. This method is based on the fact that organic substances are more soluble in organic solvents than in water. The organic substance is extracted from its aqueous solution by adopting the following process:

(1) The aqueous solution containing organic substance is shaken with a suitable organic solvent which dissolves the substance but is immiscible with water. Two layers are formed an organic layer and an aqueous layer.



Differential Extraction

(2) The solvent layer containing the organic substance (organic layer) is separated using a separating funnel. The impurities remain in the aqueous layer.

(3) The organic solvent is removed by distillation to obtain the organic substance.

Chromatography-

Chromatography is the technique for the separation, purification, and testing of compounds. In this process, we apply the mixture to be separated on a stationary phase (solid or liquid) and a pure solvent such as water or any gas is allowed to move slowly over the stationary phase, carrying the components separately as per their solubility in the pure solvent.

There are four main types of chromatography:

1. Adsorption chromatography

2. Column chromatography

3. Thin layer chromatography

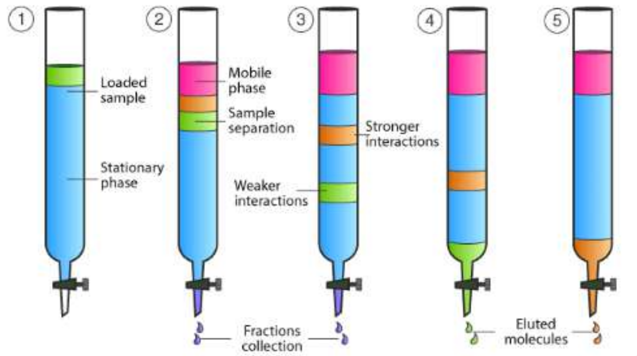
4. Partition chromatography

Adsorption chromatography

In the process of adsorption chromatography, different compounds are adsorbed on the adsorbent to different degrees based on the absorptivity of the component. Here also, a mobile phase is made to move over a stationary phase, thus carrying the components with higher absorptivity to a lower distance than those with lower absorptivity.

Column chromatography

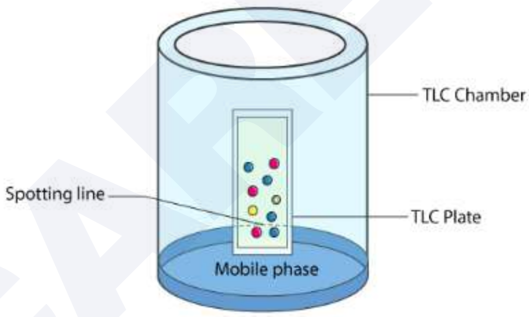
It is the technique used to separate the components of a mixture using a column of suitable adsorbent packed in a glass tube, as shown in the figure below. The mixture is placed on the top of the column, and an appropriate eluant is made to flow down the column slowly. Depending upon the degree of adsorption of the components on the wall adsorbent column, the separation of the components takes place. The component with the highest absorptivity is retained at the top, while the other flows down to different heights accordingly.



Thin layer chromatography

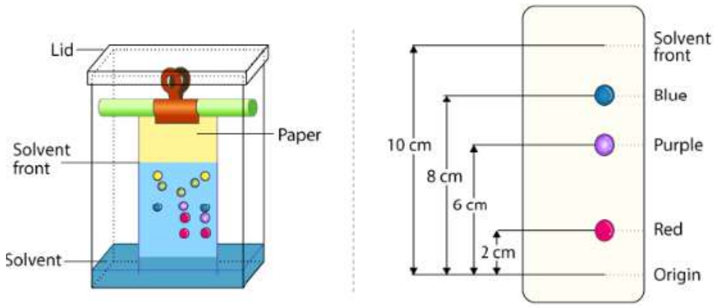
In this process, the mixture of substances is separated into its components with the help of a glass plate coated with a very thin layer of adsorbent, such as silica gel and alumina, as shown in the figure below.

The plate used for this process is known as a chrome plate. The solution of the mixture to be separated is applied as a small spot at a distance of 2 cm above one end of the plate. The plate is then placed in a closed jar containing a fluid termed an eluant, which then rises up the plate carrying different components of the mixture to different heights.



Partition chromatography

In this process, a continuous differential partitioning of components of a mixture into a stationary phase and mobile phase takes place.Paper chromatography is a type of partition chromatography. A special quality paper known as chromatography paper is used. In this process, chromatography paper is used as a stationary phase which is suspended in a mixture of solvents that act as a mobile phase. Here, we put a spot at the base of the chromatographic paper with the mixture to be separated and as the solvent rises up this paper, the components are carried to different degrees depending upon their retention on the paper. The components are thus separated at different heights.



2. Test for Hydrogen and Carbon

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

$$\underset{\text{White}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$$

3. Test for Nitrogen and Sulphur

Test for Nitrogen
The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of the Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate (II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate (II) to produce iron(III) hexacyanoferrate (II) (ferriferrocyanide) which is Prussian blue in colour.

$$6CN + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3\,[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4\,[Fe(CN)_6]_3 \,.\, \times H_2O}$$

Test for Sulphur

- The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.
  $S^{2-} + Pb^{2+} \longrightarrow PbS$
- On treating sodium fusion extract with sodium nitroprusside, the appearance of a violet colour further indicates the presence of sulphur.
  $S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood a red colour and no Prussian blue since there are no free cyanide ions.

$$Na + C + N + S \longrightarrow NaSCN$$

$$Fe^{3+} + SCN^{-} \longrightarrow [Fe(SCN)]^{2+}$$

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

4. Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

$$(X = Cl^-, Br^-, I^-)$$

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with the silver nitrate test for halogens.

5. Test for Phosphorous

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12\,(NH_4)_2\,MoO_4} + 21HNO_3 \longrightarrow \underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3\,PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

6. Liebig's Test

A known mass of organic compound is heated in the presence of pure oxygen. The carbon dioxide and water formed are collected and weighed. The percentages of carbon and hydrogen in the compound are calculated from the masses of carbon dioxide and water. The estimation of carbon and hydrogen in an organic compound is based on their conversion to CO_2 and H_2O respectively. The percentage of carbon and hydrogen are calculated from the masses of CO_2 and H_2O.

The apparatus consists of a long glass tube. This is called a combustion tube. To one end of this tube, a U-tube containing anhydrous calcium chloride and a bottle containing concentrated potassium hydroxide solution (caustic potash) are attached in series. These, in turn, are connected to a guard tube containing anhydrous calcium chloride.

The combustion tube is packed with cupric oxide and copper gauze. The other end of the tube has a provision for passing oxygen. The combustion tube is heated in a furnace. The U-tube and the caustic potash bottle are weighed before the start of the experiment. The combustion tube is heated strongly in a current of pure and dry oxygen to remove moisture and CO_2 that may be present.

A known mass of the organic compound taken in a porcelain boat is placed in the combustion tube and strongly heated. The organic compound is oxidized by cupric oxide to CO_2 and H_2O (Nitrogen, if present is also oxidized to oxides of nitrogen. These are reduced back to nitrogen by copper).

The combustion products first pass through the U-tube containing anhydrous calcium chloride (absorption of H_2O) and then through the caustic potash bottle (absorption of CO_2). The U-tube and the caustic potash bottle are weighed after cooling them to laboratory temperature.

7. Duma's Method

The nitrogen-containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)CuO \longrightarrow xCO_2 + y/2H_2O + z/2N_2 + (2x + y/2)Cu$$

Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube as shown in the figure.

Let the mass of organic compound = mg

The volume of nitrogen collected = V_1 mL

Room temperature = T_1K

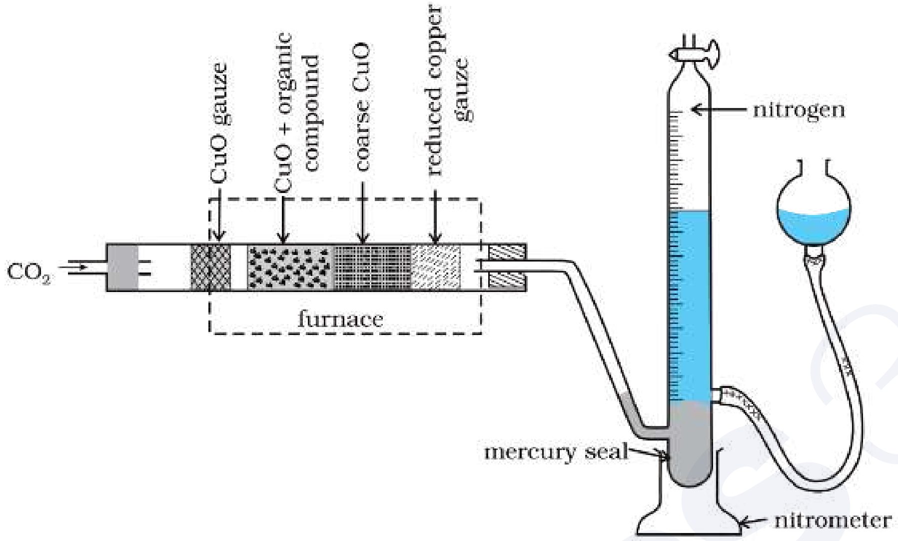
$$\text{Volume of nitrogen at STP} = \frac{p_1V_1 \times 273}{760 \times T_1}$$

Where p_1 and V_1 are the pressure and volume of nitrogen, p_1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p_1 is obtained by the relation;

p_1 = Atmospheric pressure – Aqueous tension
22400 mL N_2 at STP weighs 28g.

$$V \text{ mL } N_2 \text{ at STP weighs } = \frac{28 \times V}{22400} \text{g}$$

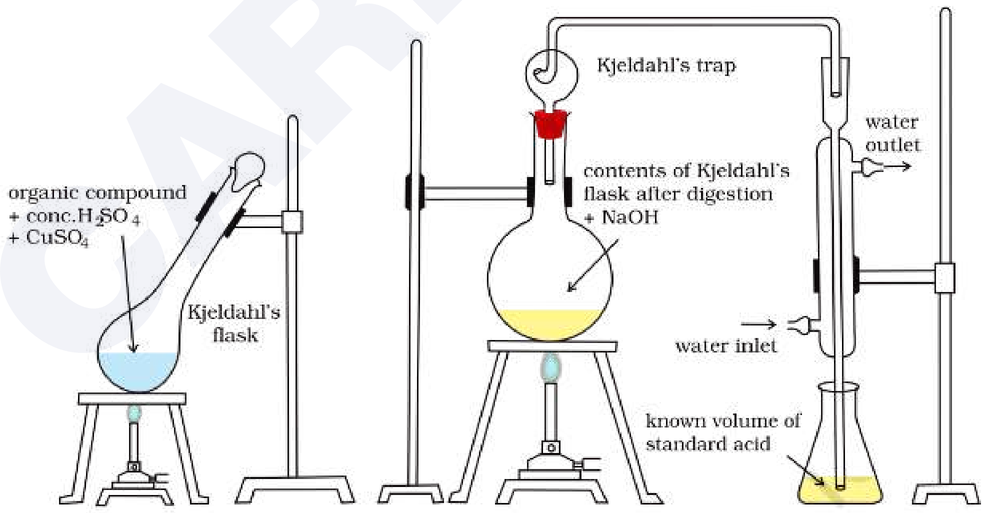
$$\text{Percentage of nitrogen } = \frac{28 \times V \times 100}{22400 \times m}$$



8. Kjeldahl's Method

The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate. The resulting acid mixture is then heated with an excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of a standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with a standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

$$\text{Organic compound } + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

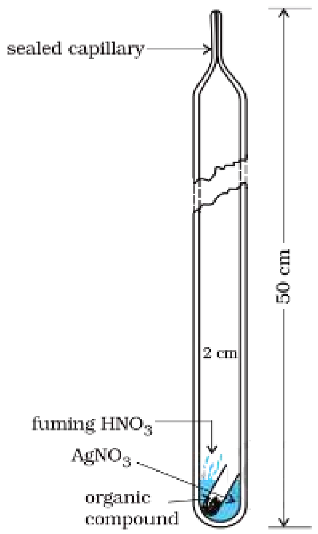


Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

9. Carius Method

Carius Method (Halogen and Sulphur)-

Halogens
A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as a Carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.



Let the mass of organic compound taken = m g
Mass of AgX formed = m_1 g
1 mol of AgX contains 1 mol of X

$$\text{Mass of halogen in } m_1\text{g of AgX} = \frac{\text{atomic mass of X} \times m_1\text{g}}{\text{molecular mass of AgX}}$$

$$\text{Percentage of halogen} = \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Sulphur
A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding an excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Let the mass of organic compound taken = m g
and the mass of barium sulphate formed = m_1 g
1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

$$m_1\text{g}BaSO_4 \text{ contains } \frac{32 \times m_1}{233}\text{g sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Carius Method (oxygen)-

The percentage of oxygen in an organic compound is usually found by the difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:
A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{ other gaseous products}$$

$$2C + O_2 \xrightarrow{1373\text{ K}} 2CO \qquad \text{(A)}$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2 \qquad \text{(B)}$$

On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbon dioxide.

$$2C + O_2 \xrightarrow{1373K} 2CO \qquad (A) \qquad \times 5$$
$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2 (B) \qquad \times 2$$

$$10C + 5O_2 + 2I_2O_5 \longrightarrow 2I_2 + 10CO_2$$

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.
Let the mass of organic compound taken be m g
Mass of carbon dioxide produced be m_1 g

$\therefore$ m_1 g carbon dioxide is obtained from $\frac{32 \times m_1}{88}$ g O_2

$$\therefore \text{ Percentage of oxygen } = \frac{32 \times m_1 \times 100}{88 \times m}\%$$

Principles Related to Practical Chemistry

Important Formulae

1. Salt Analysis

Systematic analysis of an inorganic salt involves the following steps:

(i) Preliminary examination of solid salt and its solution.

(ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.

(iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Preliminary examination of salt often gives important information, which simplifies further course of analysis. Although the results of these tests are not conclusive sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within a few minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. Heating of dry salt, blowpipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests.

Gases evolved in the preliminary tests with dil. H_2SO_4/dil. HCl and conc. H_2SO_4 also give a good indication of the presence of acid radicals. Preliminary tests should always be performed before starting the confirmatory tests for the ions.

2. Systematic Analysis of Anions

Preliminary Test with Dilute Sulphuric Acid (Systematic Analysis of Anions):-

In this test, the action of dilute sulphuric acid on the salt is noted at room temperature and on warming. Carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}), nitrite (NO_2^-) and acetate (CH_3COO^-) react with dilute sulphuric acid to evolve different gases. A study of the characteristics of the gases evolved gives information about the anions.

Procedure:
Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it

Observation	Inference	
	Gas Evolved	Possible Anion
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky	CO_2	Carbonate $(CO_3{}^{2-})$
Colourless gas with the smell of rotten egg is evolved which turns lead acetate	H_2S	Sulphide (S^{2-})

paper black.		
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO_2	Sulphite $(SO_3{}^{2-})$
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO_2	Nitrite $(NO_2{}^{-})$
Colourless vapours with the smell of vinegar turn blue litmus red	CH_3COOH Vapours	Acetate (CH_3COO^{-})

Confirmatory Test of Anions ($CO_3{}^{2-}$, S^{2-}, $SO_3{}^{2-}$, $NO_2{}^{-}$ and CH_3COO^{-}):-

Confirmatory (wet) tests for anions are performed by using water extract when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water. Confirmation of CO_3^{2-} is done by using an aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water.

Preparation of sodium carbonate extract: Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter, and collect the filtrate in a test tube and label it as sodium carbonate extract.

Anion	Confirmatory Test
Carbonate $(CO_3{}^{2-})$	Take 0.1 g of salt in a test tube, and add dilute sulphuric acid CO_2 gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide (S^{2-})	Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears
Sulphite $(SO_3{}^{2-})$	1. Take 1 ml of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved. 2. Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. H_2SO_4. The colour of the potassium permanganate solution gets discharged
Nitrite $(NO_2{}^{-})$	1. Take 1 ml of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, and acidify with acetic acid. The blue colour appears. 2. Acidify 1 mL. of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1- naphthylamine reagent. The appearance of red colour indicates the presence of nitrite ions.
Acetate (CH_3COO^{-})	1. Take 0.1 g of salt in a China dish. Add 1 ml of ethanol and 0.2 mL. conc. H_2SO_4 and heat. Fruity odour confirms the presence of acetate ions. 2. Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well, and filter if necessary. Add 1 to 2 mL of neutral ferric chloride solution to the filtrate. The deep red colour appears on boiling and a brown-red precipitate is formed.

Preliminary Test with Concentrated Sulphuric Acid-

If no positive result is obtained from dil. H_2SO_4 test, take 0.1 g of salt in a test tube and 3-4 drops of conc. H_2SO_4. Observe the change in the reaction mixture in cold and then warm it.

Observation	Inference	
	Gas	Possible
A colourless gas with a pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride (Cl^{-})
Reddish brown gas with a pungent odour has evolved. The intensity of reddish gas increases on heating the reaction mixture after the addition of solid MnO_2 to the reaction mixture. The solution also acquires red colour.	Br_2 Vapours	Bromide (Br^{-})

Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	I_2 Vapours	Iodide (I^-)
Brown fumes evolve which become dense upon heating the reaction mixture after the addition of copper turnings and the solution acquires a blue colour.	NO_2	Nitrate (NO_3^-)
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame if ignited	CO and CO_2	Oxalate, $(C_2O_4{}^{2-})$

Confirmatory tests for the anions which react with concentrated sulphuric acid are given below in the Table:
Confirmatory tests for Cl^-, Br^-, I^-, NO_3^- and $C_2O_4^{2-}$

Anion	Confirmatory Test
Chloride (Cl^-)	(a) Take 0.1 g salt in a test tube. Add a pinch of manganese dioxide and 3-4 drops of conc. Sulphuric acid, Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action. (b) Take 1 ml. of sodium carbonate extract in a test tube. Acidify it with dil. HNO_3 or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution. (c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, and add conc. H_2SO_4, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 ml of amyl alcohol followed by 1 ml of 10 % hydrogen peroxide. After gentle shaking the organic layer turns blue.
Bromide (Br^-)	(a) Take 0.1 g of salt and a pinch of MnO_2 in a test tube. Add 3-4 drops conc. sulphuric acid and heat. Intense brown fumes are evolved. (b) Neutralise 1 ml. of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 ml. carbon tetrachloride (CCl_4) /chloroform $(CHCl_3)$ /carbon disulphide (CS_2). Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ions. (c) Acidify 1 ml of sodium carbonate extract with $dil.HNO_3$ (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.
Iodide (I^-)	(a) Take 1 ml. of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A violet colour appears in the organic layer. (b) Take 1ml of sodium carbonate extract and acidify it with dil. HNO_3 (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in NH_4OH solution is obtained.
Nitrate (NO_3^-)	Take 1 mL of salt solution in water in a test tube. Add 2 ml of conc. H_2SO_4 and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.
Oxalate $(C_2O_4^{2-})$	(a) Take 1 ml. of water extract or sodium carbonate extract acidified with acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed.

	(b) Take the precipitate from test (a) and dissolve it in dilute. H_2SO_4. Add very dilute solution of $KMnO_4$ and warm. Colour of $KMnO_4$ solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.

3. Systematic Analysis of Cations

Analysis of Cations-

Preliminary Examination of the Salt for Identification of Cation:

Colour Test Observe the colour of the salt carefully, which may provide useful information about the cations.

Colour	Cations Indicated
Light green, Yellow, Brown	Fe^{2+}, Fe^{3+}
Blue	Cu^{2+}
Bright green	Ni^{2+}
Blue, Red, Violet, Pink	Co^{2+}
Light pink	Mn^{2+}

Dry Heating Test

(i) Take about 0.1 g of the dry salt in a clean and dry test tube.

(ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold.

Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence.

Colour when cold	Colour when hot	Inference
Blue	White	Cu^{2+}
Green	Dirty white or yellow	Fe^{2+}
White	Yellow	Zn^{2+}
Pink	Blue	Co^{2+}

Flame Test:

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows :

(i) Make a tiny loop at one end of a platinum wire.

(ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame

(iii) Repeat step (ii) until the wire imparts no colour to the flame.

(iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.

(v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame

(vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion.

Colour of the flame Observed by the naked eye	**Colour of the flame Observed through blue glass**	**Inference**
Green flame with blue centre	The same colour as observed without glass	Cu^{2+}
Crimson red	Purple	Sr^{2+}
Apple green	Bluish-green	Ba^{2+}
Brick red	Green	Ca^{2+}

Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

(iv) Observe the colour imparted to the bead in the non-luminous flame as well as in the luminous flame while it is hot and when it is cold.

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger.

Heating in Oxidising (non-luminous) flame		**Heating in Reducing (luminous) flame**		**Inference**
Colour in cold	Colour in hot	Colour in cold	Colour in hot	**Ion**
Blue	Green	Red Opaque	Colourless	Cu^{2+}
Reddish Brown	Violet	Grey	Grey	Ni^{2+}
Light Violet	Light Violet	Colourless	Colourless	Mn^{2+}
Yellow	Yellowish brown	Green	Green	Fe^{3+}

Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis. The first essential step is to prepare a clear and transparent solution of the salt. This is called the original solution. It is prepared as follows:

Preparation of Original Solution (O.S.):

To prepare the original solution, the following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent. The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolve, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO3 (3:1 ratio). This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

GROUP ANALYSIS:

Analysis of Zero group cation (NH_4^+ ion):

- Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.
- Pass the gas through Nessler's reagent. The brown precipitate is obtained.

Chemistry of Confirmatory Tests for NH_4^+ ion

Ammonia gas evolved by the action of sodium hydroxide on ammonium salts and reacts with hydrochloric acid to give ammonium chloride, which is visible as a dense white fume.

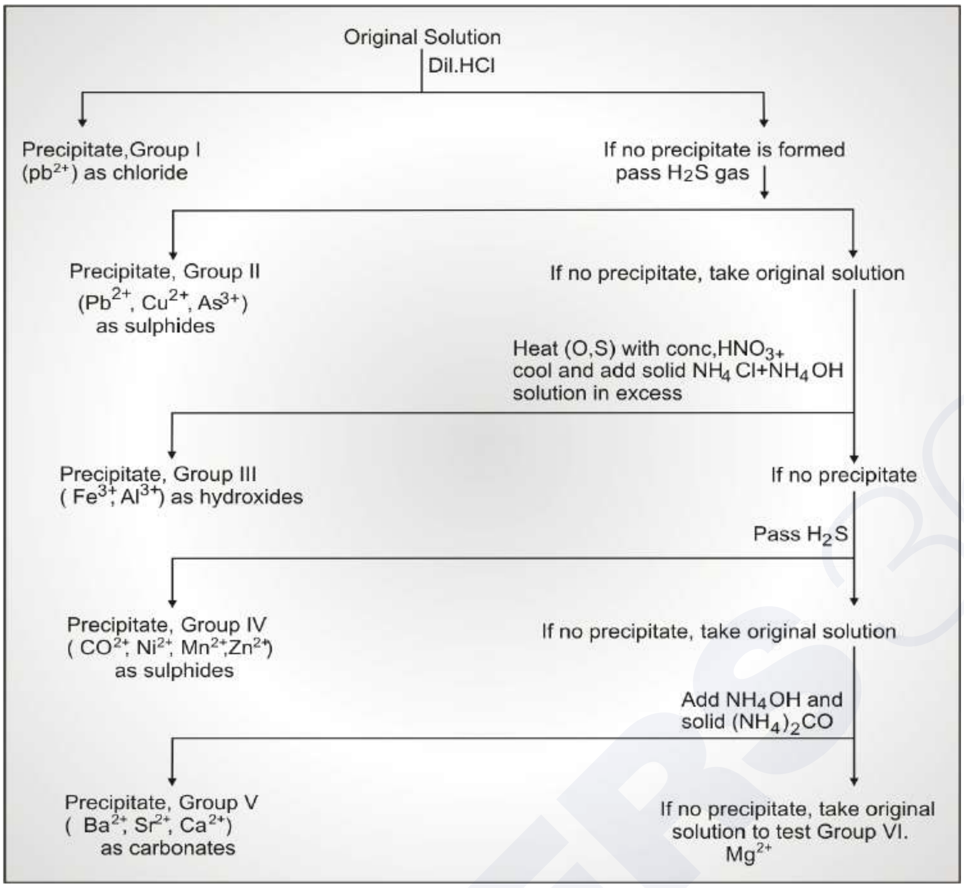
$$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$NH_3 + HCl \rightarrow NH_4Cl$$

On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.

$$2K_2HgI_4 + NH_3 + KOH \rightarrow HgO.Hg(NH_2)I + 7KI + 2H_2O$$

For the analysis of cations belonging to groups I-VI, the cations are precipitated from the original solution by using the group reagents according to the scheme shown in the flow chart given below: The separation of all the six groups is represented as below:



Group reagents for precipitating ions:

Group	Cations	Group Reagent
Group zero	NH_4^+	None
Group-I	Pb^{2+}	Dilute HCl
Group-II	$Pb^{2+}, Cu^{2+}, As^{3+}$	H_2S gas in the presence of dil. HCl
Group-III	Al^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl
Group-IV	$Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}$	H_2Sin presence of NH_4OH
Group-V	$Ba^{2+}, Sr^{2+}, Ca^{2+}$	$(NH_4)_2CO_3$ in presence of NH_4OH
Group-VI	Mg^{2+}	None

Other Useful Resources

Some useful resources for the preparation of NEET are listed below:

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