Comprehensive Questions Part I

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Dear Students,

Comprehensive questions constitute an essential segment of the Chemistry paper, carrying a weightage of 24 marks. Many available textbooks either offer excessively concise answers or include supplementary content not found in the textbook.

In the *Comprehensive Questions Part I*, an endeavor has been made to elucidate the approach for tackling lengthy questions. At the conclusion of each chapter, a compilation of significant long-form questions from past papers is provided. This compilation aims to furnish students with a clear perspective on the most probable long questions anticipated in the final exams. While this book covers the major segments of long questions, it is encouraged that students utilize it as a reference to devise their own headings and subheadings for any sections not included herein.

The primary objective of this book is to acquaint students with the requisite content and presentation techniques for handling lengthy questions. It encompasses numerical aspects, ensuring students don't overlook any steps in solving numerical problems, thus averting potential mark deductions.

Wishing you all the best for success in your examinations!

God Bless.

Table of Contents

Chapter 1
Basic Concepts
Isotopes

Definition:

Atoms of the same element can possess different masses but same atomic numbers. Such atoms of an element are called isotopes.

Explanation

This phenomenon of isotopy was first discovered by Soddy. Isotopes are different kind of atoms of the same element having same atomic number, but different atomic masses due to same number of protons and electrons but different number of neutrons. The isotopes of an element possess same chemical properties and same position in the periodic table.

Examples
- Carbon has three isotopes written as $_6C^{12}$, $_6C^{13}$ and $_6C^{14}$ and expressed as C-12, C-13 and C-14. Each of these have 6-protrons and 6 electrons. These isotopes have 6, 7 and 8 neutrons, respectively.
- Hydrogen has three isotopes written as $_1H^1$, $_1H^2$ and $_1H^3$ called protium, deuterium and tritium.
- Oxygen has three, nickel has five, calcium has six, palladium has six, cadmium has nine and tin has eleven isotopes.

Relative Abundance of Isotopes

The percentage of one isotope of an element as compared to other isotopes of the same element occurring naturally is called relative abundance of isotopes.

The properties of a particular element mostly correspond to the most abundant isotope of that element. The relative abundance of the isotopes of elements can be determined by mass spectrometry.

Facts about Isotopes
- At present above 280 different isotopes occur in nature.
- They include 40 radioactive isotopes as well.
- About 300 unstable radioactive isotopes have been produced through artificial disintegration.
- The elements like arsenic, fluorine, iodine and gold etc have only a single isotope. They are called mono-isotopic elements.
- The elements of odd atomic number almost never possess more than two stable isotopes.
- The elements of even atomic number usually have larger number of isotopes and isotopes whose mass numbers are multiples of four are particularly abundant.
- For example, O-16, Mg-24, Si-28, Ca-40 and Fe-56 form nearly 50% of the earth's crust.
- Out of 280 isotopes that occur in nature, 154 have even mass number and even atomic number.

Determination of Relative Atomic Mass of Isotopes by Mass Spectrometer

Definition:

Mass spectrometer is an instrument which is used to measure the exact masses of different isotopes of an element.

History:

- **Aston's mass spectrograph** was designed to identify the isotopes of an element on the basis of their atomic masses.
- **Dempster's mass spectrometer** was designed for the identification of elements which were available in solid state.

Construction and working:

The instrument has following components:

1. **Vaporization Chamber:**
   - The substance, the analysis of which is required, is converted into vapour state in the vaporization chamber.
   - The pressure of these vapours is kept very low, that is, 10^{-6} to 10^{-7} torr.
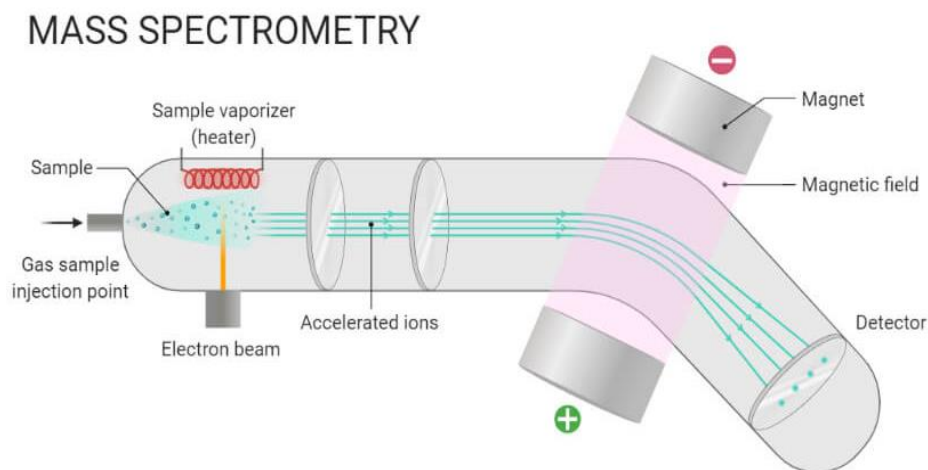
2. **Ionization Chamber:**
   - Vapors are allowed to enter the ionization chamber.
   - Fast moving electrons are thrown upon them.
   - The atoms in vapour state are ionized to cations.
   - The positively charged ions of isotopes of an element have different masses.
3. **Electric Field:**
   - The positive ions enter the electric field.
   - Electric Field is applied between perforated plates.
   - A potential difference (E) of 500-2000 volts is applied.
   - The ions are accelerated.

4. **Magnetic Field:**
   - The ions are then allowed to pass through a magnetic field of strength (H).
   - The magnetic field makes the ions to move in a circular path and then fall on the electrometer.
   - In this way ions are separated on the basis of their (m/e) values.

5. **Electrometer:**
   - It is also called ion collector and develops the electric current.
   - The strength of current thus gives the relative abundance of ions.
6. **Mathematical expression:**
   The mathematical relationship for m/e ratio of isotopic ions is:

$$\frac{m}{e} = \frac{H^2 r^2}{2E}$$

   Where   'H' is the strength of magnetic field
                      'E' is the strength of electrical field
                      'r' is the radius of circular path adopted by isotopes in the magnetic field

7. **Comparison with C-12:**
   - The same experiment is performed with C-12 and the current strength is compared.
   - This comparison allows us to measure the exact mass number of the isotope of the element under study.
8. **Modern spectrograph:**
   - In modern spectrograph ions strike a detector.
   - Ionic current is amplified and fed into recorder.
   - Recorder plots a graph.
9. **Mass spectrum:**

The graph between mass to charge ratio on x-axis and relative abundance on Y-axis is known as mass spectrum.
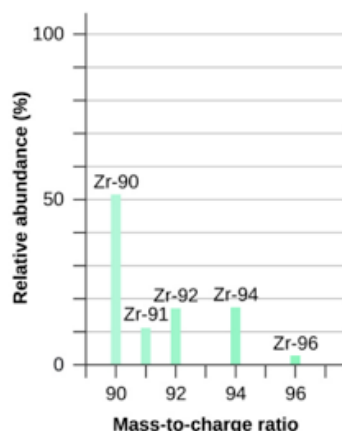
Empirical Formula

Definition
It is the simplest formula that gives the small whole number ratio between the atoms of different elements present in a compound. In an empirical formula of a compound, AxBy, there are x atoms of an element A and y atoms of an element B.

Examples
The empirical formula of glucose ($C_6H_{12}O_6$) is CH_2O and that of benzene (C_6H_6) is CH.

Steps to Calculate Empirical Formula
Empirical formula of a compound can be calculated following the steps mentioned below:

1. Percentage composition
Determination of the percentage composition.

2. Number of Gram atoms
Finding the number of gram atoms of each element. Divide the mass of each element (% of an element) by its atomic mass.

3. Determination of Atomic Ratio
Determination of the atomic ratio of each element. Divide the number of moles of each element (gram atoms) by the smallest number of moles.

4. Multiply with a Suitable Digit
If the atomic ratio is simple whole number, it gives the empirical formula, otherwise multiply with a suitable digit to get the whole number atomic ratio.

Combustion Analysis

Definition: It is a technique used for finding empirical formula of the organic compounds which simply consist of carbon, hydrogen and oxygen.

Diagram:

Working:

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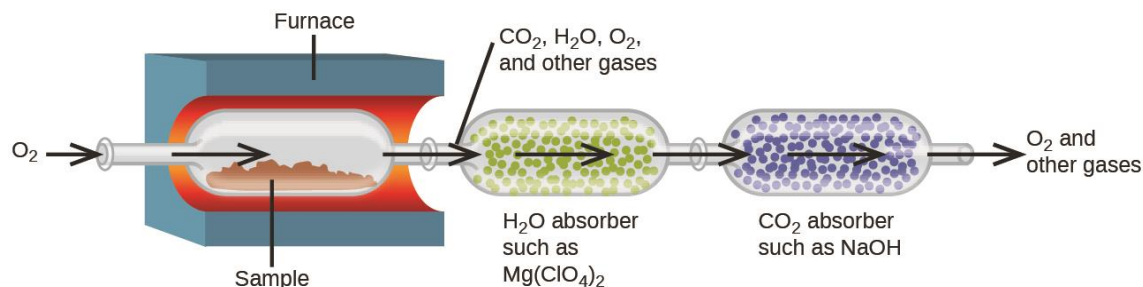
1. **Furnace**
- A weighed sample of the organic compound is placed in the combustion tube.
- This combustion tube is fitted in a furnace.
- Oxygen is supplied to burn the compound.
- Carbon and hydrogen of organic compound are converted to CO_2 and H_2O, respectively.
2. **H_2O absorber**
- H_2O vapours are absorbed in magnesium per chlorate $Mg(CIO_4)_2$ solution.
3. **CO_2 absorber**
- CO_2 gas is absorbed in 50% KOH solution.
- The difference in the masses of these absorbers before absorbing gases and after absorbing gases gives the amount of CO_2 and H_2O produced.

Formulas to calculate the percentages of the elements:

Following formulas are used to calculate the percentages of carbon, hydrogen and oxygen respectively in the unknown organic compound.

% of carbon   % of carbon $= \dfrac{mass\ of\ CO2}{mass\ of\ organic\ compound} \times \dfrac{12.00}{44.00} \times 100$

% of hydrogen   % of hydrogen $= \dfrac{mass\ of\ H2O}{mass\ of\ orgnaic\ compound} \times \dfrac{2.016}{18} \times 100$

% of oxygen   The percentage of oxygen is obtained by the method of difference.

$$\% \text{ of oxygen} = 100 - (\% \text{ of carbon} + \% \text{ of hydrogen})$$

Molecular Formula

Definition

That formula of a substance which is based on the actual molecule is called molecular formula.

Examples

Molecular formula of benzene is C_6H_6 while that of glucose is $C_6H_{12}O_6$.

The empirical formulas of benzene and glucose are CH and CH_2O respectively, so for these compounds the molecular formulas are the simple multiple of empirical formulas.

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

Where 'n' is a simple integer.

$$n= \frac{\text{Molecular formula}}{\text{Empirical formula}}$$

Compounds with Same Molecular Formula and Empirical Formula

Those compounds whose empirical and molecular formulae are the same are numerous.

Examples

H_2O, CO_2, NH_3 and $C_{12}H_{22}O_{11}$ have same empirical and molecular formulas. Their simple multiple 'n' is unity.

Mole

Definition of mole

The atomic mass, molecular mass, formula mass or ionic mass of the substance expressed in gram is called molar mass of the substance.

Formula

Number of gram atoms or moles of an element $= \dfrac{\text{Mass of an element in grams}}{\text{Molar mass of an element}}$

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Example
1 gram atom of hydrogen= 1.008 g
1 gram atom of carbon= 12.000 g
1 gram atom of uranium= 238.0 g

Formula
Number of gram molecules or moles of molecule= Mass of molecular substance in grams
                                                                                            Molar mass of the substance

Example
1 gram molecule of water= 18.0 g
1 gram molecule of H_2SO_4= 98.0 g
1 gram molecule of sucrose= 342.0 g

Formula
Number of gram formulas or moles of a substance = Mass of the ionic substance in grams
                                                                                            Formula mass of the ionic substance

Example
1 gram formula of NaCl= 58.50 g
1 gram formula of Na_2CO_3= 106 g
1 gram formula of $AgNO_3$= 170 g

Formula
Number of gram ions or moles of a species = Mass of the ionic species in grams
                                                                                            Formula mass of the ionic species

Example
1 gram ion of OH^-= 17 g
1 gram ion of SO_4^{2-}= 96 g
1 gram ion of CO_3^{2-}= 60 g

Avogadro's Number

Definition

Avogadro's number is the number of atoms, molecules and ions in one gram atom of an element, one gram molecule of a compound and one gram ion of a substance, respectively.

Examples
1.008 g of hydrogen = 1 mole of hydrogen = 6.02×10^{23} atoms of H
23 g of sodium = 1 mole of Na = 6.02×10^{23} atoms of Na
238 g of uranium = 1 mole of U = 6.02×10^{23} atoms of U
6.02×10^{23} is the number of atoms in one mole of the element.

18 g of H_2O =1 mole of water =6.02×10^{23} molecules of water
180 g of glucose = 1 mole of glucose = 6.02×10^{23} molecules of glucose
342 g of sucrose = 1 mole of sucrose = 6.02×10^{23} molecules of sucrose
One mole of different compounds has different masses but has the same number of molecules.

When we take into consideration the ions, then
96 g of SO_4^{2-} = 1 mole of SO_4^{2-} = 6.02×10^{23} ions of SO_4^{2-}
62 g of NO_3^- = 1 mole of NO_3^- = 6.02×10^{23} ions of NO_3^-

Formulas
Number of atoms of an element= Mass of the element $\times N_A$
                                                        Atomic mass

Number of molecules of a compound= $\underline{\text{Mass of the compound}} \times N_A$
Molecular mass

Number of ions of an ionic species= $\underline{\text{Mass of the ion}} \times N_A$
Ionic mass

Explanation through examples

1. In 18 g of water there are present 6.02 x 10^{23} molecules of H_2O, 2 x 6.02 x 10^{23} atoms of hydrogen and 6.02 x 10^{23} atoms of oxygen.

2. In 98g of H_2SO_4, it has twice the Avogadro's number of hydrogen atoms, four times the Avogadro's number of oxygen atoms and the Avogadro's number of sulphur atoms.

3. Dissolve 9.8 g of H_2SO_4 in sufficient quantity of H_2O to get it completely ionized. It has 0.1 moles of H_2SO_4. It will yield 0.2 mole or 0.2 x 6.02 x 10^{23} H^+ and 0.1 moles or 0.1 x 6.02 x 10^{23} SO_4^{2-} etc. Total positive charges will be 0.2 x 6.02 x 10^{23} and the total negative charges will be 0.2 x 6.02 x 10^{23}. The total mass of H^+ is (0.2 x 1.008) g and that of SO_4^{2-} is (0.1 x 96) g.

Stoichiometry

Definition

Stoichiometry is a branch of chemistry which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

Assumptions

Following are the assumptions of stoichiometry:

1. All the reactants are completely converted into the products.

2. No side reaction occurs.

3. The law of conservation of mass and the law of definite proportions are obeyed.

Studied Relationships

The following type of relationships can be studied with the help of balanced chemical equation:

a. Mass-mass Relationship

If we are given the mass of one substance, we can calculate the mass of the other substances involved in the chemical reaction.

b. Mass-mole Relationship or Mole-mass Relationship

If we are given the mass of one substance, we can calculate the moles of other substance and vice versa.

c. Mass-volume Relationship

If we are given the mass of one substance, we can calculate the volume of the other substances and vice-versa.

d. Mole-mole Relationship

If we are given the moles of one substance, we can calculate the moles of the other substances.

Limiting Reactant

Definition

The limiting reactant is a reactant that controls the amount of the product formed in a chemical reaction due to its smaller amount.

Examples

From Daily Life

1. If we have 30 "kababs" and five breads "having 58 slices", then we can only prepare 29 "sandwiches". One "kabab" will be extra (excess reactant) and "slices" will be the limiting reactant.

2. Burning of wood in excess oxygen. In this case, wood is the limiting reactant and oxygen is the excess reactant.

From Chemistry

Consider the reaction between hydrogen and oxygen to form water.

$$2H_2 \text{ (g)} + \cancel{O_2 \text{ (g)}} \longrightarrow 2H_2O \text{ (l)}$$
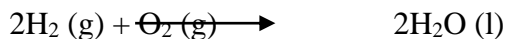
We will get 2 moles (36g) of water because 2 moles (4g) of hydrogen react with 1 mole (32 g) of oxygen according to the balanced equation. Since less hydrogen is present as compared to oxygen, so hydrogen is a limiting reactant.

Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed:

1. Calculate the number of moles from the given amount of reactant.

2. Find out the number of moles of product with the help of a balanced chemical equation.

3. Identify the reactant which produces the least amount of product as limiting reactant.

Yield

Definition

Actual Yield

The amount of the product obtained in a chemical reaction is called the actual yield.

Theoretical Yield

The amount of the product obtained through balanced chemical equation is called the theoretical yield.

Actual Yield less than Theoretical Yield

Actual yield is always less than theoretical yield due to the following reasons:

1. A practically inexperienced worker has many shortcomings and cannot get the expected yield.

2. The processes like filtration, separation by distillation, separation by a separating funnel, washing, drying and crystallization if not properly carried out, decrease the actual yield.

3. Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product.

Efficiency of Reaction

The efficiency of a reaction is expressed by comparing the actual and theoretical yields in the form of percentage (%) yield.

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Numericals

6. Silver has atomic number 47 and 16 known isotopes but only two occur naturally i-e ^{107}Ag and ^{109}Ag. Given the following mass spectrometric data. Calculate the average atomic mass of silver.

Data:

Isotopes	Mass (amu)	% Abundance
^{107}Ag	106.90509	51.84%
^{109}Ag	108.90476	48.16%

To Find:
Average atomic mass = ?
Solution:
Average atomic mass = (106.90509 x 51.84) + (108.90476 x 48.16) / 100
Average atomic mass = 107.87 amu

7. Boron with atomic number 5 has two naturally occurring isotopes. Calculate the % abundance of ^{10}B and ^{11}B from the following data:

Average atomic mass of Boron	10.81 amu
Isotopic mass of ^{10}B	10.0129 amu
Isotopic mass of ^{11}B	11.0093 amu

To Find:
Let % abundance of ^{10}B = x =?
Then % abundance of ^{11}B = 100 – x =?
Solution:
Average atomic mass = [(10.0129 .x) + (11.0093 . (100-x)] / 100 = 10.81 amu
10.0129 x + 1100.93 – 11.0093x = 1081
-0.9964x = 1081 – 1100.93
-0.9964x = -19.93
x = 19.93/ 0.9964
x = 20.002 %
Hence % abundance of ^{10}B = x = 20.002%
% abundance of ^{11}B = 100 – x = 100 – 20.002 = 79.998%

9. Justify the following statement:
(a) 23 grams of Sodium and 238 grams of Uranium have equal number of atoms in them.
1mole of Sodium = 23 grams
1 mole of Uranium = 238 grams
Since 1 mole of each element contains Avogadro's number of atoms i-e N_A = 6.02 x 10^{23} atoms. Hence 1 mole of each of Sodium and Uranium contain equal number of atoms i.e. 6.02 x 10^{23}
(b) Mg atom is twice heavier than carbon
One carbon atom contains 6 protons and 6 neutrons in its nucleus and its atomic mass is 12 amu
While one atom of Magnesium contains 12 protons and 12 neutrons in its nucleus and its atomic mass is 24 amu
Thus, Mass of Mg / Mass of Carbon = 24/ 12 = 2
Hence, One atom of Magnesium is twice heavier than that of one carbon atom
(c) 180g of glucose and 342g of sucrose have same number of molecules but different number of atoms
**180 g of glucose = 1 mole of glucose**
342 g of sucrose = 1 mole of sucrose
1 mole of each compound contains Avogadro's number of molecules. Hence both 1 mole of glucose (180grams) and 1mole of sucrose (342 grams) contain equal Avogadro's number of molecules N_A = 6.02 X 10^{23} .
Since one molecule of glucose ($C_6H_{12}O_6$) contains 24 atoms. Whereas, one molecule of sucrose ($C_{12}H_{22}O_{11}$) contains 45 atoms.
(d) 4.9g of H_2SO_4 when completely ionized in water have equal number of positive and negative charges but the number of positive charge ions are twice the number of negatively charge ions.
$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$
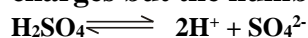
This balance equation shows that 1 molecule of H_2SO_4 produces
Number of positively charged ions = H^+ = 2
Number of negatively charged ions = SO_4^{2-} = 1
Number of positive charges = 2 (Due to two H^+ ions)
Number of negative charges = 2 (Due to two negative charges on SO_4^{2-})
Hence, whatever be the amount of H_2SO_4. It will always produce equal number of positive and negative charges but number of positively charged ions will be twice the number of negatively charged ions.

(e) One mg of K_2CrO_4 has thrice the number of ions than the number of formula units when ionized in water
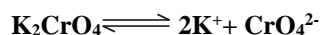
$K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{2-}$
This equation shows that 1 formula unit of K_2CrO_4 produces two K^+ ions and one CrO_4^{2-} ion in solution. Thus a total of three ions are produced by ionization of 1 formula unit of K_2CrO_4.
Hence whatever be the amount of the K_2CrO_4 number of ions in its solution will always be thrice than the number of its formula units.

(f) Two grams of H_2, 16g of CH_4 and 44 g of CO_2 occupy separately the volume of 22.414dm³, although the size and the masses of molecules of these gases are very different from each other.
2 grams of H_2 = 1 mole = N_A = 6.02 x 10^{23} molecules
16 grams of CH_4 = 1 mole = N_A = 6.02 x 10^{23} molecules
44 grams of CO_2 = 1 mole = N_A = 6.02 x 10^{23} molecules
In gases distance between two molecules is approximately 300 times than its molecular size. Thus, volume occupied by the gas molecules does not depend upon the size or the mass of molecules while it only depends upon the number of molecules.
Hence, equal number of molecules of H_2, CH_4 and CO_2 at STP will occupy same volume i.e 22.414 dm³. This is called as Avogadro's Law

10. Calculate each of the following:
(a) **Mass in grams of 2.74 moles of KMnO₄**
Data: Moles of KMnO₄=2.74 mol

To Find: Mass in grams of KMnO₄=?

KMnO4 (M=39 + 55 + 64 = 158 g mol-)

Formula: Number of moles = $\dfrac{\text{Mass in grams}}{\text{Molar mass}}$

Solution: Mass=Mole × Molar mass

Mass of KMnO₄ =No. of moles × Molar mass

$\qquad\qquad$ =$\qquad$ 2.74 × 158

$\qquad\qquad$ =$\qquad$ **432.9 g**

(b) **Moles of O atoms in 9.00g of Mg(NO₃)₂**
Data: Mass of Mg(NO₃)₂ =9g

To Find: Moles of moles of oxygen atoms =?

Mg(NO₃)₂(M=39 + 55 + 64 = 158 g mol⁻¹)

Formula: Number of moles = $\dfrac{\text{mass in grams}}{\text{molar mass}}$

Solution:

Moles of $Mg(NO_3)_2 = \dfrac{9}{148}$ = 0.061 mol

1 moles of $Mg(NO_3)_2$ contains oxygen = 6 mol

0.061 moles of $Mg(NO_3)_2$ contains oxygen = 6 × 0.0061

= 0.366 moles of Oxygen

(c) Number of O atoms in 10.037 g of $CuSO_4.5H_2O$

Data: Mass of $CuSO_4.5H_2O$ = 10.037g

To Find: No. of Oxygen atoms = ?

$CuSO_4 5H_2O$ (M=63.5 + 32 + 64 + 90=249.5 g mol^{-1})

Formula: Number of moles of $CuSO_4.5H_2O$ = $\dfrac{mass}{molar\ mass}$

Solution: Number of moles of $CuSO_4.5H_2O$ = $\dfrac{10.037}{249.5}$

= 0.04 moles of $CuSO_4.5H_2O$

1 Moles of $CuSO_4.5H_2O$ contains = 9 moles of oxygen

0.04 moles of $CuSO_4 5H_2O$ contains = 9x 0.04

= 0.36 moles of oxygen

1 mole of oxygen atoms = N_A = 6.02 x 10^{23} atoms of oxygen

0.36 moles of oxygen contain = 6.02 x 10^{23} x 0.36 = 2.167 x 10^{23} atoms of oxygen

(d) Mass in kilogram of 2.6 ×10^{20} molecules of SO_2

Data: Molecules of SO_2 = 2.6×10^{20}

To Find: Mass in kilogram of SO_2 = ?

SO_2 (M=32 + 32 = 64 g mol^{-1})

Formula: Number of particles = $\dfrac{mass}{molar\ mass}$ x N_A

Solution: Mass = $\dfrac{Number\ of\ particles\ x\ molar\ mass}{N_A}$

Mass = $\dfrac{2.6×10^{20}\ x\ 64}{6.02x10^{23}}$

= 27.64x10^{-3} g

= 27.64x10^{-3}x10^{-3}

= 27.64 x 10^{-6}kg

= 2.764x10^{-5} kg

(e) Moles of Cl atoms in 0.822 g $C_2H_4Cl_2$.

Data: Mass of $C_2H_4Cl_2$ = 0.822g

To Find: Moles of Cl atoms = ?

$C_2H_4Cl_2$ (M=24 + 4+71 = 99 g mol^{-1})

Solution:

99g of $C_2H_4Cl_2$ contains moles of Cl = 2

1g of $C_2H_4Cl_2$ contains moles of Cl = $\dfrac{2}{99}$

0.822 g $C_2H_4Cl_2$ contains moles of Cl = $\dfrac{2}{99} \times 0.822$

= **0.017 moles of Cl**

(f) Mass in grams of 5.136 moles of silver carbonate.

Data: Moles of Silver Carbonate: = 5.136 mol

To Find: Mass in grams of Silver Carbonate = ?

Ag_2CO_3 (M=2(107.87) + 12 + 48 = 275.74 g mol^{-1})

Formula: Moles = $\dfrac{mass}{molar\ mass}$

Solution: Mass = moles x molar mass

Mass of Ag_2CO_3 = No. of moles ×moles of mass

= 5.136 × 275.74

= **1416.2 g**

(g) Mass in grams of 2.78 × 10^{21} molecules of CrO_2Cl_2

Data: Molecules of $CrCO_2Cl_2$ = 2.78×10^{21}

To Find: Mass in grams of CrO_2Cl_2= ?

CrO_2Cl_2 (M=52+32+71= 155 g mol^{-1})

Formula: Number of particles = $\dfrac{mass\ in\ grams}{molar\ mass}$ x N_A

Solution: Mass = $\dfrac{Number\ of\ particles\ x\ molar\ mass}{N_A}$

Mass of CrO_2Cl_2 = $\dfrac{2.78\times10^{21}\ x\ 155}{6.02\ x\ 10^{23}}$

= **0.715 g**

(h) Number of moles and formula units in 100g of $KClO_3$

(i) **Number of K^+ ions, ClO_3^- ion, Cl atoms and O atoms in h**

Data: Mass of $KClO_3$ = 100g

To Find:

Number of moles of $KClO_3$ = ?

Number of Formula units of $KClO_3$ = ?

$KClO_3$ (M=39+35.5+48= 122.5 g mol^{-1}

$$\text{Number of moles} = \frac{\text{mas in grams}}{\text{molar mass}}$$

Number of particles = number of moles x N_A

i. **Calculation of Number of moles:**

$$\text{Moles of } KClO_3 = \frac{100}{122.5} = 0.816 \text{ moles of } KClO_3$$

ii. **Calculation of Number of formula units:**

Number of formula units of $KClO_3$ = 0.816x 6.02 $\times 10^{23}$

$$= 4.9 \times 10^2$$

Calculation of Number of K^+ ions, ClO_3^- ion, Cl atoms and O atoms

$KClO_3$: K^+ ions

1 : 1

4.9 $\times 10^{23}$: 4.9 $\times 10^{23}$

Number of K^+ ions = 4.9 $\times 10^{23}$

$KClO_3$: ClO_3^- ions

1 : 1

4.9 $\times 10^{23}$: 4.9 $\times 10^{23}$

Number of ClO_3^- ions = 4.9 $\times 10^{23}$

$KClO_3$: Chlorine atoms

1 : 1

4.9 $\times 10^{23}$: 4.9 $\times 10^{23}$

Number of Chlorineatoms = 4.9 $\times 10^{23}$

$KClO_3$: Oxygen atoms

1 : 3

$$4.9 \times 10^{23} : 3 \times 4.9 \times 10^{23}$$

$$: 1.473 \times 10^{24}$$

Number of Oxygen atoms $= 1.473 \times 10^{24}$

11. Aspartame, the artificial sweetener, has a molecular formula of $C_{14}H_{18}N_2O_5$.

(a) What is the mass of one mole of aspartame?

Data: Molecular formula of aspartame = $C_{14}H_{18}N_2O_5$

To Find: Mass of one mole of aspartame (Molar mass) = ?

Solution: Molar mass of $C_{14}H_{18}N_2O_5$ = 14(12) +18(1) +2(14) +5(16)

$$= 168+18+28+80$$

$$= 294 \text{ gmol}^{-1}$$

1 mole of aspartame $= \mathbf{294 \text{ g mol}^{-1}}$

(b) How many moles are present in 52g of Aspartame?

Data: Mass of aspartame = 52

To Find: Moles in 52 grams of aspartame = ?

Formula: Number of moles $= \dfrac{\text{mass in gram}}{\text{molar mass}}$

Solution: Mass = mole x molar mass

Moles of Aspartame = ?

Moles of aspartame $= \dfrac{52}{294} = \mathbf{0.17 \text{ mol}}$

(c) What is the mass in grams of 10.122 moles of Aspartame.

Data: Moles of aspartame = 10.122 mol

To Find: Mass in grams of Aspartame = ?

Formula: Moles $= \dfrac{\text{mass in gram}}{\text{molar mass}}$

Solution: Mass = moles x molar mass

Mass of aspartame $= 10.122 \times 294$

$$= \mathbf{2975.86 \text{ g}}$$

(d) How many hydrogen atoms are present in 2.43g of aspartame?

Data: Mass of aspartame = 2.43 g

To Find: Hydrogen atoms in Aspartame = ?

Formula: Number of particles $= \dfrac{\text{mass}}{\text{molar mass}} \times N_A$
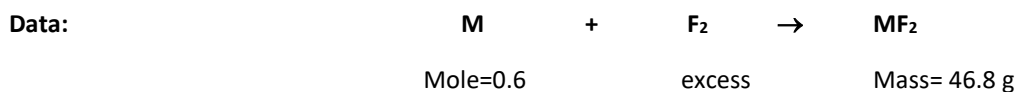
Solution: Number of particles of aspartame $= \dfrac{2.43}{294} \times 6.02 \times 10^{23} = 4.97 \times 10^{21}$

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$$C_{14}H_{18}N_2O_5 \quad : \quad \text{H atoms}$$

$$1 \quad : \quad 18$$

$$4.97 \times 10^{21} \quad : \quad 4.97 \times 10^{21} \times 18$$

$$: \quad 8.95 \times 10^{22}$$

Number of H atoms   =   **8. 95 x 10^{22} atoms of hydrogen**

12. **A sample of 0.600 mole of a metal M reacts completely with excess of fluorine to form 46.8g MF_2**

(a) **How many moles of F present in the sample of MF_2 that forms.**

Data: M   + F_2 → MF_2

Mole=0.6   excess   Mass= 46.8 g

calculation of Moles of F in MF_2

M   : MF_2

M   : MF_2

1 mole   :   1mole

0.600 mol   :   0.600 mo

Moles of MF_2 =   0.6 mole

Moles of F in MF_2 =   0.6x2=**1.2 mole**

(b) **Which element is represented by the symbol M?**

$$\text{Moles of } MF_2 = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{Molar mass} = \frac{\text{mass}}{\text{moles}}$$

$$= \frac{46.8}{0.600}$$

$$= 78g \text{ mole}^{-1}$$

Molar mass of MF_2 = 78

M + 2F   = 78

M + 2(19)   = 78

M   = 78 – 38 = 40

Molar mass of M   =   40 g mol^{-1}

Molar mass of '40' g mol^{-1} identifies Calcium (Ca)

14. **(a) Calculate the percentage of nitrogen in the four important fertilizer i.e.**

(i) NH_3 (ii) NH_2CONH_2 (iii) $(NH_4)_2SO_4$ (iv) NH_4NO_3

To Find: % age of Nitrogen =   ?

Formula: %age of Nitrogen $= \dfrac{\text{Mass of Nitrogen in fertilizer}}{\text{Molar mass}} \times 100$

(i) **NH_3 (Ammonia)**

        Molar mass of NH_3 $=$ $14 + 3 = 17 \text{ g mol}^{-1}$

        %age of Nitrogen $=$ $\dfrac{\text{Mass of Nitrogen in fertilizer}}{\text{Molar mass}} \times 100$

                                 $=$ $\dfrac{14}{17} \times 100 = \textbf{82.35 \%}$

(ii) **Urea (NH_2CONH_2)**

        Molar mass of NH_2CONH_2 $=$ 60 g mol^{-1}

        %age of N $=$ $\dfrac{28}{60} \times 100 = \textbf{46.67 \%}$

(iii) **$(NH_4)_2SO_4$ (Ammonium Sulphate)**

        Molar mass of $(NH_4)_2SO_4$ $=$ 132 g mol^{-1}

        %age of N $=$ $\dfrac{28}{132} \times 100 = \textbf{21.2 \%}$

(iv) **NH_4NO_3 (Ammonium Nitrate)**

        Molar mass of NH_4NO_3 $=$ 80 g mol^{-1}

        % age of N $=$ $\dfrac{28}{80} \times 100 = \textbf{35 \%}$

(b) Calculate the percentage of nitrogen and phosphorus in each of the following:

(i) $NH_4H_2PO_4$ **(ii)** $(NH_4)_2HPO_4$ **(iii)** $(NH_4)_3PO_4$

(i) **$NH_4H_2PO_4$ Ammonium hydrogen phosphate**

        Molar mass of $NH_4H_2PO_4$ $=$ 115 g mol^{-1}

        % age of N $=$ $\dfrac{14}{115} \times 100 = \textbf{12.17\%}$

        % age of P $=$ $\dfrac{31}{115} \times 100 = \textbf{26.96\%}$

(ii) **$(NH_4)_2HPO_4$ (Diammonium Hydrogen Phosphate)**

        Molar mass of $(NH_4)_2HPO_4 =$ 132 g mol^{-1}

        % age of N $=$ $\dfrac{28}{132} \times 100 = \textbf{21.21\%}$

        % age of P $=$ $\dfrac{31}{132} \times 100 = \textbf{23.48\%}$

(iii) **$(NH_4)_3PO_4$ (Ammonium Phosphate)**

Molar mass of $(NH_4)_3PO_4$ = $3(14 + 4) + 31 + 4 (16)$

= $3(18) + 31 + 64$

= $54 + 31 + 64 = 149$ g mol^{-1}

% age of N = $\frac{42}{149} \times 100$

= **28.19%**

% age of P = $\frac{\text{Mass of P}}{\text{Molar mass}} \times 100$

= $\frac{31}{149} \times 100$

= **20.8 %**

15. **Glucose $C_6H_{12}O_6$ is the most important nutrient in the cell for generating chemical potential energy. Calculate the mass % of each element in glucose and determine the number of C, H and O atoms in 10.5 g of the sample.**

Data: Mass of Glucose = 10.5 g

To Find:

(i) Mass % of each element in Glucose = ?

(ii) No. of atoms of C, H & O in 10.5g Glucose = ?

(i) Molar mass of $C_6H_{12}O_6$ = $72 + 12 + 96$

= 180 g mol^{-1}

% of C = $\frac{\text{Mass of Carbon}}{\text{Molar mass}} \times 100$

= $\frac{72}{180} \times 100 = $ **40 %**

% of H = $\frac{12}{180} \times 100 = $ **6.66 %**

% of O = $\frac{96}{180} \times 100 = $ **53.34 %**

(ii) Mass of glucose = 10.5g

Moles of glucose = $\frac{10.5}{180} = 0.058$ mol

1 mole glucose contain C-atoms = $6 \times 6.02 \times 10^{23}$

0.058 mole glucose contains C-atoms = $6 \times 6.02 \times 10^{23} \times 0.058$

= **2.1×10^{23} atoms**

1 mole glucose contains H-atoms = $12 \times 6.02 \times 10^{23} \times 0.058$

0.058 moles glucose contains H-atoms	=	$12 \times 6.02 \times 10^{23} \times 0.058$
	=	**4.2×10^{23} atoms**
1 mole $C_6H_{12}O_6$ contains O-atoms	=	$6 \times 6.02 \times 10^{23}$
0.058 mole $C_6H_{12}O_6$ contains O-atoms	=	$6 \times 6.02 \times 10^{23} \times 0.058$
	=	**2.1×10^{23} atoms**

16. Ethylene glycol is used as automobile antifreeze. It has 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. Its molar mass is 62.1 grams mol. Determine its empirical formula.

Data:

% of Carbon	=	38.7%
% of Hydrogen	=	9.7%
% of Oxygen	=	51.6%
Molar mass of Ethylene glycol	=	62.1 g mol^{-1}

To Find:

Empirical formula of Ethylene glycol	=	?
Molecular formula of Ethylene glycol	=	?

	C	:	H	:	O
Moles	$\dfrac{38.7}{12}$	:	$\dfrac{9.7}{1}$	:	$\dfrac{51.6}{16}$
	3.225	:	9.7	:	3.225
Mole ratios	$\dfrac{3.225}{3.225}$	:	$\dfrac{9.7}{3.225}$	:	$\dfrac{3.225}{3.225}$
Atomic ratio	1	:	3	:	1

Empirical formula of Ethylene glycol is CH_3O

Empirical formula mass = CH_3O = 12 + (1x 3) + 16 = 31 gmol^{-1}

Molecular Mass = n (Empirical Mass)

n= Molecular mass/ Empirical mass

n = 62.1 gmol^{-1} / 32 gmol^{-1}

n= 2

Molecular Formula = n (Empirical Formula)

= 2 (CH_3O)

Molecular Formula = $C_2H_6O_2$

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17. Serotenin (Molar mass = 176g mol-1) is a compound that conducts nerve impulses in brain and muscles. H contains 68.2% C, 6.86% H, 15.09% N and 9.089%O. What is its molecular formula?

Data: %ages of elements in Serotenin:

% age of Carbon	=	68.2%
% age of Hydrogen	=	6.86%
% age of Oxygen	=	9.08%
Molar mass of Serotenin	=	176 g mol^{-1}

To Find: Molecular formula of Serotenin = ?

i.   Finding empirical formula:

	C	:	H	:	N	:	O
Moles	$\dfrac{68.2}{12}$:		$\dfrac{6.86}{1}$:		$\dfrac{15.09}{14}$:		$\dfrac{9.08}{16}$
	5.68 :		6.86 :		1.08 :		0.57
Molar ratios	$\dfrac{5.68}{0.57}$:		$\dfrac{6.86}{0.57}$:		$\dfrac{1.08}{0.57}$:		$\dfrac{0.57}{0.57}$
Atomic ratio	10 :		12 :		2 :		1

Empirical formula is C$_{10}$H$_{12}$N$_2$O

ii.   Finding Molecular formula:

Empirical formula mass	=	120+12+28+16
	=	176g
$n = \dfrac{\text{Molar mass}}{\text{Empirical mass}}$	=	$\dfrac{176}{176} = 1$
Molecular formula	=	n × empirical formula
	=	1 (C$_{10}$H$_{12}$N$_2$O)

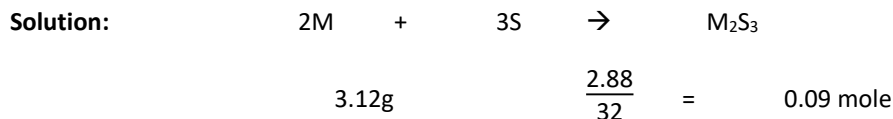**Molecular formula of Serotenin is C$_{16}$H$_{12}$N$_2$O**

18. An unknown metal M reacts with S to form a compound with a formula M$_2$S$_3$. If 3.12g of M reacts with exactly 2.88 g of Sulphur. What are the names of metal M and the compound M$_2$S$_3$.

Data:

Mass of M	=	3.12 g
Mass of S	=	2.88

To Find:

Unknown metal M	=	?
Compound M$_2$S$_3$	=	?

Solution: $2M$ $+$ $3S$ → M_2S_3

$3.12g$ $\dfrac{2.88}{32}$ $=$ 0.09 mole

Identification $=$?

S :   **M**

According to equation: $3mol$: 2 mol

$3/3$: $2/3$

1 : $2/3$

1×0.09 : $0.09 \times 2/3$

0.09 :   **0.06 mol**

Moles of M $=$ **0.06**

Moles $=$ $\dfrac{Mass}{Molar\ mass}$

Molar mass $=$ $\underline{Mass}$

Moles

$=$ $3.12/0.06 = 52$ g mol^{-1} = molar mass of Chromium

The metal 'M' is Chromium and compound 'M$_2$S$_3$' is Cr$_2$S$_3$

19. The octane present in gasoline burns according to the following equation

$$2C_8H_{18(l)} + 25O_{2(g)} → 16CO_{2(g)} + 18H_2O_{(l)}$$
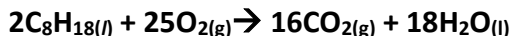
(a)   How many moles of O$_2$ are needed to react fully with 4 moles of octane?

$2C_8H_{18\,(l)} + 25O_{2\,(g)}$ → $16CO_{2\,(g)} + 18H_2O_{\,(l)}$
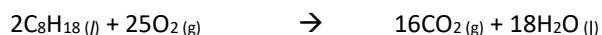
(Octane)

To Find: Moles of O$_2$ $=$?

2 moles of C$_8$H$_{18}$ need O$_2$ $=$ 25 mol

1 moles of C$_8$H$_{18}$ need O$_2$ $=$ $\dfrac{25}{2}$

4 moles of C$_8$H$_{18}$ need O$_2$ $=$ $\dfrac{25}{2} \times 4$

$=$ 50 moles of O$_2$ are required

(b) How many moles of CO$_2$can be produced from one mole of Octane?

To Find: Moles of CO$_2$ $=$?

2 moles C$_8$H$_{18}$ produce CO$_2$ $=$ 16 moles

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$$1 \text{ mole } C_8H_{18} \text{ produce } CO_2 \qquad = \qquad \frac{16}{2}$$

= 8 moles of CO_2 can be produced

(c)How many moles of water are produced by the combustion of 6 moles of Octane?

To Find: Moles of Water   =   ?

2 moles C_8H_{18} produce H_2O =   18 moles

$$1 \text{ mole } C_8H_{18} \text{ produce } H_2O \qquad = \qquad \frac{18}{2}$$

$$6 \text{ mole } C_8H_{18} \text{ produce } H_2O \qquad = \qquad \frac{18}{2} \times 6 = 54 \text{ moles of water are produced}$$

(d) If this reaction is to be used to synthesize 8 moles of CO_2, how many grams of

oxygen are needed? How many grams of octane will be used?

To Find:

Mass of Oxygen needed   =   ?

Mass of Octane used   =   ?

16 moles CO_2 need O_2 =   25 moles

$$8 \text{ moles } CO_2 \text{ need } O_2 \qquad = \qquad \frac{25}{16} \times 8 = 12.5 \text{ moles}$$

Mass of O_2 = $12.5 \times 32 =$ **400 g**

16 moles CO_2 need C_8H_{18} =   2 moles

$$8 \text{ moles } CO_2 \text{ need } C_8H_{18} \qquad = \qquad \frac{2}{16} \times 8 = 1 \text{ mol}$$

=   **114 g** mass of Octane used

20. Calculate the number of grams of Al_2S_3 which can be prepared by the reaction of 20g of Al and 30g of Sulphur. How much the non-limiting reactant is in excess?

Data:

2Al	+	3S	→	Al_2S_3
mass=20 g		mass=30 g		mass=?
molar mass=27 gmol^{-1}		molar mass=32 gmol^{-1}		molar mass=150 gmol^{-1}
mole=20/27		mole=30/32		
= 0.74mol		= 0.9375mol		
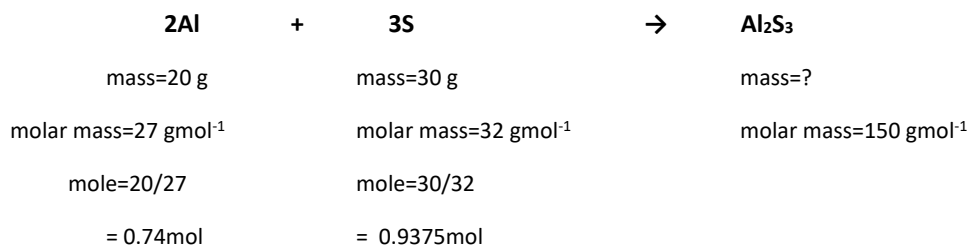
i. **Identification of limiting reactant and calculation of mass of Al_2S_3**

Solution: To identify limiting reactant moles of both reactants shall be compared with product

	Al	:	Al_2S_3
According to equation:	2 mole	:	1 mole
	2/2	:	1/2
	1	:	1/2
	1x0.74	:	0.74 x 1/2
	3.125	:	0.37 moles of Al_2S_3

	S	:	Al_2S_3
According to equation:	3 mole	:	1 mole
	3/3	:	1/3
	1	:	1/3
	0.9375 x 1	:	0.9375 x 1/3
		:	0.3125 moles of Al_2S_3

As number of moles of product obtained from Sulphur are less so Sulphur is limiting reactant.

Actually 0.3125 mole Al_2S_3 shall be obtained.

Mass of Al_2S_3	=	No. of moles $\times$ Molar mass
	=	0.3125×150
	=	**46.87 g**

ii. **Calculation of excess amount of non-limiting reactant:**

Solution: For this purpose, moles of both reactants shall be compared

	S	:	Al
According to equation:	3 mole	:	2 mole
	3/3	:	2/3
	1	:	2/3
	0.9375 x 1	:	0.9375 x 2/3
		:	0.625 moles of Al

For 0.9375 moles of S, we need only 0.623 moles of Al, however we have been provided 0.74 moles of Al.

Excess moles of Al	=	given mole- required mole
	=	0.74 - 0.625
	=	0.115
Excess mass of Al	=	mole x molar mass
	=	0.115 x 27
	=	**3.105 g**

21. A mixture of two liquids, hydrazine N_2H_4 and $N_2O_4$are used as a fuel in rockets. They produce N_2 and water vapors. How many grams of N_2 gas will be formed by reacting 100g of N_2H_4 and 200g of N_2O_4.

Data: $2N_2H_4 + N_2H_4 \rightarrow 3N_2 + 4H_2O$

mass of N_2H_4=100 g   mass of N_2O_4=200 g   mass=?

molar mass=32 gmol^{-1}molar mass= 92 gmol^{-1} Molar mass=28 gmol^{-1}

mole=100/32=3.125   mole=200/92=2.17

Identification of limiting reactant and calculation of mass of N_2:

Solution: To identify limiting reactant moles of both reactants shall be compared with product

	N_2H_4	:	N_2
According to equation:	2mol	:	3 mol
	2/2	:	3/2
	1	:	3/2
	1x3.125	:	3.125 x 3/2
	3.125mol	:	4.6875mol
	N_2O_4	:	N_2
According to equation:	1mol	:	3 mol
	1x 2.17	:	3x 2.17
	2.17	:	6.51 mol

As number of moles of product obtained from N_2H_4 are less so N_2H_4 is limiting reactant. Actually 4.6875 moles of N_2 shall be obtained.

Mass of N_2	=	No. of moles × Mol. Mass
	=	4.6875× 28
	=	**131.25 g**

22. Silicon Chloride (SiC) is an important ceramic material. It is produced by allowing sand (SiO$_2$) to react with carbon at high temperature.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

When 100kg sand is reacted with an excess of carbon, 51.4 kg of SiCis produced.

What is the % yield?

Data: SiO_2 +   3C $\rightarrow$ SiC   +   2CO

Mass=100Kg   mass = 51.4Kg

=100,000 g   = 514,00 g(Actual yield)

Molar mass= 60 gmol^{-1} Molar mass   = 40 gmol^{-1}

To Find: % age yield   =   ?

Formula: % age Yield : $\dfrac{\text{actual yield}}{\text{theoretical yield}}$ x 100

i.   Calculation of Theoretical yield of SiC

According to Equation

60g SiO$_2$ produces   =   40g SiC

100,000 g SiO$_2$ produces   = $\dfrac{40}{60}$ x 100,000

=   **66666.6 g SiC**

ii.   Calculation of % age yield of SiC

% age yield   = $\dfrac{\text{actual yield}}{\text{theoretical yield}} \times 100$

= $\dfrac{51400}{66666.6} \times 100$

=   **77.1 %**

Important long questions according to past papers.

1. Define mass spectrometer. Explain the construction and working of mass spectrometer.
2. Describe combustion analysis. OR How can the %age of Carbon, Hydrogen and Oxygen in the given organic compound be estimated by combustion analysis?
3. What is the difference between actual yield and theoretical yield?
4. Define limiting reactant. How is it helpful to control chemical reaction?
5. What is stoichiometry? Give its assumptions and relationships studied. Mention two important laws which help to perform the stoichiometric calculations.
6. Example# 5, 10, 11, 12, 13
7. Exercise Numerical 16, 17, 20, 21

Chapter 2

Experimental Techniques in Chemistry

Filtration

Definition

The process of filtration is used to separate insoluble particles from liquids.

Filter Media

The filter media used are:

a. Filter paper

b. Filter crucible

Nature of the precipitate and other factors dictate which filter medium must be used.

Filtration through Filter Paper

Filtration by a glass funnel and filter paper is usually a slow process. Filter papers are available in a variety of porosites (pore sizes). Which pore size is to be used, depends upon the size of particles in the precipitate.

Procedure

1. The mixture is poured onto the filter paper.
2. The solvent (water) passes through leaving behind the suspended particles on the filter paper. 3. The filter paper should be large enough so that it is one-fourth to one-half full of precipitate at the end of filtration.
4. The funnel should be large enough for its rim to extend 1 to 2 cm above the top circumference of the paper.
5. The stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.
6. The stem of the funnel should be several inches long so that it can extend a few centimeters down into the receiving beaker.
7. The tip should touch the side of the beaker. The filtrate runs down the side of beaker without splashing.

Folding of Filter Paper

The paper should be folded twice.
The first fold should be along the diameter of the paper.
The second fold should be such that edges do not quite match.
The paper should be opened on the slightly larger section. This provides a cone with three fold thickness halfway around and one thickness the other halfway around.
An apex angle very slightly greater than 60 degrees is formed.
The paper is inserted into 60 degree funnel, moistened with water and firmly pressed down.
The filtering operation should be aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper tightly fits all around its upper circumference.

Fluted Filter Paper

Ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained.

Advantage

The rate of filtration through conical funnel can be considerably increased using a fluted filter paper.

Filtration through Filter Crucibles

Another convenient way to filter a precipitate is by suction through a crucible.

Gooch Crucible

Assembly

It is made of porcelain having a perforated bottom which is covered with paper pulp or a filter paper cut to its size. Quick filtration can be done by placing the Gooch crucible in a suction filtering apparatus.

Advantage

1. It is useful for the filtration of precipitates, which need to be ignited at high temperature.
2. Concentrated HCl and $KMnO_4$ solutions are filtered by covering its perforations with asbestos mat.

Sintered Glass Crucible

Assembly

Sintered glass crucible is a glass crucible with a porous glass disc sealed into the bottom.

Advantage

It is very convenient to use because no preparation is needed as with the gooch crucible.

Crystallization

Definition

Crystallization is the removal of a solid from solution by increasing its concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals.

Principle

The solute should be soluble in a suitable solvent at high temperature and the excess amount of the solute is thrown out as crystals when it is cooled.

Choice of a Solvent

Following are the characteristics of an ideal solvent:

i. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.

ii. It should not react chemically with the solute.

iii. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.

iv. On cooling it should deposit well-formed crystals of the pure compound.

v. It should be inexpensive.

vi. It should be safe to use and should be easily removable.

Solvents Commonly Employed

Water, rectified spirit (95% ethanol), absolute ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, acetic acid and petroleum ether.

Preparation of the Saturated Solution

The substance is dissolved in a minimum amount of a suitable solvent and is heated directly or on a water bath with constant stirring. More solvent is added to the boiling solution until all the solute has dissolved.

Filtration

The hot saturated solution is filtered through a normal or a fluted filter paper to avoid the premature crystallization of the solute on the filter paper or in the funnel stem. Hot water funnel is used for this purpose.

Cooling

The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed. Slow cooling yields bigger crystals which include solvent and impurities.

Collecting the Crystals

When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump with full suction. The filter cake is pressed firmly with a cork to drain the left-

over liquid. The crystals are washed with a small portion of cold solvent and the process is repeated several times. The mother liquor is concentrated by evaporation and cooled to obtain a fresh crop of crystals.

Drying of the Crystallized Substance

The drying methods employed are:

1. Pressing it between several folds of filter papers and repeating the process several times.

Disadvantage

The crystals are crushed to a fine powder and sometimes the fibres of filter paper contaminate the product.

2. The crystals are dried in an oven provided the substance does not melt or decompose on heating at 100° C.

Best Method

3. A safe and reliable method of drying crystals is through a vacuum desiccator. The crystals are spread over a watch glass and kept in a vacuum desiccator for several hours.

Drying agents

$CaCl_2$, silica gel or phosphorus pentaoxide.

Decolourization of Undesirable Colours

The colouring matter or resinous products make the product coloured on crystallization. The product is boiled in the solvent with finely powdered animal charcoal. The hot solution is then filtered. The coloured impurities are adsorbed by animal charcoal and the pure decolourized substance crystallizes out on cooling.

Sublimation

Definition

It is a process in which a solid, when heated, vapourizes directly without passing through the liquid phase and these vapours can be condensed to form the solid again.

Use

It is frequently used to purify a solid.

Examples

Ammonium chloride, iodine, naphthalene, benzoic acid.

Procedure

The substance is taken in a watch glass covered with an inverted funnel. The substance is then heated slowly over a sand-bath and the funnel is cooled with wet cotton. The pure solid deposits on the inner side of the funnel.
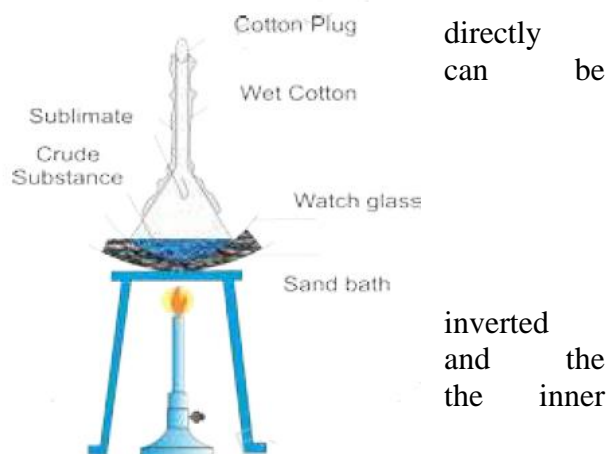
Solvent Extraction

Definition

A solute can be separated from a solution by shaking the solution with a solvent in which the solute is more soluble and the added solvent does not mix with the solution.

Apparatus used

Usually it is done by placing the solution and the second liquid into a separating funnel.

Example

Ether extraction

This is used to separate the products of organic synthesis from water. The aqueous solution containing the organic product is shaken up with ether in a separating funnel and allowed to separate.

Aqueous phase: Inorganic impurities

Ether layer by evaporation: Organic product

Efficiency of the process

Repeated extractions using small portions of solvent are more efficient than using a single but larger volume of solvent.

Applicability

The technique is particularly useful when the product is volatile or thermally unstable.

Distribution law or Partition law

This law states that a solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

Example

The distribution of iodine between two immiscible solvents, water in the presence of KI and carbon tetrachloride. Iodine reacts with iodide ion to produce tri-iodide ion in a reversible reaction.

$$I_2 + I^- (aq) \rightleftharpoons I_3^- (aq)$$

Soluble in CCl_4 Soluble in water
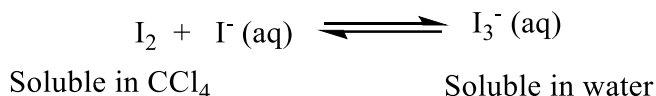
If we add CCl_4 to an aqueous solution of I_3^- ions, the iodine will transfer from the aqueous layer into the organic layer. The brown colour of the tri-iodide ions fades and the purple colour of free iodine molecules appears in organic phase. No matter how much iodine is used, the ratio of the final concentrations at equilibrium is constant. The constant is called distribution coefficient, K and is given by

$$K = \frac{[I_2(CCl_4)]}{[I_3^- (aq)]}$$

Chromatography

Definition

The word chromatography originates from the Greek word "Khromatos" meaning colour writing.

Primary use

Chromatography is a method used primarily for the separation of a sample of mixture.

It involves the distribution of a solute between a stationary phase and a mobile phase.

Stationary phase

The stationary phase may be a solid or a liquid supported as a thin film on the surface of an inert solid.

Mobile phase

The mobile phase flowing over the surface of the stationary phase may be a gas or a liquid.

In chromatography, substances are separated due to their relative affinities for the stationary and mobile phases.

Distribution coefficient

The distribution of the components of a mixture between the two phases is governed by distribution coefficient K.

$$K = \frac{\text{Concentration of a component in the moving phase}}{\text{Concentration of that component in the stationary phase}}$$

The component of a mixture with a small value of K mostly remains in the stationary phase. The component with a greater value of K remains largely dissolved in the mobile phase.

Types of chromatography

Adsorption chromatography

In it the stationary phase is a solid. A substance leaves the mobile phase to become adsorbed on the surface of the solid phase.

Partition chromatography

In it the stationary phase is a liquid. The substances being separated are distributed throughout both the stationary and mobile phases.

Techniques of Chromatography

Paper Chromatography

It is a technique of partition chromatography.

Stationary phase

The stationary phase is a liquid (say H_2O) adsorbed on paper. The adsorbed water behaves as an immiscible liquid towards the mobile phase, which passes over the paper.

Mobile phase

The mobile phase is usually an organic liquid.

Methods to Perform Chromatography

(i) ascending (ii) descending (iii) radial/circular.

Procedure

1. The solvent is in a pool at the bottom of a vessel in which the paper is supported and the solvent travels upwards by capillary action.

2. A solvent mixture is poured into the chromatographic tank.

3. Cover the tank to homogenize its inner atmosphere.

4. Take about 20 cm strip of Whatmann's chromatographic paper No.1 and draw on it a thin pencil line about 2.5 cm from one end.

5. Spot a point, on the pencil line, with the sample mixture solution.

6. Spots of the known compounds may also be placed alongside for identification.

7. When the spots have dried, suspend the paper with clips so that the impregnated end dips into solvent mixture to a depth of 5-6 mm.

8. Cover the tank.

9. As the solvent front passes the spots, the solutes begin to move upward.

10. The rate at which they move depends on their distribution coefficients.

11. When the solvent front has risen to about 3/4th of the length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry.

12. Once the paper is dried, the pattern on the paper is called a chromatogram.

13. The different components of the mixture, if coloured, can visually be identified.

14. If colourless, the chromatogram has to be developed by chemical methods or physical techniques used to identify the spots.

15. Each component has a specific retardation factor called R_f value. The R_f value is related to its distribution coefficient and is given by:

$$R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$$

Uses of Chromatography

- In organic synthesis for separation, isolation and purification of the products.
- In qualitative and quantitative analyses.
- For determination of the purity of a substance.
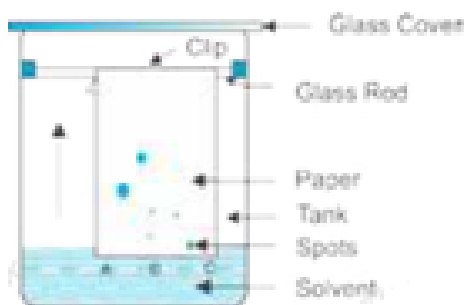
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Gases

Boyle's Law

Statement

Boyle's law is stated as follows:-

The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas.

Expression

$$V \alpha 1/P \qquad \text{(T \& n constant)}$$

$$V = k/P$$

$$PV = k \text{ ……. (1)}$$

'k' is proportionality constant.

The value of k is different for the different amounts of the same gas.

From eq (1) Boyle's law can be stated as:

The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity.

$$P_1V_1 = k \text{ and } P_2V_2 = k$$

$$P_1V_1 = P_2V_2$$

P_1= Initial value of pressure, V_1= Initial value of volume, P_2= Final value of pressure, V_2= Final value of volume

Experimental Verification of Boyle's Law

Let us take a gas in a cylinder having a moveable piston.
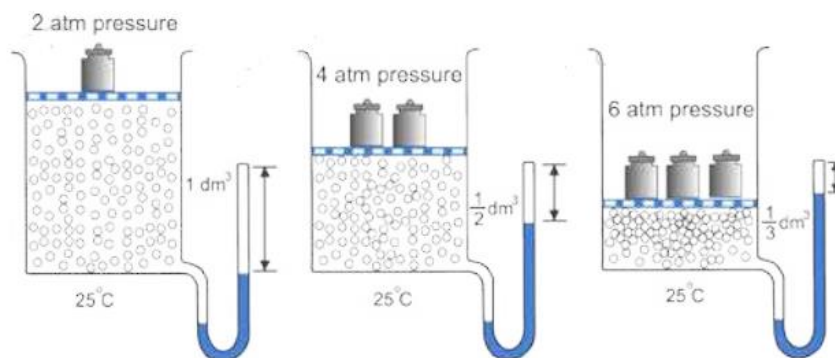
The cylinder is also attached with a manometer to read the pressure of the gas directly.

Experiment and Results

1. Let the initial volume of gas is 1 dm^3 and its pressure is 2 atmospheres when the piston has one weight on it.
2. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres.
3. When the piston is loaded with a mass three times greater, then the pressure becomes six atmospheres.

Calculations

$$P_1V_1 = 2 \text{ atm x } 1 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

$$P_2V_2 = 4 \text{ atm x } 1/2 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

$$P_3V_3 = 6 \text{ atm x } 1/3 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

Conclusion

At constant temperature the volume of a given quantity of a gas is reduced in proportion to the increase in pressure.

<center>**Boyle's law is verified**</center>

Graphical Explanation of Boyle's Law

Plot of pressure and volume at 0 ⁰C

- Take a particular amount of a gas at a constant temperature say 0 ⁰C and enclose it in a cylinder having a piston in it.
- Increase in pressure decreases the volume.
- If a graph is plotted between pressure on the x-axis and volume on the y-axis, then a curve is obtained.
- This curve is called isotherm "iso" means same, "therm" means heat.
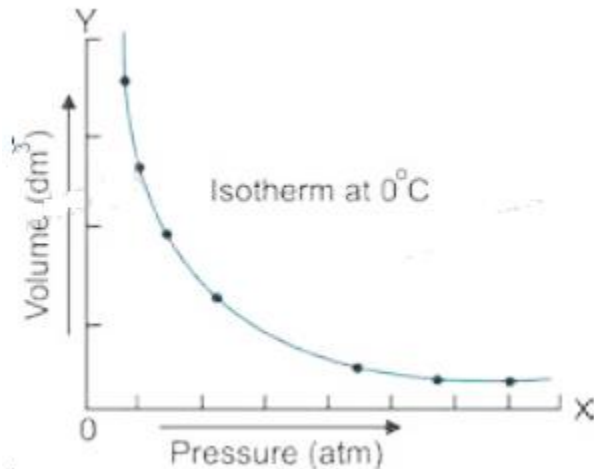
Plot of pressure and volume at 25 ⁰C

- Increase the temperature of the gas to 25°C.
- Keep this temperature constant and again vary the pressure and volume and plot the isotherm.
- It goes away from both the axes.
- The reason is that at higher temperature the volume of the gas has increased.
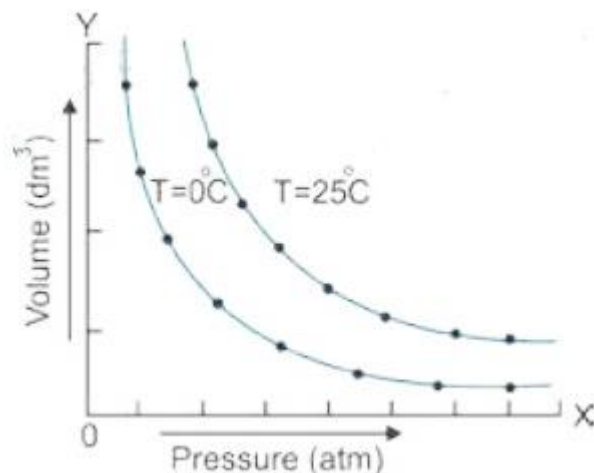
Plot of pressure and 1/volume

- If a graph is plotted between 1/V on x-axis and the pressure P on the y-axis then a straight line is obtained.
- This shows that the pressure and inverse of volume are directly proportional to each other.
- This straight line will meet at the origin which means that when the pressure is very close to zero, then the volume is so high that its inverse is very close to zero.
- By increasing the temperature of the same gas from T_1 to T_2 and keeping it constant, one can vary pressure and volume.
- The graph of this data between P and 1/V will give another straight line.
- This straight line at T_2 will be closer to the pressure-axis
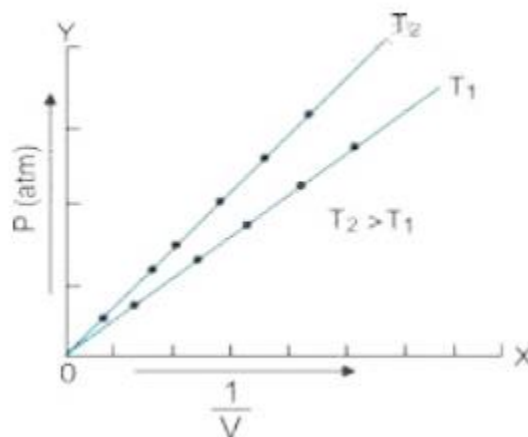
Plot of PV and P

- Plot a graph between pressure on x-axis and the product PV on Y-axis.
- A straight line parallel to the pressure axis is obtained.
- This straight line indicates that 'k' is a constant quantity.
- At higher constant temperature, the volume increase and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained.

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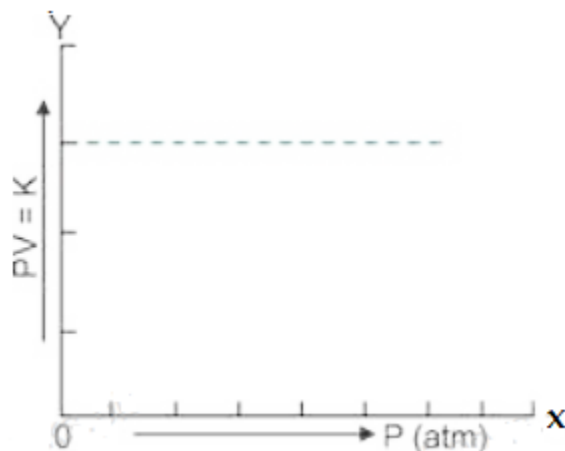
Charles's Law

Statement

Charles's law is stated as:

The volume of the given mass of a gas is directly proportional to the absolute temperature when the pressure is kept constant.

Expression

$$V \propto T \ (P \ \& \ n \ constant)$$

$$V = kT$$

$$V/T = k$$

If the temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2, then

$$V_1/T_1 = V_2/T_2 = k$$

$$V_1/T_1 = V_2/T_2$$

Experimental Verification of Charles's Law

Consider a certain amount of a gas enclosed in a cylinder fitted with a movable piston. The volume of the gas is V_1 and its temperature is T_1. When the gas in the cylinder is heated, both volume and the temperature of the gas increase.
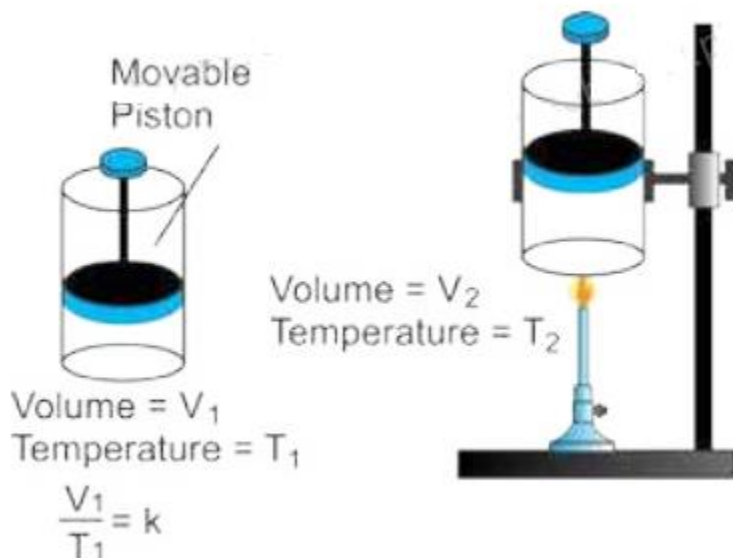
The new values of volume and temperature are V_2 and T_2, respectively.

Conclusion

The ratio of volume to temperature remains constant for same amount of gas at same pressure.

Charles' law is verified

Derivation of Absolute Zero

Quantitative Definition of Charles's Law

At constant pressure, the volume of the given mass of a gas increases or decreases by 1/273 of its original volume at 0 ⁰C for every 1 °C rise or fall in temperature, respectively.

General Equation for Calculating Volumes

$$V_t = V_o\left(1 + \frac{t}{273}\right)$$

V_t= volume of gas at temperature T

V_o= volume of gas at 0 ⁰C

t= Temperature on centigrade or Celsius scale

Celsius Scale does not Obey Charles' Law

Temperature volume data of a hypothetical gas is considered.

- At 0 ⁰C the volume of the gas taken is 546 cm^3 which is twice of 273 cm^3.
- At 273 ⁰C, the volume of the gas has doubled (1092 cm^3) and it should become practically zero at -273 ⁰C.
- Since original volume is 546 cm^3, so, for 1 ⁰C rise in temperature, 2 cm^3 increase in volume will take place.

- $2cm^3$ is the 1/273 of 546 cm^3.
- For 100 ºC rise in temperature, a change of 200 cm^3 will take place.
- The volume does not increase corresponding to increase in temperature on Celsius scale.
- The increase in temperature from 10 ºC to 100 ºC increases the volume from 566 cm^3 to 746 cm^3.

$$V_1/T_1 = V_2/T_2$$

$$566/10 \neq 746/100$$

Charles's law is not obeyed if temperature is measured on Celsius scale

Kelvin Scale Obeys Charles's Law

A new temperature scale was developed. It starts from 273 °C (more precisely -273.16 °C) which is called zero Kelvin or zero absolute.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = K$$

$$\frac{566}{283} = \frac{746}{373} = 2 = K$$

- **Development of Kelvin Scale**

A graph is plotted between the variables of Charles's law.
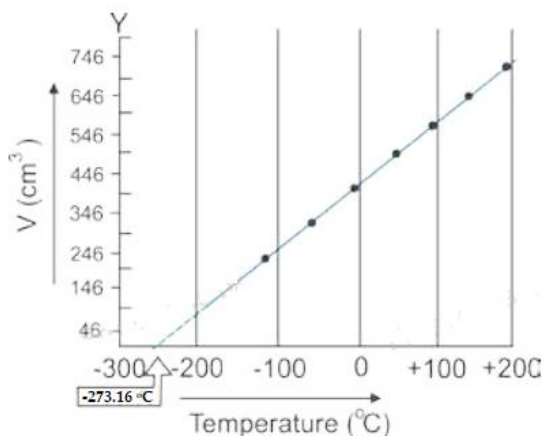
If we plot a graph between temperature on x-axis and the volume of one mole of an ideal gas on y-axis, we get a straight line which cuts the temperature axis at -273.16 °C by extrapolation method.

Greater the mass of gas taken, greater will be the slope of straight line as there will be greater number of moles and volume.

Absolute Zero

The temperature of 0K or -273.16 ⁰C is called absolute zero. This is the lowest possible temperature which would have been obtained if the substance remains in the gaseous phase. Actually all the gases are converted to liquid even before reaching this temperature. Real gases never attain this temperature.

General Gas Equation

Boyle's Law

According to Boyle's law:

$$V \propto \frac{1}{P} \quad \text{(when 'n' and 'T' are held constant)}$$

Charles's Law

According to Charles's law:

$$V \propto T \quad \text{(when n and P are held constant)}$$

Avogadro's Law

According to Avogadro's law:

$$V \alpha n \text{ (when P \& T are held constant)}$$

Combining the three equations

$$V \propto \frac{nT}{P}$$

$$V = \text{Constant } \frac{nT}{P}$$

The constant is 'R' which is called **general gas constant**

$$V = R \frac{nT}{P}$$

$$PV = nRT$$

This is called an ideal gas equation or general gas equation.
Reduction to Individual Laws

$$PV = nRT, \text{ when T and n are held constant, } PV = k \text{ (Boyle's law)}$$

$$V = R \frac{nT}{P}, \text{ when P and n are held constant, } V = kT \text{ (Charles's law)}$$

$$V = R \frac{nT}{P}, \text{ when P and T are held constant } V = kn \text{ (Avogadro's law)}$$

For one mole of a gas

$$PV = RT \text{ or } PV/T = R$$

The ratio of PV to T is a constant quantity (molar gas constant)

$$P_1V_1/T_1 = R \quad P_2V_2/T_2 = R$$

Therefore,

$$P_1V_1/T_1 = P_2V_2/T_2$$

Calculation of Ideal Gas Constant
According to STP
The volume of one mole of an ideal gas at STP (one atmospheric pressure and 273.16 K) is 22.414 dm^3.

$$R = \frac{PV}{nT}$$
$$R = \frac{1 \text{ atm} \times 22.414 \text{ dm}^3}{1 \text{ mole} \times 273.16 \text{ K}}$$
$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

Physical meaning of R
If we have one mole of an ideal gas at 273.16 K and one atmospheric pressure and its temperature is increased by 1 K, then it will absorb 0.0821 dm^3 -atm of energy, dm^3 -atm is the unit of energy in this situation.
Pressure in mm of mercury or torr and the volume in cm^3

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$
$$= 0.0821 \times 760 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1}$$
$$= 62.4 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1} \text{ Since, (1 mm of Hg = 1 torr)}$$
$$= 62.4 \text{ dm}^3 \text{ torr K}^{-1} \text{ mol}^{-1}$$
$$= 62400 \text{ cm}^3 \text{ torr K}^{-1} \text{ mol}^{-1} \text{ As, (1 dm}^3 = 1000 \text{ cm}^3)$$

According to SI units
The SI units of pressure are Nm^{-2} and of volume are m^3. By using Avogadro's principle:

$$1 \text{ atm} = 760 \text{ torr} = 101\,325 \text{ Nm}^{-2}$$

$$1\text{m}^3 = 1000 \text{ dm}^3$$

$$n = 1 \text{ mole}$$

$$T = 273.16 \text{ K}$$

$$P = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$$

$$V = 22.414 \text{ dm}^3 = 0.022414 \text{ m}^3$$

Putting their values, alongwith units.

$$R = \frac{PV}{nT} = \frac{101325 \text{ N m}^{-2} \times 0.02241 \text{ m}^3}{1 \text{ mol} \times 273.16 \text{ K}}$$

$$R = 8.3143 \text{ Nm K}^{-1} \text{ mol}^{-1} = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \ (1 \text{ Nm} = 1\text{J})$$

Since $1\text{cal.} = 4.18 \text{ J}$

$$\text{so } R = \frac{8.3143}{4.18} = 1.989 \text{cal K}^{-1} \text{mol}^{-1}$$

Dalton's Law of Partial Pressures

Statement
The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures.

Explanation
Let the gases are designated as 1,2,3, and their partial pressures are p_1, p_2, p_3. The total pressure (P_t) of the mixture of gases is given by:

$$P_t = p_1 + p_2 + p_3$$

Partial pressure
The partial pressure of a gas in a mixture of gases is the pressure that it would exert on the walls of the container, if it were present all alone in that same volume under the same temperature.

Example
Take four cylinders of 10 dm^3 each and three gases H_2, CH_4 and O_2 are separately enclosed in first three of them at the same temperature. Let their partial pressures be 400 torr, 500 torr and 100 torr, respectively. All these gases are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law:

$$P_t = p_{H2} + p_{CH4} + p_{O2} = (400 + 500 + 100) \text{ torr}$$
$$P_t = 1000 \text{ torr}$$

The total pressure is the result of total number of collisions per unit area in a given time.

Application of general gas equation to individual gases

Adding these three equations

$$P_t = p_{H_2} + p_{CH_4} + p_{O_2}$$

$$P_t = (n_{H_2} + n_{CH_4} + n_{O_2}) \frac{RT}{V}$$

$$P_t = n_t \frac{RT}{V} \qquad \text{where } n_t = n_{H_2} + n_{CH_4} + n_{O_2}$$

$$P_t V = n_t RT$$

The total pressure of the mixture of gases depends upon the total number of moles of the gases.

Calculation of Partial Pressure of a Gas

Suppose we have a mixture of gas A and gas B. This mixture is enclosed in a container having volume (V). The total pressure is one atm. The number of moles of the gases A and B are n_A and n_B, respectively. If they are maintained at temperature T, then

$$P_t V = n_t RT \dots.. \text{(equation for the mixture of gases)}$$
$$p_A V = n_A RT \dots\dots. \text{(equation for gas A)}$$
$$p_B V = n_B RT \dots\dots.. \text{(equation for gas B)}$$

Divide the first two equations

$$\frac{p_A V}{P_t V} = \frac{n_A RT}{n_t RT}$$

$$\frac{p_A}{P_t} = \frac{n_A}{n_t}$$

$$p_A = \frac{n_A}{n_t} P_t$$

$$p_A = x_A \, P_t \qquad (x_A \text{ is mole fraction of gas A})$$

$$p_B = x_B \, P_t$$

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure of the mixture. Mole fraction of any one gas in the mixture is less than unity. The sum of mole fractions is always equal to unity.

Applications of Dalton's Law of Partial Pressures

1. Collection of gases over water

Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is the sum of the partial pressures of the dry gas and water vapours. The partial pressure exerted by the water vapours is called aqueous tension.

$$P_{moist} = p_{dry} + p_{w.vap}$$
$$P_{moist} = p_{dry} + \text{aqueous tension}$$
$$p_{dry} = P_{moist} - \text{aqueous tension}$$

2. Process of respiration

The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of oxygen in the lungs is 116 torr. Carbon dioxide produced during respiration moves out in the opposite direction, as its partial pressure is more in the lungs than that in air.

3. Breathing at higher altitudes

At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

4. Breathing under sea

Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. In sea, after every 100 feet depth, the diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. The pressure of N_2 increases in depth of sea and it diffuses in the blood.

Graham's Law of Diffusion

Statement

The rate of diffusion or effusion of a gas is inversely proportional to the square root of its density at constant temperature and pressure.

Expression

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \quad \text{(at constant temperature and pressure)}$$

$$\text{Rate of diffusion} = \frac{k}{\sqrt{d}}$$

$$\text{Rate of diffusion} \times \sqrt{d} = k$$

$$\text{or Rate} \times \sqrt{d} = k$$

The constant k is same for all gases, when they are all studied at the same temperature and pressure.

Explanation

Let us have two gases 1 and 2, having rates of diffusion as r_1 and r_2 and densities as d_1 and d_2 respectively.

According to Graham's law

$$r_1 \times \sqrt{d_1} = k$$

$$r_2 \times \sqrt{d_2} = k$$

Divide the two equations and rearrange

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

The density of a given gas is directly proportional to its molecular mass. Graham's law of diffusion can also be written as follows:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Where M_1 and M_2 are the molar masses of gases.

Demonstration of Graham's Law

1. Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously.
2. HCl molecules travel a distance of 40.5 cm while NH_3 molecules cover 59.5 cm in the same duration.
3. They produce dense white fumes of ammonium chloride at the point of junction.

Calculations through Law

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}}$$

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

$$1.46 = 1.46$$
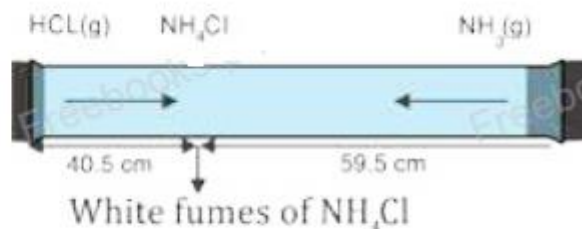
Graham's Law is verified

Kinetic Molecular Theory of Gases

History

For illustrating the behaviour of gases quantitatively, Bernoulli (1738) put forward kinetic molecular theory of gases. Clausius (1857) derived the kinetic equation and deduced all the gas laws from it. The theory was elaborated and extended by Maxwell, who gave the law of distribution of velocities. Boltzmann also contributed and studied the distribution of energies among the gas molecules. Among some other names Van der Waal is the prominent scientist in this field.

Postulates of Kinetic Molecular Theory

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have monoatomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of the gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.
8. The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

Kinetic Equation of Gas

R.J Clausius deduced an expression for the pressure of an ideal gas. Due to the collisions of gas molecules, a force is exerted on the walls of the container. This force when divided by the area of the vessel gives force per unit area, which is called pressure. In this way, the final form of kinetic equation is as follows:

$$PV = \frac{1}{3} mN\overline{c^2}$$

P = pressure
V = volume
m = mass of one molecule of the gas
N = number of molecules of gas in the vessel
$\overline{c^2}$ = mean square velocity

Explanation of Gas Laws from Kinetic Theory of Gases

(a) Boyle's Law

The kinetic energy is directly proportional to the absolute temperature of the gas. The kinetic energy of N molecules is:

$$\frac{1}{2} mN\overline{c^2}$$

$$\frac{1}{2} mN\overline{c^2} \propto T$$

$$\frac{1}{2} mN\overline{c^2} = kT$$

Where k is the proportionality constant. According to the kinetic equation of gases:

$$PV = \frac{1}{3} mN\overline{c^2}$$

Multiplying and dividing by 2 on right hand side

$$PV = \frac{2}{3} \left(\frac{1}{2}mN\overline{c^2}\right)$$

$$PV = \frac{2}{3} kT$$

If the temperature (T) is constant then right hand side of equation 2/3 kT is constant. Let that constant be k'.
So, PV = k' (which is Boyle's law)
Hence at constant temperature and number of moles, the product PV is a constant quantity.

(b) Charles' Law
Consider the following equation:

$$PV = \frac{2}{3} kT$$

$$V = \frac{2}{3} \frac{kT}{P} = \left(\frac{2k}{3P}\right) T$$

At constant pressure. Therefore,

$$\frac{2k}{3P} = k'' \text{ (a new constant)}$$

$$V = k'' T$$

$$\frac{V}{T} = k'' \text{ (which is Charles's law)}$$

(c) Avogadro's Law

Consider two gases 1 and 2 at the same pressure P and having the same volume V. Their number of molecules
are N_1 and N_2, masses of molecules are m_1 and m_2 and mean square velocities are $\overline{c_1^2}$ $\overline{c_2^2}$
  Their kinetic equations can be written as follows:

$$PV = \frac{1}{3} m_1 N_1 \overline{c_1}^2 \text{ for gas(1)}$$

$$PV = \frac{1}{3} m_2 N_2 \overline{c_2}^2 \text{ for gas(2)}$$

$$\text{Equalizing } \frac{1}{3} m_1 N_1 \overline{c_1}^2 = \frac{1}{3} m_2 N_2 \overline{c_2}^2$$

$$\text{Hence, } m_1 N_1 \overline{c_1}^2 = m_2 N_2 \overline{c_2}^2 \qquad \cdots$$
$$\text{(eq 1)}$$

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2} m_1 \overline{c_1}^2 = \frac{1}{2} m_2 \overline{c_2}^2$$

$$m_1 \overline{c_1}^2 = m_2 \overline{c_2}^2$$
$$\text{(eq 2)}$$

Dividing eq (1) by eq (2)
$$N_1 = N_2$$

Equal volumes of all the gases at the same temperature and pressure contain equal number of molecules, which
is Avogadro's law.

(d) Graham's Law of Diffusion

$$PV = \frac{1}{3} mN\overline{c^2}$$

Applying the kinetic equation

$$PV = \frac{1}{3} mN_A \overline{c^2}$$

If we take one mole of a gas having Avogadro's number of molecules (N = NA) then the equation can be written as:

$$PV = \frac{1}{3} M\overline{c^2} \quad (M = mN_A)$$

$$\overline{c^2} = \frac{3PV}{M}$$

Where M is the molecular mass of the gas. Taking square root:

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3PV}{M}}$$

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad (\frac{M}{V} = d)$$

'V' is the molar volume of gas at given conditions. Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas.

$$\sqrt{\overline{c^2}} \propto r$$

$$r \propto \sqrt{\frac{3P}{d}}$$

At constant pressure

$$r \propto \sqrt{\frac{1}{d}}$$

Graham's law verified.

Kinetic Interpretation of Temperature

According to kinetic molecular theory of gases the molecules of a gas move randomly with elastic collisions. The kinetic equation of gases can be re-written as:

$$PV = \frac{1}{3} mN\overline{c^2}$$

Here m is the mass of one molecule of the gas, N is the number of molecules in the vessel and $\overline{c^2}$ is their mean square velocity. The average kinetic energy associated with one molecule of a gas due to its translational motion is given by the following equation.

$$E_k = \frac{1}{2} m\overline{c^2} \qquad \text{(eq 1)}$$

E_k is the average translational kinetic energy of gas molecules.

$$PV = \frac{2}{3} N \left(\frac{1}{2} m\overline{c^2} \right) \qquad \text{(eq 2)}$$

$$PV = \frac{2}{3} N E_k$$

To get insight into the meaning of temperature consider one mole of a gas.

$$N = N_A$$

$$PV = \frac{2}{3} N_A E_k$$

According to the general gas equation for one mole of a gas

$$PV = RT$$

Hence,

$$\frac{2}{3} N_A E_k = RT$$

$$E_k = \frac{3R}{2N_A} T$$

A new definition of temperature

The kelvin temperature of a gas is directly proportional to the average translational kinetic energy of its molecules. This suggests that a change in temperature means change in the intensity of molecular motion.

Linde's Method of Liquefaction of Gases

Principle

Joule-Thomson Effect

When a compressed gas is allowed to expand into a region of low pressure it gets cooled.

Assembly

The assembly consists of the following parts:

1. Compressor
2. Refrigerating liquid
3. Spiral tube
4. Expansion chamber

Working

1. Air is compressed to about 200 atmospheres.
2. It is passed though water cooled pipe where the heat of compression is removed.
3. It is then allowed to pass through a spiral pipe having a jet at the end.
4. When the air comes out of the jet the expansion takes place from 200 atm to 1 atm leading to fall of temperature.
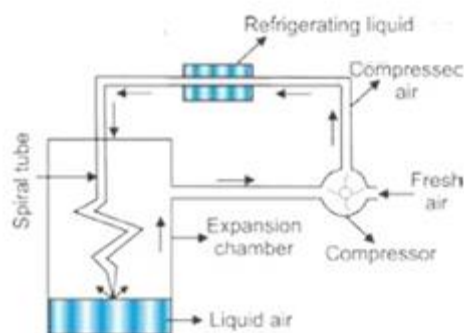
5. This cooled air goes up and cools the incoming compressed air.
6. It returns to the compression pump.
7. This process is repeated again and again.
8. The liquid air is collected at the bottom of the expansion chamber.

All gases except H_2 and He can be liquefied by this procedure.

Van der Waals Equation for Real Gases

Volume Correction

Compression of gas

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them.

The molecules have definite volume, no doubt very small as compared to the vessel, but it is not negligible.

Van der Waals postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas.

b= The effective volume of the molecules per mole of a gas

b= excluded volume which is constant and characteristic of a gas. Its value depends upon the size of gas molecules.

The volume available to gas molecules is the volume of the vessel minus the volume of gas molecules.

$$V_{free} = V_{vessel} - b$$

V_{free}= volume available to the gas molecules.
The excluded volume b is not equal to the actual volume of gas molecules.
It is four times the actual volume of molecules.

$$b= 4V_m$$

V_m= volume of one mole of gas molecules in a highly compressed state but not liquid state.

Pressure Correction
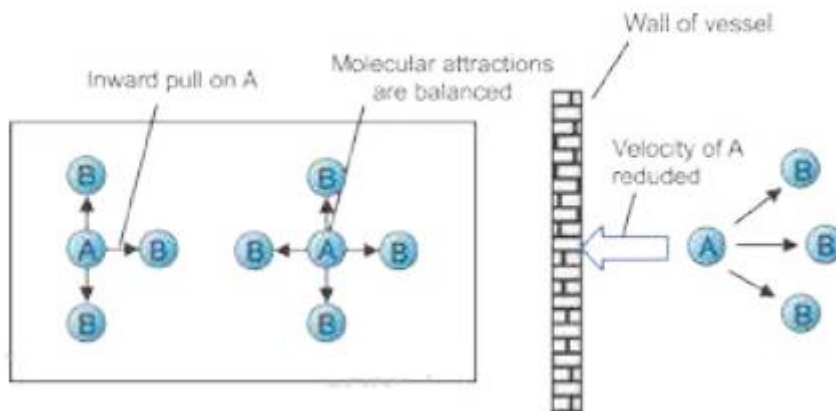
A molecule in the interior of a gas is attracted by other molecules on all sides, so the attractive forces are cancelled out. When a molecule strikes the wall of a container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall.

Explanation

Consider the molecule "A" which is unable to create pressure on the wall due to the presence of attractive forces due to 'B' type molecules. Let the observed pressure on the wall of the container is P. This pressure is less than the actual pressure Pi, by an amount P', so

$$P = P_i - P'$$

P_i= true kinetic pressure if the forces of attraction would have been absent.
P'= lessened pressure due to attractive forces

$$P_i = P + P'$$

The pressure P for one mole of a gas used up against intermolecular attractions should decrease as volume increases. The value of P' in terms of a constant 'a' which accounts for the attractive forces and the volume V of vessel can be written as:

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$$P' = \frac{a}{V^2}$$

Proof

P' is determined by the forces of attraction between molecules of type A, which are striking the wall of the container and molecules of type B, which are pulling them inward. The net force of attraction is proportional to the concentrations of A type and B type molecules.

$$P' \propto C_A . C_B$$

n= the number of moles o f A and B separately and total volume of both types of molecules is 'V'.
V= total volume of both types of molecules
n/V= moles dm^{-3}

$$P' \propto \frac{n}{V} . \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' \propto \frac{an^2}{V^2}$$

'a' is a constant of proportionality

If, n = 1 (one mole of gas)

$$P' = \frac{a}{V^2}$$

Greater the attractive forces among the gas molecules, smaller the volume of vessel, greater the value of lessened pressure P'.
a= coefficient of attraction or attraction per unit volume. It has a constant value for a particular real gas.

$$P_i = P + \frac{a}{V^2}$$

Van der Waal's Equation
Putting the values in PV = nRT

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For 'n' moles of a gas $\qquad \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

Units of a

$$P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P'V^2}{n^2}$$

$$a = \frac{atm \times (dm^3)^2}{(mol)^2}$$

$$a = atm\ dm^6\ mol^{-2}$$

In S.I. units, pressure is in Nm^{-2} and volume in m^3

$$a = \frac{Nm^{-2} \times (m^3)^2}{(mol)^2}$$

$$a = Nm^{+4}\ mol^{-2}$$

Units of b

$dm^3\ mol^{-1}$ or $m^3\ mol^{-1}$

Plasma State

Plasma is the "fourth state of matter". Plasma was identified by the English scientist William Crookes in 1879.
Definition
The ionized gas mixture, consisting of ions, electrons and neutral atoms is called plasma.
<div align="center">OR</div>
Plasma is a distinct state of matter containing a significant number of electrically charged particles a number sufficient to affect its electrical properties and behaviour.
Formation of Plasma

When more heat is supplied, the atoms or molecules may be ionized. The atom loses one electron and develops a net positive charge. It becomes an ion. In a sufficiently heated gas, ionization happens many times, creating clouds of free electrons and ions. All the atoms are not ionized, and some of them remain completely intact with no net charge.

Diatomic molecules (25°C)

Atomic hydrogen 2000°C

Ions, electrons (plasma) 100,000°C
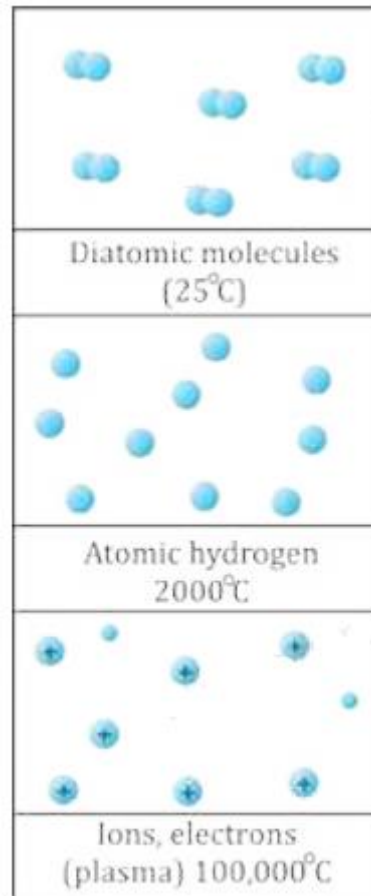
Natural and Artificial Plasma
Characteristics of Artificial Plasma
Artificial plasma can be created by ionization of a gas as in neon signs.
Plasma at low temperatures is hard to maintain because outside a vacuum low temperature plasma reacts rapidly with any molecule it encounters.
Characteristics of Natural Plasma
Natural plasma exists only at very high temperatures, or low temperature vacuums.
Natural plasma does not breakdown or react rapidly, but is extremely hot (over 20,000°C minimum).
Their energy is so high that they vaporize any material they touch.
Characteristics of Plasma
1. Electromagnetically responsive
Plasma must have sufficient number of charged particles. It exhibits a collective response to electric and magnetic fields. The motion of the particles in the plasma generates fields and electric currents from within plasma density. It refers to the density of the charged particles. This complex set of interactions makes plasma a unique, fascinating, and complex state of matter.
2. Macroscopically neutral
It is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.
Existence of Plasma
1. Entire universe is almost of plasma.
2. Plasmas are found in everything from the sun to quarks.
3. It is the stuff of stars. A majority of the matter in inner-stellar space is plasma.

4. The sun is a 1.5 million kilometer ball of plasma heated by nuclear fusion.
5. On earth it only occurs in a few limited places, like lightning bolts, flames, auroras, and fluorescent lights.
6. When an electric current is passed through neon gas, it produces both plasma and light.

Applications of Plasma

In fluorescent light bulbs

Inside the long tube of a fluorescent light bulb is a gas. When the light is turned on, electricity flows through the tube. This electricity charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.

In neon signs

Neon signs are glass tubes filled with gas. When they are turned on then the electricity flows through the tube. The electricity charges the gas and creates a plasma inside the tube. The plasma glows with a special colour depending on what kind of gas is inside.

Generation of electrical energy

It generates electrical energy from fusion pollution control and removal of hazardous chemicals.

Use in offices and homes

Plasma light up our offices and homes, make our computers and electronic equipment work.

Use in lasers and particle accelerator

They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant.

Miscellaneous uses

They find applications such as plasma processing of semiconductors, sterilization of some medical products, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches.

Future Horizons

The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which create molecules in metastable state. These metastable molecules survive long enough to react with designated molecules and are selective in their reactivity. They give solution to radioactive contamination. Scientists are experimenting with mixtures of gases to work as metastable agents on plutonium and uranium.

Numericals

5. **(b) A sample of carbon monoxide gas occupies 150.0ml at 25.0⁰C. It is then cooled at constant pressure until it occupies 100.0 ml. What is the new temperature?**

Data:

V_1 = 150 cm³

T_1 = 25°C + 273 = 298K

V_2 = 100 cm³

To Find: T_2=?

Formula:

Using the equation from Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Solution: $T_2 = \dfrac{V_2 \times T_1}{V_1}$

$T_2 = \dfrac{100 \times 298}{150}$ =**198.6 K**

As K = °C + 273

°C = K − 273 = 198.6 − 273 = −**74.3⁰C**

16. **Helium gas in 100cm³ container at a pressure of 500 torris transferred to a container with a volume of 250 cm³. What will be the new pressure?**

(a) No change in temperature occurs (Isothermal: Boyle's Law)

Data:
Initial volume of He gas $= V_1 = 100 cm^3$
Initial pressure of He gas $= P_1 = 500$ torr
Final volume of He gas $= V_2 = 250 cm^3$
To Find: Final pressure of He gas $= P_2 = ?$

Formula: $P_1 V_1 = P_2 V_2$

Solution: $P_2 = \dfrac{P_1 V_1}{V_2}$

$P_2 = \dfrac{500 \text{ torr} \times 100 \text{ cm}^3}{250 cm^3}$

$P_2 = \textbf{200 tor}$

(b) When the temperature changes from $T_1 = 20^{\circ}C$ to $T_2 = 15^{\circ}C$. Then general gas equation for one mole is to be applied.

T_1	=	$20^{\circ}C$
T_2	=	$15^{\circ}C$
T_1	=	$20^{\circ}C + 273 = 293$ K
T_2	=	$15^{\circ}C + 273 = 288$ K

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{V_2}$$

$$P_2 = \frac{500 \times 100}{293} \times \frac{288}{250}$$

$$= \textbf{196.58 torr}$$

17. **What are the densities in Kgm^{-3} for following gases at S.T.P (P = 101325 Nm^{-2} T = 273 K, Molecular mass are in $Kg.mol^{-}$ (i)Methane (ii)Oxygen(iii)Hydrogen**

(i)

Data: Temperature of CH_4 = 273 K
Pressure of CH_4 = 101325 Nm^{-2}
General gas constant R = 8.3143 $JK^{-}mol^{-}$

Convert gram into kilogram
Molar mass of CH_4 = 16 $gmol^{-}$
= 16×10^{-3} kg mol

Formula: $d = \dfrac{PM}{RT}$

Soultion:

$d = \dfrac{101325 Nm^{-2} \times 16 \times 10^{-3} \text{ kg mol}^{-1}}{8.3143 JK^{-1} mol^{-1} \times 273K}$

$$d = \frac{101325 Nm^{-2} \times 16 \times 10^{-3} \text{ kg}}{8.3143 \times 273 Nm}$$

As J = N.m

$$d = \frac{1621.2}{2269.8}$$

$$= \mathbf{0.714 \text{ kg m}^{-3}}$$

(ii)
Data: Convert gram into kilogram

Molar mass of O_2 = 32 $gmol^{-1}$

= 32×10^{-3} kg mol^{-1}

Formula: $d = \dfrac{PM}{RT}$

Solution:

$$d = \frac{101325 Nm^{-2} \times 2 \times 10^{-3} \text{ kg mol}^{-1}}{8.3143 JK^{-1} \text{ mol}^{-1} \times 273K}$$

$$d = \frac{101325 \times 2 \times 10^{-3}}{8.3143 \times 273K} \frac{Nm^{-2} \times \text{ kg}}{J}$$

Since J = Nm

$$d = \frac{3242.4}{2269.8} \text{ Kgm}^{-3}$$

$$= \mathbf{1.428 \text{ kg m}^{-3}}$$

(iii)
Data: Convert gram into kilogram

Molar mass of H_2 = 2 $gmol^{-1}$

= 2×10^{-3} kg mol^{-1}

Formula: $d = \dfrac{PM}{RT}$

Solution: $d = \dfrac{101325 Nm^{-2} \times 2 \times 10^{-3} \text{ kg mol}^{-1}}{8.3143 JK^{-1} \text{ mol}^{-1} \times 273K}$

$$d = \frac{101325 \times 2 \times 10^{-3}}{8.3143 \times 273K} \frac{Nm^{-2} \times \text{ kg}}{J}$$

Since J = Nm

$$d = \frac{202.65}{2269.8}$$

$$= \mathbf{0.089 \text{ kgm}^{-3}}$$

Compare the values of densities in proportion to their mole masses.

Ans.

d_{H_2}	:	d_{CH_4}	:	d_{O_2}
0.089	:	0.714	:	1.428
0.089/0.089	:	0.714/0.089	:	1.428/0.089
1	:	8	:	16

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> **How do you justify that increase of volume up to 100 dm³ at 27°C of 2 moles of NH₃ will allow the gas behave ideally, as compared to S.T.P conditions.**

Ans.

> 2 moles of NH_3 at 0°C and 1 atm pressure will be having volume around 44.828 dm^3. Under these conditions it will be close to ideal behavior, but not perfect ideal. The reason is that NH_3 is a polar gas and same forces of attractions are present at 0°C.
>
> When the temperature is increased to 27°C and volume is increased upto 100 dm^3 , then NH_3 will definitely behave more ideally.

18. A sample of Krypton with a volume of 6.25 dm³ and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm³ and a pressure of 375 torr. What will be its final temperature (in °C)

Data:

> Initial volume of gas = V_1= 6.25 dm^3
> Initial pressure of gas = P_1 =765 torr
> Initial pressure of gas = T_1=20°C
> Final volume of gas = V_2= 9.55 dm^3
> Final pressure of gas=P_2 =375 torr
>
> Initial pressure of gas = T_1 =20°C + 273
> $\qquad\qquad\qquad\qquad$ = 293 K
>
> **To Find:** Final temperature of gas = T_2= ?
>
> **Formula:** $\qquad \dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$
>
> **Solution:** $\qquad T_2 \qquad = \dfrac{P_2V_2}{P_1V_1} \times T_1$
>
> $\qquad T_2 \quad = \dfrac{375 \text{torr} \times 9.55 \text{ dm}^3 \times 293\text{K}}{765 \text{ torr} \times 6.25\text{dm}^3}$
>
> $\qquad\quad = \dfrac{375 \times 9.55 \times 293}{765 \times 6.25} \text{K}$
>
> $\qquad T_2 \quad = \qquad 219.5$
> $\qquad T_2 \quad = \qquad 219.5 - 273$
> $\qquad\qquad\quad = \qquad \mathbf{-53.5°C}$

19. Working at a vacuum line a chemist isolated a gas in weighing bulb with a volume of 255 cm³ at a temperature of 25°C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. what was the formula mass of this gas?

Data:

Pressure of gas $\qquad\qquad$ = $\qquad$ 10 torr

= $\dfrac{10}{760}$ = 0.0132atm

Volume of gas $\qquad\qquad$ = $\qquad$ 255 cm^3 = 0.255 dm^3

Temperature of gas $\qquad$ = $\qquad$ 25°C

$\qquad\qquad\qquad\qquad\qquad$ = $\qquad$ 25°C + 273 = 298 K

Mass of gas $\qquad\qquad\quad$ = $\qquad$ 12.1 mg = 0.0121 g

General Gas Constant(R) $\quad$ = $\qquad$ 0.0821 dm^3atmK^{-1}mol^{-1}

To Find: Formula mass (M) = ?

Formula: $PV = \dfrac{m}{M}RT$

Solution: $M = \dfrac{WRT}{PV}$

$$M = \frac{0.0121\text{g} \times 0.0821\text{dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}\text{ 298k}}{0.0132\text{ atm} \times 0.255\text{dm}^3}$$

$$= \frac{0.0121 \times 0.0821 \times 298}{0.0132\text{ atm} \times 0.255}\text{ gmol}^{-1}$$

$$M = \frac{0.296}{0.003366} = \textbf{87.93 gmol}^{-1}$$

20. What pressure is exerted by a mixture of 2.00g of H_2 and 8.00g of N_2 at 273K in a 10 dm^3 vessel?

Data:

Mass of H_2	=	2.00g
Mass of N_2	=	8.00 g
Temperature of mixture	=	273K
Volume of the gas	=	10dm^3

To Find: Pressure of mixture of gases = ?

Formula: $PV = nRT$

Solution: $P = \dfrac{nRT}{V}$

Calculation of moles:

First of all convert masses of H_2 and N_2 into moles.

Number of moles of H_2 = $\dfrac{\text{Mass of } H_2}{\text{Molar mass of } H_2}$

Since, molar mass of H_2 = 2.00g mol^{-1}
Putting the values

Number of moles of H_2 = $\dfrac{2.00}{2.00}$ = 1 mole

Mass of N_2 = 8.00g

Number of moles of N_2 = $\dfrac{\text{Mass of } N_2}{\text{Molar Mass of } N_2}$

Putting the values

Number of moles of N_2 = $\dfrac{8.00}{28}$ = 0.286

To calculate pressure of mixture of gases, we take total number of moles.

Total number of moles = 1 + 0.286 = **1.286**

Calculation of total pressure of gaseous mixture:

$$P = \frac{1.286 \text{ moles} \times 0.0821 \text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 273 \text{K}}{10 \text{dm}^3}$$

$$= \frac{28.82}{10} \text{ atm} = \textbf{2.88 atm}$$

21. (a) The relative densities of two gases A and B are 1:1.5 Find out the volume of B which will diffuse in the same time in which 150 dm³ of A will diffuse?

Data:

Density of gas A	=	1.00
Density of gas B	=	1.5
Volume of A diffused	=	150 dm³

To Find:

Volume of B disused   =   ?

Formula: $\dfrac{r_A}{r_B} = \sqrt{\dfrac{d_B}{d_A}}$

Solution: Volumes of gases differ correspond to the rates of diffusions.

$$\frac{150}{r_B} = \sqrt{\frac{1.5}{1}}$$

Taking square on both sides

$$\frac{(150)^2}{r_B^2} = \frac{1.5}{1}$$

$$r_B^2 = \frac{(150)^2}{1.5}$$

$$= 15000 \text{ dm}^6$$

$$r_B = \sqrt{15000}$$

$$= \textbf{122.47dm}^3$$

(b) Hydrogen (H₂) diffuses through a porous plate at a rate of 500 cm³ per minute at 0°C. What is the rate of diffusion of oxygen through the same porous plate of 0°C.

Data:

Rate of diffusion of H_2 at 0°C   =   500cm³min⁻¹

To Find: Rate of diffusion O_2 at 0°C =   ?

Formula: $\dfrac{r_{O2}}{r_{H2}} = \sqrt{\dfrac{M_{H2}}{M_{O2}}}$

Molar mass of H_2 =   2 g mol⁻¹

Molar mass of O_2 =   32 g mol⁻¹

$$\frac{r_{O_2}}{500} = \sqrt{\frac{2}{32}}$$

$$\frac{r_{O_2}}{500} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$r_{O_2} = \frac{500}{4} = \textbf{125 cm}^3 \textbf{ min}^{-1}$$

So the rate of diffusion of O_2 is 125 cm³/min

(c)The rate of effusion of an unknown gas A through a pinhole is found to be 0.279 times the rate of effusion of H₂ gas through the same pinhole. Calculate the molecular mass of the unknown gas at S.T.P.

Data:

Rate of effusion of H_2	=	1
Rate of effusion of A	=	0.279
To Find: Molar Mass of A	=	?

Formula:
$$\frac{r_{H_2}}{R_A} = \sqrt{\frac{M_A}{M_{H2}}}$$

Solution: Taking square on both sides

$$\left(\frac{1}{0.279}\right)^2 = \frac{M_A}{2}$$

$$M_A = \frac{2}{0.0778}$$

$$= \textbf{25.7 gmol}^{-1}$$

22. Calculate the number of molecules and the number of atoms in given amount of each gas.

(a) 20 cm³ of CH₄ at 0°C and pressure of 700 mm of mercury(Hg)

Data:

Volume of CH_4	=	$20cm^3$
Volume of CH_4	=	$0.02dm^3$
Temperature of CH_4	=	$0°C$
=	$0°C + 273 K = 273 K$	
Pressure of CH_4	=	700 mm Hg
	=	$\frac{700}{760}$ = 0.92 atm

General Gas Constant (R) = 0.0821 dm³atm K⁻¹ mol⁻¹

To Find: Number of moles of CH_4 =   ?

Formula: $\quad PV \quad = \quad nRT$

Solution: $\quad n \quad = \quad \dfrac{PV}{RT}$

$$n = \frac{0.92\,atm \times 0.02\,dm^3}{0.0821\,dm^3\ atm\ K^{-1}\ mol^{-1} \times 273K}$$

$$= \frac{0.92 \times 0.02}{0.0821 \times 273}\ moles$$

$$n = \frac{0.0184}{22.356}\ moles$$

$n \quad = \quad 8.2 \times 10^{-4}$ moles of CH_4

Number of molecules of $CH_4 = 8.2 \times 10^{-4} \times 6.02 \times 10^{23}$

$$= 49.36 \times 10^{19}$$

$$= \textbf{4.936} \times \textbf{10}^{\textbf{20}}$$

One molecule of CH_4 has number of atoms = 5

Number of atoms in $CH_4 = 5 \times 4.936 \times 10^{20}$

$$= \textbf{2.47} \times \textbf{10}^{\textbf{21}}\textbf{atoms}$$

(b) 1 ml of NH₃ at 100°C and pressure of 1.5 atm

Data: Volume of NH_3 $\quad = \quad$ 1 ml

$= 1ml = 1\ cm^3 = 0.001\ dm^3$

Temperature of NH_3 $\quad = \quad 100°C$

= 100°C + 273 = 373 K

Pressure of NH_3 = 1.5 atm

General Gas Constant (R) = 0.0821 dm^3atm. $K^{-1}mol^{-1}$

To Find: Number of moles of NH_3 = ?

Formula: PV = nRT

Solution: n = $\dfrac{PV}{RT}$

Calculation of moles

$$n = \frac{1.5\,atm \times 0.001\ dm^3}{0.0821\ dm^3\ atm.\ K^{-1}\ mol^{-1} \times 373K}$$

$$= \frac{1.5 \times 0.001}{30.62}\ moles$$

$$= 4.89 \times 10^{-5}\ moles$$

Calculation of number of molecules and number of atoms

Number of molecules of

NH_3 = moles × N_A

= $4.89 \times 10^{-5} \times 6.02 \times 10^{23}$

= **2.95×10^{19}molecules**

One molecule of NH_3 has number of atoms =4

2.94×10^{19} molecules have number of atoms

= $4 \times 2.943 \times 10^{19}$

= **1.179×10^{20}atoms**

23. **Calculate the masses of 10^{20} molecules of each H_2, O_2 and CO_2 at S.T.P what will happen to the masses of these gases, when the temperature of the gases are increased by 100°C and the pressure is decreased by 100 mm of Hg.**

Data:

Molecules of H_2 = 10^{20}

Molecules of O_2 = 10^{20}

Molecules of CO_2 = 10^{20}

Increase of temperature= 100°C

Increase of pressure = 100 mm of Hg

Molar mass of H_2 = 2g mol^{-1}

Mass of H_2 = ?

Mass of O_2 = ?

Mass of CO_2 = ?

Mass of H_2 molecules = $\dfrac{\text{Molar mass} \times \text{number of molecules of } H_2}{N_A}$

Since 1 mole of H_2 at S.T.P has number of molecules = 6.02×10^{23}

6.02×10^{23} molecules of H_2 at S.T.P. have Mass = 2.00g

Mass of H_2 molecules at S.T.P = $\dfrac{2}{6.02 \times 10^{23}} \times 10^{20}$

Mass of H_2 molecules at S.T.P = $\dfrac{2}{6.02} \times 10^{-3}$ =**3.3×10^{-4} g**

Molar mass O_2 $\qquad = \qquad$ 32 gmol^{-1}

Mass of O_2 molecules $= \dfrac{\text{Molar mass} \times \text{number of molecules of } O_2}{N_A}$

Mass of 10^{20} molecules of O_2 at S.T.P $= \dfrac{32}{6.02 \times 10^{23}} \times 10^{20}$ g

$\qquad\qquad = \qquad$ **5.31 × 10^{-3}g**

Molar mass of CO_2 $\qquad = \qquad$ 44 g mol^{-1}

Mass of CO_2 molecules $\qquad = \dfrac{\text{Molar mass} \times \text{number of molecules of } CO_2}{N_A}$

Mass of 10^{20} molecules of CO_2 at S.T.P $= \dfrac{44}{6.02 \times 10^{23}} \times 10^{20}$

$\qquad\qquad = \qquad$ **7.30 × 10^{-3} g**

The change of temperature and pressure does not affect the masses because mass can neither be created nor bedestroyed so it remains constant.

24. Two moles of NH_3 are enclosed in a 5dm^3 flask at 27°C
(a) Calculate the pressure exerted by the gas assuming that
i. Gas behaves like an ideal gas

Data:
Volume = V = 5dm^3
Temperature = T = 27°C
$\qquad\qquad$ = 27° + 273 = 300K
Number of moles = n = 2 moles
General gas constant = R = 0.0821 atm.dm^3. mol^{-1}K^{-1}
To Find: Pressure = P = ?
Formula: PV = nRT
Solution:
$$P = \frac{nRT}{V}$$
$$P = \frac{2 \times 0.0821 \times 300}{5}$$

P = 9.852 atm
ii. Gas behaves like a real gas (a= 4.17 atmdm^6 mol^{-2} , b= 0.0371 dm^{3}mol^{-1})

Data:
Volume = V = 5dm^3
Temperature = T = 27°C
$\qquad\qquad$ = 27° + 273 = 300K
Number of moles = n = 2 moles
General gas constant = R = 0.0821 atm.dm^3. mol^{-1}K^{-1}
a= 4.17 atmdm^6 mol^{-2}
b= 0.0371 dm^{3}mol^{-1}
To Find: Pressure = P = ?
Formula: According to Van der waal's equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Solution: $\left(P + \frac{an^2}{V^2}\right) = \frac{nRT}{(V-nb)}$

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Putting the values

$$P = \frac{2 \times (0.0821) \times 300}{5 - 2 \times (0.0371)} - \frac{4.17 \times 2^2}{5^2}$$

$$P = \frac{49.26}{4.926} - \frac{16.68}{25}$$

$P = 10 - 0.67 = 9.33$ atm

(b) Also calculate the amount of pressure lessened due to forces of attraction at these conditions of volume and temperature

Amount of pressure lessened = 9.85 − 9.33 = 0.52 atm

Important long questions from past papers
1. State Charles's law. Explain its experimental verification.
2. Describe Dalton's law of partial pressures. Write its three applications.
3. State and explain Graham's law of diffusion of gases.
4. State Joule-Thomson effect. Explain Linde's method of liquefaction.
5. How pressure and volume were corrected by Van der Waal?
6. Derive Boyle's law and Charles' law from kinetic equation of gases.
7. Give postulates of Kinetic Molecular Theory of Gases.
8. Example# 3, 4, 5, 7, 8

Ch 4

Liquids and Solids

Intermolecular Forces

Definition

The force of attraction between the molecules is called intermolecular force. For example, the force of attraction between HCl molecules.

Types of Intermolecular Forces

Following are the four types:

1. Dipole-dipole forces

2. Ion-dipole forces

3. Dipole-induced dipole forces

4. Instantaneous dipole-induced dipole forces or London dispersion forces

Dipole-dipole Forces

The positive end of one molecule attracts the negative end of the other molecule and these electrostatic forces of attraction are called dipole-dipole forces.

Example

In HCl molecule chlorine develops the partial negative charge and hydrogen develops the partial positive charge.

$$\overset{\delta^-}{Cl} — \overset{\delta^+}{H} - - - - - \overset{\delta^+}{H} — \overset{\delta^-}{Cl}$$
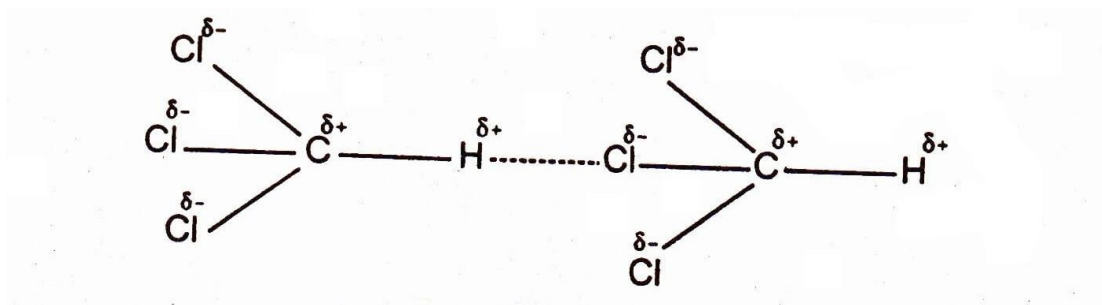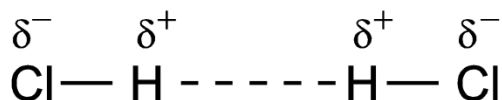
Dipole-dipole forces are approximately one percent as effective as a covalent bond.

Factors

The strength of these forces depends upon:

1. The electronegativity difference between the bonded atoms.

2. The distance between the molecules.

Strength of Forces in Different Phases

The distances between molecules in the gaseous phase are greater so these forces are very weak in this phase. In liquids these forces are reasonably strong.

Effect on Thermodynamic Parameters

Greater the strength of these dipole-dipole forces, greater are the values of thermodynamic parameters like melting points, boiling points, heats of vapourization and heats of sublimation.

Dipole-induced Dipole Forces

In a mixture of substances containing polar and non-polar molecules the positive end of the polar molecule attracts the mobile electrons of the nearby non-polar molecule. Polarity is induced in non-polar molecule, and both molecules become dipoles. These forces are called dipole-induced dipole forces or as Debye forces.
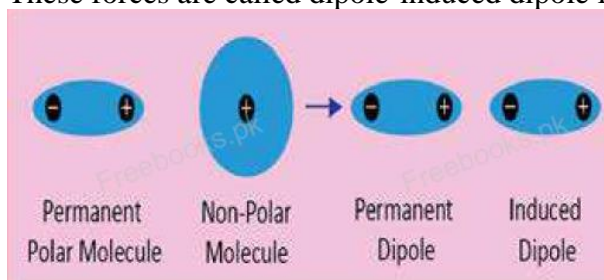
Instantaneous dipole-induced dipole forces or London Dispersion Forces

Definition

The momentary force of attraction created between instantaneous dipole and the induced dipole is called instantaneous dipole-induced dipole interaction or London force.

Explanation

A German physicist Fritz London in 1930 offered a simple explanation for these weak attractive forces between non-polar molecules.

Attractive forces among He atoms

1) **Generation of instantaneous dipole**
- In helium gas, the electrons of one atom influence the moving electrons of the other atom.
- Electrons repel each other and they tend to stay as far apart as possible.
- When the electrons of one atom come close to the electron of other atom, they are pushed away from each other.
- In this way, a temporary dipole is created in the atom.
- At any moment the electron density of the atom is no more symmetrical.
- It has more negative charge on one side than on the other.
- At that particular instant, the helium atom becomes a dipole.
- This is called **instantaneous dipole**.

2) **Generation of induced dipole**
- The instantaneous dipole then disturbs the electronic cloud of the other nearby atom.
- A dipole is induced in the second atom.
- This is called **induced dipole**.

Characteristics
- It is a very short-lived attraction because the electrons keep moving.
- London forces are present in all types of molecules whether polar or non-polar, but they are very' significant for non-polar molecules like Cl_2, H_2 and noble gases.

Factors Affecting the London Forces

1. Size of atom

When the size of the atom or molecule is large then the dispersion becomes easy and these forces become more prominent.

2. Atomic number

The atomic number increases down the group and the outermost electrons move away from the nuclei. The dispersion of the electronic clouds becomes more and more easy. So the polarizability of these atoms goes on increasing.

3. Polarizability

Polarizability is the quantitative measurement of the extent to which the electronic cloud can be polarized or distorted. This increased distortion of electronic cloud creates stronger London forces and hence the boiling points are increased down the group.

4. Boiling points of halogens

The boiling points of halogens in group VII-A also increase from fluorine to iodine. Fluorine is a gas and boils at -188.1 °C, while iodine is a solid at room temperature which boils at +184.4 °C. The polarizability of iodine molecule is much greater than that of fluorine.

5. Number of atoms

Greater the number of atoms in a molecule greater is its polarizability.

Example

The boiling points of C_2H_6 and C_6H_{14} are - 88.6 °C and 68.7 ºC, respectively. The reason is that longer molecules have more places along its length where they can be attracted to other molecules. With the increasing molecular mass of these hydrocarbons, they change from gaseous to liquid and then to solids.

Hydrogen Bonding

Definition

Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom.

Example
Hydrogen bonding in the molecule of water.
Explanation
- Oxygen is more electronegative element as compared to hydrogen, so water is a polar molecule.
- There is dipole-dipole interactions between partial positively charged hydrogen atoms and partial negatively charged oxygen atoms.
- Oxygen atom has two lone pairs.
- Hydrogen has sufficient partial positive charge.
- Both the hydrogen atoms of water molecule create strong electrical field due to their small sizes.
- The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons.
Electronegative atoms creating hydrogen bonding
- Fluorine
- Oxygen
- Nitrogen
- Rarely chlorine
Strength of hydrogen bond
The strength of hydrogen bond is generally twenty times less than that of a covalent bond.
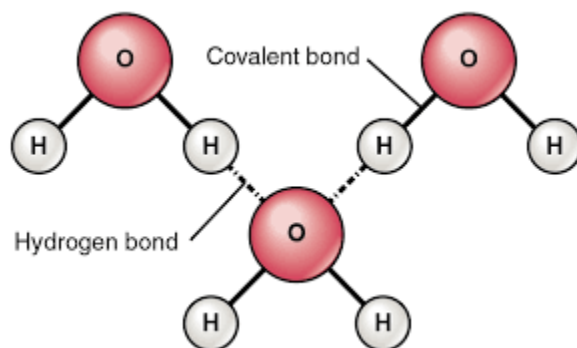
Other Examples of Hydrogen Bonding
Hydrogen bonding between acetone and chloroform
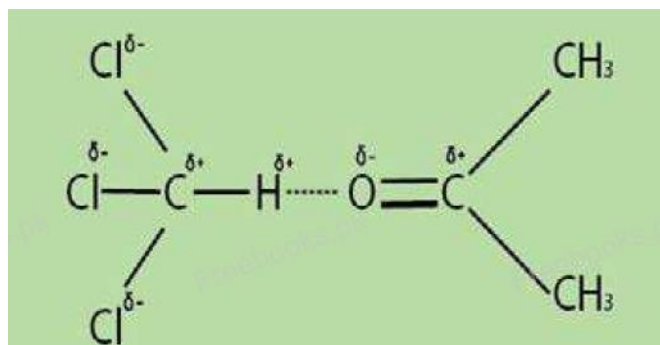
Hydrogen bonding in ammonia and hydrofluoric acid
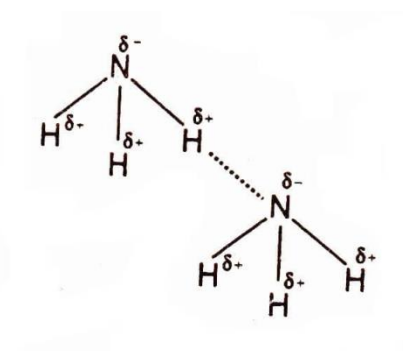
The molecules of HF join with each other in a zig-zag manner.

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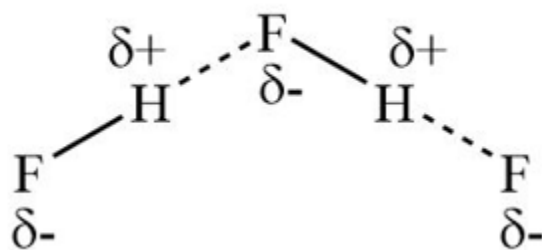
The bond angle is 120 º

Low Acidic Strength of HF

The low acidic strength of HF molecule as compared to HCl, HBr and HI is due to the strong hydrogen bonding, because the partial positively charged hydrogen is entrapped between two highly electronegative atoms.

Properties and Application of Compounds containing Hydrogen Bonding

1. Thermodynamic Properties of Covalent Hydrides

Hydrogen bonding influences the physical properties like melting and boiling points.

Comparison of the physical properties of hydrides of IV-A, V-A, VI-A and VII-A

For comparison the graphs are plotted between the period number of the periodic table on x-axis and boiling points in kelvin on y-axis.

Hydndes	B.P (ºC)
CH_4	-164
SiH_4	-112
GeH_4	-88
SnH_4	-52
NH_3	-33.4
PH_3	-88
AsH_3	-55
SbH_3	-17
H_2O	100
H_2S	-61
H_2Se	-42
H_2Te	-2
HF	19.9
HCl	-85
HBr	-67
HI	-38
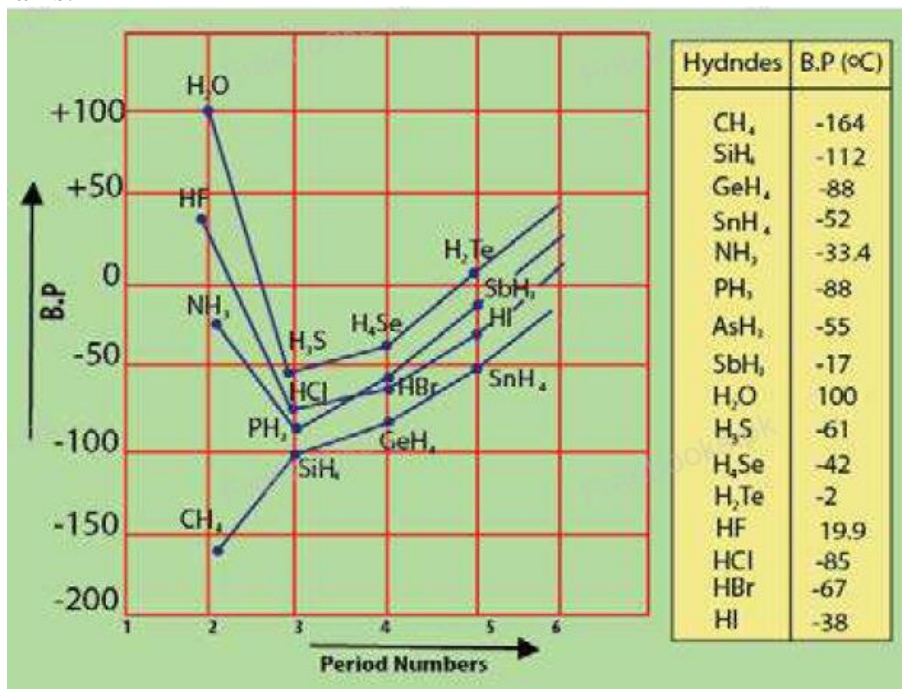
Conclusions from the graph

Boiling point of hydrides of group IV-A

Hydrides of group IV-A have low boiling points as compared to those of group V-A, VI-A, VII-A. **Reason:** These elements are least electronegative. Methane has the lowest boiling point because it is a very small molecule and its polarizability is the least.

Boiling point of hydrides of V-A, VI-A, VII-A

The hydrides of group V-A, VI-A, VII-A NH₃, H₂O and HF show maximum boiling points in the respective series. **Reason:** The reason is the enhanced electronegative character of N, O and F.

➢ Water is liquid at room temperature, but H_2S and H_2Se are gases.

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➢ Fluorine is more electronegative than oxygen. So, H-bonding in HF is expected to be stronger than that in water and the boiling point of HF higher than that of H_2O. However, it is lower and the reason is that the fluorine atom can make only one hydrogen bond per molecule.
➢ Water can form two hydrogen bonds per molecule, as it has two hydrogen atoms and two lone pairs on oxygen atom.
➢ Ammonia can form only one hydrogen bond per molecule as it has only one lone pair.

Boiling point of halogen acids
The boiling point of HBr is slightly higher than that of HCl. It means that chlorine is electronegative enough to form a hydrogen bond. It seems that HCl has a strong dipole-dipole interaction but it is a border line case.

Boiling point of hydrides of fourth period
The hydrides of fourth period GeH_4, AsH_3, H_2Se, HBr show greater boiling points than those of third period due to greater size and enhanced polarizabilities.

2. Solubility of Hydrogen-Bonded Molecules
Example 1
Water is the best example of H-bonded system. Similarly ethyl alcohol (C_2H_5OH) also has the tendency to form hydrogen bonds. Ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other.

Example 2
Small-sized carboxylic acids are soluble in water. Hydrocarbons are not soluble in water because they are non-polar compounds and there is no hydrogen bonding between water and hydrocarbon molecules.

3. Structure of Ice
1. The molecules of water have tetrahedral structure.
2. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron.
3. In the liquid state, water molecules are extensively associated with each other and these associations break and are reformed because the molecules of water are mobile.
4. When the temperature of water is decreased and ice is formed then the molecules become more regular and this regularity extends throughout the whole structure.
5. Empty spaces are created in the structure.
6. When water freezes it occupies 9% more space and its density decreases.
7. The result is that ice floats on water. The structure of ice is just like that of a diamond being tetrahedral.
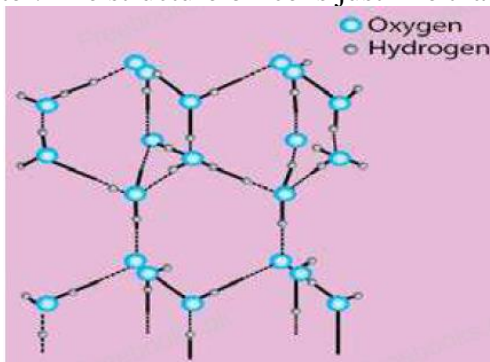
Hydrogen Bonding and Life Sustenance under frozen water
The lower density of ice than liquid water at 0 ºC causes water in ponds and lakes to freeze from surface to the downward direction. The less dense water below 4 ºC stays on the top of slightly warm water underneath and ultimately it freezes. This layer of ice insulates the water underneath and fish and plants survive under this blanket of ice.

4. Cleansing Action of Soaps and Detergents
Soaps and detergents perform the cleansing action because:
1. The polar part of their molecules are water soluble due to hydrogen-bonding
2. The non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.

5. Hydrogen Bonding in Biological Compounds and Food Materials
Hydrogen bonding exists in the molecules of living system.

Structure of Proteins
1. Hair, silk and muscle fibres consist of long chains of amino acids.
2. These chains are coiled about one another into a spiral called a helix.
3. Helix may be right handed or left handed.
4. In right handed helix the groups like >N H and > C = O are vertically adjacent to one another linked by hydrogen bonds.
5. These H-bonds link one spiral to the other. X-ray analysis confirms 27 amino acid units on average for each turn of the helix.
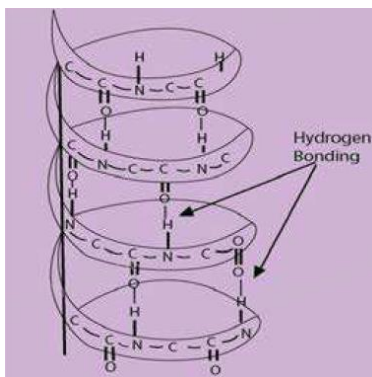
Structure of DNA
1. Deoxyribonucleic acid (DNA) has two spiral chains.
2. These are coiled about each other on a common axis.
3. They give a double helix 18-20 Å in diameter.
4. They are linked together by H-bonding between their sub units.
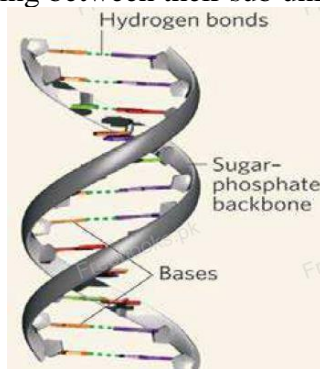
Hydrogen Bonding in Carbohydrates
The food materials like carbohydrates include glucose, fructose and sucrose. They all have -OH groups in them which are responsible for hydrogen bonding in them.

6. Hydrogen Bonding in Paints, Dyes and Textile Materials

H-bonding in paints and dyes
The adhesive action of paints and dyes is due to hydrogen bonding.

H-bonding in glue and honey
Hydrogen bonding makes glue and honey as sticky substances.

H-bonding in cotton, silk or synthetic fibres
Hydrogen bonding is of vital importance in the thread making materials. This hydrogen bonding is responsible for their rigidity and tensile strength.

Manometric Method

Vapour Pressure

Definition

The vapour pressure of a liquid is a pressure exerted by the vapours of the liquid in equilibrium with the liquid at a given temperature.
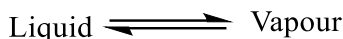
$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

Manometric method is an accurate method for determining vapour pressure.

Assembly

Liquid in flask

The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat.

Manometer and Vacuum pump

One end of the tube from the flask is connected to a manometer and the other end is connected to a vacuum pump.
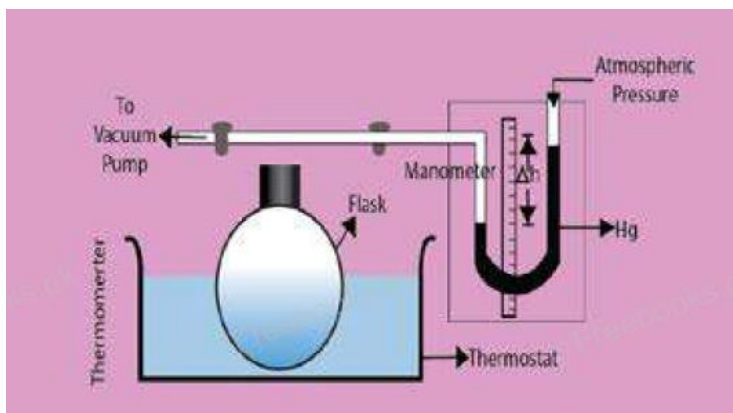
Working

Freezing of liquid

1. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated.
2. The air is removed from the surface of the liquid along with the vapours of that liquid.
3. The frozen liquid is then melted to release any entrapped air.
4. Liquid is again frozen and released air is evacuated.
5. This process is repeated many times till almost all the air is removed.

Warming of liquid

6. The liquid is warmed in the thermostat to that temperature at which its vapour pressure in the flask is to be determined.

Determination of vapour pressure

7. Difference in the heights of the columns of Hg in liquid determines the vapour pressure of the liquid.
8. The column of mercury in the manometer facing the vapours of the liquid is depressed.
9. The other column which faces the atmospheric pressure rises.
10. The pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and the vapour pressure of liquid.
11. The column of manometer facing the liquid is more depressed than facing the atmosphere.

Equation used

$$\mathbf{P = Pa + \Delta h}$$

P= vapour pressure of the liquid at one atm pressure.
Pa=Atmospheric pressure
Δh= Difference in the heights of the mercury levels in the two limbs of the manometer giving us the vapour pressure of liquid

Liquid Crystals

Historical Background

In 1888, Frederick Reinitzer, an Austrian botanist discovered a universal property. He was studying an organic compound cholesteryl benzoate. This compound turns milky liquid at 145°C and becomes a clear liquid at 179°C. When the substance is cooled, the reverse process occurs. This turbid liquid phase was called liquid crystal.

Definition

Liquid crystalline state exists between two temperatures i.e. melting temperature and clearing temperature.

$$\text{Crystal} \rightleftharpoons \text{Liquid crystal} \rightleftharpoons \text{Liquid}$$
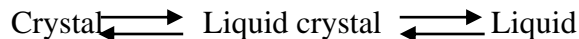
Properties

1. Behave as liquids

Liquid crystals can flow as liquids. They have the properties like liquids as surface tension, viscosity, etc.

2. Behave as solids

Liquid crystals have some degree of order. It means that they resemble crystals in certain properties like optical ones.

3. Structure

Those substances which make the liquid crystals are often composed of long rod like molecules. In the normal liquid phase, these molecules are oriented in random directions. In liquid crystalline phase, they develop some ordering of molecules. Depending upon the nature of ordering, liquid crystals can be divided into nematic, smectic and cholesteric.

4. Anisotropic

The properties of liquid crystals are intermediate between those of crystals and isotropic liquids. They have the fluidity of the liquids and the optical properties of the crystals. A crystalline solid may be isotropic or anisotropic, but liquid crystals are always anistropic.

Uses of Liquid Crystals

1. As temperature sensors

Liquid crystals can diffract light. When one of the wavelengths of white light is reflected from a liquid crystal it appears coloured. With temperature change the distances between the layers of the molecules of liquid crystals change. The colour of the reflected light changes accordingly. Liquid crystals can he used as temperature sensors.

2. Detection of potential failure in electrical circuits

Liquid crystals are used to find the point of potential failure in electrical circuits.

3. In room thermometers

Room thermometers also contain liquid crystals with a suitable temperature range. As the temperature changes, figures show up in different colours.

4. Medical applications

Blockages in veins

Liquid crystalline substances are used to locate the veins, arteries, infections and tumors. The reason is that these parts of the body are warmer than the surrounding tissues. Specialists can use the techniques of skin thermography to detect blockages in veins and arteries.

Early diagnosis of breast cancer

When a layer of liquid crystal is painted on the surface of the breast, a tumor shows up as a hot area which is coloured blue. This technique has been successful in the early diagnosis of breast cancer.

4. Display of electrical devices

Liquid crystals are used in the display of electrical devices such as digital watches, calculators and laptop computers. These devices operate due to the fact that temperature, pressure and electro-magnetic fields easily affect the weak bonds, which hold molecules together in liquid crystals.

5. Use in chromatography

In chromatographic separations, liquid crystals are used as solvents.

6. Oscillography and TV display

Oscillographic and TV displays also use liquid crystal screens.

Classification of Solids

Ionic Solids

Definition

Crystalline solids in which the particles forming the crystal are positively and negatively charged ions are called ionic solids. These ions are held together by strong electrostatic forces of attraction. These attractive forces are also called ionic bonds.

Examples

NaCl, KBr etc.

Properties of Ionic Solids

1. Well-defined geometrical pattern

The cations and anions are arranged in a well defined geometrical pattern, so they are crystalline solids at room temperature.

2. Stable compounds

Under ordinary conditions of temperature and pressure they never exist in the form of liquids or gases. Ionic crystals are very stable compounds.

3. High melting and boiling points

Very high energy is required to separate the cations and anions from each other against the forces of attraction. That is why ionic crystals are very hard, have low volatility and high melting and boiling points.

4. Non-existence as neutral molecules

Ionic solids do not exist as individual neutral independent molecules.

5. Non-directional bonds

The cations and anions attract each other and these forces are non-directional.

6. Close packing

The close packing of the ions enables them to occupy minimum space.

7. Systematic arrangement of ions

A crystal lattice is developed when the ions arrange themselves systematically in an alternate manner. The structure of the ionic crystals depends upon the radius ratio of cations and anions. For example, NaCl and CsF have the same geometry because the radius ratio in both the cases is the same.

8. Formula mass

The term formula mass for the ionic substances is used and not the molecular mass, because they do not exist in the form of molecules.

9. Non-conductors in solid state

Ionic crystals do not conduct electricity in the solid state, because on account of electrostatic force existing between them the cations and anions remain tightly held together and hence occupy fixed positions. Ionic crystals conduct electricity when they are in solution or in the molten state. In both cases ions become free.

10. Brittleness

Ionic crystals are highly brittle because ionic solids are composed of parallel layers which contain cations and anions in alternate positions, so that the opposite ions in the various parallel layers lie over each other. When an external force is applied, one layer of the ions slides a bit over the other layer along a plane. In this way the like ions come in front of each other and repel. This causes brittleness.
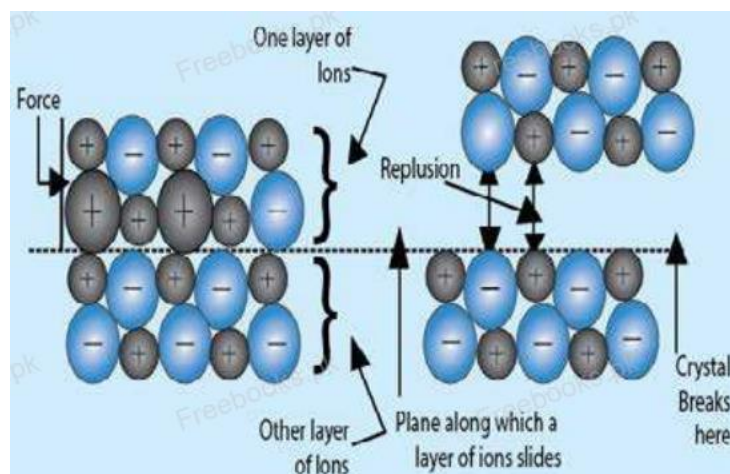
11. High density

Ionic solids are mostly of high density due to close packing of ions.

12. Ionic reactions

Such compounds having the ionic crystals give ionic reactions in polar solvents and these are very fast reactions.

13. Isomorphism and polymorphism

The properties like isomorphism and polymorphism are also associated with the ionic crystals.

Structure of Sodium Chloride

Structure and size of ions

1. The structure of ionic crystals depends upon the structure and the size of their ions.
2. Each ion is surrounded by a certain number of ions of opposite charge.

3. In the structure of NaCl each Na^+ ion is surrounded by six chloride ions.
4. It is clear that Na^+ has ten electrons while Cl^- has total 18 electrons.
5. The size of the Cl^- is bigger than that of Na^+.

Distance between ions

1. The distance between two nearest ions of the same kind i.e., Cl^- ions is 5.63 ^{o}A .
2. The distance between two adjacent ions of different kind is 5.63/2 = 2.815 ^{o}A.

Coordination number

1. Each Na^+ is surrounded by six Cl^- placed at the corners of a regular octahedron.
2. The coordination number of each Na^+ is six.
3. Each Cl^- is also surrounded by six Na^+.

Formula unit

1. Na^+ and $C1^-$ are not connected to one another by pairs because all six Cl^- ions are at the same distance away from one Na^+.
2. Independent molecules of NaCl do exist in the vapour phase.
3. In solid NaCl there are no independent molecules of NaCl.
4. Sodium chloride is said to have formula unit of NaCl.

Chlorides at the corners and face centres of cube

1. There are eight Cl^- at the comers of the cube, and each is being shared amongst eight cubes.
2. $1/8^{th}$ part of each Cl^- ion is considered for this unit cell.
3. One complete Cl^- is contributed by eight corners.
4. Six chloride ions are present at the face centres and each is being shared between two cells.
5. Per unit cell there are 8/8 + 6/2 = 4 Cl^- ions.
6. Justification of 4 Na^+ can be given, if a unit cell has 8 Na^+ at eight corners and 6 Na^+ at faces.
7. There are equal number of Na^+ ions
8. Four NaCl units are present per unit cell.
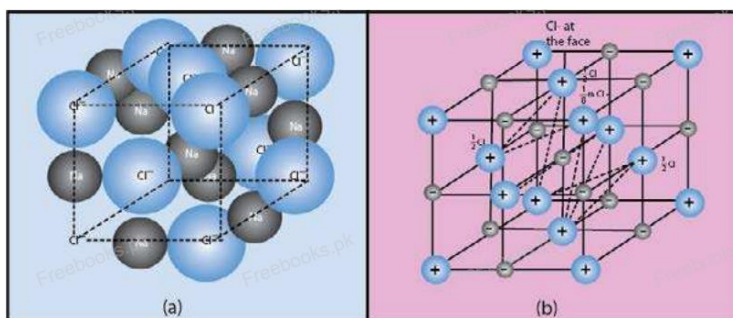
Covalent Solids

Definition
Covalent solids are also called atomic solids, because they are composed of neutral atoms of the same or of different elements. These atoms are held together by covalent bonds.
Types of covalent solids
Covalent solids are of two types.

Giant molecules
(i) When the covalent bonds join to form giant molecules like diamond, silicon carbide or aluminium nitride.
Layered structures
(ii) When atoms join to form the covalent bonds and separate layers are produced like that of graphite, cadmium iodide and boron nitride.
Properties of covalent solids
1. Three dimensional structure
The bonding in covalent crystals extend in three dimensions. They contain a network of atoms.
2. Directional bond and open structure
The valencies of atoms are directed in definite directions, so the packing of atoms in these crystals is looser than those of ionic and metallic crystals. Covalent crystals have open structure.
3. High melting and boiling points
These crystals are very hard and considerable amount of energy is required to break them. They have high melting points and their volatility is very low.
4. Bad conductors of electricity
Due to the absence of free electrons and ions they are bad conductors of electricity. Graphite has a layered structure and the electrons are available in between the layers. These electrons are delocalized and conductivity becomes possible. Graphite is not a conductor perpendicular to the layers.
5. Solubility in non-polar solvents
These solids are insoluble in polar solvents like water but they are readily soluble in non-polar solvents like benzene and carbon tetrachloride.
6. Rate of chemical reaction of giant molecules
The covalent crystals having giant molecules like diamond and silicon carbide are insoluble in all the solvents. Because of their big size, they do not interact with the solvent molecules. The chemical reactions of such crystalline solids are very slow.
Structure of diamond
sp^3 hybridization
The four atomic orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbitals. They are directed in space along the four corners of a tetrahedron.
sp^3-sp^3 overlap
This is the unit cell of diamond and a large number of such unit cells undergo sp^3-sp^3 overlapping to form a huge structure. Each carbon atom is linked with four other carbon atoms. The bonds between carbon atoms are covalent which run through the crystal in three-dimensions.
Bond angles and bond lengths
All the bond angles are 109.5° and the bond lengths are 154 pm.
Continuous three dimensional structure
The whole lattice is continuous and because of the continuity of C-C covalent bonding the entire diamond crystal behaves as a huge or giant three-dimensional carbon molecule.
Face centred-cubic structure
The overall structure of diamond looks face centred-cubic.
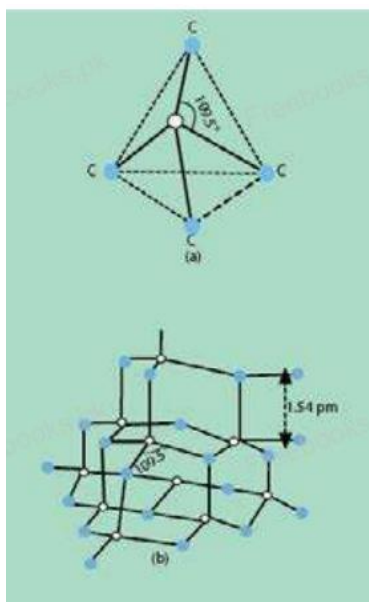
Molecular Solids

Definition
Those solid substances in which the particles forming the crystals are polar or non-polar molecules or atoms are called molecular solids.

Types of intermolecular forces
Two types of intermolecular forces hold them together.
(i) Dipole-dipole interactions.
(ii) van der Waals forces.
These intermolecular forces are much weaker than those in ionic crystals and covalent crystals.

Polar molecules
Ice and sugar are the best examples of crystals having polar molecules.

Non-polar molecules
Iodine, sulphur, phosphorus, carbon dioxide and solidified noble gases form the non-polar molecules.

Melting and boiling points
Polar molecular solids have usually higher melting and boiling points as compared to non-polar molecular solids.

Properties of the molecular solids

1. Regular arrangement of atoms
X-ray analysis has shown the regular arrangements of atoms in constituent molecules of these solids and we get the exact positions of all the atoms.

2. Weak forces
The forces, which hold the molecules together in molecular crystals, are very weak so they are soft and easily compressible.

3. Volatile and low melting and boiling points
They are mostly volatile and have low melting and boiling points.

4. Bad conductors of electricity
They are bad conductors of electricity.

5. Low densities
They have low densities.

6. Transparency to light
They are sometimes transparent to light.

7. Solubility
Polar molecular crystals are mostly soluble in polar solvents, while non-polar molecular crystals are usually soluble in non-polar solvents.

Structure of iodine
Layer lattice
In the solid state the molecules of iodine align in the form of layer lattice.
I-I bond distance
 I-I bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine (266.6 pm).
Poor conductor of electricity
As expected from its structure, iodine is a poor conductor of electricity.
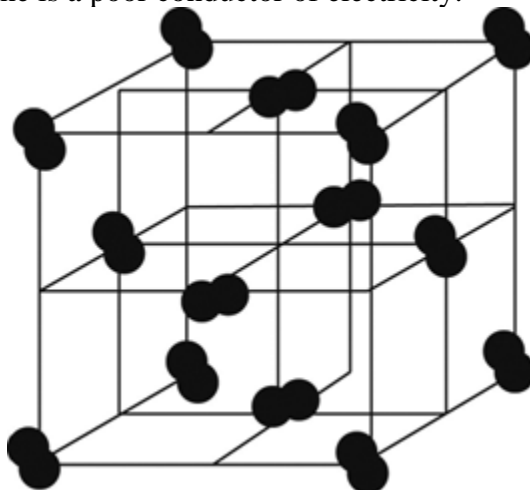
Metallic Solids

Definition
The force which binds a metal cation to a number of electrons within its sphere of influence is known as metallic bond.
Theories of Metallic Bonding
Electron pool or electron gas theory
The first theory of metallic bonding is called electron pool or electron gas theory. This theory was **proposed by Drude and extended by Loren (1923)**.

According to this theory:
> Each atom in a metal crystal
> loses all of its valence electrons. These
> valence electrons form a pool or a gas.
> The positively charged metal ions are
> believed to be held together by electron
> pool or gas.

Explanation
1. The positively charged ions occupy definite positions at measurable distances from each other in the crystal lattice.
2. Valence electrons are not attached to any individual ion or pair of ions rather belong to the crystal as a whole.
3. These electrons are free to move about from one part of the crystal to the other.
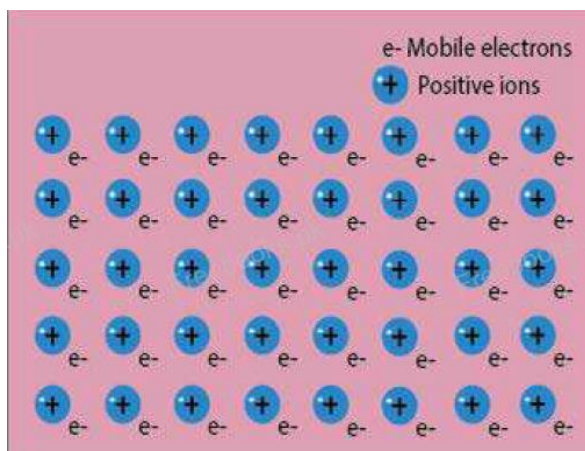
Valence Bond Theory
L. Pauling explained the metallic bond according to valence bond theory.
Statement
According to this theory:
The metallic bond is treated essentially as covalent in character. It is assumed that the covalent bonds are not localized but are highly delocalized in metal structure.
Molecular Orbital Theory
Molecular orbital theory was applied to explain the characteristics of metallic solids.
Statement
According to this theory:
It is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals.
Explanation
1. The delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice.
2. Such a combination of atomic orbitals produce as a large number of closely spaced states.
3. These states of energy are known as **bands of energy**.
4. It is called a **band theory**.
5. The energy gap between two bands determines the properties of the metallic solids.

Properties of metallic solids
1. Electrical conduction
Metals are good conductor of electricity. When electric field is applied between two ends of a metal then the mobile electrons begin to move towards the positive pole and the new electrons from the negative pole take their place.
2. Effect of temperature on electrical conduction
The electrical conductivity of metals decreases with the increase in temperature. With the increase in temperature the positive metal ions also begin to oscillate and the motion hinders the free movement of mobile electrons between the positive ions. This hindrance decreases the electrical conductivity.
3. Thermal conductivity
When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy and move towards the cooler end. During the process they collide with adjacent electrons and transfer their heat energy to them.
4. Metallic luster
Whenever the metals are freshly cut, most of them possess metallic luster. When light falls on the metallic surface, the incident light collides with the mobile electrons and they are excited. These electrons when de-excited give of some energy in the form of light. This light appears to be reflected from the surface of the metal which gives a shining look.
5. Malleable and ductile
Metals are malleable and ductile whenever stress is applied on them. Their layers slip pass each other. The structure of the metal changes without fracturing.

Important long questions from past papers

8. Define hydrogen bonding. Explain the structure of Ice on the basis of Hydrogen Boding.
9. Discuss hydrogen bonding in biological compounds.
10. Explain hydrogen bonding in NH_3, H_2O and HF.
11. Classify solids on the basis of Bonding.
12. Write brief not on isomorphism, anisotropy, polymorphism, transition temperature
13. What are ionic solids? Give their properties in detail.
14. What are covalent solids? Write their properties in detail.
15. What are liquid crystals? Give their uses in daily life.
16. What are molecular solids? Give their important characteristics?
17. Define vapor pressure? Discuss its measurement by Manometric method.
18. Discuss London dispersion forces. Elaborate factors on which it depends.
19. Give Postulates of Kinetic Molecular theory (K.M.T).

<center>**Chapter 5**</center>

<center>**Atomic Structure**</center>

Discovery of Electron (Cathode Rays)

Cathode rays are produced in a gas discharge tube.

Assembly

1. A gas discharge tube fitted with two metallic electrodes acting as cathode and anode.

2. The tube is filled with a gas, air or vapours of a substance at any desired pressure.

3. The electrodes are connected to a source of high voltage.

4. The exact voltage required depends upon the length of the tube and the pressure inside the tube.

5. The tube is attached to a vacuum pump by means of a small side tube so that the conduction of electricity may be studied at any value of low pressure.

Value of voltage for production of cathode rays

1. Current does not flow through the gas at ordinary pressure even at high voltage of 5000 volts.

2. When the pressure inside the tube is reduced and a high voltage of 5000-10000 volts is applied, then an electric discharge takes place through the gas producing a uniform glow inside the tube.

3. When the pressure is reduced further to about 0.01 torr, the original glow disappears.

4. Some rays are produced which create fluorescence on the glass wall opposite to the cathode. These rays are called cathode rays.

<center>**The colour of the glow or the fluorescence produced on the walls of the glass tube depends upon the composition of glass.**</center>
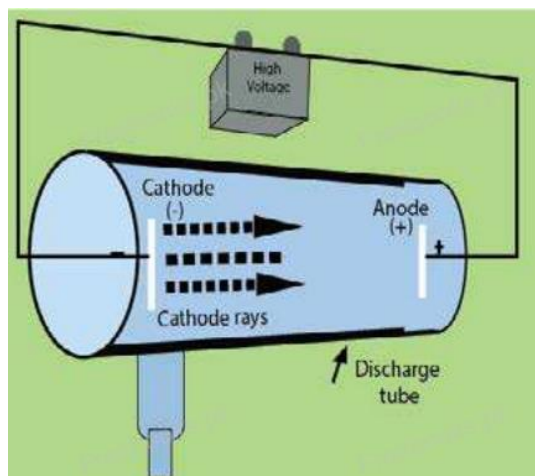
Properties of Cathode Rays

Following are the properties of cathode rays:

1. Cathode rays are negatively charged

Cathode rays are negatively charged.

Work of J.Perrin

In 1895, J Perrin showed that when the cathode rays passed between the poles of the magnet, the path of the negatively charged particles was curved downward to point 2 by the magnetic field.

Work of J. Thomson

In 1897, J. Thomson established their electric charge by the application of electric field, the cathode ray particles were deflected upwards (towards the positive plate) to point 3. Thomson found that by carefully controlling the charge on the plates when the plates and the magnet were both around the tube, he could make the cathode rays strike the tube at point 1 again.
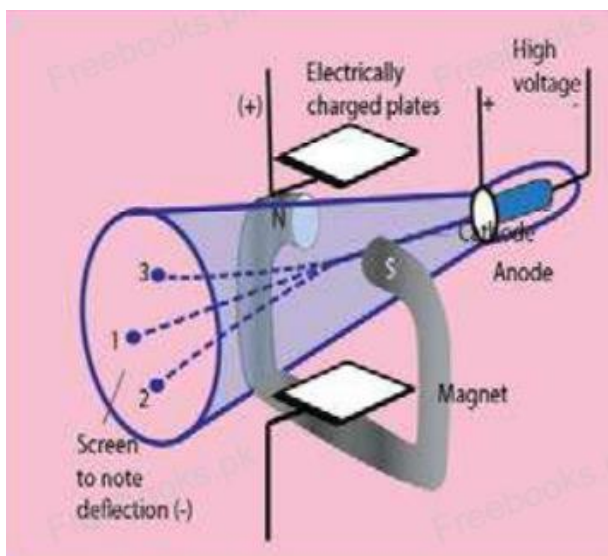
2. Production of fluorescence

They produce a greenish fluorescence on striking the walls of the glass tube. These rays also produce fluorescence in rare earths and minerals. When placed in the path of these rays, alumina glows red and tin stone yellow.

3. Shadow casting

Cathode rays cast a shadow when an opaque object is placed in their path. This proves that they travel in straight line perpendicular to the surface of cathode.
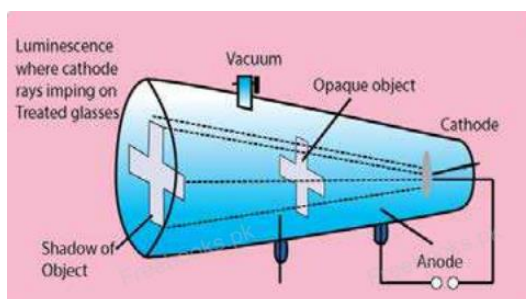
4. Cathode rays possess momentum

These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. Cathode rays are not rays but material particles having a definite mass and velocity.
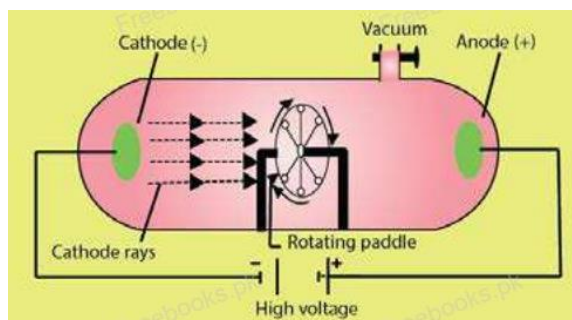
5. X-ray production

Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass.

6. Heat production

Cathode rays can produce heat when they fall on matter e.g. when cathode rays from a concave cathode are focussed on a platinum foil, it begins to glow.

7. Ionization of gases

Cathode rays can ionize gases.

8. Reducing effect

They can cause a chemical change, because they have a reducing effect.

9. Passage through metal foil

Cathode rays can pass through a thin metal foil like aluminum or gold foil.

10. e/m ratio equal to electrons

The e/m value of cathode rays shows that they are simply electrons.

Work of J.J. Thomson

He concluded from his experiments that cathode rays consist of streams of negatively charged particles. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube. He concluded that all atoms contained electrons.

Work of Stoney

He named these particles as electrons.

Discovery of Proton (Positive Rays)

Historical Background

In 1886, German physicist, E. Goldstein carried out the experiment for the discovery of proton.

Experimental Work

1. A discharge tube with a cathode having extremely fine holes in it was used.

2. A large potential difference is applied between electrodes

Observation

1. There are rays, other than cathode rays, produced in opposite direction.

2. These rays after passing through the perforated cathode produce a glow on the wall opposite to the anode.

3. These rays pass through the canals or the holes of cathode, they are called canal rays.

Origin of name

These rays are named as positive rays owing to the fact that they carry positive charge.
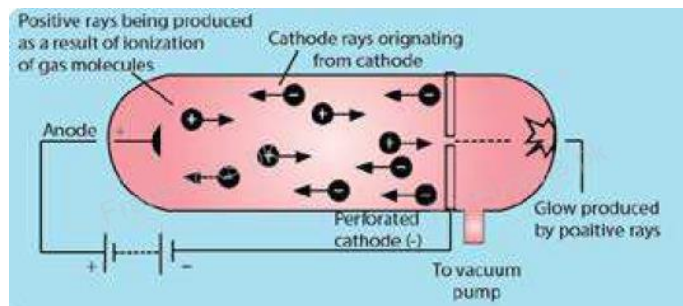
Reason for the Production of Positive Rays

The high speed cathode rays (electrons) strike the molecules of a gas enclosed in the discharge tube. They knock out electrons from the gas molecules and positive ions are produced.

$$M + e^- \longrightarrow M^+ + 2e^-$$

Properties of Positive Rays

1. Effect of Electric and Magnetic Field
They are deflected by an electric as well as a magnetic field showing that these are positively charged.
2. Travel in straight lines
These rays travel in a straight line in a direction opposite to the cathode rays.
3. Produce Flashes
They produce flashes on ZnS plate.
4. The charge/mass ratio
The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of the gas used in the discharge tube. Heavier the gas, smaller is the e/m value.
Highest e/m ratio
The e/m value is found to be the maximum for hydrogen because the value of 'm' is the lowest for the hydrogen gas. The positive particle obtained from hydrogen gas is the lightest.
5. Name of the Positive Particle
This particle is called proton, a name suggested by Rutherford.
6. Mass of Proton
The mass of a proton is 1836 times more than that of an electron.

Discovery of Neutron

Historical Background
Proton and electron were discovered in 1886 and their properties were completely determined till 1895. Up to 1932 it was thought that an atom was composed of only electrons and protons. Rutherford predicted in 1920

that some kind of neutral particle having mass equal to that of proton must be present in an atom as atomic masses of atoms could not be explained otherwise.

Experimental Work

Chadwick discovered neutron in 1932 and was awarded Nobel Prize in Physics in 1935. A stream of α-particles produced from a polonium source was directed at beryllium ($_4Be^9$) target. It was noticed that some penetrating radiations were produced. These radiations were called neutrons because the charge detector showed them to be neutral.

Reaction involved

$$_2He^4 + _4Be^9 \longrightarrow {} _6C^{12} + _0n^1$$
(α-particle)
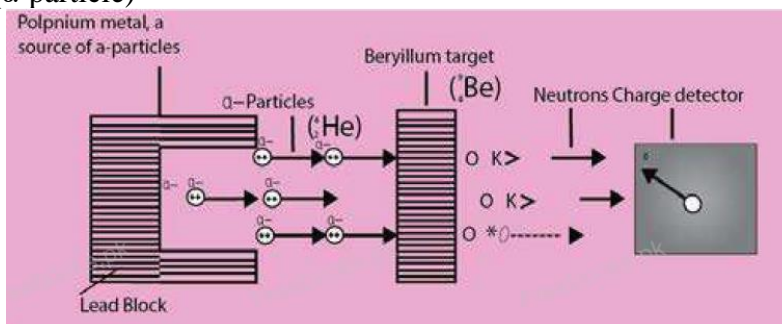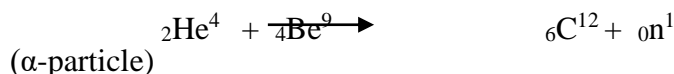
Properties of Neutron

1. Decay of a Neutron

Free neutron decays into a proton with the emission of an electron and a neutrino.

$$_0^1n \rightarrow {}_{+1}^1P + {}_{-1}^0e + {}_0^0n$$
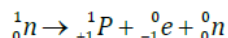
2. Gas ionization

Neutrons cannot ionize gases.

3. Penetrating Particles

Neutrons are highly penetrating particles.

4. Expelling Protons

They can expel high speed protons from paraffin, water, paper and cellulose.

5. Fast and Slow Neutrons

When neutrons travel with energy of 1.2 Mev they are called fast neutrons but with energy below 1ev are called slow neutrons. Slow neutrons are usually more effective than fast ones for the fission purposes.

6. Neutrons as Projectiles

When neutrons are used as projectiles they can carry out the nuclear reactions. A fast neutron ejects an α-particle from the nucleus of nitrogen atom and boron is produced along with α-particles.

$$_7^{14}N + _0^1n \rightarrow {}_5^{11}B + _2^4He$$
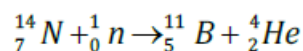
7. Radioactivity

When slow moving neutrons hit the Cu metal then γ gamma radiations are emitted. The radioactive $_{29}Cu^{66}$ is converted into $_{30}Zn^{66}$.

$$_{29}^{65}Cu + _0^1n \rightarrow {}_{29}^{66}Cu + hv(\gamma - raditions)$$

$$^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e \text{ (electron)}$$
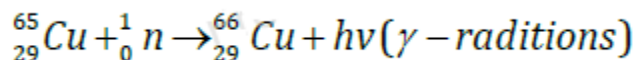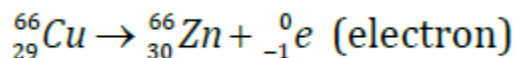
The radioactive copper emits an electron (β-particle) and its atomic number increases by one unit.

Application

Because of their intense biological effects they are being used in the treatment of cancer.

Rutherford's Model of Atom

In 1911, Lord Rutherford performed a classic experiment.

Experiment

He studied the scattering of high speed α-particles which were emitted from a radioactive metal (radium or polonium).

Setting

- A beam of α-particles was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate.
- A photographic plate or a screen coated with zinc sulphide was used as a detector.
- Whenever, an α-particle struck the screen, flash of light was produced at that point. It was observed that most of the particles went through the foil undeflected. Some were deflected at fairly large angles and a few were deflected backward.

Proposals

- Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which he called as nucleus.
- On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons.
- Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.
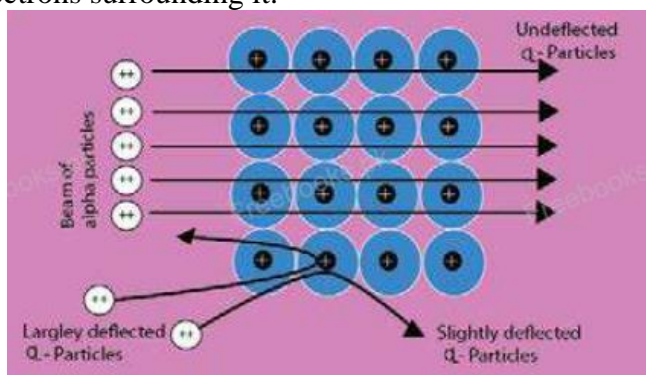
In Rutherford's model for the structure of an atom, the outer electrons could not be stationary as they could be attracted by the nucleus and ultimately fall into it. To have a stable atomic structure the electrons were supposed to be moving around the nucleus in closed orbits.

Defects

- Rutherford's planet-like picture was Electron defective and unsatisfactory because the moving electron must be accelerated towards the nucleus.
- The radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. An atomic structure proposed by Rutherford would collapse.
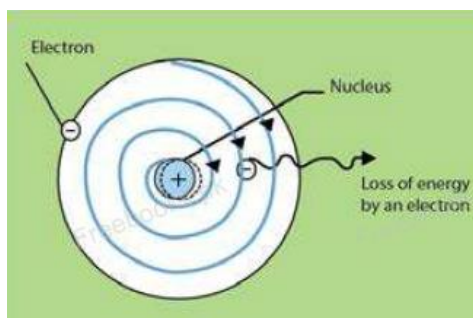
Measurement of e/m Value of Electron

In 1897, J.J Thomson devised an instrument to measure the e/m value of electron.

Apparatus

The apparatus consists of a discharge tube.

Working

Passage of cathode rays through electric and magnetic fields

1. The cathode rays are allowed to pass through electric and magnetic fields.
   When both fields are off
2. When both the fields are off then a beam of cathode rays, consisting of electrons, produces bright luminous spot at **P1** on the fluorescent screen.
3. The north and south poles of magnetic field are perpendicular to the plane of paper in the diagram.
4. The electrical field is in the plane of paper.
   When only magnetic field is applied
5. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point **P3**.
   When only electric field is applied
6. When only electric field is applied, the cathode rays produce a spot at **P2**.
   When both fields are applied simultaneously
7. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point **P1**.
   Determination of e/m value of electrons
8. In this way by comparing the strengths of the two fields one can determine the e/m value of electrons. It comes out to be **1.7588×10^{11} coulombs kg^{-1}**.

This means that 1 kg of electrons have 1.7588×10^{11} coulombs of charge.
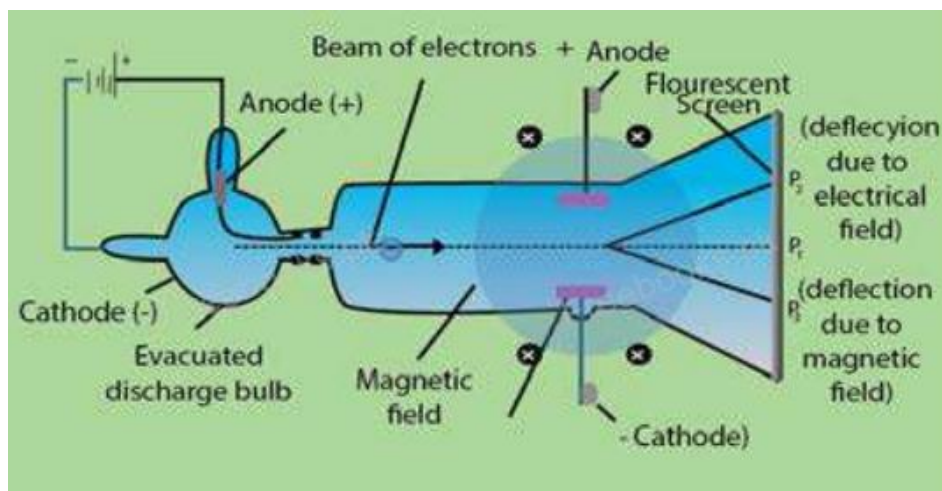
Measurement of Charge on Electron-Millikan's Oil Drop Method

In 1909, Millikan determined the charge on electron by a simple arrangement.

Apparatus

Metallic Chamber

1. The apparatus consists of a metallic chamber.
2. It has two parts.
3. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump.

Electrodes

1. There are two electrodes A and A'.
2. These electrodes are used to generate an electrical field in the space between the electrodes.
3. The upper electrode has a hole in it.

Working

1. Atomizer

A fine spray of oil droplets is created by an atomizer.

2. Microscope
A few droplets pass through the hole in the top plate and into the region between the charged plates, where one of them is observed though a microscope.

3. Illumination

This droplet, when illuminated perpendicularly to the direction of view, appears in the microscope as bright speck against a dark background.

4. Force of gravity

1. The droplet falls under the force of gravity without applying the electric field.
2. The velocity of the droplet is determined.
3. The velocity of the droplet (V_1) depends upon its weight, mg.

$$v_1 \alpha \; mg \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

Where
m=mass of the droplet
g= acceleration due to gravity

5. Ionization of air

The air between the electrodes is ionized by X-rays.
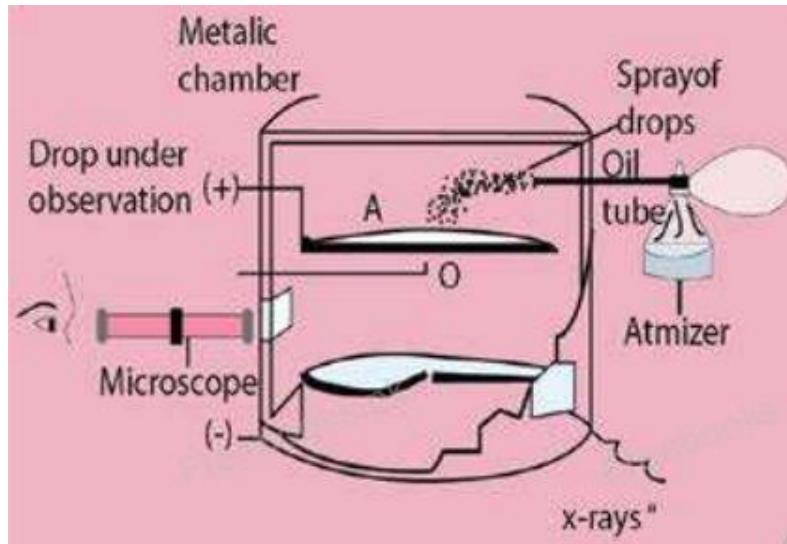
6. Taking up of electron by droplet

The droplet under observation takes up an electron and gets charged.

7. Battery connection

Now, connect A and A' to a battery which generates an electric field having a strength, E.

8. Movement against the action of gravity

The droplet moves upwards against the action of gravity with a velocity (v_2).

$$v_2 \alpha \; Ee - mg \qquad \ldots\ldots\ldots\ldots \qquad (2)$$

Where
e=charge on the electron
Ee=upward driving force on the droplet due to applied electrical field of strength E

Dividing eq (1) by (2)

$$\frac{v_1}{v_2} = \frac{mg}{Ee-mg} \quad \cdots\cdots\cdots\cdots \quad (3)$$

The values of v_1 and v_2 are recorded with the help of microscope.
The factors like g and E are also known.
Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber.
Hence 'e' can be calculated.

Calculation of charge on each droplet
1. By changing the strength of electrical field, Millikan found that the charge on each droplet was different.
2. The smallest charge which he found was 1.59×10^{-19} coulomb which is very close to the recent value of 1.6022×10^{-19} coulombs.
3. This smallest charge on any droplet is the charge of one electron.
4. The other drops having more than one electron on them have double or triple the amount of this charge.
5. The charge present on an electron is the smallest charge of electricity that has been measured so far.

Calculation of mass of electron

The value of charge on electron is 1.602×10^{-19} coulombs, while e/m of electron is 1.7588×10^{11} coulombs kg^{-1}. So,

$$\frac{e}{m} = \frac{1.6022 \times 10^{-19} \text{coulombs}}{\text{Mass of electrons}} = = 1.7588 \times 10^{11} \text{ coulombs kg}^{-1}$$

$$\text{Mass of electron} = \frac{1.6022 \times 10^{-19} \text{coulombs}}{1.7588 \times 10^{11} \text{coulombs kg}^{-1}}$$

Rearranging

Mass of electron= 9.1095×10^{-31} kg

Derivation of Radius of Revolving Electron in nth Orbit
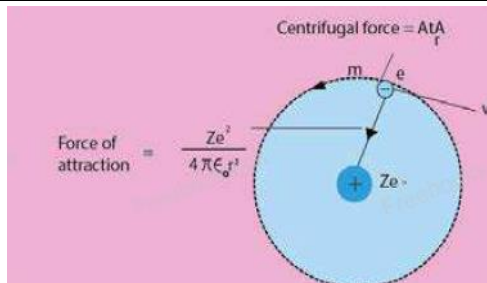
For a general atom, consider an electron of charge 'e' revolving around the nucleus having charge Ze+.
Z =proton number
e+ =charge on the proton
m =mass of electron
r =radius of the orbit

v =velocity of the revolving electron.

Coulomb's law

According to Coulombs law, the electrostatic force of attraction between the electron and the nucleus will be given by the following formula.

$$\frac{Ze^+ \cdot e^-}{4\pi \epsilon_0 r^2} = \frac{Ze^2}{4\pi \epsilon_0 r^2}$$

ϵ_0 is the vacuum permittivity and its value is $8.84 \times 10^{-12}C^2J^{-1}m^{-1}$.

Balanced by mv^2/r

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi \epsilon_0 r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi \epsilon_0 r} \qquad \text{eq (1)}$$

Rearrangement

$$r = \frac{Ze^2}{4\pi \epsilon_0 mv^2} \qquad \text{eq (2)}$$

The radius of a moving electron is inversely proportional to the square of its velocity. Electron should move faster nearer to the nucleus in an orbit of smaller radius. If hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

Angular momentum

The angular momentum of the electron is given by:

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

$$v = \frac{nh}{2\pi mr} \qquad \text{eq (3)}$$

Taking square root

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \text{eq (4)}$$

v^2 value substitution

$$r = \frac{Ze^2 \times 4\pi^2m^2r^2}{4\pi\varepsilon_0 mn^2h^2}$$

Rearrangement

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m Z e^2}$$

eq (5)

For Z=1

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2} = \left(\frac{\varepsilon_0 h^2}{\pi m e^2}\right) n^2$$

eq (6)

The radius of hydrogen atom is directly proportional to the square of number of orbit (n). Higher orbits have more radii and vice versa.

$$\left(\frac{\varepsilon_0 h^2}{\pi m e^2}\right)$$

Constant factor

Value= 0.529 x I0^{-10} m or 0.529 A° (10^{-10} m = 1 A°)

$$r = 0.529 \ \text{Å} \ (n^2)$$

eq (7)

Calculation of radii

By putting the values of n = 1,2.3,4............. the radii of orbits of hydrogen atom are:

n=1	r_1=0.529 Å	n=4	r_4=8.4 Å
n=2	r_2=2.11 Å	n=5	r_5=13.22 Å
n= 3	r_3=4.75 Å		

Orbits not equally spaced

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \ \text{.........................}$$

The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

Energy of Revolving Electron

Total energy of an electron= Kinetic energy + Potential energy

Kinetic energy= ½ mv^2

Electrostatic force of attraction

$$\frac{Ze^2}{4\pi \varepsilon_0 r^2}$$

Work done

If the electron moves through a small distance dr, then the work done for moving electron is given by:

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2} dr \quad \text{because work=(force x distance)}$$

Calculation of potential energy

Calculation of the potential energy of the electron at a distance r from the nucleus.

We calculate the total work done for bringing the electron from infinity to a point at a distance r from the nucleus. This can be obtained by integrating the above expression between the limits of infinity and r.

$$\int_{\infty}^{r} \frac{Ze^2 dr}{4\pi \in_0 r^2} = \frac{Ze^2}{4\pi \in_0} \int_{\infty}^{r} \frac{dr}{r^2} = \frac{Ze^2}{4\pi \in_0} \left[\frac{-1}{r}\right]_{\infty}^{r} = \frac{Ze^2}{4\pi \in_0} \left[\frac{-1}{r}\right] = -\frac{Ze^2}{4\pi \in_0 r}$$

$$\text{Work done} = E_{potential} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

eq (1)

The minus sign indicates that the potential energy of electron decreases, when it is brought from infinity to a point at a distance 'r' from the nucleus.

$$E = E_{kinetic} + E_{potential}$$

$$= \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi\varepsilon_o r}$$

eq (2)

We know

$$mv^2 = \frac{Ze^2}{4\pi \in_0 r}$$

$$E = \frac{Ze^2}{8\pi \in_0 r} - \frac{Ze^2}{4\pi \in_0 r}$$

$$E = -\frac{Ze^2}{8\pi \in_0 r}$$

eq (3)

As

$$\frac{\in n^2 h^2}{mZe}$$

$$E_n = \frac{-mZ^2 e^4}{8 \in_0^2 n^2 h^2}$$

eq (4)

Where En is the energy of nth orbit.
For hydrogen atom , the number of protons in nucleus is one, so (Z = 1).

$$E_n = -\frac{me^4}{8\in_0^2 h^2}\left[\frac{1}{n^2}\right]$$

eq (5)

When the values of these constants are substituted along with their units, then it comes out to be 2.178 x 10 $^{-18}$ J.

$$E_n = -2.178 \times 10^{-18}\left[\frac{1}{n^2}\right] J$$

eq (6)

Gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value shows that electron is bound by the nucleus i.e. electron is under the force of attraction of the nucleus.

The value of energy obtained for the electron is in joules/atom. If, this quantity is multiplied by Avogadro's number and divided by 1000, the value of En will become

$$E_n = \frac{6.02 \times 10^{23} \times 2.18 \times 10^{-18}}{1000}\left[\frac{1}{n^2}\right] kJmol^{-1}$$

$$E_n = -\frac{1313.315}{n^2} kJmol^{-1} \qquad \text{................} \qquad \text{eq (7)}$$

Substituting, the values of n as 1,2,3,4,5, etc. in equation 7

$$E_1 = -\frac{1313.31}{1^2} = -1313.31 \ kJmol^{-1}$$

$$E_2 = -\frac{1313.31}{2^2} = -328.32 \ kJmol^{-1}$$

$$E_3 = -\frac{1313.31}{3^2} = -145.92 \ kJmol^{-1}$$

$$E = -\frac{1313.31}{} = -82.08 \ kJmol^{-1}$$

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \ kJmol^{-1}$$

$$E_\infty = -\frac{1313.31}{\infty^2} = 0 \ kJmol^{-1} \ \text{(electron is free from the nucleus)}$$

Calculation of energy differences

$$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99 \ kJmol^{-1}$$
$$E_3 - E_2 = (-145.92) - (-328.32) = 182.40 \ kJmol^{-1}$$
$$E_4 - E_3 = (-82.08) - (-145.92) = 63.84 \ kJmol^{-1}$$

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \text{........................}$$

These values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply.

Calculation of ionization energy of hydrogen

$$E_n - E_1 = 0 - (-1313.31) = 1313.31 \ kJmol^{-1}$$

1313.31 kJmol^{-1} is the ionization energy of hydrogen. This value is the same as determined experimentally.

<center>**Defects of Bohr's Atomic Model**</center>

1. Applicable to single electron system

Bohr's theory can successfully explain the origin of the spectrum of H-atom and ions like He^{+1}, Li^{+2} and Be^{+3}, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons system like He, Li and Be, etc.

2. Fine structure

When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very fine lines, i.e. original lines are seen divided into other lines. The Hα- line in the Balmer series consists of five -component lines. This is called fine structure or multiple structure. The appearance of several lines in a single line suggests that only one quantum number is not sufficient to explain the origin of various spectral lines.

3. Three dimensional space

Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. The atomic model is not flat.

4. Zeeman effect and Stark effect

When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called Zeeman effect. When the excited hydrogen atoms are placed in an electrical field, then similar splitting of spectral lines takes place which is called Stark effect.

Bohr's theory does not explain either Zeeman or Stark effect.

<div align="center">

Quantum numbers

</div>

Definition

Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom. An electron in an atom is completely described by its four quantum numbers. Quantum numbers serve as identification numbers or labels, which completely describe an electron. These quantum numbers specify position of electron in an atom.

(1) Principal quantum number (n)

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger.

Values

Its values are non-zero, positive integers up to infinity.

$$n = 1, 2, 3, 4, 5,.........................$$

Advantages

1. The value of n represents the shell or energy level.

2. Letter notations K, L, M, N, etc are also used to denote the various shells.

For example, when n =1, it is called K shell, for n = 2, it is L shell and so on.

3. The values of n also determine the location of electron in an atom, i.e the distance of electron from the nucleus.

4. Greater the value of 'n' greater will be the distance of electron from the nucleus.

5. It is a quantitative measure of the size of an electronic shell, 'n' also provides us the energy of electron in a shell.

(2) Azimuthal quantum number (l)

A spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. Each shell is divided into subshells. Azimuthal quantum number represents the sub-shells.

Values

The values of azimuthal quantum number (l) are:

$$l = 0, 1, 2, 3, ...(n-1)$$

Its value depends upon n. The values of azimuthal quantum number always start from zero.

Advantages

1. These values represent different sub-shells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffused and fundamental, respectively.

2. A subshell may have different shapes depending upon the value of (l). It may be spherical, dumb-bell, or some other complicated shapes.

3. The value of ' l ' is related to the shape of the sub-shell as follows:

$\ell = 0$	s-subshell	spherical
$\ell = 1$	p-subshell	dumb-bell
$\ell = 2$	d-subshell	(complicated shape)

Relationship between principal and azimuthal quantum number

| n = 1 | K-shell | $\{\ell = 0$ | {s-subshell | should be called as | 1s |

| n = 2 | L-shell | $\begin{cases}\ell = 0 \\ \ell = 1\end{cases}$ | $\begin{cases}\text{s-subshell} \\ \text{p-subshell}\end{cases}$ | 2s / 2p |

| n = 3 | M-shell | $\begin{cases}\ell = 0 \\ \ell = 1 \\ \ell = 2\end{cases}$ | $\begin{cases}\text{s-subshell} \\ \text{p-subshell} \\ \text{d-subshell}\end{cases}$ | 3s / 3p / 3d |

| n = 4 | N-shell | $\begin{cases}\ell = 0 \\ \ell = 1 \\ \ell = 2 \\ \ell = 3\end{cases}$ | $\begin{cases}\text{s-subshell} \\ \text{p-subshell} \\ \text{d-subshell} \\ \text{f-subshell}\end{cases}$ | 4s / 4p / 4d / 4f |

Formula for calculating electrons

$$2 (2l + 1)$$

$\ell = 0$	s-subshell	total electrons = 2
$\ell = 1$	p-subshell	total electrons = 6
$\ell = 2$	d-subshell	total electrons = 10
$\ell = 3$	f-subshell	total electrons = 14

(3) Magnetic quantum number (m)

Strong magnetic field splits the spectral lines further. In order to explain this splitting, a third quantum number called the magnetic quantum number (m) has been proposed. It is also called orientation quantum number.

Values

Its values are

$$m = 0, \pm 1, \pm 2, \pm 3, \dots\dots\dots\dots\dots\dots$$

The value of 'm' depends upon values of 'l'

$\ell = 0$	s-subshell	m=0
$\ell = 1$	p-subshell	m=0, ±1(p-subshell has three degenerate orbitals)
$\ell = 2$	d-subshell	m=0,±1, ±2(d-subshell has five degenerate orbitals)
$\ell = 3$	f-subshell	m=0,±1, ±2, ±3(f-subshell has seven degenerate orbitals)

For a given value of ' l ' the total values of 'm' values are (2 l +1).

Advantages

1. It tells about degeneracy of orbitals in space.

2. It tells us the number of different ways in which a given s, p, d or f-subshell can be arranged along x, y and z-axes in the presence of a magnetic field.

For s-subshell
- In case of s-subshell $l = 0$, so, $m = 0$.
- s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes.
- s-subshell is not sub-divided into any other orbital.
- The shape of 's' orbital is such that the probability of finding the electron in all the directions from the nucleus is the same.
- It is a spherical and symmetrical orbital.

For p-subshell
- For p-subshell, $l = 1$ and $m = 0, \pm1$.
- These values of 'm' imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y, and z axes.
- These three orbitals are perpendicular to each other and named as px, py, and pz.
- They have egg shaped lobes which touch each other at the origin.
- In the absence of the magnetic field, all the three p-orbitals have the same energy and are called degenerate orbitals.
- These orbitals are said to be 3-fold degenerate or triply degenerate.

For d-subshell
- For d-subshell $l = 2$ so $m = 0, \pm1, \pm2$.
- It implies that it has five space orientations and are designated as dxy ($m = -2$), dyz ($m = -1$), dzx ($m = +1$), dx^2-y^2 ($m = +2$) and dz^2 ($m - 0$)
- All these five d-orbitals are not identical in shape.
- In the absence of a magnetic field, all five d-orbitals have the same energy and they are said to be five-fold degenerate orbitals.

For f-subshell
- For f-subshell, $l = 3$ and $m = 0, \pm1, \pm2, \pm3$.
- They have complicated shapes.

(4) Spin quantum number (s)
In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates about its own axis either in a clockwise or anti-clockwise direction. This is also called self-rotation. Opposite magnetic fields are generated by the clockwise and anti-clockwise spins of electrons.

Background
Alkali metals have one electron in their outermost shell. Their emission spectra are observed by means of high resolving power spectrometer and each line in the spectrum is found to consist of pair of lines. This is called doublet line structure. Lines of doublet line structure are widely separated from each other. This spin motion is responsible for doublet line structure in the spectrum.

Important long questions from past papers
1. Write any four properties of cathode rays.
2. How did Rutherford discover the nucleus of atom?
3. Give properties of neutron in detail.
4. Write down the experiment how neutron was discovered.
5. Describe J.J Thomson's experiment for determining e/m value of electron.

6. Describe Millikan's oil drop method for the measurement of charge on electron.
7. Write four defects of Bohr's atomic model.
8. Derive the formula for calculating the energy of an electron in n^{th} orbit using Bohr's model.
9. Derive an expression to determine the radius of an orbit using Bohr Model.
10. Define Quantum numbers. Discuss briefly Azimuthal quantum number/principal quantum number/magnetic quantum number and spin quantum number.

<center>

Ch 6

Chemical Bonding

Atomic Sizes

</center>

Definition

The atomic radius means the average distance between the nucleus of the atom and its outermost electronic shell.

Reasons of less precision of radius determination

The radius of an atom cannot be determined precisely due to the following reasons:

(i) There is no sharp boundary of an atom. The probability of finding an electron never becomes exactly zero even at large distances from the nucleus.

(ii) The electronic probability distribution is affected by neighbouring atoms. For this reason, the size of an atom may change from one compound to another.

Techniques for radius measurement

Atomic radii can be determined, by measuring the distances between the centres of adjacent atoms with the help of X-rays or by spectroscopic measurements.

Variation of Atomic Radii in the Periodic Table

Along periods

The atomic radii decrease from left to the right in a period. The decreasing trend in a period is due to:

1. The increase in the nuclear charge. As the nuclear charge increases the pull on the electrons is increased and size of an atom decreases.

2. The shielding effect remains the same from left to right in a period.

Shielding effect/screening effect

The screening effect is also called shielding effect. This is responsible for the decrease in force of attraction of the nucleus for the electrons present in the valence shell.

Decrease of atomic radii in higher periods

The decrease of atomic radii is very prominent in second period, but less in higher periods. The decrease is small when we travel from left to right in transition elements Sc(21)-Zn(30), Y(39)-Cd(48) due to the intervening electrons.

Along groups

The atomic radii increase from top to bottom in a group. The increase in atomic radii in a group is due to:

1. Increase in the number of shells

2. Increase in screening effect

<center>

Ionic Radii

</center>

Definition

The ionic radius of an ion is the radius of the ion while considering it to be spherical in shape.

Ionic radii of cations and anions

The ionic radius of a cation is smaller than the atomic radius of the element from which it is derived. The ionic radius of an anion is greater than the atomic radius of the corresponding atom.

Examples

The radius of Na atom, for example, reduces from 186 pm to 95 pm after conversion into Na+ ion. The ionic radius of Cl- ion increases from 99 pm to 181 pm. The cationic radius decreases with the increase in the effective nuclear charge on the ion.

Decrease in radius with increasing positive charge

The decrease in radius is larger for divalent ions (Mg^{2+}) and still larger for trivalent ions (Al^{3+}).

Reason

This is due to the reason that with the successive loss of electrons, the nuclear charge attracts the remaining electrons with a greater force.

Increase in radius with increasing negative charge
The increase in the size of the anion is due to the increase in the electron-electron repulsion because of the increase in the valence shell electrons. Greater the amount of negative charge on an atom greater the size of ion.

Trend in the periodic table
The variation of ionic radii in groups and periods has the same trend as for atomic radii. Ionic radius for metals is for positive ions and for elements of group number VA to VII A is for negative ions.

Calculation of ionic radii
Let us consider, the positive and negative ions, which are held together by electrostatic forces of attraction in a crystal lattice. r+ and r- are the values of radii of cation and anion, respectively.

1. Interionic distance
The interionic distance 'R' in a crystal lattice is equal to the sum of the cationic radius r+ and the anionic radius r-

$$R = r_+ + r_-$$

2. Pauling's study
Pauling was able to determine the distance between K+ and Cl- ions in potassium chloride crystal.
$$R = 133pm + 181\ pm = 314\ pm$$
The ionic radius appeared to be an additive property. Pauling extended this concept to other K^+ salts and calculated the radii of other ions from the relationship:

$$r_- = R - r_+$$

The ionic radii of different cations can also be determined.
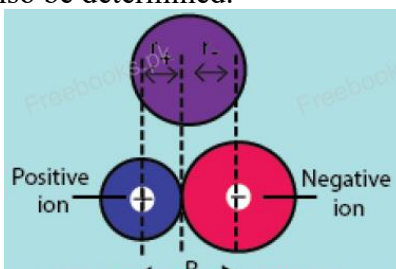
Covalent Radii

Definition
The covalent radius of an element is defined as half of the single bond length between two similar atoms covalently bonded in a molecule.

Example
The covalent radius of hydrogen, for example, is 37.7 pm. It is half of the single bond length (75.4 pm) between the two H atoms in H-H molecule.
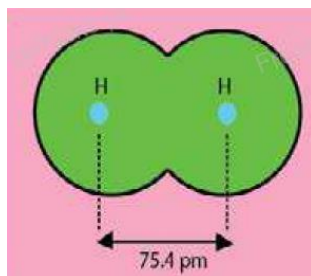
Determination of covalent radius
The covalent radius of an atom can be used to determine the covalent radius of another atom. For example, the experimentally determined bond length of C-Cl in CH_3Cl is 176.7 pm. The covalent radius of Cl-atom being known as 99.4 pm, that of C-atom can be calculated by subtracting this value from C-Cl bond length. So, the covalent radius of C-atom = 176.7- 99.4 = 77.3 pm.

Variation along periodic table

The variation of covalent radii in groups and periods is almost the same as of atomic radii.

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Ionization Energy

</div>

Definition

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization.

Example

$$Mg \rightarrow Mg^+ + e^- \qquad \Delta H = 738 kJmol^{-1}$$

Factors Influencing Ionization Energies

Following are the factors influencing ionization energies:

(i) Atomic radius of atom

(ii) Nuclear charge or proton number of the atom

(iii) Shielding effect of inner electrons

(iv) Nature of orbital

Variation in the Periodic Table

Along periods

The ionization energies increase from left to right in a period due to:

1. Increase in the proton number.

This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell.

2. Increase in nuclear charge

It leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

Along groups

The ionization energy decrease in spite of the increase in proton number or nuclear charge due to:

1. Successive addition of electronic shells

The valence electrons are placed at a larger distance from the nucleus.

2. Effective nuclear charge decreases

As the force of attraction between the nucleus and the outer electron decreases with the increase in distance the electron can be removed more easily or with less energy.

2. Increasing shielding effect

The force of attraction also decreases due to increasing shielding effect of the intervening electrons.

Higher Ionization Energies

The energy required to remove an electron after the removal of first electron is called second ionization energy.

$$Mg \rightarrow Mg^{++} + e^- \qquad \Delta H = 1450 kJmol^{-1}$$

Similarly, the energy required to remove third electron after the removal of second one is called the third ionization energy, and it is 7730kJ for Mg.

Reason

Second electron is removed from a positively charged ion rather than a neutral atom. The dominant positive charge holds the electrons more tightly and thus further removal of electrons becomes more difficult.

Ionization energy is index to the metallic character

Ionization energy is an index to the metallic character. The elements having low ionization energies are metals and those having high ionization energies are non-metals. Those with intermediate values are mostly metalloids.

Valency determination

The gaps in the first, second, third and higher ionization energies help us to guess the valency of an element. If, there is sufficient gap between first ionization energy and second one, then the element shows valency of one.

Electron Affinity

Definition

The electron affinity of an atom is the energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge.

Example

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H = -349 kJmol^{-1}$$

Factors Influencing the Electron Affinity

Following factors influence the electron affinity:

1. Atomic radius
2. Nuclear charge
3. Shielding effect

Variation in the Periodic Table

Along periods

The electron affinities of elements increase from left to right in the periodic table due to:

1. Increase in the nuclear charge.
2. Decrease in atomic radius
3. Constant shielding effect

The alkali metals have the lowest and the halogens have the highest electron affinities.

Along groups

The electron affinities usually decrease from top to bottom due to:

1. Increase in atomic radii
2. Decrease in effective nuclear charge
3. Increase in shielding effect

Exceptions

1. Fluorine has electron affinity less than that of chlorine.

Reason

Fluorine has very small size and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick cloud repels the incoming electron.

2. The elements of group IIA, VA and VIII show abnormally low values in every period of the periodic table. This can be understood from their electronic configurations.

Electronegativity

Definition

The tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

Factors influencing electronegativity

Following factors influence the electronegativity:

1. Atomic radius
2. Nuclear charge
3. Shielding effect

It is related to the ionization energy and the electron affinity of the element. Thus, fluorine atom is more electronegative than hydrogen atom.

Calculation of electronegativity values

Pauling calculated the electronegativity values of elements from the difference between the expected bond energies for their normal covalent bond and the experimentally determined values. He devised an electronegativity scale on which fluorine is given an arbitrary standard value 4.0. It is the most electronegative element. The electronegativity values of other elements are compared with fluorine.

Units
Electronegativity has no units.

Variation in the Periodic Table

Along periods
The electronegativity of elements increase from left to right in the periodic table due to:
1. Increase in the nuclear charge
2. Decrease in atomic radius
3. Constant shielding effect

Along groups
The electronegativity decreases from top to bottom down the group due to:
1. Increase in atomic radii
2. Decrease in effective nuclear charge
3. Increase in shielding effect

Bond type and electronegativity
The electronegativity differences of the elements can be related to dipole moments and bond energies. The difference in the electronegativity values of the bonded atoms is an index to the polar nature of the covalent bond.
1. When the difference is zero the bond between the two atoms is non-polar.
Thus, all the bonds which are formed between similar atoms are non-polar in character, while those formed between different elements are mostly polar.
2. Elements of widely different electronegativities form ionic bonds.
3. A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds.

Types of Bonds

Chemical bonds can be classified as:
(i) Ionic bond
(ii) Covalent bond
(iii) Coordinate covalent bond

Ionic Bond

Definition
According to the Lewis theory, ionic bond is formed by the complete transfer of electron or electrons from an atom with low ionization energy to another atom with high electron affinity.

Example
Formation of potassium chloride

Ionization of potassium
The electronic configuration of potassium is:
$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$$
It may be represented as K (2,8,8,1)
It tends to lose the outermost electron to form K^+ ion.
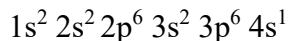
$$K(2,8,8,1) \rightarrow K^+(2,8,8) + e^- \qquad \Delta H = 419.0 kJmol^{-1}$$
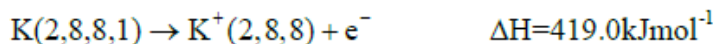
After the loss of an electron, potassium attains the nearest inert gas configuration of Ar (2,8,8). This is first ionization energy of potassium.

Electron affinity of chlorine
Chlorine atom has the electronic configuration $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or Cl (2,8,7). It tends to attain the nearest inert gas configuration of Ar (2,8,8) releasing 348.6 $kJmol^{-1}$ energy. It is the electron affinity of chlorine.

$$:\ddot{C}l \cdot + e^- \rightarrow :\ddot{C}l^- : \qquad \Delta H = -349 kJmol^{-1}$$

The oppositely charged K^+ and Cl^- ions are held together by strong electrostatic force of attraction. The lattice energy of KCl is 690 $kJmol^{-1}$.

Other examples

$$Ca\ (2,8,8,2) \longrightarrow Ca^{2+}\ (2,8,8) + 2e^-$$
$$Al\ (2,8,3) \longrightarrow Al^{3+}\ (2,8) + 3e^-$$
$$O\ (2,6) + 2e^- \longrightarrow O^{2-}\ (2,8)$$
$$S\ (2,8,6) + 2e^- \longrightarrow S^{2-}\ (2,8,8)$$
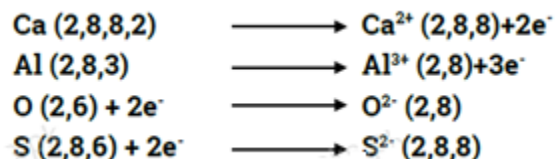
Calcium oxide contains ions in the ratio of $Ca^{2+} : O^{2-}$ and its formula is CaO, while in aluminium oxide, Al^{3+} and O^{2-} ions are present in the ratio 2:3. Its formula is Al_2O_3. Similarly, CaS and Al_2S_3 are also ionic compounds to some extent.

Percentage of ionic character

In order to decide the % of ionic nature in a compound note the difference of electronegativity between the bonded atoms.

If the difference is 1.7 or more then the bond is said to be ionic.

Example

NaCl has 72% ionic character.

CsF has 92% ionic character.

There is no bond with 100% ionic character.

Covalent Bond

Definition

According to Lewis and Kossel, a covalent bond is formed by the mutual sharing of electrons between two atoms.

Types of covalent bond

1. Non-polar covalent bond
2. Polar covalent bond

Non-polar covalent bonds

In such bonds, the bonding electron pairs are equally shared and thus bonds are electrically neutral.

Example

In H_2 or Cl_2 molecules, the two electrons forming the covalent bond are equally shared by the two identical atoms having same electronegativities.

$$H : H \quad or \quad H - H \qquad\qquad :\ddot{C}l : \ddot{C}l: \quad or\ Cl---Cl$$

Other examples

F_2, Br_2 and I_2

CCl_4

Reason

This is due to cancellation of all the dipoles of this molecule due to its symmetry. All the C-Cl bonds are polar but molecule is non-polar overall.

$$:\ddot{C}l:$$
$$:\ddot{C}l \quad :C: \quad \ddot{C}l:$$
$$:\ddot{C}l:$$

or
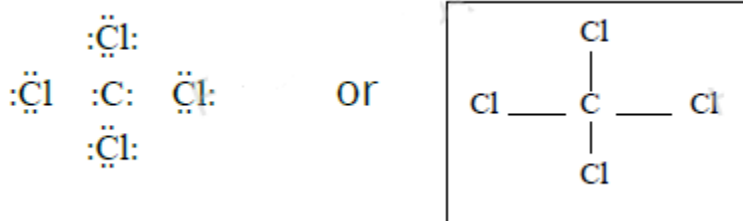
Similar molecular geometry

CH_4, SiH_4, and $SiCl_4$

Polar covalent bond

When two different atoms are joined by a covalent bond, the electron pair is not equally shared between the bonded atoms. The bonding pair of electrons will be displaced towards the more electronegative atom

Examples

One end of the molecule is partially positive and the other partially negative.

Hydrogen fluoride

$$H \times \ddot{F}: \quad or \quad H^{\delta+} \times F^{\delta-}$$

Water

$$H \times \ddot{O} \times H$$

Methyl chloride

$$H: \; C \; \ddot{\underset{xx}{Cl}}^{x}$$

or

Methanol

$$H: \; C \; \underset{xx}{\overset{xx}{O}} \; {}^{x}_{x}H$$

or
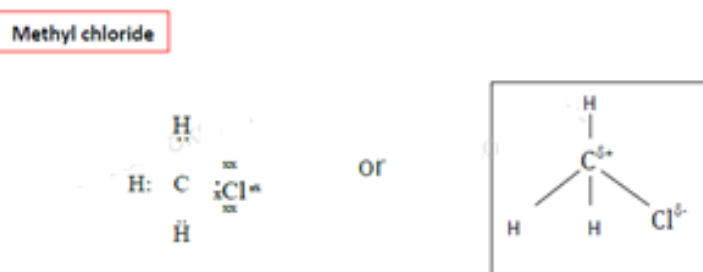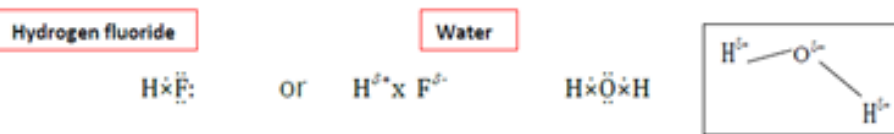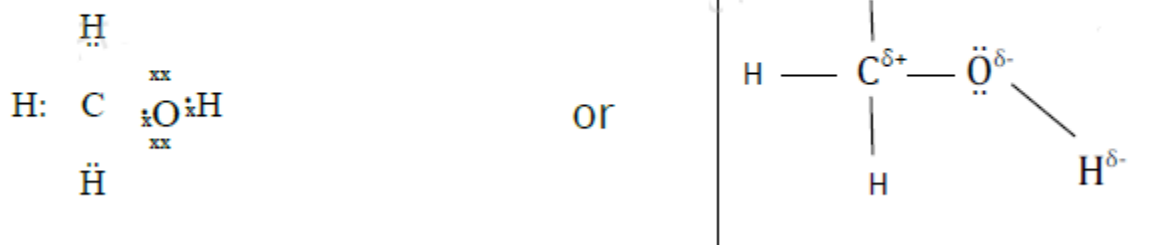
Molecules with double and triple bond

$$:N:::N: \quad or \quad :N \equiv N:$$

$$\ddot{O}::\ddot{O} \quad or \quad \ddot{O}=\ddot{O}$$

Carbon dioxide

$$:\ddot{O}::C::\ddot{O}: \quad \text{or} \quad \ddot{O}=C=\ddot{O}$$
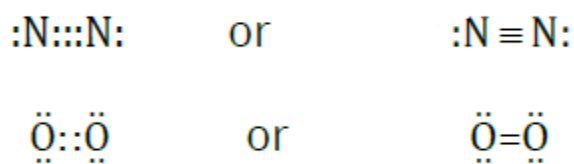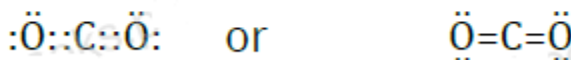
Each bond represents a pair of electrons.

In a double bond (=), two shared pairs and in a triple bond (≡), three shared pairs of electrons are involved.

Carbon compounds

Some of the non-metallic atoms, particularly carbon atoms, mutually share their electrons with each other. This leads to the formation of macromolecules. Diamond, graphite and SiC are the best examples of such molecules. Carbon can make single, double and triple covalent bonds in alkanes, alkenes and alkynes.

Ethane

H   H
H :C̈: C̈: H   or
H   H

Disilane

H   H
H :S̈i: S̈i: H   or
H   H

Ethene and ethyne

H   H
:C: :C: or
H   H

$$H:C::C:H \quad \text{or} \quad H\text{-}C\equiv C\text{-}H$$
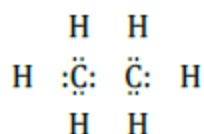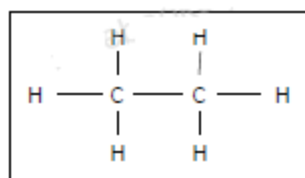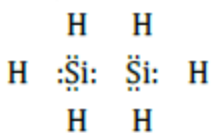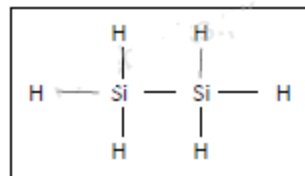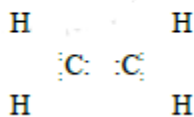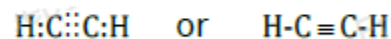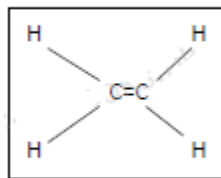
Coordinate Covalent Bond

Definition

A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.

Examples

1. Bond formation between NH_3 and BF_3

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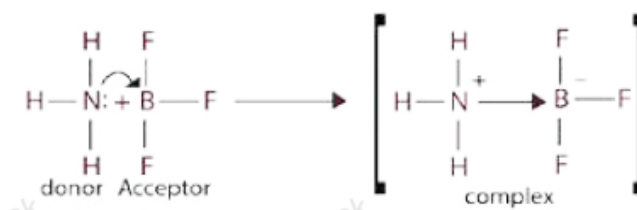
NH_3 has three covalent bonds and there is a lone pair of electrons on nitrogen atom. Boron atom in BF_3 is deficient in electrons. The octet of B is not complete in BF_3. Nitrogen can donate the pair of electrons to the acceptor BF_3 and this result in the formation of a coordinate covalent bond.

Adduct/complex formation
The complex so produced is overall neutral and charges are indicated on N and B atoms.

In some of the compounds, after the formation of a coordinate covalent bond, the distinction between covalent bond and coordinate bond vanishes.

2. Bond formation between H_2O and H^+
Water donates its electron pair to H+ ion to give H_3O^+ ion. All the three bonds between oxygen and hydrogen have equal status. Every bond is 33% coordinate covalent and 66% covalent.
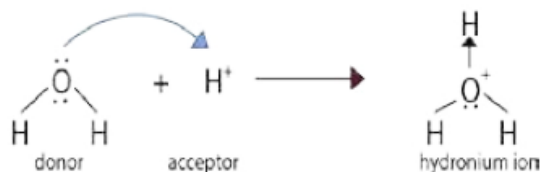
3. Oxonium ion formation
All the alcohols and ethers offer their lone pairs to H^+ to give coordinate covalent bonds. The ions so produced are called oxonium ions.
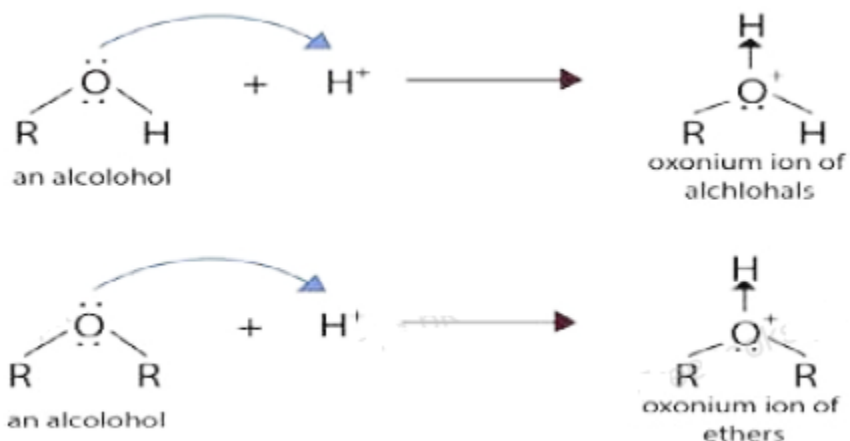
4. Bond formation between NH_3 and H^+
Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ ion.
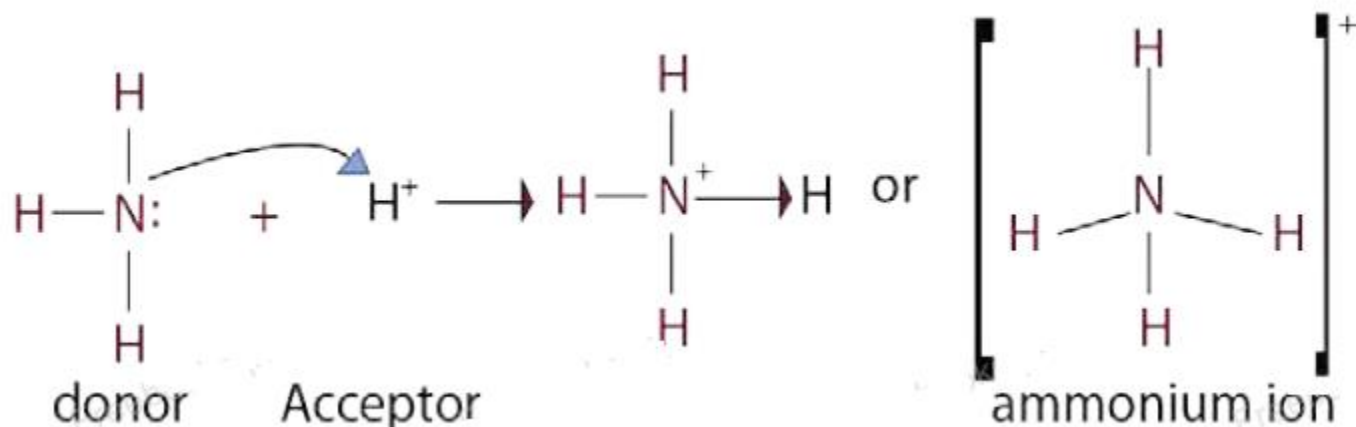
5. Other examples

(a) All the primary, secondary and tertiary amines like ammonia make such bonds with H^+.

(b) PH_3 combines with H^+ to give PH_4^+ ion called phosphonium ion.

(c) Coordinate covalent bonds are present in HNO_3.

(d) Many oxyacids of halogens, like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bonds between chlorine and oxygen.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Postulates:

1. Both lone pairs as well as the bond pairs participate in determining the geometry of the molecules.
2. All electron pairs remain at maximum distance apart to avoid repulsions.
3. Lone pairs occupy more space than bond pairs because bond pair is attracted by two nuclei whereas lone pair is under the influence of one nucleus.
4. Lone pairs exert greater repulsion forces than bond pairs.
5. The magnitude of repulsions between the electron pairs is of the following order:
   lone pair-lone pair>lone pair-bond pair>bond pair-bond pair

These repulsions are called Vander Waals Repulsions.

6. Two electron pairs of double bond and three electron pairs of triple bond occupy more space than one electron pair of single bond.
7. Electron pairs of double bond and single bond are considered as single electron pair in determining the geometry of the molecule.

Types of Molecules:

Let us consider

A= As central polyvalent atom

B= Types of atom bonded to A

More than one 'B' type atoms are linked to A to give **AB₂, AB₃, AB₄** type molecules.

1. **AB₂ Type molecules:**

   Total electron pairs= 2
   Bond pairs= 2
   Lone pairs= 0
   Geometry= Linear
   Angle= 180°

   Shape:
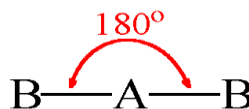
   Examples: $BeCl_2$, $HgCl_2$

2. **AB₃ Type molecules:**
   Total no of electron pair= 3. We can have two sub-types of AB₃ molecules.

   a. **AB₃ Type with no lone pair:**
      Bond pairs= 3

      Lone pairs= 0

      Geometry= Trigonal planar

      Angle= 120°

Shape:

104
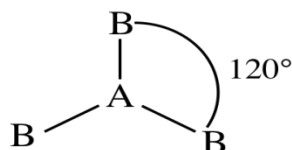
Example (with single bond): BF$_3$ **Shape:**

Example (with multiple bond): SO$_3$
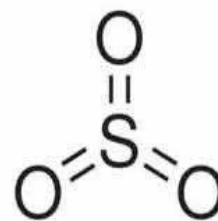
b. AB$_3$ Type with one lone pair:
Bond pairs= 2

Lone pairs= 1

Geometry= Bent or angular

Angle= less than 120°

Shape:

Example (with single bonds): SnCl$_2$

Example (with multiple bond): SO$_2$

1.431 Å **Shape**

119°
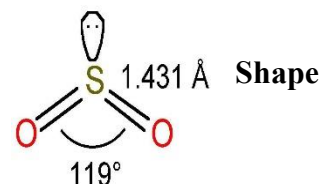
3. AB$_4$ Type Molecules:
Total electron pairs= 4
We can have 3 sub types of AB$_4$ molecules.

a. AB$_4$ with no lone pair:
Bond pairs= 4
Lone pairs= 0
Geometry= Tetrahedral
Angle= 109.5°
Shape:
Example: CH$_4$, BF$_3$

109.5°

b. AB$_4$ type with no lone pair:
Bond pairs= 3

Lone pairs= 1

Geometry= Trigonal Pyramidal

Angle= less than 109.5°

Example: NH$_3$. Angle is 107.5° in NH$_3$

Shape:

107°
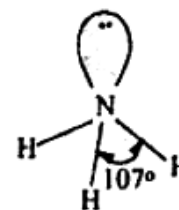
Pyramidal shape

c. AB$_4$ with two lone pairs:

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Bond pairs= 2

Lone pairs= 2

Geometry= Bent or angular

Angle= less than 109.5°

Shape:
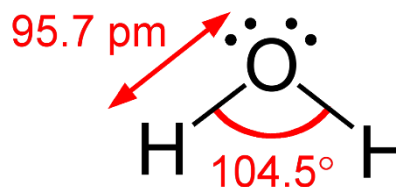
Example: H_2O angle in water is 104.5°

95.7 pm

H   104.5°   H

Valence Bond Theory(VBT)

VBT is concerned with both bond formation and the shapes of the molecules.

Main Points:

1. This theory considers molecule as a combination of atoms.
2. According to this, a covalent bond is formed when half-filled orbitals (in valence shell) of two atoms overlap.
3. Pair of electrons (one from each atom) then occupies the overlapped orbital (thus bond formation take place).
4. Larger the overlap stronger is the bond.
5. Direction of the bond is determined by the direction of the overlap.
6. Depending upon the overlap covalent bond can either be σ (sigma) or π (pi).

sigma bond (σ bond):

When two orbitals overlap in such a way that probability of finding an electron is maximum around the line joining the two nuclei it is called sigma bond.

pi bonds (π bond):

When two orbitals overlap in such a way that probability of finding an electron is above and below the inter-nuclear axis it is called pi bond.

Types of overlaps with examples:

1. s-s overlap:

s-s overlap gives rise to sigma bond

For Example: H_2 molecule

H= $1=1s^1$

H   H H_2

1   +   1   →   1↓

1s   1s   ss overlapping

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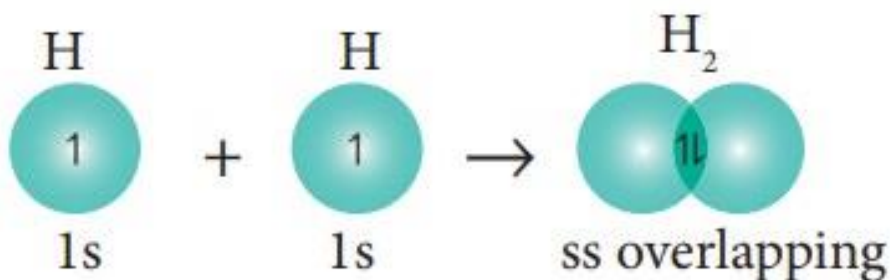
2. s-p overlap:

When s and p orbitals overlap sigma bond is formed.

For example: In HF molecule 1s of H and 2pz of F overlap to form sigma bond

$H= 1=1s^1$

$F= 9= 1s^2,2s^2,2p_x^2,2p_y^2,2p_z^1$
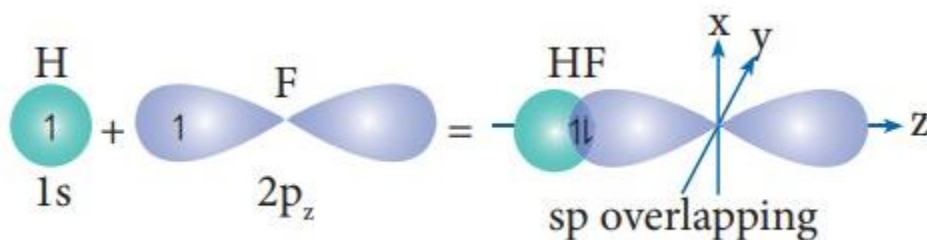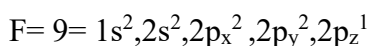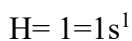
3. p-p overlapping:

Type1: When there is a single bond then p-p overlap gives rise to sigma bond.

For example: F_2 molecule (half-filled 2pz orbitals of both fluorine atoms overlap with each other)

$$F=9=1s^2,2s^2,2p_x^2,2p_y^2,2p_z^1$$
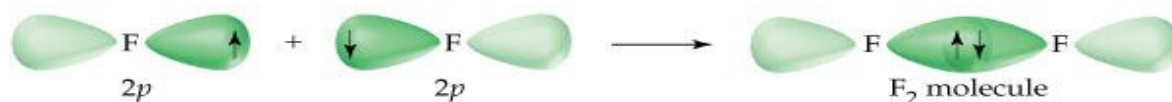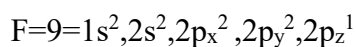
Type 2When there is a double or a triple bond then pi bond is also formed in addition to sigma bond

For example:N_2 molecule

$$N_7 = 1s^2,2s^2,2p_x^1,2p_y^1,2p_z^1$$
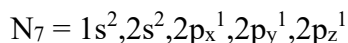
All the three partially filled p orbitals of one N atom overlap with p orbitals of other N atom

- $p_x$overlaps with p_x to form a sigma bond
- p_y overlaps with p_y to form a pi bond

- p_z overlaps with p_z to form a pi bond

Hence, triple covalent bond is formed
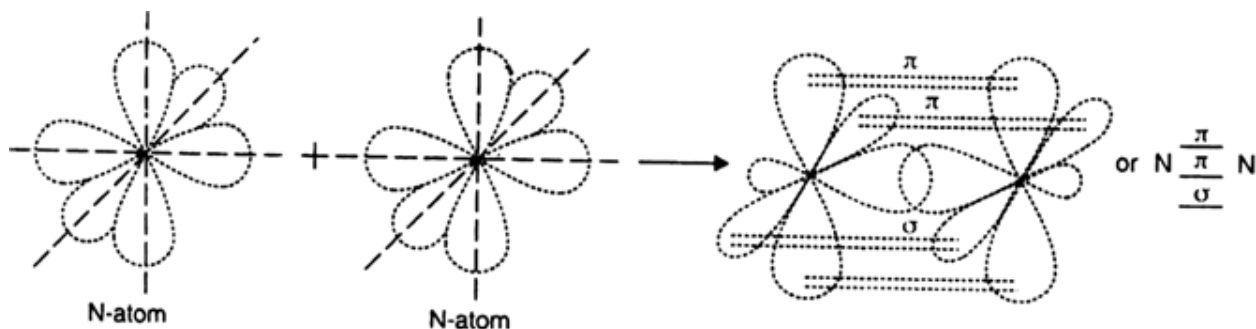
Hybridization

Definition

Hybridization is the concept in which atomic orbitals of different energy and shape intermix to form a new set of orbitals of same shape and energy.

OR

According to this, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.

Types

There are three basic types of hybridization:

1. sp^3
2. sp^2
3. sp

sp^3 Hybridization

Definition

One s and three p orbitals intermix to form a set of four equivalent sp^3 hybrid orbitals.

All these four sp^3 hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5^0 in space to give a tetrahedral geometry.

Examples

CH_4, NH_3 and H_2O

Methane
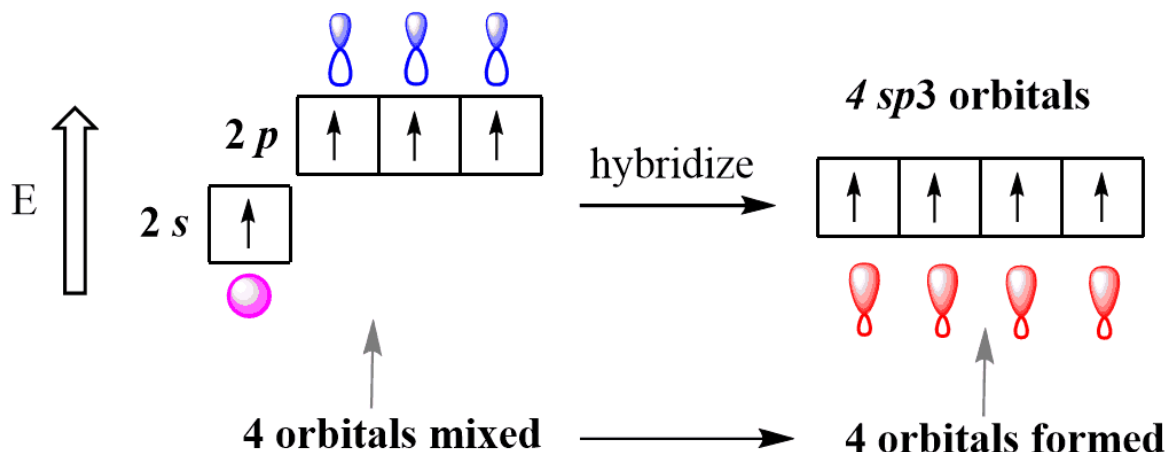
The energies of hybrid orbitals are lower than unhybridized orbitals.

unhybridized atomic orbitals of carbon

Four hybridized sp3 atomic orbitals
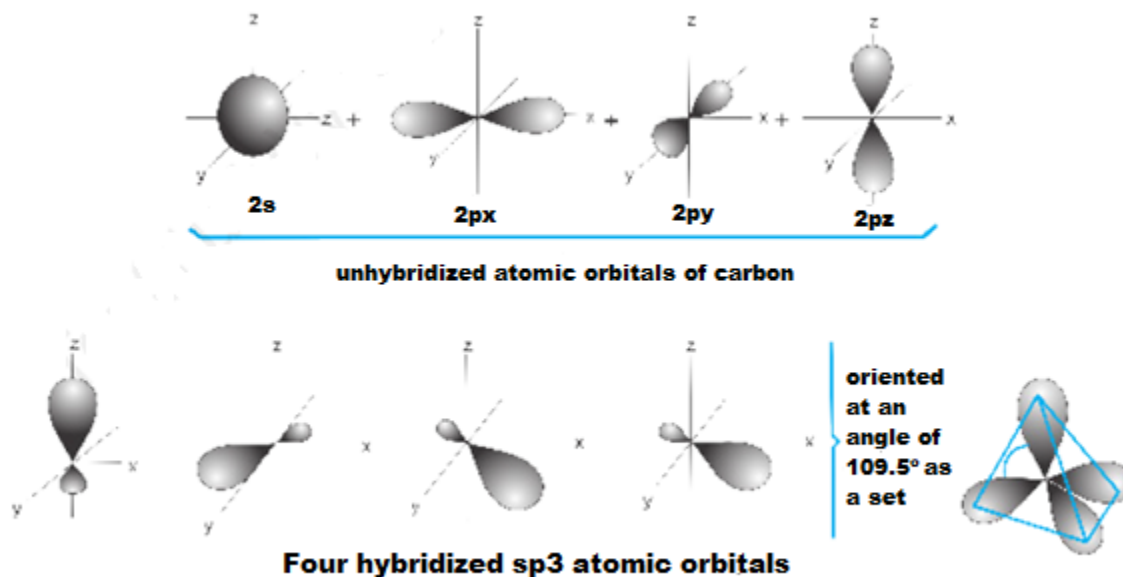
Structure of methane

Explanation of Structure of Methane

Hydrid orbitals: Four sp^3 hybrid orbitals consisting of two lobes formed due to overlap of one s and three p orbitals. Each orbital has one larger lobe and the other smaller lobe.

Overlap of orbitals: Each sp^3 hybrid orbital combines with s orbital of hydrogen to give sp^3-s sigma bonds.

Geometry: Tetrahedral geometry with carbon at center.

Bond angles: Total six bond angles of 109.5⁰.

Total bonds: Four sigma bonds formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms.

Arrangement of bonds: The four C-H bonds which result from sp^3-s overlap are directed towards the corners of a regular tetrahedron. All the four hydrogen atoms do not lie in the same plane.

Faces, corners, edges: The tetrahedral structure of CH_4 has four faces, four corners and six edges.
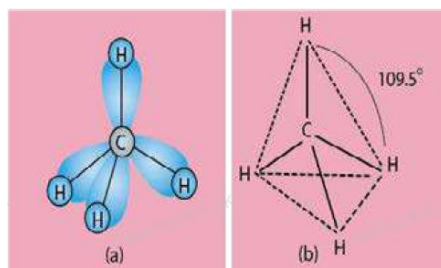
Structure of methane

Ammonia
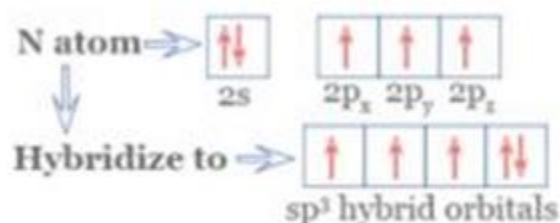
Explanation of Structure of Ammonia
> **Hybrid orbitals:** One s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals.
> **Overlap of orbitals:** Three sp^3 orbitals overlap with three s-orbitals of hydrogen atoms.
> **Geometry:** One corner of the tetrahedron is occupied by lone pair of electrons. The other three corners have single electron. Shape of ammonia is a pyramidal molecule due to repulsion of bond pairs by lone pair of electrons.
> **Total bonds:** Three sigma bonds formed by sp^3-s orbital overlap.
> **Bond angle:** The bond angle in ammonia is 107.5°.
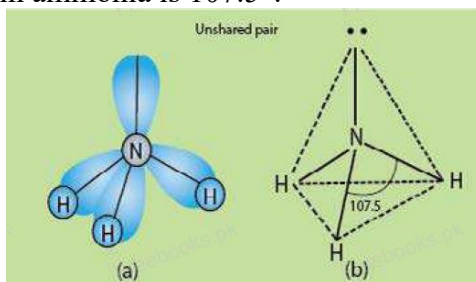
Structure of ammonia

Water H₂O
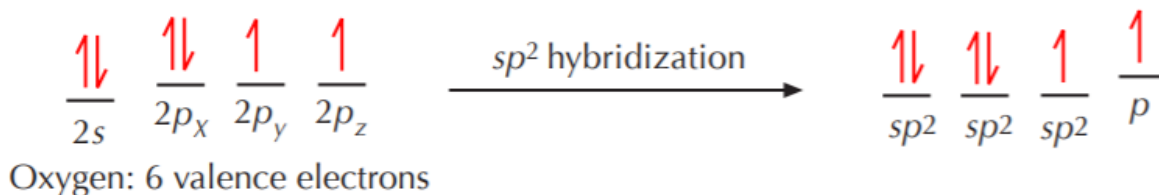
Explanation of Structure of Water
> **Hybrid orbitals:** 2s and three 2p orbitals of oxygen hybridize to form four sp^3 hybrid orbitals.
> **Overlap of orbitals:** The sp^3 orbitals overlap with s orbital of H atoms to form two sigma bonds.

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Geometry: The hybrid orbitals will have a tetrahedral arrangement. The two corners of the tetrahedron are occupied by lone pair of electrons and the other two corners by single electron. The molecule of water has bent or angular structure (distorted tetrahedron) because of the repulsion of lone pairs on bond pairs.

Total bonds: Two sigma bonds formed by sp^3-s orbital overlap.

Bond angle: The bond angle in water is 104.5°.
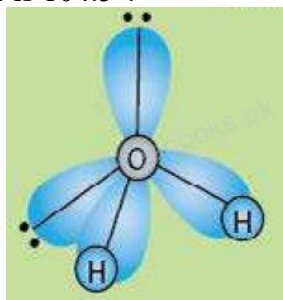
Structure of water

sp^2 hybridization

Definition

In sp^2 hybridization, one 's' and two 'p' atomic orbitals of an atom intermix three orbitals called sp^2 hybrid orbitals.

Examples

BF_3

Ethene (ethylene)
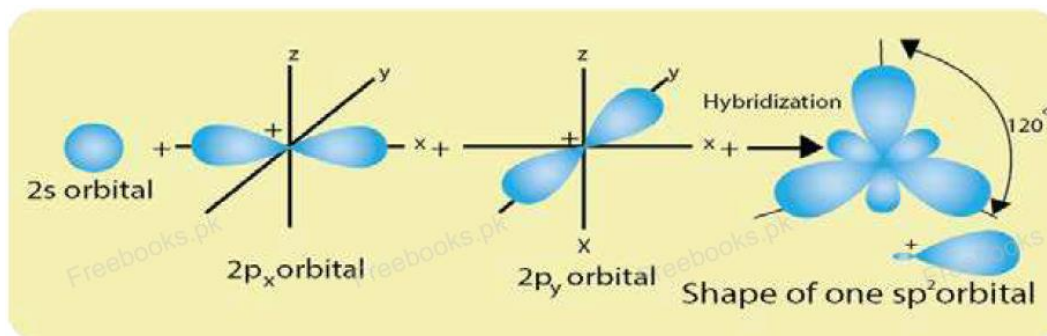
Boron Trifluoride

Unhybridized Boron
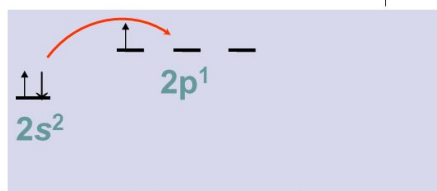
For BF_3, 3 hybrid orbitals are needed, so 3 atomic orbitals are required as follows: $(s + p + p) = sp^2$

hybridized Boron
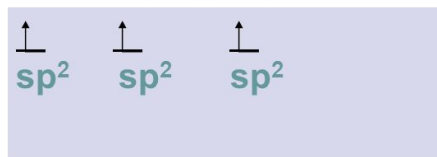
Explanation of Structure of BF_3

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Hybrid orbitals: One s and two 2p atomic orbitals of boron overlap to form three sp^2 hybrid orbitals.
Overlap of orbitals: BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms.
Geometry: The structure is triangular planar.
Total bonds: Three bonds formed by sp^2-$2p_z$ orbital overlap.
Bond angle: The three bond angles are each of 120^0.
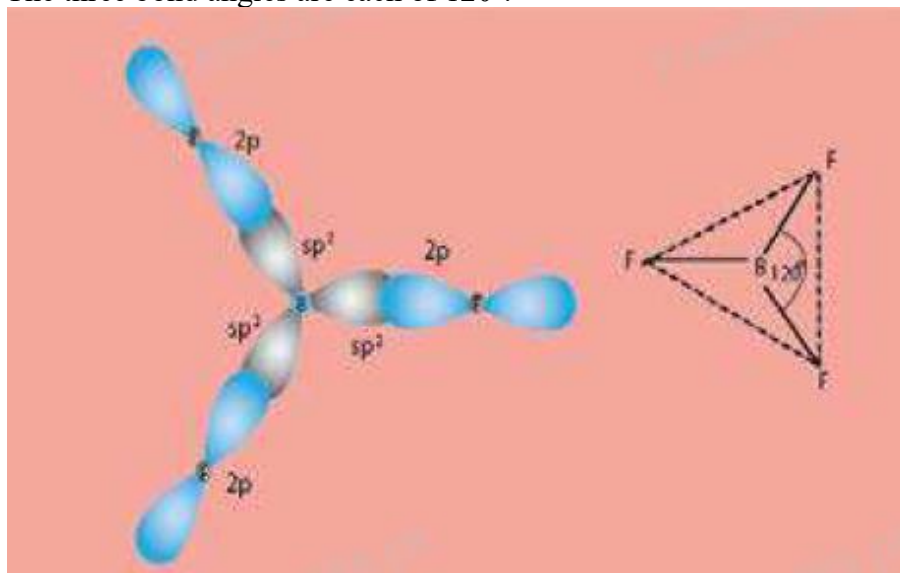
Ethene $H_2C=CH_2$ /Ethylene
The structure of alkenes can be understood through sp^2 hybridization.
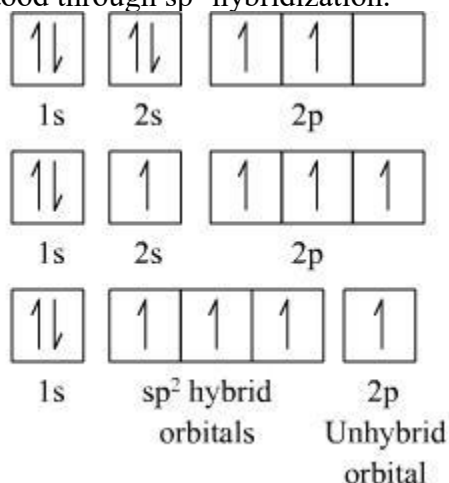
Explanation of Structure of ethene
Hybrid orbitals: Three sp^2 hybrid orbitals formed by one s and two 2p orbitals of carbon.
Unhybridized orbitals: The unhybridized $2p_z$ orbital will remain perpendicular to the hybridized orbitals.
Overlap of orbitals: sp^2 hybrid orbital of each carbon overlaps to give sp^2-sp^2 sigma bond and the other two sp^2 orbitals overlap with 1s orbitals of hydrogen to give sp^2-s sigma bonds. The unhybridized $2p_z$ orbitals overlap sideways to give a π-bond.
Geometry: Trigonal planar.
Bond angle: The bond angle between any two sp^2 hybrid orbitals is $120°$.

combine to generate three sp^2 hybrid orbitals

which are represented as the set
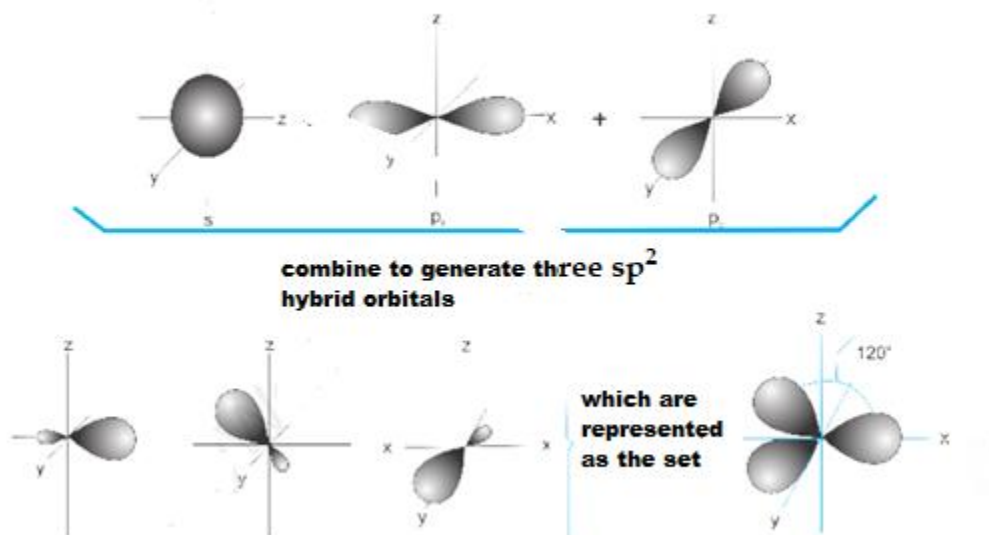
Total bonds: One sp^2-sp^2 sigma bond and two sp^2-s sigma bonds. One $2p_z$-$2p_z$ π-bond.

π - bond
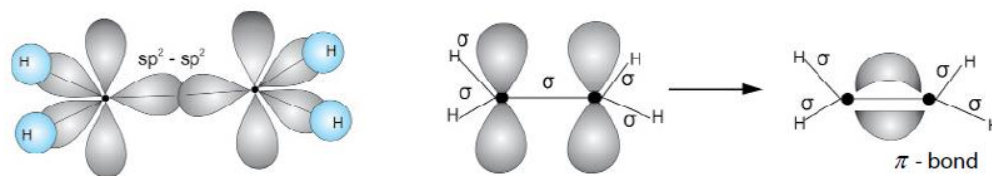
Structure of ethene

sp Hybridization
Definition
In sp hybridization, one 's' and one 'p' orbitals intermix to form two sp-hybrid orbitals called sp hybrid orbitals.
Examples
Ethylene, $BeCl_2$
Beryllium Dichloride

Unhybridized Be

$2s^2$

2p

For $BeCl_2$, 2 hybrid orbitals are needed, so 2 atomic orbitals are required as follows: $(s + p) = sp$

hybridized Be

sp   sp

Explanation of Structure of BeCl₂
- **Hybrid orbitals:** One s and one p orbital of Be overlap to give two sp hybrid orbitals.

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- **Overlap of orbitals:** Two sp hybrid orbitals of Be atom overlap with the half-filled $3p_z$-orbitals of chlorine atoms.
- **Geometry:** Linear shape.
- **Total bonds:** Two sp-$3p_z$ sigma bonds.
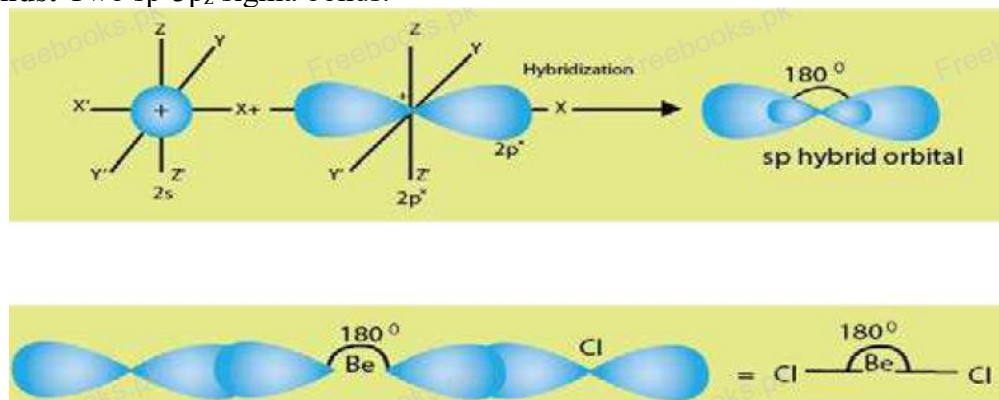
Structure of Beryllium dichloride

- **Bond angle:** The Cl-Be-Cl bond angle is 180°.

Ethyne (HC≡CH) Acetylene

Hybrid orbitals: One 2s and one 2p orbitals of the carbon atom mix together to give rise to two degenerate sp hybridized atomic orbitals.

Unhybridized orbitals: The unhybridized 2py and 2pz orbitals are perpendicular to the hybridized orbitals.

Overlap of orbitals: Two sp hybridized carbon atoms join together to form a sigma bond by sp-sp overlap. The other sp orbital forms a sigma bond with 1s orbital of hydrogen atom. The two unhybridized p orbitals on each carbon atom overlap sideways give two π -bonds.

Geometry: Linear shape.

Total bonds: One sp-sp sigma bond and two sp-s sigma bonds. Two, $2p_y$-$2p_y$ and $2p_z$-$2p_z$, π-bonds.

Bond angles: These orbitals have a bond angle of 180º.
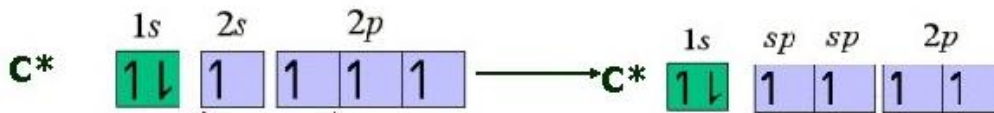
In sp hybridization, there are still two unhybridized 2p orbital

sp hybridized carbon atom

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combine **to generate
two sp orbitals**

**Which are
represented
as the set**

180°

| Formation of σbonds | Formation of π bonds | Space filling model |
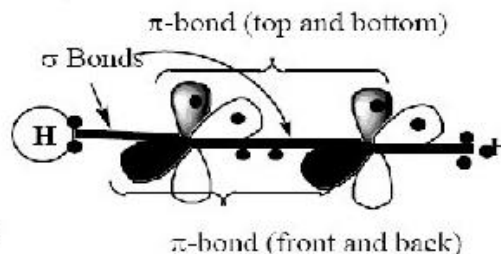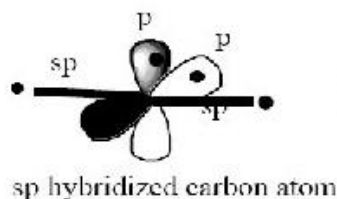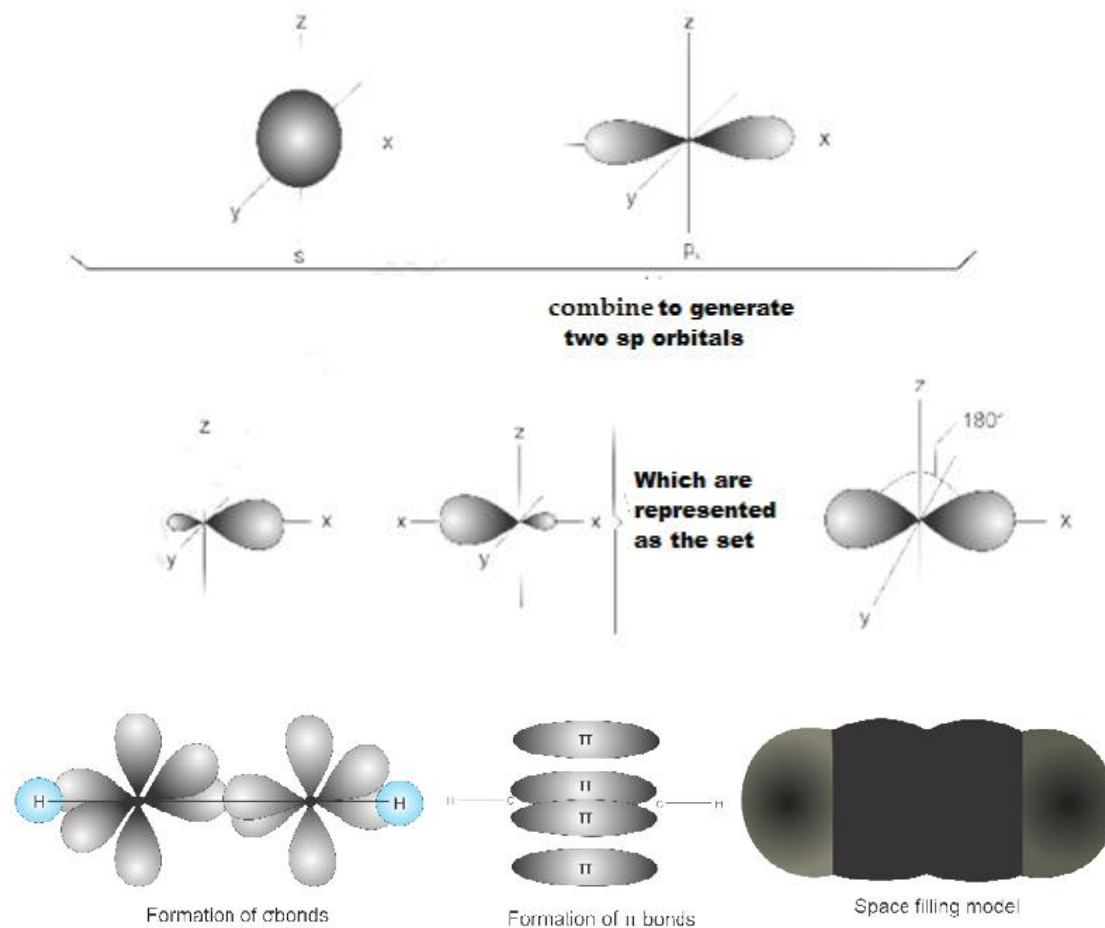
Molecular Orbital Theory

Postulates

1. It considers the whole molecule as a single unit.

2. It assumes that the atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals which are characteristic of the whole molecule.

3. Two atomic orbitals, after overlapping, form two molecular orbitals which differ in energy. One of them, having lower energy, is called bonding molecular orbital while the other having higher energy is called anti-bonding molecular orbital.
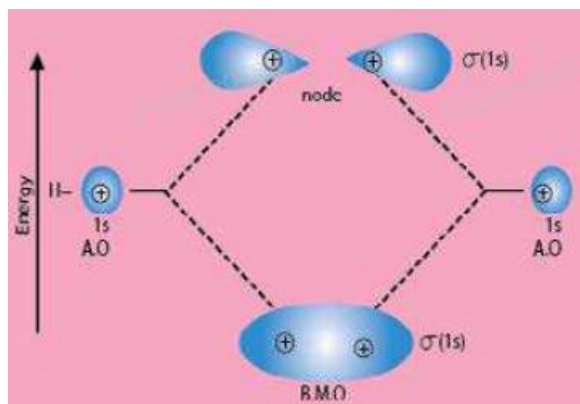
4. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital while the antibonding molecular orbital, is called σ*.

5. The filling of electrons into the molecular orbitals takes place according to the Aufbau principle, Pauli's exclusion principle and Hund's rule.

6. Overalapping of orbitals occurs in two ways:

(a) Head on Approach

The p-orbitals of the two atoms approach along the same axis (i.e. p_x axis). This combination of the atomic orbitals gives rise to σ (2px) bonding and σ* (2px) anti-bonding molecular orbitals. Both are symmetrical about the nuclear axis.
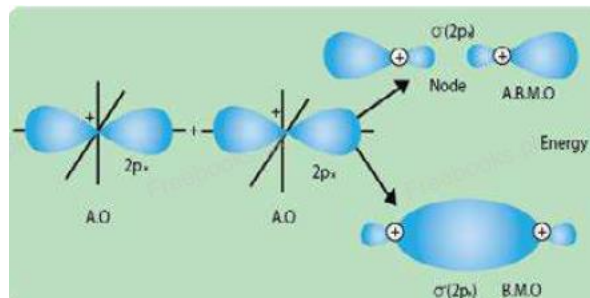
(b) Sideways Approach

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals.
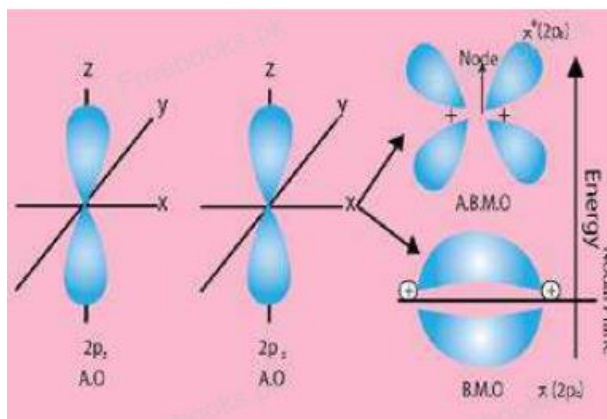
7. The bonding molecular orbitals π (2py) or π (2pz) have zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane.

8. The anti-bonding molecular orbitals π* (2py) and π* (2pz) have the least electron density in the π inter-nuclear region. Since the 2py and 2pz atomic orbitals are degenerate, the p molecular orbitals i.e. π (2py) and π (2pz) are also degenerate. So, are also the π*(2py) and π*(2pz) molecular orbitals.

9. Overall six molecular orbitals (three bonding and three anti-bonding) are formed from two sets of 2p atomic orbitals.

10. The bond formed as a result of linear overlap is σ bond, while that formed as a result of sideways overlap is called a p (pi) bond.

11. There are three bonding molecular orbitals, the p-orbitals overlap can lead to the formation of at the most three bonds: one sigma and two π-bonds.

12. The number of bonds formed between two atoms after the atomic orbitals overlap is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No. of electrons in the B.M.O} - \text{No. of electrons in the A.B.M.O}}{2}$$

MOT Diagram of Hydrogen Molecule

Bond order $= \dfrac{2-0}{2} \quad = 1$
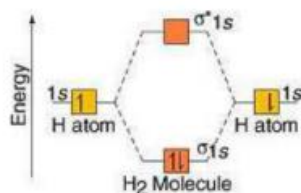
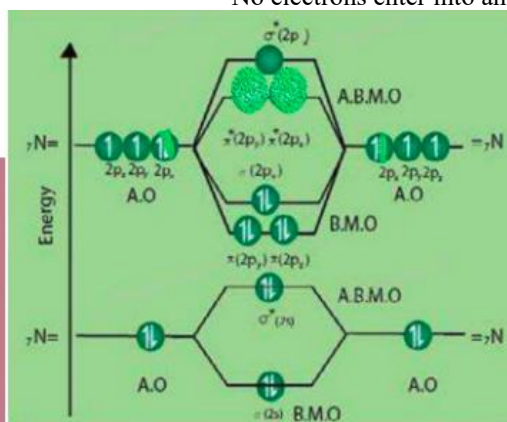## MOT Diagram of He, N₂ and O₂

Helium
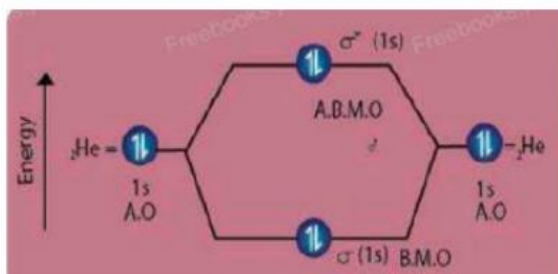
Nitrogen (diamagnetic, repelled by the magnetic field)

Triple bond :one sigma and two π bonds.
The bond dissociation energy=941kJmol^{-1}.
Six electrons enter into three outermost bonding orbitals.
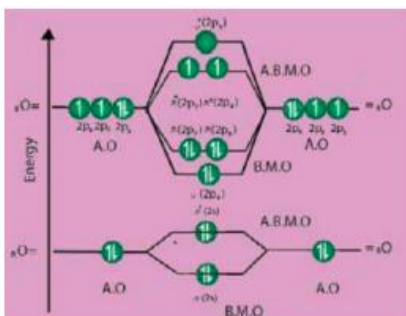No electrons enter into anti-bonding orbitals.

$\dfrac{2-2}{2} = 0$

$6(1s^2)<6^*(1s^2)<6(2s^2)<6^*(2s^2)<\pi(2p^2_y)=\pi(2p^2_z)<6(2p^2_x)<\pi^*(2p_y)=\pi^*$

$(2p_z)<6^*(2p_x)$

$\dfrac{6-0}{2}=\dfrac{6}{2}=3$

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Oxygen (paramagnetic gets attracted by magnetic field in liquid state)

$$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi_z^*(2p_z)^1 < \sigma^* 2p_x$$

Bond order= $\underline{6\text{-}2}$ = 2
2

It corresponds to a double bond.
This is consistent with the large bond energy of 496kJ mol^{-1} of oxygen molecule.

Dipole Moment

Definition

The dipole moment (μ) is defined as the product of the electric charge (q) and the distance between the positive and negative centres (r).

Formula Applied

$$\mu = q \times r$$

Vector quantity

The dipole moment is a vector quantity which has a magnitude as well as a direction.

Example

In HCl the molecule becomes polar due to the electronegativity difference.

The separation of positive and negative charges on the molecule is called a dipole and the molecule is said to have a dipole moment.
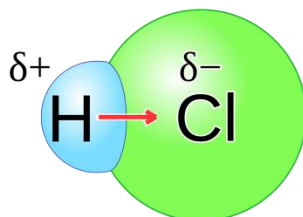
The dipole moments of HF, HCl, HBr. HI, CO, NO, etc. are directed from electropositive ends to electronegative ends.

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Units

The dipole moments are measured in Debye (D) units.

Measurement of Dipole Moment

Let us consider a hypothetical molecule (A*—B⁻), or a unit negative charge separated from a unit positive charge by distance r = 100 pm (1 Å).

The dipole moment of such a molecule can be calculated by multiplying the distance 100pm to charge of one electron or proton.

$$1.6 \times 10^{-19}C \text{ m} = (1.6022 \times 10^{-19}C) \times (100 \times 10^{-12}m) = 1.6022 \times 10^{-29} \text{ mC}$$

Another unit of dipole moment is Debye. The equivalence of Debye and mC is $1\ D = 3.336 \times 10^{-30}$mC. So, the dipole moment of the above system in Debye units is:

$$= \frac{1.6022 \times 10^{-29} \text{mC}}{3.336 \times 10^{-30} \text{mC}} = 4.8\ D$$

If the molecule is polyatomic and contains two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments.

Examples

Examples of CO_2 and H_2O are:
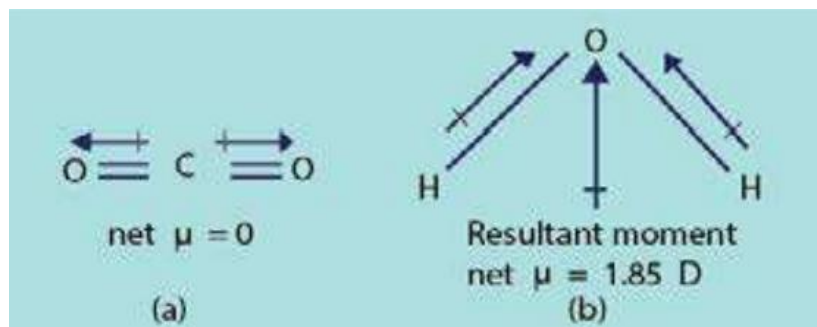
Dipole Moments and Molecular Structures

Information about the molecular structure

Dipole moment provides two types of information about the molecular structure:

(i) Percentage ionic character of a bond

(ii) Angles between the bonds or the geometry of molecules

(1) Percentage ionic character

For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond length. The dipole moment of 100% ionic compound is represented as μ_{ionic}.

$$\%age \text{ of ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

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(2) Bond Angles or the Geometry of Molecules

Dipole moment of water

The dipole moment of water is 1.85 D which **ruled out its linear structure**.
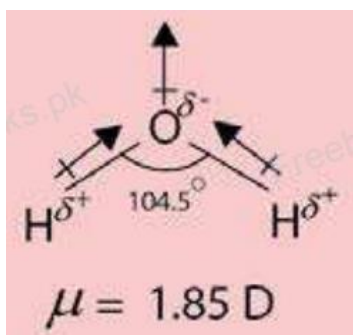
The calculations show that water has an angular structure with a bond angle 104.5° between the two O-H bonds.

A linear H_2O molecule (H-O-H) would have **zero dipole moment**.
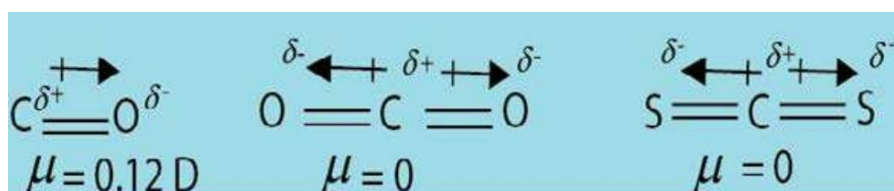
Other examples

H_2S and SO_2

The triatomic molecules H_2S or SO_2 etc. are also bent like H_2O.

CO, CO_2 and CS_2

CO has a dipole moment while CO_2 does not have any.

The reason is that CO_2 has **a linear structure**, where the dipoles being equal and opposite, cancel out each other's effect. Similarly, CS_2 has **zero dipole moment**.

BF_3, $AlCl_3$, CH_4, SiH_4 and CCl_4

Symmetrical triangular planar molecules of BF_3, $AlCl_3$ and perfectly tetrahedral molecules like CH_4, SiH_4, CCl_4 also **have zero dipole moments**.
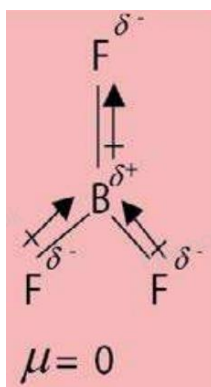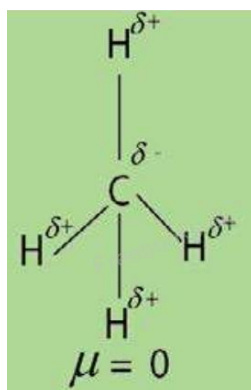
This is all due to the cancellation of individual bond moments.

Important long questions from past papers

1. Write note on ionic bond OR covalent bond OR coordinate covalent bond.
2. Write the main postulates of VSEPR theory and explain the structure of Ammonia on the basis of this theory.
3. Explain sp hybridization.
4. Explain sp^3 hybridization.
5. What is sp^2 hybridization.
6. Explain the molecular orbital structure of N_2 and O_2 molecules on the basis of MOT.
7. Explain important points of Molecular orbital theory.
8. Define ionization energy. Write factors affecting it and trends in the periodic table.
9. Define electron affinity. Name the factors affecting it and trends in the periodic table.
10. Discuss the valence bond theory. How are the sigma and pi bonds formed?
11. Define dipole moment. Give its units. How is it used to determine the geometry of molecule? Give an example.

Ch 7

Thermochemistry

Internal Energy and First Law of Thermodynamics

Energy of the system

A system containing some quantity of matter has definite amount of energy present in it. This energy is the sum of kinetic as well as the potential energies of the particles contained in the system.

Kinetic energy

The kinetic energy is due to the translational, rotational and vibrational movements of particles.

Potential energy

The potential energy accounts for all the types of attractive forces present in the system. These attractive forces include all the types of bonds and the van der Waal's forces present among the particles.

Internal energy

The total of all the possible kinds of energies of the system is called its internal energy, E.

Internal energy as state function

The change in internal energy of the system ΔE is a state function.

Measurement of Internal energy

It is not possible to measure the absolute value of internal energy of a system but it is often possible to measure the value of ΔE for a change in the state of the system.

Ways to transfer energy

There are two fundamental ways of transferring energy to or from a system.

1. Heat
2. Work.

Heat

It is defined as the quantity of energy that lows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings.

Heat is not a property of a system. It is not a state function. Heat evolved or absorbed by the system is represented by a symbol q.

Work

Work is also a form in which energy is transferred from one system to another. It is defined as the product of force and distance.
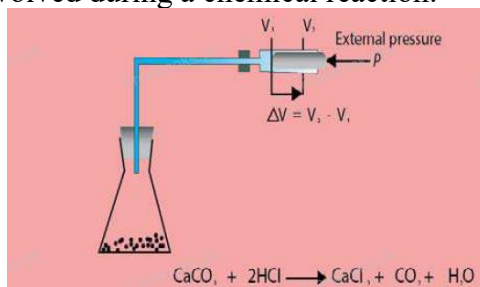
$$W = F \times S$$

Units

Work is measured in Joules in SI units.

Type of work in thermochemistry

Pressure-volume work.

Example

Expansion can occur when a gas is evolved during a chemical reaction.

The work W done by the system is given by

$$W = -P \Delta V$$

Force = pressure
Distance =volume change
P =external pressure
ΔV =change in volume.
Work is not a state function.
The sign of W is positive when work is done on the system and it is negative when work is done by the system.
The sign of q is positive when heat is absorbed by the system from surroundings, and it is negative when heat is absorbed by the surroundings from the system.

First Law of Thermodynamics

Statement

The first law of thermodynamics, also called the law of conservation of energy, states that

Energy can neither be created nor destroyed, but can be changed from one form to another.

OR

A system cannot destroy or create energy. However, it can exchange energy with its surroundings in the form of heat and work.

The energy change is the sum of both heat and work so that the total energy of the system and its surroundings remains constant.

Experimental

Consider, a gas enclosed in a cylinder having a frictionless piston. When a quantity of heat 'q' is supplied to the system, its internal energy E_1 changes to E_2 and piston moves upwards. The change in internal energy ΔE is given by the following equation.

$$\Delta E = E_2 - E_1 = q + w$$

$$\Delta E = q + w \qquad ..\text{eq } 1$$

q =amount of heat absorbed by the system
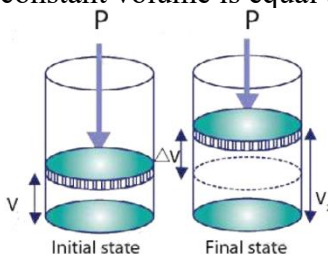W =work done by the system in moving the piston up
For pressure-volume work the above expression assumes the following form:

$$\Delta E = q - P\Delta V \qquad ... \text{eq } 2$$

When the volume of the gas is not allowed to change then $\Delta V = 0$ and equation (2) will take the following form.

$$\Delta E = q_v \qquad ..\text{eq } (3)$$

A change in internal energy of a system at constant volume is equal to heat absorbed by the system.

Initial state   Final state

Enthalpy

Definition

To take account of increase in internal energy and accompanying work done by the gas, there is another property of the system called enthalpy or heat content. It is represented by H. Enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV).

$$H = E + PV$$

Units
Joules

Enthalpy is a state function.
Experimental Proof
A quantity of heat q is given to the system (gas) which is now kept at constant atmospheric pressure. A part of this heat is used to increase the internal energy of the gas and the rest is used to do work on the surroundings. This work is done by the gas when it expands against a constant pressure.
Measurement
It is not possible to measure the enthalpy of a system in a given state. Change in enthalpy (ΔH) can be measured for a change in the state of system.
Mathematical Equation
A change in enthalpy of a system can be written as:

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + V\Delta P + P\Delta V \quad ..eq\ (1)$$

At constant pressure, $\Delta P = 0$. Hence,

$$\Delta H = \Delta E + P\Delta V$$
$$..eq\ (2)$$

For Solids and Liquids
In case of liquids and solids, the changes in state do not cause significant volume change i.e.
$\Delta V = 0$. For such process, ΔH and ΔE are approximately the same i.e. $\Delta H \approx \Delta E$
First Law of Thermodynamics

$$\Delta E = q + w$$
$$..eq\ (3)$$

If W is pressure-volume work done by the system, then:

$$w = -P\Delta V$$
$$..eq\ (4)$$

$$\Delta E = q - P\Delta V \quad ..eq\ (5)$$

Putting the value of ΔE in equation (5)

$$\Delta H = q - P\Delta V + P\Delta V$$
$$\Delta H = q$$

Since the pressure is constant.

$$\Delta H = q_p$$

Change in enthalpy is equal to heat of reaction at constant pressure.
Work with ΔH value

The reactions are carried out at constant pressure more frequently than at constant volume. So, working with ΔH is more convenient rather than ΔE.

Glass Calorimeter

Purpose

It is used to determine the enthalpy of neutralization. It determines the value of ΔH.

Enthalpy of Neutralization

The standard enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions [H^+] from an acid, react with one mole of hydroxide ions from a base to form one mole of water. For example, the enthalpy of neutralization of sodium hydroxide by hydrochloric (OH^-) acid is -57.4 kJ mol^{-1}.

Assembly

Following are the key features of the assembly of glass calorimeter:

1. This usual type of calorimeter is basically an insulated container. To serve the purpose of insulation broken pieces of glass or cotton wool is used.

2. It has a thermometer.

3. It has a stirrer.
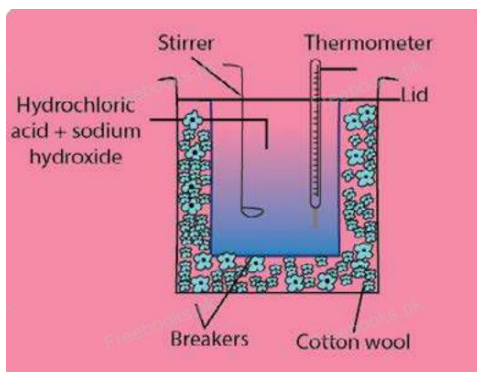
Working

Following are the steps involved in working of glass calorimeter:

1. Reactants in stoichiometric amounts are placed in the calorimeter.
2. When the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system.
3. The temperature of the system is recorded before and after the chemical reaction.
4. Knowing the temperature change the mass of reactants present and the specific heat of water, we can calculate the quantity of heat q evolved or absorbed during the reaction. Thus:

$$q = m \times s \times \Delta T$$

Where m = mass of reactants

s = specific heat of the reaction mixture

ΔT = change in temperature

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Heat Capacity

The product of mass and specific heat of water is called heat capacity of the whole system.

Bomb Calorimeter

Purpose

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds.

Enthalpy of combustion

The standard enthalpy of combustion of the substance is the amount of heat evolved when one mole of the substance is completely burnt in excess of oxygen under standard conditions. It is denoted by $\Delta H \, ^{\circ}C$.

Example

Standard enthalpy of combustion of ethanol $\Delta H \, ^{\circ}_C$ is -1368 kJ mol^{-1}.

Assembly

Following are the key features of assembly of bomb calorimeter:

1. It consists of a strong cylindrical steel vessel
2. It is lined with enamel to prevent corrosion.
3. It is provided with a thermometer and a stirrer.
4. Platinum crucible is inside the steel bomb to hold the sample.
5. Ignition coil is also provided.
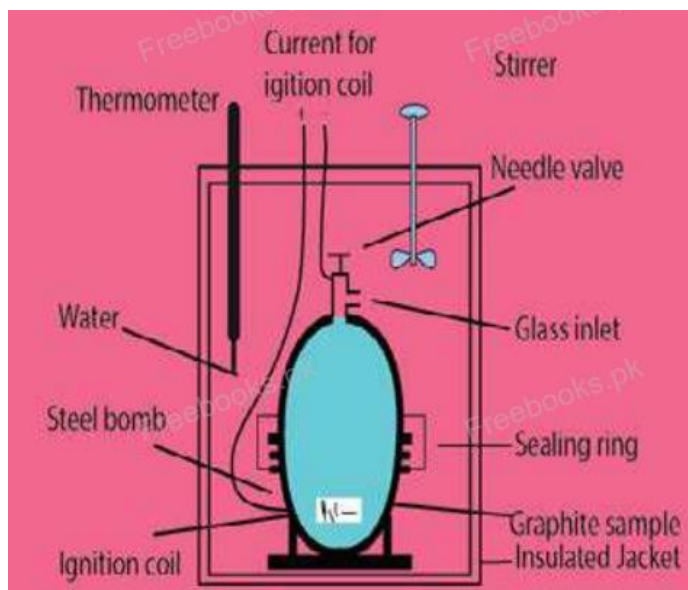
Working
Following are the key points of working of bomb calorimeter:

1. A known mass (about one gram) of the test substance is placed in a platinum crucible inside the bomb.
2. The lid is screwed on tightly and oxygen is provided in through a valve until the pressure inside is about 20 atm.
3. After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well insulated calorimeter.
4. It is allowed to attain a steady temperature.
5. The initial temperature is measured, by using the thermometer present in the calorimeter.
6. The test substance is then ignited electrically by passing the current through the ignition coil.
7. The temperature of water, which is stirred continuously, is recorded at 30 sec intervals.
8. From the increase of temperature ΔT, heat capacity (c) in kJK^{-1} of bomb calorimeter including bomb, water etc., we can calculate the enthalpy of combustion.

$$q = c \times \Delta T$$

Where c=heat capacity
ΔT=change in temperature
Heat capacity
The heat capacity 'c' of a body or a system is defined as the quantity of heat required to change its temperature by 1 Kelvin.

Hess's Law of Constant Heat Summation

Statement
If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.
**Explanation**
For many reactions, ΔH cannot be measured directly by calorimetric method.
Examples
1. Preparation of tetrachloromethane (CCl_4) from carbon and chlorine.
2. Decomposition of tetrachloromethane into its constituent elements.
3. Boron oxide (B_2O_3) and aluminium oxide (Al_2O_3) provide problems for the measurement of standard enthalpies of their formation as it is difficult to burn these elements completely in oxygen because a protective layer of oxides covers the surface of the unreacted element.
4. Heat of formation of CO cannot be measured directly due to the formation of CO_2 with it.
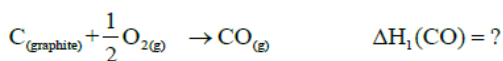**Mathematical Expression**
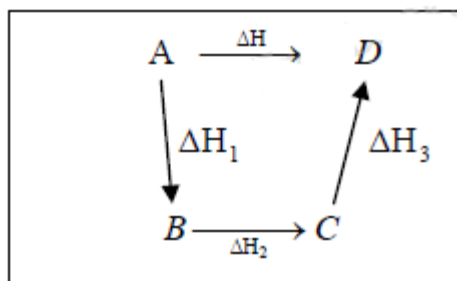
$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ …eq (1)

Oxidation of carbon

The reaction occurs in two steps.

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$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{(graphite)} = -393.7 \text{kJ mol}^{-1}$$

$$CO_{(gas)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2(CO) = -283 \text{kJ mol}^{-1}$$

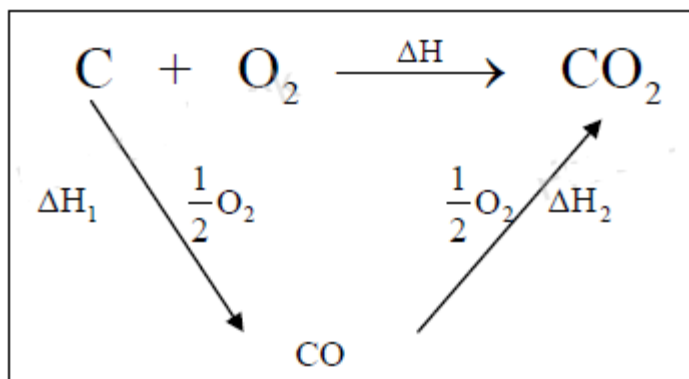$$C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_1(CO) = ?$$

Calculations

$\Delta H = \Delta H_1 + \Delta H_2$

$\Delta H_1 = \Delta H - \Delta H_2$

$= -393 - (-283)$

$= -110 \text{kJ mol}^{-1}$

Formation of Sodium Carbonate from Sodium Hydrogen Carbonate
Single Step Process

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H = -89.08 \text{ kJ}$$

Two Step Process

$$NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)} \qquad \Delta H_1 = -48.06 \text{ kJ}$$

$$NaHCO_{3(aq)} + NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H_2 = -41.02 \text{ kJ}$$
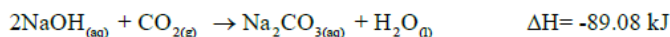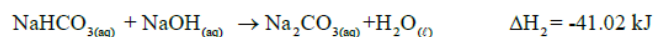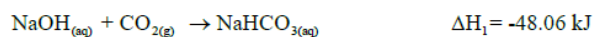
According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$-89.08 = -48.06 - 41.02$$
$$-89.08 = -89.08$$

This proves Hess's law.

The Born-Haber Cycle

Statement
Energy change in a cyclic process is always zero.
Application
It enables us, to calculate the lattice energies of binary ionic compounds such as M^+X^-.

The lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under standard conditions.

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)} \qquad \Delta H^{\circ}_{Latt} = -787 \text{ kJ mol}^{-1}$$

Lattice energies cannot be determined directly but values can be obtained indirectly by means of an energy cycle.
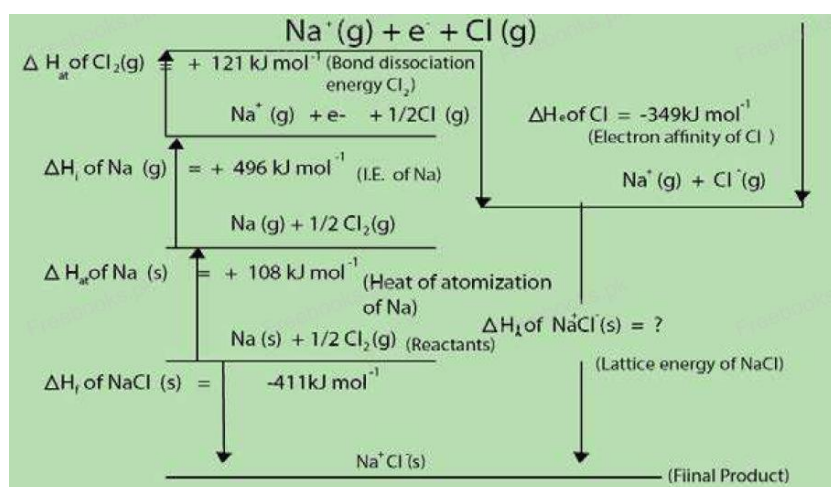
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Energy triangle
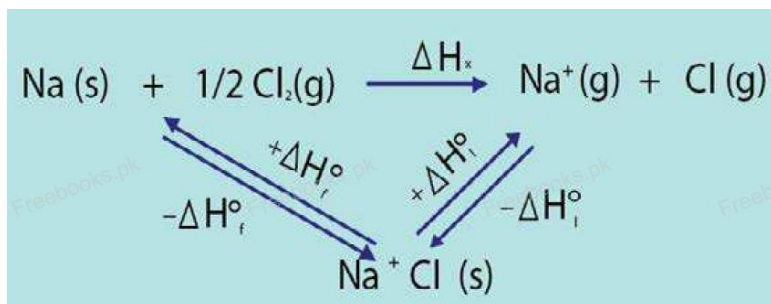
ΔH°_f can be measured conveniently in a calorimeter.

ΔH°_l can be obtained if ΔH_x, which is the total energy involved in changing sodium and chlorine from their normal physical states to gaseous ions, can be calculated.

Born-Haber Cycle

$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{i(Na)} + \Delta H_{at(Cl)} + \Delta H_{e(Cl)}$$

Atomization and Ionization

$$Na_{(s)} \rightarrow Na_{(g)} \qquad\qquad \Delta H_{at}=108kJ\ mol^{-1}$$

$$Na_{(g)} \rightarrow Na_{(g)} +1e^{-} \qquad\qquad \Delta H_i=496kJ\ mol^{-1}$$

Atomization of chlorine

$$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)} \qquad\qquad \Delta H_{at}=121\ kJ\ mol^{-1}$$

Absorption of electron by chlorine

$$Cl_{(g)} +e^{-} \rightarrow Cl^{-}_{(g)} \qquad\qquad \Delta H_e = -349\ kJ\ mol^{-1}$$

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$$\Delta H_x = (108+496+121-349) = 376 \text{ kJ mol}^{-1}$$

Lattice energy for sodium chloride

$$\Delta H^o{}_f = \Delta H^o{}_\ell + \Delta H_x$$

$$\Delta H^o{}_\ell = \Delta H^o{}_f - \Delta H_x$$

ΔH_ℓ= -411-376= -787 KJ/mol

It gives idea of the force of attraction between Na^+ and Cl^- ions in crystalline sodium chloride.

Important long questions from past papers
12. Define Enthalpy and prove that $\Delta H= q_p$
13. State and explain Hess's law of constant heat summation.
14. State 1st law of thermodynamics. Prove that $\Delta E=q_v$
15. Define Enthalpy of reaction. How is it measured by Glass Calorimeter?
16. What is molar heat of combustion? How is it measured by bomb calorimeter?

All definitions (any four) may come for long question.

Ch 8

Chemical Equilibrium

Law of Mass Action

Statement

The rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants.

General reaction

Consider a general reaction in which A and B are the reactants and C and D are the products.

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$
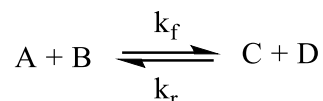
The equilibrium concentrations, called active mass, of A, B, C and D are represented in square brackets like [A], [B], [C] and [D] respectively and they are expressed in moles dm^{-3}.

Rate of forward reaction

According to the law of mass action, the rate of the forward reaction, is proportional to the product of molar concentrations of A and B.

$$\text{Rate of forward reaction } (R_f) \, \alpha \, [A][B]$$

$$\text{OR}$$

$$R_f = k_f[A][B]$$

k_f = proportionality constant and is called rate constant for forward reaction.

R_f = rate of forward reaction.

Rate of reverse reaction

The rate of reverse reaction (R_r) is given by:

$$\text{Rate of reverse reaction } (R_r) \, \alpha \, [C][D]$$

$$R_r = k_r[C][D]$$

k_r = proportionality constant and is called the rate constant for backward reaction.

At equilibrium

$$\text{Rate of forward reaction} = \text{Rate of reverse reaction}$$

$$\mathbf{R_f = R_r}$$

Putting the values

$$k_f[A][B] = k_r[C][D]$$

Rearrangement

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

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$$K_c = \frac{\text{rate constant for forward step}}{\text{rate constant for reverse step}}$$

K_c = equilibrium constant

General reaction

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$
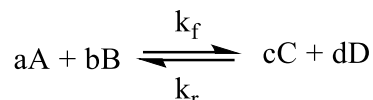
Where a, b, c and d are the coefficients of balanced chemical equation.

Equilibrium constant

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Applications of Equilibrium Constant

Following are the applications of equilibrium constant:
1. Direction of reaction   2. Extent of reaction
3. Effect of various factors on equilibrium constant and equilibrium position

1. Direction of reaction

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium.

Possibilities

The value of [product] / [reactants] ratio leads to one of the following three possibilities:
(a) The ratio is less than K_c. The reaction will proceed in the forward direction.
(b) The ratio is greater than K_c. The reaction will proceed in the reverse direction.
(c) The ratio is equal to K_c. The reaction is at equilibrium.

2. Extent of reaction

(a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.
(b) If the value of K_c is small, it reflects that the reaction does not proceed appreciably in the forward direction.
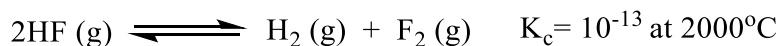(c) If the value of K_c is very small, this shows a very little forward reaction.

Examples

1. Equilibrium constant for the decomposition of ozone to oxygen is 10^{55} at 25°C.

$$2O_3 \rightleftharpoons 3O_2 \qquad K_c = 10^{55} \text{ at } 25 \text{ °C}$$
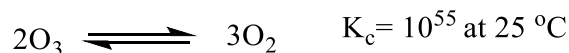
This reaction is almost complete.

2. The value of equilibrium constant for the decomposition of HF at 2000°C is 10^{-13}.

$$2HF\,(g) \rightleftharpoons H_2\,(g) + F_2\,(g) \qquad K_c = 10^{-13} \text{ at } 2000\text{°C}$$

It indicates high stability and slow decomposition of HF even at 2000°C.

3. The Effect of Conditions on the Position of Equilibrium

Equilibrium constant and position of equilibrium are two different entities.

Difference between equilibrium constant and equilibrium position

K_c is equilibrium constant and has constant value at a particular temperature whereas the ratio of products to reactants in equilibrium mixture is described as the position of equilibrium

Change of equilibrium position

Equilibrium position can change if the external conditions e.g. temperature, pressure and concentrations are altered.

Value of Kc and equilibrium position

For a reversible reaction:

If K_c is large the position of equilibrium lies on the right.

If K_c is small the position of equilibrium lies on the left.

The Le-Chatelier's Principle

Statement

If a stress is applied to a system at equilibrium the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

(a) Effect of Change in Concentration

Consider the reaction in which $BiCl_3$ reacts with water to give a white insoluble compound BiOCl.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$
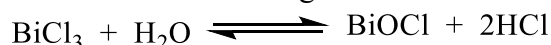
Equilibrium constant

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

Aqueous solution of $BiCl_3$ is cloudy because of hydrolysis and formation of BiOCl.

Addition of HCl

If a small amount of HCl is added to this solution, it will disturb the equilibrium and force the system to move in such a way so that effect of addition of HCl is minimized. The reaction will move in the backward direction to restore the equilibrium again and a clear solution will be obtained.

Addition of H₂O

However, if water is added to the above solution the system will move in the forward direction and the solution will again become cloudy.

The shifting of reaction to forward and backward direction by disturbing the concentration is just according to Le-Chatelier's principle.

Conclusion

Addition of a substance among the reactants or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction. The addition of a substance among the products or the removal of a substance among the reactants will derive the equilibrium towards the backward direction. Removing one of the products formed can increase the yield of a reversible reaction. The value of K_c remains constant.
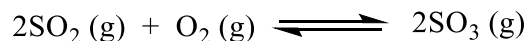
(b) Effect of Change in Pressure or Volume

The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

Example

Take the example of formation of SO_3 gas from SO_2 gas and O_2 gas.

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$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2SO_3 \text{ (g)}$$

This gas phase reaction proceeds with the decrease in the number of moles and hence decreases in volume at equilibrium stage.

Effect of pressure/volume change at equilibrium

When the reaction approaches the equilibrium stage the volume of the equilibrium mixture is less than the volume of reactants taken initially. If one decreases the volume further at equilibrium stage the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant. The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.

(c) Quantitative Effect of Volume on Equilibrium Position

The quantitative effect of change of volume or pressure can be inferred from the mathematical expression of K_c for SO_3 (g) synthesis.

$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2SO_3 \text{ (g)}$$
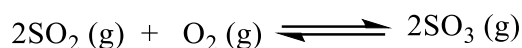
Equilibrium constant expression

$$K_c = \frac{4x\ V}{(a-2x)\ (b-x)}$$

V= volume of reaction mixture at equilibrium stage
a and b= the number of moles of SO_2 and O_2 present initially
Y= the number of moles of oxygen which has reacted at equilibrium.

Effect of volume change at equilibrium

According to the above equation, when volume is increased, then 'x' has to be decreased to keep K_c constant. The decrease of x means that reaction is pushed to the backward direction. From the amount of the increase in volume, we can calculate the amount of x which has to be decreased to keep K_c constant.

Effect of pressure change at equilibrium

Increasing the pressure on the above reaction at equilibrium will decrease the volume and the value of K_c will increase. In order to keep the value of K_c constant the reaction will move in the forward direction.
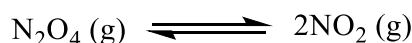
Dissociation of PCl₅

PCl_5 dissociates to give PCl_3 and Cl_2

$$PCl_5 \text{ (g)} \rightleftharpoons PCl_3 \text{ (g)} + Cl_2 \text{ (g)}$$
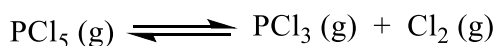
Equilibrium constant

$$K_c = \frac{x^2}{V(a-x)}$$

Dissociation of N₂O₄

$$N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)}$$

Equilibrium constant

$$K_c = \frac{4x^2}{V(a-x)}$$

Both these reactions have the factor of volume present in the denominator.

Reason

The reason is that numbers of moles of products are greater than those of reactants. So, increase in pressure will decrease x to keep the value of K_c constant and the reaction will be pushed to the backward direction.

Effect on K_c and equilibrium position

The equilibrium position is disturbed but not the K_c value.

Reactions not affected by pressure/volume change

Those gaseous reactions, in which number of moles of reactants and products are same, are not affected by change in pressure or volume. Same is the case for reactions in which the participating substances are either liquids or solids.

(d) Effect of Change in Temperature

Most of the reversible chemical reactions are disturbed by change in temperature. A temperature increase favours the endothermic reactions and a temperature decrease favours the exothermic reactions.

Change of equilibrium constant

The equilibrium constant changes by the change of temperature because the equilibrium position shifts without any substance being added or removed.

Example 1

Consider the following exothermic reaction in gas phase at equilibrium taking place at a known temperature.

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g)\ +\ H_2\ (g) \qquad \triangle H = - 41.84\ KJ/mol$$
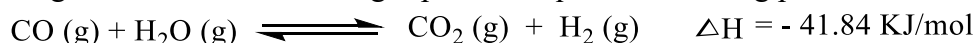
Temperature change at equilibrium

At equilibrium stage, if we take out heat and keep the system at this new lower temperature, the system will readjust itself, so as to compensate the loss of heat energy. More of CO and H_2O molecules will react to form CO_2 and H_2 molecules, thereby, liberating heat because reaction is exothermic in the forward direction. It means by decreasing temperature, we shift the initial equilibrium position to the right until a new equilibrium position is established. Heating the reaction at equilibrium will shift the reaction to the backward direction because the backward reaction is endothermic.

Example 2

Consider a salt such as KI. It dissolves in water and absorbs heat.

$$KI\ (s) \rightleftharpoons KI\ (aq) \qquad \triangle H = 21.4\ KJ/mol$$
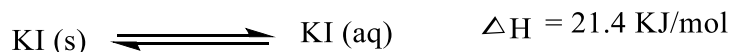
Let us have a saturated solution of KI in water at a given temperature at equilibrium.

Effect of temperature on equilibrium

A rise in temperature at equilibrium favours more dissolution of the salt. Equilibrium is shifted to the forward direction. Cooling will favour crystallization of salt.

Zero heat of solution

For some salts the heat of solution is close to zero. The solubility of these salts in water is not affected by the change in temperature.

Example

Formation of aqueous solution of NaCl is an example of such a salt.

Negative heat of solution

Those substances, whose heats of solutions are negative (exothermic), decrease their solubilities by increasing temperature, as LiCl and Li_2CO_3 etc.

(e) Effect of Catalyst on Equilibrium Constant

In most of the reversible reactions the equilibrium is not always reached within a suitable short time. So, an appropriate catalyst is added.

Role of catalyst

1. Time to attain equilibrium lowered

A catalyst does not affect the equilibrium position of the reaction. It increases the rates of both forward and backward reactions and this reduces the time to attain the state of equilibrium.

2. Energy of activation lowered

A catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

Applications of Chemical Equilibrium in Industry

Concept of chemical equilibrium is widely applicable for preparation of certain materials on industrial scale.

1. Synthesis of Ammonia by Haber's Process

The process of ammonia synthesis was developed by German chemist F. Haber and first used in 1933.

Chemical equation

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g)} \quad \triangle H = -92.46 \text{ KJ/mol}$$

Ways to maximize yield

(i) By continual withdrawal of ammonia after intervals the equilibrium will shift to forward direction.

ii) Increase the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of the products. High pressure will shift the equilibrium position to right to give more and more ammonia.

(iii) Decreasing the temperature will shift it to the forward direction.

Graphical representation
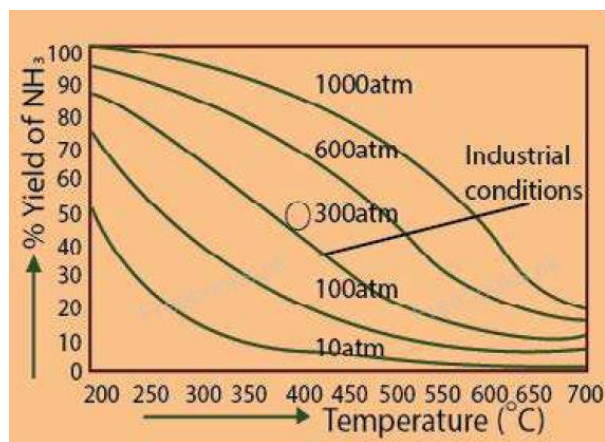
At very high pressure and low temperature the yield of NH_3 is high but the rate of formation is low.

Industrial conditions

Industrial conditions denoted by circle are between 200 and 300 atmospheres at about 400 ºC.

Low temperature yield

The yield of NH_3 is favoured at low temperature, but the rate of its formation does not remain favourable.

Optimum conditions

The optimum conditions are the pressure of 200-300 atm and temperature around 673 K (400 ºC). The catalyst is the pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

Equilibrium mixture

The equilibrium mixture has 35% by volume of ammonia.

Cooling of equilibrium mixture

The mixture is cooled by refrigeration coils until ammonia condenses (B.P = -33.4 ºC) and is removed.

Recycling of gases

Boiling points of nitrogen and hydrogen are very low they remain in the gaseous state and are recycled by pumps back into the reaction chamber.

Advantages of Haber's process

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tons of ammonia in the world. About 80% of this is used for the production of fertilizers and some is used in manufacture of explosives or the production of nylon and other polymers.

1. Preparation of Sulphur Trioxide

In the contact process for manufacture of H_2SO_4 the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2SO_3 \text{ (g)} \qquad \triangle H = -194 \text{ KJ/mol}$$
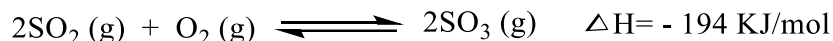
Low temperature
At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly.
High temperature
As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle.
High pressure
High pressure tends to increase yield of SO_3.
High oxygen level
The concentration of O_2 (air) is increased to increase the yield of SO_3. During the process pressure is kept at one atmosphere.
Optimum conditions
Effect of temperature reasonable time, a mixture of SO_2 and O_2 (air) at 1 atm pressure is passed over a solid catalyst at 650 ^{0}C. The equilibrium mixture is then recycled at lower temperature, 400 to 500 ºC, to increase the yield of SO_3. The most effective catalysts are V_2O_5 and finely divided platinum.
Oleum and sulphuric acid
SO_3 is dissolved in H_2SO_4 to get oleum which is diluted to get H_2SO_4. H_2SO_4 is the king of chemicals.

<div align="center">

Common Ion Effect
</div>

Definition
The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.
Examples
1. Purification of sodium chloride
Pass hydrogen chloride gas through saturated brine. Sodium chloride is fully ionized in the solution.
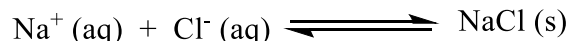
$$NaCl \text{ (s)} \rightleftharpoons Na^+ \text{ (aq)} + Cl^- \text{ (aq)}$$

Equilibrium constant expression for this process can be written as follows:

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

HCl ionizes in solution

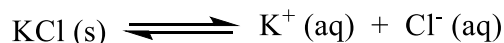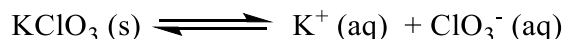$$HCl \text{ (aq)} \rightleftharpoons H^+ \text{ (aq)} + Cl^- \text{ (aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant.

$$Na^+ \text{ (aq)} + Cl^- \text{ (aq)} \rightleftharpoons NaCl \text{ (s)}$$

2. Suppression of KClO₃ ionization
The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion.

$$KClO_3 \text{ (s)} \rightleftharpoons K^+ \text{ (aq)} + ClO_3^- \text{ (aq)}$$

$$KCl \text{ (s)} \rightleftharpoons K^+ \text{ (aq)} + Cl^- \text{ (aq)}$$

3. Suppression of H₂S dissociation
The dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion.

$$H_2S \ (aq) \rightleftharpoons 2H^+ \ (aq) \ + \ S^{2-} \ (aq)$$

$$HCl \ (aq) \rightleftharpoons H^+ \ (aq) \ + \ Cl^- \ (aq)$$
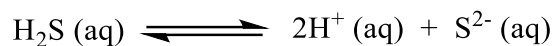
Application

This low concentration of S^{-2} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

4. Suppression of NH₄OH ionization

An addition of NH_4Cl in NH_4OH solution suppresses the concentration of OH^- (aq) due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte.

$$NH_4Cl \ (aq) \rightleftharpoons NH_4^+ \ (aq) \ + \ Cl^- \ (aq)$$

$$NH_4OH \ (aq) \rightleftharpoons NH_4^+ \ (aq) \ + \ OH^- \ (aq)$$

Application

The combination of these two substances is used as a group reagent in third group basic radicals.

5. Qualitative analysis and buffer preparation

Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

Numericals

4. Write K_c for the following reactions.

(i) $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

$$K_c = \frac{[Sn^{4+}][Fe^{2+}]^2}{[Sn^{2+}][Fe^{3+}]^2}$$

(ii) $Ag^+_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Ag_{(s)} + Fe^{3+}_{(aq)}$

$$K_c = \frac{[Ag][Fe^{3+}]}{[Ag^+][Fe^{2+}]}$$

(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

(iv) $4NH_{3(g)} + 5O_2 \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
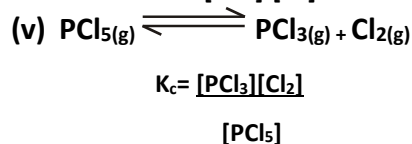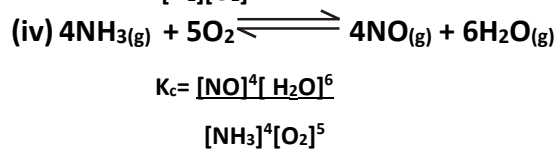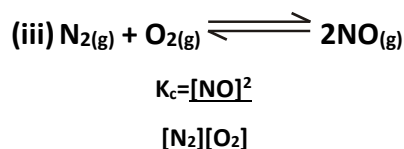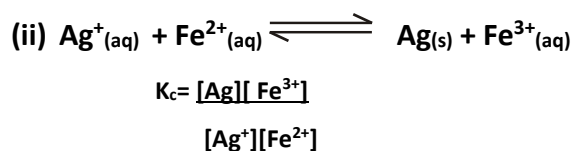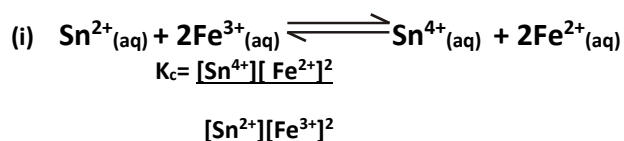
11. How would you prove that at 25°C, 1dm³ of water contains 10^{-7} moles of H_3O^+ and 10^{-7} moles of OH^-

Ans: In neutral water, at 25°C, The product of $[H^+][OH^-]$ is equal to 10^{-14}

As $\qquad [H^+] \quad = \quad [OH^-]$

or $[H^+][H^+]$ = 10^{-14}

                      $[H^+]^2$ = 10^{-14}

                      $[H^+]$ = 10^{-7} mol dm^{-3}

and $[OH^-]$ = 10^{-7} mol dm^{-3}

19. K$_c$ for the following reaction is 0.016 at 520°C

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The equilibrium mixture contains [HI] = 0.08 M, [H₂] = 0.01 M and [I₂] = 0.01 M. To this mixture more HI is added so that its new concentration is 0.096 M. What will be the concentrations of HI, H₂ and I₂ when equilibrium is re-established?

Data:

$[HI]$ =   0.08 M

$[H_2]$ =   0.01 M and

$[I_2]$ =   0.096 M

  K$_c$ =   0.0016
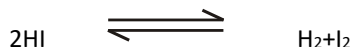
$$2HI \rightleftharpoons H_2+I_2$$

To Find:

At equilibrium

$[HI]$ = ?

$[H_2]$ = ?

$[I_2]$ = ?

Calculation and Result:

$$2HI \rightleftharpoons H_2 + I_2$$

Initial conc. in moles dm^{-3}

            0.08 $\rightleftharpoons$ 0.01 + 0.01

On adding more HI the new concentration of HI

            0.096 $\rightleftharpoons$ 0.01 + 0.01

Change in conc.

            0.096 $\rightleftharpoons$ 0.01 + 0.01

Equilibrium conc. in moles/dm^{-3}
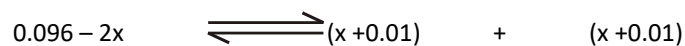
$$0.096 - 2x \quad \rightleftharpoons \quad (x + 0.01) \quad + \quad (x + 0.01)$$

The equilibrium expression for the reaction can be written as:

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

On substituting the values we get

$$0.016 = \frac{(0.01 + x) \times (0.01 + x)}{(0.096 - 2x)^2}$$

$$0.016 = \frac{(0.01 + x)^2}{(0.096 - 2x)^2}$$

Taking square root on both sides

$$\sqrt{0.016} = \sqrt{\frac{(0.01 + x)^2}{(0.096 - 2x)^2}}$$

$$0.126 = \frac{0.01 + x}{0.096 - 2x}$$

$$0.126 \, (0.096 - 2x) = 0.01 + x$$

$$0.012 - 0.252x = 0.01 + x$$

$$0.012 - 0.01 = 0.252x + x$$

$$1.252x = 0.002$$

$$X = \frac{0.002}{1.252}$$

$$= \textbf{0.0016 moldm}^{-3} = [I_2] = [H_2]$$

Conc. of HI at equilibrium = 0.096-0.0016=**0.095 mol dm^{-3}**

20. The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4.0. A mixture of 3 moles of acetic acid and 1 moleof C_2H_5OH (ethyl alcohol) is allowed to come to equilibrium. Calculate the amount of ethyl acetate present at equilibrium state in number of moles and grams. Also calculate the masses of reactants left behind.

Data:

Equilibrium constant K_c = 4

Initial conc. of acetic acid, (CH_3COOH) = 3

Initial conc. of ethyl alcohol C_2H_5OH = 1 mol

To Find:

Amount of ethyl acetate present at equilibrium = ?

Let the number of moles of ethyl acetate at equilibrium = x moles

Chemical Equation:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initial conc. in moles:

$$3 \qquad 1 \rightleftharpoons 0 \qquad 0$$

Equilibrium conc. in moles dm^{-3}

$$(3-x) \quad (1-x) \rightleftharpoons x \qquad x$$
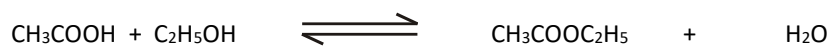
Formula:

Equilibrium constant expression for the reaction can be written as:

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Subsisting the values

$$4 = \frac{(x)(x)}{(3-x)(1-x)}$$

$$4 = \frac{x^2}{x^2-4x+3}$$

By cross multiplying

$$4(x^2 - 4x + 3) = x^2$$

$$4x^2 - 16x + 12 = x^2$$

$$3x^2 - 16x + 12 = 0$$

To find out the values of x, since

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here a = 3, b = -16 and c = 12

Putting these values

$$x = \frac{+16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2(3)}$$

$$= \frac{+16 \pm \sqrt{256 - 144}}{6}$$

$$= \frac{+16 \pm \sqrt{116}}{6}$$

$$= 4.43 \text{ or } 0.9 \text{ mol}$$

The values, x = 4.43 moles is not possible as it is greater than the concentrations of the reactant. Thus 0.9 mole of ethyl acetate is present at equilibrium.

Number of moles of ethyl acetate at equilibrium = 0.9 moles

Molar mass of ethyl acetate = 88 g mol^{-1}

Mass of ethyl acetate = 0.9 × 88 **= 79.46 g**

Number of moles of water produced = 0.9 moles

Molar mass of water= 18 g mol^{-1}

Mass of water produced = 0.9 × 18 = **16.2 g**

Moles of acetic acid left behind = 3 − x = 3 - 0.9 = 2.1 moles

Molar mass of acetic acid = 60 g mol^{-1}

Mass of alcohol left behind = 2.1×60 = **126 g**

Moles of alcohol left behind = 1.0 − 0.9 = 0.1

Molar mass of ethyl alcohol= 46 g mol^{-1}

Mass of alcohol left behind = 0.1 × 46 = **4.6 g**

21. Study the equilibrium

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2\ (g)}$$

(a) Write an expression of K_p

(b) When 1.00 mole of steam and 1.00 mole of carbon monoxide are allowed to reach equilibrium,33.3% of the equilibrium mixture is hydrogen. Calculate the value of K_p. State the unit of K_p.

Solution (a):

(a) $K_p = \dfrac{P_{H_2}P_{CO_2}}{P_{H_2O}.P_{CO}}$

Solution(b):

Data:

Moles of steam	=	1.00
Moles of CO$_2$	=	1.00
Conc. Of H$_2$ in equilibrium mixture	=	33.3%

To Find:

Value and units of K_p	=	?

Calculation and Result:

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2\ (g)}$$

Initial conc.   1 mole   1 mole   0 mole   0 mole

Eq. Conc.　　1 – X　1 – X moles　　x moles　　x moles

Total moles of reactants and products　　　=　　(1 – x) +(1 – x) + x + x

　Total moles at equilibrium　　　=　　2 moles

　Conc. of H_2 at equilibrium　　=　　33%

$$= \frac{33}{100} \times 2 = 0.66 \text{ mole}$$

$$X = 0.66$$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

$$= \frac{(x)\ (x)}{(1-x)\ (1-x)}$$

$$= \frac{(0.66)\ (0.66)}{(1-0.66)\ (1-0.66)}$$

$$= \frac{(0.66)\ (0.66)}{(0.33)\ (0.33)}$$

$$K_c = 4$$

Since $K_P = K_C (RT)^{\Delta n}$

$\Delta n = n_{products} - n_{reactants} = 2 - 2 = 0$

As number of moles of reactants are equal to that of products so $K_p = K_c = 4$

22. Calculate the pH of following:

(a) 10^{-4} moldm^{-3} of HCl

HCl ionizes as

HCl $\rightleftharpoons$ H^+ + Cl^-
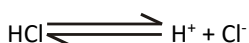
Since HCl is strong acid and it is 100% dissociated. Hence 10^{-4} mol/dm^3 of HCl produces 10^{-4} mol/dm^3 of H^+ ions

Thus,

$[H^+] = 10^{-4}$ mol/dm^3

pH = -log $[H^+]$

pH = -log $[10^{-4}]$

pH = 4

(b) 10^{-4} moldm^{-3} of Ba(OH)$_2$

Ba(OH)$_2$ ionizes as

Ba(OH)$_2$ $\rightleftharpoons$ Ba^{2+} + $2OH^-$
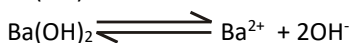
Since Ba(OH)2 is strong base and it is 100% dissociated. Hence 2 x 10^{-4} mol/dm^3 of Ba(OH)$_2$ produces 10^{-4} mol/dm^3 of OH$^-$ ions

$[OH^-] = 10^{-4}$ mol/dm^3

pOH = - log $[OH^-]$

pOH = - log (2 x 10^{-4})

pOH = 3.699

Since: pH + pOH = 14

　pH = 14 – pOH

143

pH = 14 – 3.699

pH = 10.301

(c) 1 moldm^{-3} of H$_2$X , which is 50% dissociated

H$_2$X ionizes as

H$_2$X $\rightleftharpoons$ 2H$^+$ + X$^-$
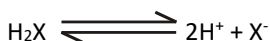
1 mole of H$_2$X produces 2 moles of H$^+$ ions if 100% dissociated

However, since H$_2$X is 50% dissociated therefore 1 mole of H$_2$X produce 1 mole of H$^+$ ion
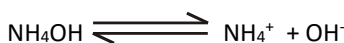
Thus,

[H$^+$] = 1mol/dm^3

pH = -log [1]

pH = 0

(d) 1 mol/dm^3 of NH$_4$OH that is 1% dissociated

NH$_4$OH ionizes as

NH$_4$OH $\rightleftharpoons$ NH$_4^+$ + OH$^-$

It shows that 1mole of NH$_4$OH produces 1 mole of OH$^-$ ions. NH$_4$OH is only 1% dissociated

Hence

$$\% \ dissociation = \frac{mol \ of \ OH^-}{Total \ moles \ of \ NH_4 \ OH} X \ 100$$

$$1 = \frac{mol \ of \ OH^-}{1} X \ 100$$

$$mol \ of \ OH^- = \frac{1}{100} X \ 1$$

OH$^-$ = 0.01 moldm^{-3}

pOH = -log [OH$^-$]

pOH = -log [0.01]

pOH = 2

pH + pOH = 14

pH = 14 – pOH

pH = 14 – 2

pH = 12

23. (a) Benzoic acid, C$_6$H$_5$COOH, is a weak non-basic (Ka = 6.4 × 10^{-5}mol dm^{-3}). What is the pH of a solution containing 7.2g of sodium benzoate in one dm^3 of 0.02 mole dm^{-3} of benzoic acid?

Data:

Ka of Benzoic acid   =   6.4 × 10^{-5}

Mass of sodium benzoate, C$_6$H$_5$COONa   =   7.2 g

Moles of benzoic acid   =   0.02 moles

To Find:

pH of the Solution   =   ?

Calculation and Result:

Molar mass of C$_6$H$_5$COONa   =   144g/mole

Moles of C$_6$H$_5$COONa   = $\frac{7.2}{144}$

144

$$= \quad 0.05 \text{ moles}$$

Moles of benzoic acid $\quad = \quad 0.02 \text{ moles}$

$$pH \quad = pK_a + \log \frac{[Salt]}{[Acdi]}$$

$$= -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$= -\log (6.4 \times 10^{-5}) + \log \frac{[0.05]}{[0.02]}$$

$$= -(0.80 - 5) + \log 2.5$$

$$= 5 - 0.80 + 0.39$$

$$\textbf{pH} \quad = \quad \textbf{4.59}$$

(b) A buffer solution has been prepared by mixing 0.2 M CH₃COONa and 0.5 M CH₃COOH in 1 dm³ of solution. Calculate the pH of solution. pKₐ of acid=4.74 at 25°C. How the value of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl.

Data:

$[CH_3COOH] = 0.5 \text{ M}$ $\quad\quad [CH_3COONa] = 0.2 \text{ M}$

$pK_a \quad\quad = \quad\quad 4.74$

To Find:

$pH \quad\quad = \quad\quad ?$

Calculation and Result:

$$pH \quad = \quad pka + \log \frac{[Salt]}{[Acid]}$$

$$pH \quad = \quad pka + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH \quad = \quad 4.74 + \log \frac{0.2}{0.5}$$

$$pH \quad = \quad 4.74 + \log 0.4$$

$$pH \quad = \quad 4.74 - 0.4 \text{ or pH} = \textbf{4.34}$$

By adding 0.1 M NaOH, concentration of CH₃COOH decreases to 0.4 M and that of CH₃COONa increases 0.3 M, thus new concentrations are

$[CH_3COOH] = 0.4 \text{ M } [CH_3COONa] = 0.3 \text{ M}$

$$pH \quad = \quad pka + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

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$$pH \quad = \quad 4.74 + \log \frac{0.3}{0.4}$$

$$pH \quad = \quad 4.74 + \log (0.75)$$

$$pH \quad = \quad 4.74 - 0.12 = \mathbf{4.62}$$

By adding 0.1 m HCl, concentration of CH_3COONa decreases from 0.2 M to 0.1 M and that of CH_3COOH increases from 0.5 M to 0.6 M.

$[CH_3COOH] = 0.6\ M[CH_3COONa] = 0.1\ M$

$$pH \quad = \quad pka + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH \quad = \quad 4.74 + \log \left(\frac{0.1}{0.6} \right)$$

$$pH \quad = \quad 4.74 - 0.78 = \mathbf{3.96}$$

24. The solubility of CaF_2 in water at 25°C is found to be 2.05×10^{-4} mol dm^{-3}. What is the value of K_{sp} at this temperature?

Data:

Solubility or concentration of CaF_2 = 2.05×10^{-4} mol dm^{-3}

To Find:

Value of K_{sp} = ?

Calculation and Result:

$$CaF_2 \quad \rightleftharpoons \quad Ca^{+2} \quad + \quad 2F^-$$

t = 0 sec	2.05×10^{-4} M	0	0
t = equilibrium	0 mol dm^{-3}	2.05×10^{-4} mol dm^{-3}	$2 \times 2.05 \times 10^{-4}$ mol dm^{-3}

$$K_{sp} \quad = \quad [Ca^{+2}][F^-]^2$$

$$= \quad (2.05 \times 10^{-4})\ (2 \times 2.05 \times 10^{-4})^2$$

$$= \quad (2.05 \times 10^{-4})\ (4.10 \times 10^{-4})^2$$

$$= \quad (2.05 \times 10^{-4})\ (16.81 \times 10^{-8})$$
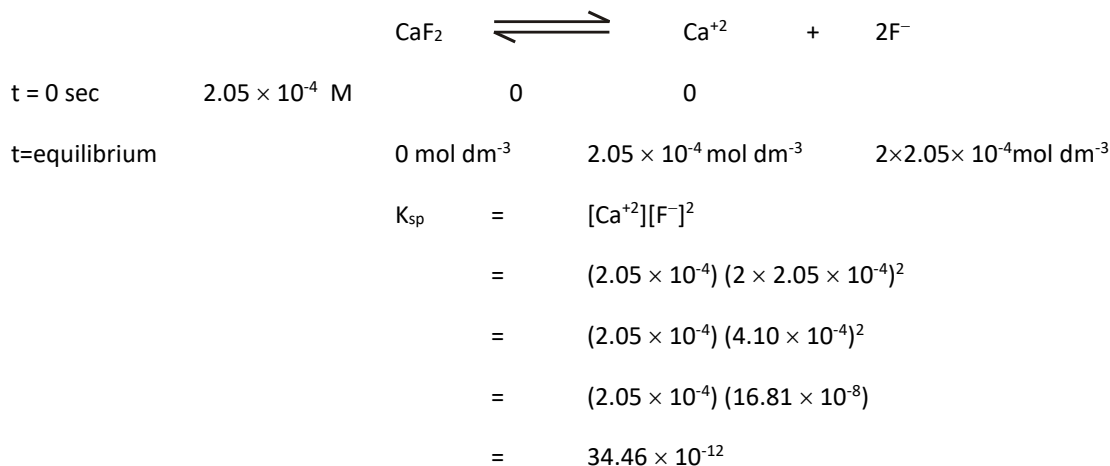
$$= \quad 34.46 \times 10^{-12}$$

$K_{sp} = \quad \mathbf{3.446 \times 10^{-11}\ mol^3 dm^{-9}}$

25. The solubility product of Ag_2CrO_4 is 2.6×10^{-2} at 25°C. Calculate the solubility of the compound.
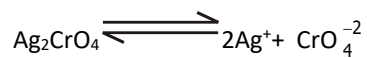
Data:

Solubility product of Ag_2CrO_4 = K_{sp} = 2.6×10^{-2}

To Find:

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Solubility of Ag_2CrO_4 = ?

Calculation and Result:

Let solubility of Ag_2CrO_4 be 'S'

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

Initial stage	S	0	0
Equilibrium stage	S	2S	S

$$K_{sp} = [Ag^+]^2[CrO_4^{-2}]$$

$$2.6 \times 10^{-2} = (2S)^2 (S)$$

$$2.6 \times 10^{-2} = 4S^3$$

Or

$$S^3 = \frac{2.6 \times 10^{-2}}{4}$$

$$= 0.0065$$

$$S = \sqrt[3]{0.0065}$$

$$\mathbf{S = 0.1866 \ mol \ dm^{-3}}$$

Important long questions from past papers

17. Example# 2, 4, 5, 6, 7
18. Exercise Q. 23 (a, b), 24, 25
19. Write a note on synthesis of ammonia by Haber's process keeping in mind the applications of chemical equilibrium in industry.
20. State le-Chatelier's principle. Describe the effect of change in temperature of a system in equilibrium by this Principle.
21. State le-Chatelier's principle. How is this principle used to explain the effect of change in concentration on equilibrium constant of a reaction?
22. What is common ion effect? Explain it.

Ch 9

Solutions

Phenol-Water System

Partial miscibility
If equal volumes of water and phenol are mixed together, they show partial miscibility.
Effect of temperature
1. Room temperature
It has been observed that around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot of phenol giving us the lower layer.
2. At 25 ⁰C
At 25 ⁰C the upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. These two solutions are conjugate solutions to each other. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer.
3. Increase of temperature
When the temperature of water-phenol system is increased the compositions of both layers change. Water starts travelling from upper to the lower layer and phenol travels from lower to the upper layer.
4. At 65.9 ⁰C
When the temperature of this system approaches 65.9 ⁰C, a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water. The temperature of 65.9 ⁰C at which two conjugate solutions merge into one another, is called critical solution temperature or upper consulate temperature.
Partially miscible pairs of liquids
Some other partially miscible pairs of liquids have their own consulate temperatures with definite compositions. For example, water-aniline system has a single layer at 167.00 ⁰C with 15% water. Methanol-cyclohexane system has consulate temperature of 49.10 ⁰C with 29% methanol.

Raoult's Law

Statement 1
The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.
Mathematical expression

$$p = p^{\circ}x_1$$

..eq (1)

p = vapour pressure of solvent in the solution
p° = vapour pressure of pure solvent
x_1 = mole fraction of solvent

$$X_1 + X_2 = 1$$

(x_2 is the mole fraction of solute)

Putting the value of x_1 in eq (1)

$$X_1 = 1 - X_2$$

$$p = p°(1 - X_2)$$

$$p = p° - p°X_2$$

$$p° - p = p°X_2$$

$$\Delta p = p°X_2 \qquad \text{...eq (2)}$$

Statement 2
The lowering of vapour pressure is directly proportional to the mole of fraction of solute.

$$\frac{\Delta p}{p°} = X_2$$

$$\text{...eq (3)}$$

$\Delta p/p°$ = relative lowering of vapour pressure
Δp = actual lowering of vapour pressure

Statement 3
The relative lowering of vapour pressure is equal to the mole fraction of solute.
Factors affecting relative lowering of vapour pressure
(i) Is independent of the temperature
(ii) Depends upon the concentration of solute.
(iii) Is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

<u>**Raoult's Law (when both components are volatile)**</u>

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution.
Explanation
Consider two liquids 'A' and 'B' with vapour pressures $p°_A$ and $p°_B$ in the pure state at a given temperature. After making the solution, the vapour pressures of both liquids are changed. Let the vapour pressures of these liquids in solution state be p_A and p_B with their mole fractions x_A and x_B, respectively. The liquid A is low boiling and B is high boiling.
Application of Raoult's law

$$p_A = p°_A x_A$$

$$p_B = p°_B x_B$$

$$P_t = p_A + p_B = p°_A x_A + p°_B x_B$$

P_t = total vapour pressure

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$$x_A + x_B = 1$$
$$x_B = 1 - x_A$$

$$P_t = p_A^{\circ}x_A + p_B^{\circ}(1 - x_A)$$

$$P_t = p_A^{\circ}x_A + p_B^{\circ} - p_B^{\circ}x_A$$

$$P_t = (p_A^{\circ} - p_B^{\circ})x_A + p_B^{\circ}$$
$$\qquad \dots eq\ (4)$$

Eq (4) is a straight line equation.

Plotting of graph

If a graph is plotted between x_B or mole % of B on x-axis and P_t on y-axis, a straight line will be obtained. Only those pairs of liquids give straight lines which form ideal solutions.

- Solutions of two components A and B which are ideal have their vapour pressures on the straight line connecting p°$_A$ with p°$_B$.
- Each point on this straight line represents the vapour pressure of a solution, at a given temperature, with the corresponding contribution of both the components A and B.
- The two dotted lines represent the partial pressures of the individual components of solution. They show the increase of vapour pressure of a component with increase in its mole fraction in solution.
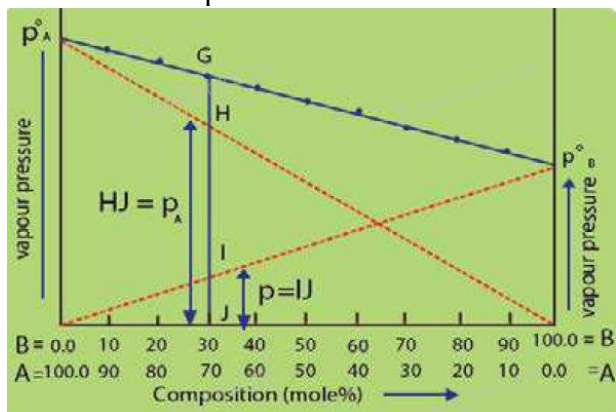
Explanation of graph

1. Consider a point G on the straight line.
2. This point represents the vapour pressure of solution with 30% moles contribution of the component B and 70% of component A.
3. Since, A is more volatile component, so its contribution towards the vapour pressure of solution is represented by p_A. The contribution of the less volatile component B is represented by p_B.
4. We can calculate the relative contributions of A and B towards the total vapour pressure of solution by taking other points along the line joining p°$_A$ to p°$_B$.
5. The total vapour pressure of the solution (Pt) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components ($p_A + p_B$).

Fractional Distillation of Ideal Mixture of Two Liquids

Let us have two liquids A and B which form a completely miscible solution. A is more volatile component so its boiling point is less than B. If we have various solutions of these two components and a graph is plotted between compositions on x-axis and temperature on y-axis, then two curves are obtained.

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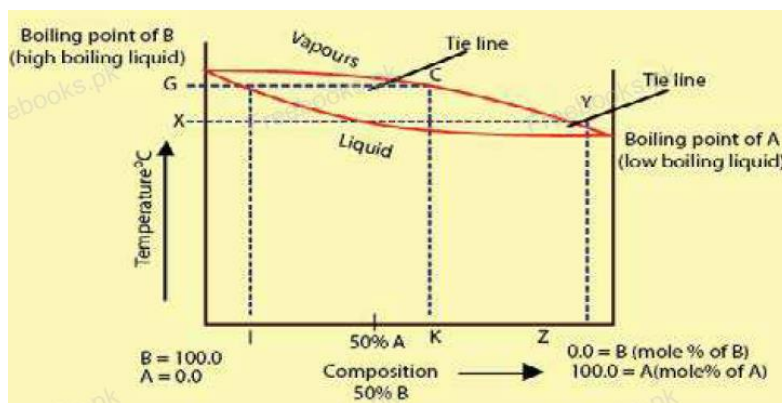
Explanation of graph

- The upper curve represents the composition of the vapours of different solutions while the lower curve represents the composition of the liquid mixtures.
  Reason
  At any temperature the composition of vapours is different from the composition of liquid mixture.
- The point G is the boiling point of solution corresponding to composition I. It meets liquid curve at point H and the vapour curve at point C.
- The composition of liquid mixture corresponding to point H is shown by point I. At point I the mixture has greater percentage of B and less percentage of A. At the same temperature the vapours of the mixture have the composition K.
- At point K, the percentage of A is comparatively greater than B when we compare it with composition of liquid mixture corresponding to point I. Because A is a low boiling liquid it is present in the vapour state in greater percentage than at point I.
- If the temperature of the mixture is maintained corresponding to point G the distillate will have greater percentage of A and the residue will have greater percentage of B.
  Reason
  The fraction going to distillate is that which is in vapour state and it has greater % of A.
- The distillate of composition K is again subjected to distillation. Its boiling point is X and at this temperature the distillate of composition Z is obtained.
- This distillate of composition Z is further distilled. The distillate becomes richer in A and residue is more and more rich in B.
- Process of distillation is repeated to get the pure component A.
- We can completely separate the components by fractional distillation.
  Zeotropic mixtures
  Such liquid mixtures, which distil with a change in composition, are called zeotropic mixtures.
  Example
  Methyl alcohol-water solution can be separated into pure components by distillation.

Non-Ideal Solutions (Azeotropic mixtures)

Why solutions deviate from Raoult's law

Solutions show deviations from Raoult's Law due to differences in their molecular structures i.e. size, shape and intermolecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy.

Vapour pressure deviations

The vapour pressure deviations may be positive or negative in such solutions.

Azeotropic mixtures

Azeotropic mixtures are those which boil at constant temperature and distil over without change in composition at any temperature like a pure chemical compound. Such mixtures cannot be regarded as chemical compounds as changing the total pressure along with the boiling point changes their composition.
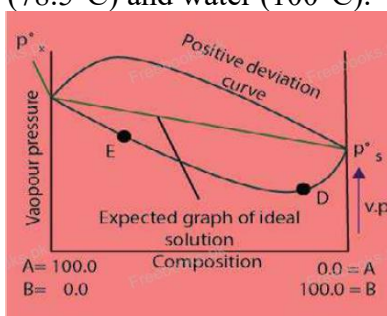
(a) Positive Deviations

If a graph is plotted between composition and vapour pressure of a solution which shows positive deviation from Raoult's law, the total vapour pressure curve rises to a maximum. The vapour pressure of some of the solutions is above the vapour pressure of either of the pure components.

Example

Let us consider the mixture of A and B components at point C where the mixture has the highest vapour pressure and the lowest boiling point. On distilling this type of solution, the first fraction will be a constant boiling point mixture i.e. azeotropic mixture having a fixed composition corresponding to the maximum point. For this type of solution, it is not possible to bring about complete separation of components by fractional distillation.

Example

Ethanol-water mixture is an example of this type. It boils at 78.1°C with 4.5% water and 95.5 % alcohol. 78.1ºC is lower than the boiling point of ethanol (78.5°C) and water (100°C).

(b) Negative Deviations

For this type of solution, the vapour pressure curve shows a minimum.

Example

Consider a point E. The more volatile component A is in excess. On distilling this solution, the vapours will contain more of A and the remaining mixture becomes richer in less volatile component B. Finally, we reach the point D where vapour pressure is minimum and the boiling point is maximum. At this point, the mixture will distill over unchanged in composition. Therefore, it is not possible to separate this type of solution completely into its components.

Example

Hydrochloric acid solution in water. HCl forms an azeotropic mixture with water, boiling at 110 ºC and containing 20.24% of the acid.

<u>**Solubility and Solubility Curves**</u>

Solubility

Definition

The solubility is defined as the concentration of the solute in the solution when it is in equilibrium with the solid substance at a particular temperature.

Example

Saturated solution of NaCl in water at 0°C contains 37.5g of NaCl in l00g of water. The solubility of $CuSO_4$ in water at 0°C is 14.3g/100g, while at 100°C it is 75.4g/100g.

Explanation

Whenever a solute is put in a solvent then the molecules or ions break away from the surface of the solid and pass into the solvent to give a uniform solution. Some of the particles of the solute may come back towards the solid due to collisions. This is called re-crystallization or precipitation.

Dynamic equilibrium

If excess of solid is present in the solution then the rate of dissolution and rate of crystallization become equal. This is a state of dynamic equilibrium.

The concentration of the solute at equilibrium with the solution is constant for a particular solvent and at a fixed temperature. The solution is called saturated solution and the concentration is termed as its solubility.
Solubility Curves

A graphical representation between temperature and solubility of solution is called solubility curves. There are two types of solubility curves.
(a) Continuous solubility curves
(b) Discontinuous solubility curves

(a) Continuous Solubility Curves
Continuous solubility curves don't show sharp breaks anywhere.
Examples
- $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCl_2$ are showing continuous solubility curves.
- The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines.
- NaCl shows a very small change of solubility from 0°C to 100°C increase of temperature.
- $Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40°C onwards. It shows continuous solubility curve.
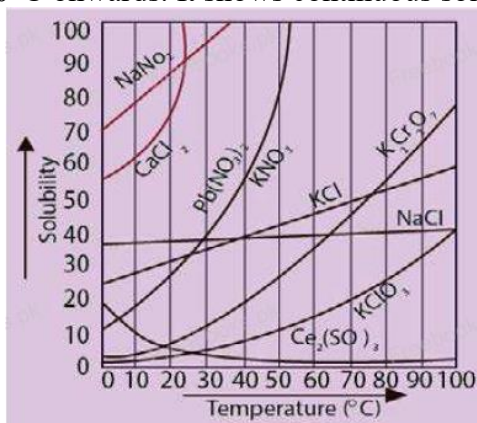
(b) Discontinuous Solubility Curves
The solubility curves show sudden changes of solubilities and these curves are called discontinuous solubility curves.
Examples
$Na_2SO_4.10\,H_2O$, $CaCl_2.6\,H_2O$.
Explanation
These curves are combination of two or more solubility curves. At the break a new solid phase appears and another solubility curve of that new phase begins. It is the number of molecules of water crystallization which changes and hence solubility changes.

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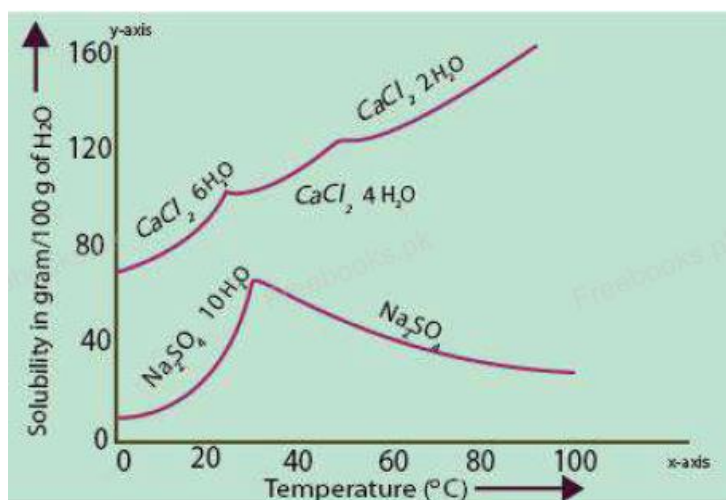
Lowering of Vapour Pressure

When the solvent is containing dissolved non-volatile non-electrolyte solute particles, the escaping tendency of solvent particles from the surface of the solution decreases and its vapour pressure is lowered.
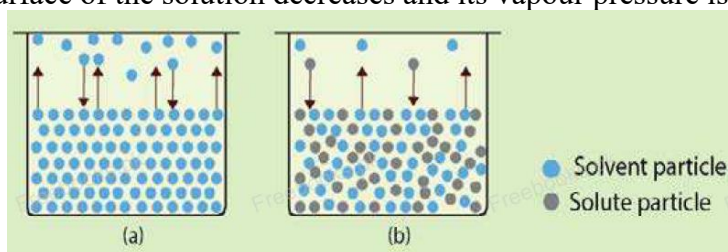
Explanation through Raoult's law

A quantitative relationship between the change of vapour pressure of a solvent due to addition of non-volatile and non-electrolyte solute and the mole fraction of solute has been given by Raoult's law.

According to Raoult's law the relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta p}{p^\circ} = x_2$$

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then

$$x_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1 + n_2}$$

For a dilute solution, n_2 can be ignored in denominator

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1}$$

Calculation of number of moles

If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses receptively, then

$$n_1 = \frac{W_1}{M_1} \qquad \text{and} \qquad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^\circ} = \frac{\dfrac{W_2}{M_2}}{\dfrac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

...eq (1)

Calculation of Molecular mass of solute

The molecular mass (M_2) of a non-volatile solute can be calculated from the equation (1).

$$M_2 = \frac{p^\circ}{\Delta p} \times \frac{W_2 M_1}{W_1}$$

Elevation of Boiling Point

Reason for the elevation of boiling point
The presence of a non-volatile non-electrolyte solute in the solution decreases the vapour pressure of the solvent. Greater the concentration of solute greater will be the lowering of vapour pressure. The temperature at which a solvent in the solution state boils is increased.
Graph for determination of vapour pressure
Plot a graph between temperatures on x-axis and vapour pressures on y-axis.
Curve and slope
- A rising curve is obtained with the increase of temperature.
- The slope of the curve at high temperature is greater which shows that at high temperature the vapour pressure increases more rapidly.
- Temperature T_1 on the curve AB which is for the pure solvent corresponds to the boiling point of the solvent.
- The solvent boils when its vapour pressure becomes equal to the external pressure represented by p°.
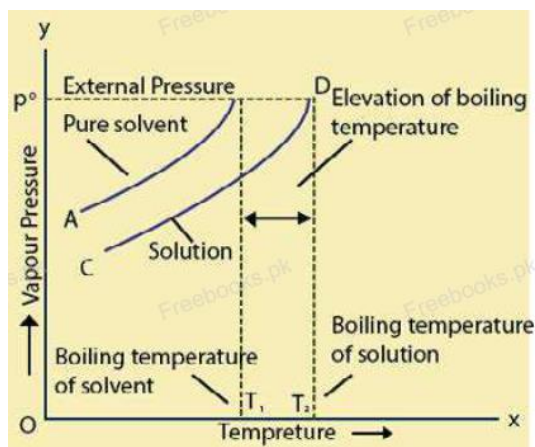
Temperature vs vapour pressure

Addition of solute
- When the solute is added in the solvent then a curve CD is obtained.
- This curve is lower than the curve AB because vapour pressures of solution are less than those of pure solvent.
- Solution will boil at higher temperature T_2 to equalize its pressure to p°.
- The difference of two boiling points gives the elevation of the boiling point ΔT_b.

Expression of ΔT_b

Elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b = K_b m$$

eq (1)

Where K_b is called the ebullioscopic constant or molal boiling point constant.

According to equation (1), molality of any solute determines the elevation of boiling point of a solvent.

ΔT_b is a colligative property

Dissolve 6 g of urea in 500 g of H_2O or 18 g of glucose in 500 g of H_2O. Both give 0.2 molal solution and both have same elevation of boiling points i.e. 0.1 °C which is 1/5th of 0.52 °C. Therefore, ΔT_b is a colligative property.

$$\text{Molality(m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

$$m = \frac{W_2}{M_2} \frac{1}{W_1/1000} = \frac{1000 \, W_2}{M_2 W_1}$$

eq (2)

Putting the value of m from equation (2) into equation (1)

$$\Delta T_b = K_b \frac{1000 \, W_2}{M_2 W_1}$$

$$\text{Molecular mass } (M_2) = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000$$

eq (3)

Equation (3) can be used to determine the molar mass of a non-volatile and non-electrolyte solute in a volatile solvent.

Measurement of Boiling Point Elevation: Landsberger's Method

The best method for the determination of boiling point elevation of a solution is Landsberger's method.

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Apparatus

The apparatus consists of four major parts:

(a) An inner tube with a hole in its side. This tube is graduated.

(b) A boiling flask which sends the solvent vapours into the graduated tube through a rosehead.

(c) An outer tube, which receives hot solvent vapours coming from the side hole of the inner tube.

(d) A thermometer which can read up to 0.01K.
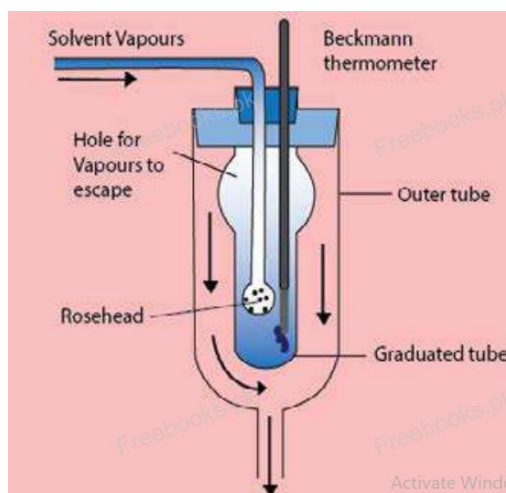
Working

1. The solvent is placed in the inner tube.
2. Some solvent is also taken in a separate flask and its vapours are sent into this tube.
3. These vapours cause the solvent in the tube to boil by its latent heat of condensation.
4. This temperature is noted which is the boiling point of the pure solvent.
5. The supply of the vapours is temporarily cut off and a weighed pellet of the solute is dropped in the inner tube.
6. The vapours of the solvent are again passed through it until the solution is boiled.
7. This temperature is again noted.
8. The supply of the solvent vapours is cut off.
9. The thermometer and the rosehead are removed and the volume of the solution is measured. The difference of the two boiling points gives the value of ΔT_b.

Formula Applied

The following formula is used to calculate the molecular mass of solute:

$$M_2 = \frac{K_b}{\Delta T_b} \frac{1000\, W_2}{W_1}$$

Measurement of Freezing Point Depression: Beckmann's Freezing Point Apparatus

An easy method to perform measurement of freezing point depression is Beckmann's freezing point apparatus.

Apparatus

The apparatus consists of three major parts:

a. A freezing tube with a side arm. It contains solvent or solution and is fitted with a stirrer and a Beckmann's thermometer.

b. An outer larger tube into which the freezing tube is adjusted. The air jacket in between these tubes helps to achieve a slower and more uniform rate of cooling.

c. A large jar containing a freezing mixture.
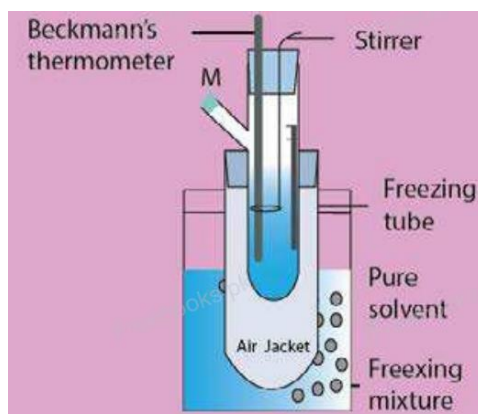
Working

1. Around 20 to 25g of the solvent is taken in the freezing tube.
2. The bulb of the thermometer is immersed in the solvent.
3. Approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.
4. The freezing tube is then put in the air jacket and cooled slowly. In this way, accurate freezing point of the solvent is determined.
5. The solvent is re-melted by removing the tube from the bath and weighed amount of 0.2 to 0.3 g of the solute is introduced in the side tube.
6. The freezing point of the solution is determined while stirring the solution.
7. The difference of the two freezing points gives the value of ΔT_f

Formula Applied

The following formula is used to calculate the molar mass of solute:

$$M_2 = \frac{K_f}{\Delta T_f} \frac{1000 \, W_2}{W_1}$$

Depression of Freezing Point

Freezing point:

Temperature at which the vapour pressure of liquid becomes equal to vapour pressure of solid is called the freezing point of a substance. In order to determine the molecular mass of solute depression of freezing point is determined.

Freezing point of solvent:

- Take pure solvent.
- Note its vapour pressure change with decrease of temperature till it freezes.
- Plot a graph between temperature (X-axis) and Vapor pressure (Y-axis)
- Curve ABC is obtained.
- AB shows liquid phase and BC the solid phase.
- T_1 is the freezing point of solvent.
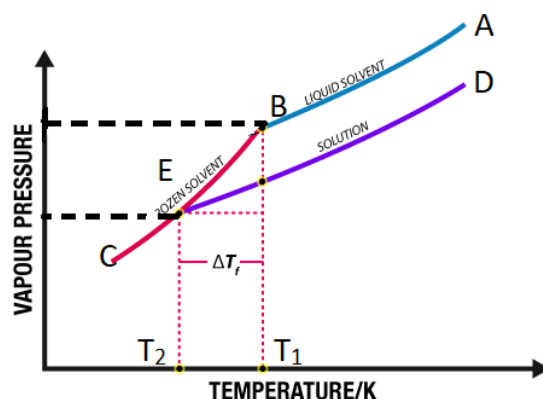
FreezingPoint of solution:

- Now add a pallet of solute in solvent.
- Decrease the temperature till it freezes.
- Note the vapour pressure change with temperature.
- Plot a graph between temperature and vapour pressure.
- Curve DEC is obtained.
- T_2 is the freezing point of solution
- Depression of freezing point $\Delta T_f = -T_1 - T_2$

Determination of molar mass of solute:

$$\Delta T_f \propto m$$

$$\Delta T_f \propto k_f m \quad \_\_\_ (1)$$

$k_f \rightarrow$ Cryoscopic constant

$m \rightarrow$ Molatity

$$\text{Molality (m)} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in Kg}}$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1/1000}$$

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} \qquad (2)$$

Where $W_1 \rightarrow$ mass of solvent

$W_2 \rightarrow$ mass of solute

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$M_2 \rightarrow$ molar mass of solute

Putting values of m in equation 1

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 W_1}$$

$$\Delta T_f \times M_2 \times W_1 = K_f \times W_2 \times 1000$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

Numericals

17. (a) Calculate the molarity of glucose solution when 9g of it are dissolved in 250 cm³ of solution

Data:

Mass of glucose	=	9 g
Volume of solution	=	250 cm³
	=	$\frac{250}{1000} = 0.25$ dm³

To Find:

Molarity of glucose	=	?

Formula:

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of clute}} \times \frac{1}{\text{vol. of soluton in dm}^3}$$

Calculation and Result:

Molar mass of glucose = 180g/mole

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of clute}} \times \frac{1}{\text{vol. of soluton in dm}^3}$$

$$= \frac{9}{180} \times \frac{1}{0.25} = 0.2 \text{ M}$$

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(b) Calculate the mass of urea in 100g of H_2O in 0.3 molal solution

Data:

Mass of water $=$ 100 g

$=$ $\frac{100}{1000}$ = 0.1 kg

Molarity of solution $=$ 0.3 M

To Find:

Mass of urea $=$?

Formula:

Molality $=$ $\frac{\text{mass of urea}}{\text{molar mass of urea}} \times \frac{1}{\text{mass of solvent in kg}}$

Calculation and Result:

Molar mass of urea, $(NH_2)_2CO$ $=$ 60 g mol^{-1}

$=$ $\frac{\text{mass of urea}}{\text{molar mass of urea}} \times \frac{1}{\text{mass of solvent in kg}}$

Mass of Urea $=$ Molarity $\times$ molar mass $\times$ mass of solvent in kg

$=$ $0.3 \times 60 \times 0.1$

$=$ 1.8 g

(c) Calculate the concentration of solution in terms of molality Kg^{-1} which is obtained by mixing 250g of 20% solution NaCl with 200g of 40% solution of NaCl.

Data:

250 of 20% NaCl, 200 g of 40% NaCl solution

To Find:

Concentration of Solution $=$?

Formula applied:

Molality $=$ $\frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$

Calculation and Result:

First Solution	Second Solution

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250 of 20% NaCl,	200 g of 40% NaCl solution
Mass of NaCl = $\frac{20}{100} \times 250$	Mass of NaCl = $\frac{20}{100} \times 200$
= 50g	= 80 g

Total mass of NaCl in two solution =   50 + 80 = 130 g

Total mass of solution   =   250 g + 200 g = 450 g

Mass of solute (NaCl)   =   130g

Mass of solvent   =   450 – 130 – 320 g

= $\frac{320}{1000}$ = 0.32 kg

Molality = $\frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$

= $\frac{130}{58.5} \times \frac{1}{0.32}$

=   **6.94 mol kg^{-1}**

18. (a) An aqueous solution of sucrose has been labeled as 1 Molar. Find the mole fraction of the solute and solvent.

Data:

Molarity of Sucrose solution   =   1M

To Find:

Mole fraction of Solute and Solvent=   ?

Calculation and Result:

1 Molar aqueous solution of ($C_{12}H_{22}O_{11}$) means that 1mole sucrose is present in 1000 g of water. Moles of sucrose (solute)

n_2 =   1 moles

Mass of solvent   =   1000g

Moles of solvent (H_2O), n_1 = $\frac{1000}{18}$ = 55.5 mol

Total moles   =   1 + 55.5

=   56.5 moles

Moles fraction of solute, X_2 = $\frac{n_2}{n_1+n_2} = \frac{1}{56.6}$

$X_{sucrose}$ / X_2   =   **0.0176**

Moles fraction of solvent, X_1 = $\dfrac{n_1}{n_1+n_2}$

$= \dfrac{55.5}{56.5}$

X_{H2O} / X_2 = 0.98

(b) You are provided with 80% H_2SO_4 having density 1.8 g cm^{-3}. How much volume of this H_2SO_4 sample is required to obtain one dm^3 of 20% W/W H_2SO_4 which has a density of 1.25 g cm^{-3}

Data:

Provided solution (80% H_2SO_4 having density 1.8 g cm^{-3})

Density = 1.8 g cm^{-3}

To Find:

Volume of H_2SO_4 sample = ?

Calculation and Result:

It means that 1 cm^3 of H_2SO_4 has mass = 1.8 g

1000 cm^3 of H_2SO_4 has mass = 1.8 × 1000

= 1800 g

Because acid is 80% so

100 g H_2SO_4 solution has H_2SO_4 = 80 g

1 g H_2SO_4 solution has H_2SO_4 = $\dfrac{80}{100}$

1800 g H_2SO_4 solution has $H2SO4$ = $\dfrac{80}{100} \times 1800$

= 1440 g

Moles of H_2SO_4 = $\dfrac{\text{mass of } H_2SO_4}{\text{Molar mass}}$

= $\dfrac{1440}{98}$ = 14.7 M

Required solution (20% H_2SO_4 having density 1.25 g cm^{-3})

Density = 1.25 g/cm^{-3}

1 cm^3 of H_2SO_4 has mass = 1.25 g

1000 of H_2SO_4 has mass = 1.25 × 1000 = 1250 g

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Because acid is 20%, so

100 H_2SO_4 solution contains H_2SO_4 = 20 g

1250 g H_2SO_4 solution contains H_2SO_4 = $\frac{20}{100} \times 1250 = 250$ g

Moles of H_2SO_4 = $\frac{250}{98} = 2.55$ mol

Provided H_2SO_4	=	**Requirement H_2SO_4**
M_1V_1	=	M_2V_2
$14.7 \times V_1$	=	2.55×1000
V_1	=	$\frac{2.55 \times 1000}{14.7}$
	=	173.47 cm^3 (Requirement volume)

Note: Measure 173.47cm^3 of "provided solution", add water to get 1dm^3 of required solution.

19. 250 cm^3 of 0.2 molar K_2SO_4 solution is mixed with 250 cm^3 of 0.2 molar KCl solution. Calculate the molar concentration of K^+ ions in the solution.

Data:

Volume of K_2SO_4 = 250 cm^3

Molarity of K_2SO_4 = 0.2 M

Volume KCl = 250cm^3

Molarity KCl = 0.2 M

To Find:

Molar Conc. of K^+ ions = ?

Calculation and Result:

K_2SO_4 solution			**KCl solution**		
Volume	=	250 cm^3	Volume	=	250cm^3
Molarity	=	0.2 M	Molarity	=	0.2 M
$K_2SO_4 \rightarrow 2K^+ + SO^-_4$			$KCl \rightarrow K^+ + Cl^-$		
0.2 M	2(0.2) (0.2)		0.2 M 0.2 M		
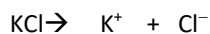
0.4 M | **0.2M**

Total concentration of K⁺ ions = 0.4 + 0.2

= 0.6 M

Total volume of two solutions = 250 + 250 = 500 cm³

= $\frac{500}{1000}$ = 0.5 dm³

1 dm³ solution contains K⁺ ions = 0.6 mol

0.5 dm³ solution contains K⁺ ions = 0.6 × 0.5 = **0.3 mol/dm³**

20. **5g of NaCl are dissolved in 1000 g of water. The density of resulting solutions is 0.997 g/cm³. Calculate molality, molarity and mole fraction of this solution. Assume that the volume of the solution is equal to that of solvent.**

Data:

Mass of NaCl = 5 g

Mass of H₂O = 1000g

Density of solution = 0.987 g cm⁻³

Requirement:

Molarity, Molality, Mole fraction of Solution = ?

Calculation and Result:

Molality = $\frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$

= $\frac{5}{58.5} \times \frac{1}{1}$ = **0.0854 m**

Density of solution = 0.987 g cm⁻³

Mass of solution = 5 + 1000 = 1005 g

Density = $\frac{\text{mass}}{\text{volume}}$

Volume of solution = $\frac{\text{mass}}{\text{density}} = \frac{1005}{0.987}$ = 1018.2 cm³

= 1.018 dm³

Molarity = $\frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{volume of solvent in dm}^3}$

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$$= \frac{5}{58.5} \times \frac{1}{1.018} = \textbf{0.084 M}$$

Mass of NaCl $= 5\ g$

Moles of NaCl $= \frac{5}{58.5} = 0.085$

Mass of H_2O $= 1000g$

Mole of H_2O $= \frac{1000}{18} = 55.5$

X_{NaCl} $= \frac{0.085}{55.5 + 0.085} = \frac{0.085}{55.585}$

$= \textbf{0.0015}$

X_{H2O} $= \frac{55.5}{55.5 + 0.085} = \frac{55.5}{55.585}$

$= \textbf{0.99}$

21. **4.675 of a compound with empirical formula C_3H_5O were dissolved in 212.5 g of pure benzene. The freezing point of solution was found 1.02°C less than that of pure benzene. The molar freezing point constant of benzene is 5.1°C calculate (i) the relative molar mass and (ii) the molecular formula of the compound.**

Data:

Mass of solute W_2 $= 4.675\ g$

Mass of solvent W_1 $= 212.5\ g$

Depression in freezing point ΔT_F $= 1.02°C$

Molal freezing point constant K_f $= 5.1°C$

To Find:

Molar mass of solute, M_2 $= ?$

Formula:

$$M_2 = \frac{K_f \times 1000 \times W_2}{\Delta T_1 \times W_1}$$

Calculation and Result:

$$M_2 = \frac{K_f \times 1000 \times W_2}{\Delta T_1 \times W_1}$$

$$= \frac{5.1 \times 1000 \times 4.675}{1.02 \times 212.5} = 110 \text{ g mol}^{-1}$$

Empirical formula of compound $\quad = \quad C_3H_3O$

Empirical formula mass $\quad = \quad 36 + 3 + 16 = 55 \text{ gmol}^{-1}$

Molar mass of compound $\quad = \quad 110 \text{ gmol}^{-1}$

$$n = \frac{\text{Molar Mass}}{\text{Empirical formula mass}}$$

$$= \frac{110}{55} = 2$$

Molecular formula $\quad = \quad$ n (empirical formula)

$$= \quad 2 \times (C_3H_3O)$$

$$= \quad \mathbf{C_6H_6O_2}$$

22. **The boiling point of a solution containing 0.2 g of a substance A in 20 g of ether (molar mass = 74) is 0.17 K higher than that of pure ether. Calculate the molar mass of A. Molal boiling point constant of ether is 2.16 K.**

Data:

Mass of solute (W_2) $\quad = \quad$ 0.2 g

Mass of solvent (W_1) $\quad = \quad$ 20 g

Elevation of boiling point (ΔT_b) $\quad = \quad$ 0.17 K

Molal boiling point constant (K_b) $\quad = \quad$ 2.16 K

To Find:

Molar mass of solute (M_2) $\quad = \quad$?

Formula:

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{1000 \ W_2}{W_1}$$

Calculation and Result:

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{1000 \ W_2}{W_1}$$

$$= \frac{2.16 \times 1000 \times 0.2}{0.17 \times 20}$$

$$= \mathbf{127 \text{ g mol}^{-1}}$$

23. **3g of a non-volatile non-electrolyte solute X are dissolved in 50g of ether (molar mass = 74) at 239 K. The vapour pressure of ether falls from 442 torr to 426 torr under these conditions. Calculate the molar mass of solute X.**

Data:

Mass of solute = W_2= 3g

Mass of solvent = W_1 = 50 g

Molar mass of solvent = M_1 = 74 g mol^{-1}

Pressure of pure solvent = P^o= 442 torr

Pressure of solution = P = 426 torr

To Find:

Molar mass of solute X = ?

Formula:

$$M_2 = \frac{W_2 M_1 P^o}{\Delta P W_1}$$

Calculation and Result:

Change in pressure

$$\Delta P = P^o - P$$

$$= 442 - 426$$

$$= 16 \text{ torr}$$

$$M_2 = \frac{W_2 M_1 P^o}{\Delta P W_1}$$

$$= \frac{3 \times 74 \times 442}{16 \times 50}$$

$$= \frac{98124}{800}$$

$$= \textbf{122.6 g mol}^{-1}$$

Important long questions from past papers

23. Define Solubility curves. Explain continuous and discontinuous solubility curves.
24. Give graphical explanation of boiling point elevation of solution.
25. What are Colligative properties of solutions? Explain elevation of boiling point.
26. State and explain Raoult's law in three forms.
27. What are ideal solutions? Explain the fractional distillation of ideal mixture of two liquids.
28. Differentiate between ideal and non-ideal solutions.
29. Describe freezing point depression method to determine the molecular mass of an organic compound.

30. Describe one method to determine the boiling elevation of a solution.
31. The boiling point of water is 99.725 °C. To a sample of 600g of water are added 24g of solute having molar mass of 58 g.mol^{-1} to form a solution. Calculate the boiling point of solution.
32. The freezing point of pure camphor is 178.4°C. Find the freezing point of solution containing 2 g of a non-volatile compound having molar mass of 140 gmol^{-} in 40 g of camphor. The molal freezing point constant (K_f) of camphor is 37.7 °C. Kg^{-1}.mol^{-1}.

Any four definitions from chapter may come as long question.

Chapter 10

Electrochemistry

Definition

"Electrochemistry is concerned with the conversion of electrical energy into chemical energy in electrolytic cells as well as conversion of chemical energy into electrical energy in galvanic or voltaic cell"

Electronic Conduction	Electrolytic Conduction
1. This type of conduction is present in metals	1. This type of conduction is present in molten salts or their aqueous solutions
2. This conduction is due to the movement of free electrons present in metals	2. This conduction is due to the movement of positive and negative ions
3. No physical or chemical change take place in conductor during electronic conduction	3. Ions undergo oxidation and reduction reactions at respective electrodes
4. Example: copper, iron etc	4. Example: Electrolysis of molten NaCl to Cl_2 and Na

Ionization

When some electrolyte is dissolved in water the process is called ionization.

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Electrolysis

A chemical change caused by passage of electricity through molten compound or through its aqueous solution is called electrolysis.

$$2\ NaCl\ (s) + 2\ H_2O\ (l) \longrightarrow 2NaOH\ (aq) + H_2\ (g) + Cl_2\ (g)$$
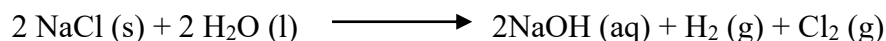
Electrochemical Cells

Definition

"The cell in which a chemical reaction utilizes electrical energy or produces electrical energy is called electrochemical cell"

There are two types of electrochemical cells:

1. Electrolytic cells

Definition

"An electrochemical cell in which electric current is used to drive a non-spontaneous reaction is called electrolytic cell"
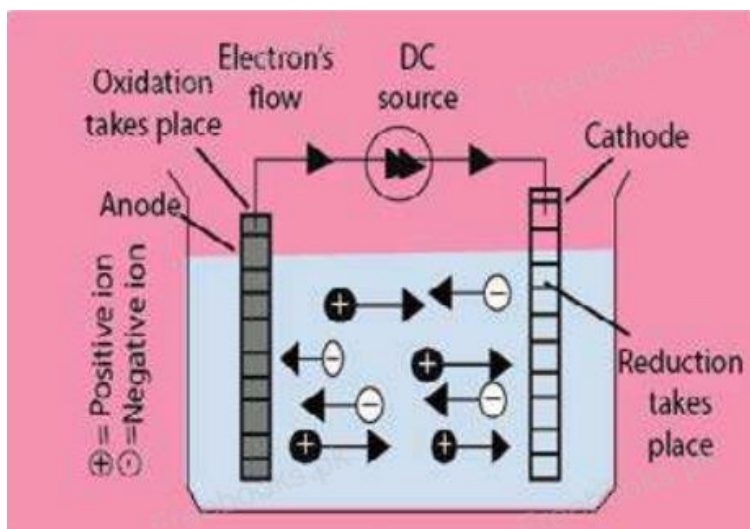
Electrolytic cell consists of two electrodes i.e. cathode and anode dipped in an electrolyte and connected through an external DC source of electricity.
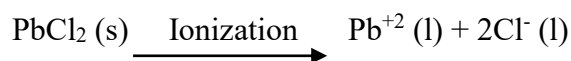
Working

When electricity is passed through the solution, positive ions move towards negative electrode i.e. cathode. They pick up electrons from cathode and are reduced.
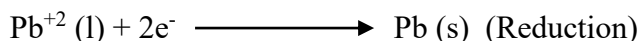
On the other hand, negative ions move towards positive electrode i.e. anode where they give up their electrons and are oxidized.

Oxidation takes place at anode while reduction takes place at cathode. The whole process is known as electrolysis.

<div align="center">Electrolysis of Fused Salts</div>

$$PbCl_2 \text{ (s)} \xrightarrow{\text{Ionization}} Pb^{+2} \text{ (l)} + 2Cl^- \text{ (l)}$$

At cathode:

$$Pb^{+2} \text{ (l)} + 2e^- \longrightarrow Pb \text{ (s) (Reduction)}$$

At anode:

$$2\,Cl^- \text{ (l)} \longrightarrow Cl_2 \text{ (g)} + 2e^- \text{ (Oxidation)}$$

Net Cell Reaction

$$PbCl_2 \text{ (s)} \xrightarrow{\text{Electrolysis}} Pb \text{ (s)} + Cl_2 \text{ (g)}$$

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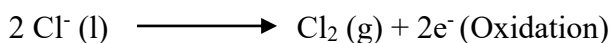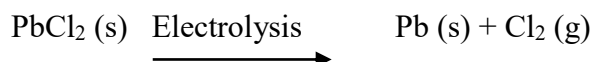
Electrolysis of aqueous solution of salts (using inert electrodes)
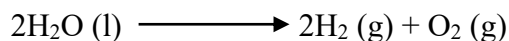
1. Electtrolysis of aqueous solution of $NaNO_3$

$$NaNO_3 \longrightarrow Na^+ + NO_3^-$$

$$2\ H_2O\ (l) \longrightarrow H_3O^+ (aq) + OH^- (aq)$$

At cathode

$$4H_3O^+ (aq) + 4e^- \longrightarrow 4H\ (g) + 4H_2O\ (l)$$

$$4H\ (g) \longrightarrow 4H_2\ (g)$$

At anode

$$4OH^- (aq) \longrightarrow 4\ OH\ (aq) + 4\ e^-$$

$$4\ OH \longrightarrow O_2\ (g) + 2\ H_2O\ (l)$$

Net cell reaction

$$2H_2O\ (l) \longrightarrow 2H_2\ (g) + O_2\ (g)$$
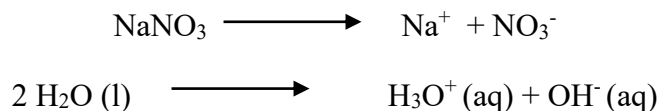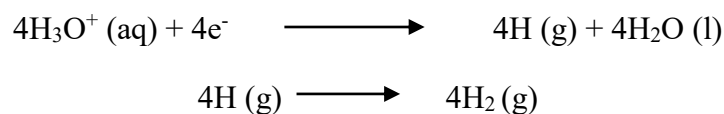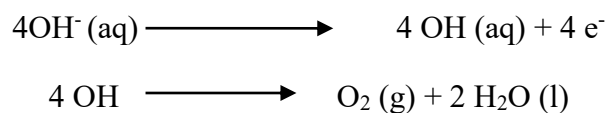
Examples of electrolysis

(When electrodes take part in reaction)

a. Electrolysis of $CuSO_4$ using Cu electrode

Electrolyte: aqueous $CuSO_4$

Cathode: pure copper

Anode: impure copper

$$CuSO_4\ (s) \rightleftharpoons Cu^{+2}\ (aq) + SO_4^{-2}\ (aq)$$

At anode:

$$Cu\ (s) \longrightarrow Cu^{+2}\ (aq) + 2e^-$$

At cathode:

$$Cu^{+2}\ (aq) + 2e^- \longrightarrow Cu\ (s)$$
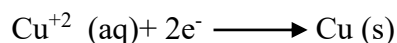
b. Electrolysis of $AgNO_3$ using Ag electrodes

Cathode: pure Ag

Anode: Impure Ag

Electrolyte: $AgNO_3$

$$AgNO_3 \text{ (s)} \rightleftharpoons Ag^+ \text{ (aq)} + NO_3^- \text{ (aq)}$$

At anode:

$$Ag \text{ (s)} \quad\quad Ag^+ \text{ (aq)} + e^-$$

At cathode:

$$Ag^+ \text{ (aq)} + e^- \longrightarrow Ag \text{ (s)}$$
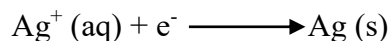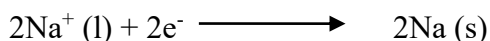
Electrolytic processes of Industrial Importance

a. Electrolysis of Molten NaCl

Sodium metal and Cl_2 is prepared in Down's cell using iron cathode and graphite anode.

$$NaCl \text{ (s)} \longrightarrow Na^+ \text{ (l)} + Cl^- \text{ (l)}$$

At cathode:

$$2Na^+ \text{ (l)} + 2e^- \longrightarrow 2Na \text{ (s)}$$

At anode:

$$2Cl^- \text{ (l)} \longrightarrow 2Cl \text{ (g)} + 2 e^-$$

$$Cl \text{ (g)} + Cl \text{ (g)} \longrightarrow Cl_2 \text{ (g)}$$

Net cell reaction:

$$2 \ NaCl \text{ (l)} \longrightarrow 2 \ Na \text{ (s)} + Cl_2 \text{ (g)}$$
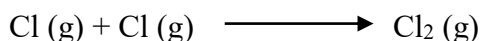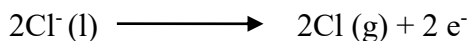
b. Electrolysis of conc. aqueous solution of NaCl

Caustic soda is obtained on industrial scale by the electrolysis of concentrated aqueous solution of NaCl using titanium anode and mercury or steel cathode in Nelson's cell. Saturated aqueous solution of NaCl is called brine.
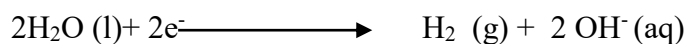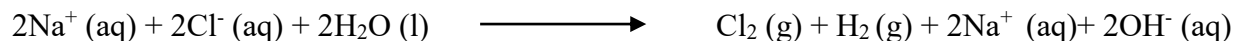
$$NaCl \text{ (s)} \longrightarrow Na^+ \text{ (aq)} + Cl^- \text{ (aq)}$$

$$2H_2O \text{ (l)} \longrightarrow H_3O^+ \text{ (aq)} + OH^- \text{ (aq)}$$

At anode:

$$2Cl^- \text{ (g)} \longrightarrow Cl_2 \text{ (g)} + 2e^-$$

At cathode:

$$2H_2O \text{ (l)} + 2e^- \longrightarrow H_2 \text{ (g)} + 2\ OH^- \text{ (aq)}$$

Overall reaction:

$$2Na^+ \text{ (aq)} + 2Cl^- \text{ (aq)} + 2H_2O \text{ (l)} \longrightarrow Cl_2 \text{ (g)} + H_2 \text{ (g)} + 2Na^+ \text{ (aq)} + 2OH^- \text{ (aq)}$$
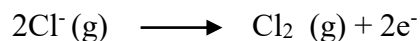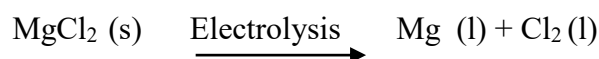
c. Extraction of magnesium and calcium

Magnesium and calcium metals are extracted by the electrolysis of their fused chlorides.

$$MgCl_2 \text{ (s)} \xrightarrow{\text{Electrolysis}} Mg \text{ (l)} + Cl_2 \text{ (l)}$$

d. Extraction of aluminium

Aluminium is extracted by electrolyzing fused bauxite ($Al_2O_3.2H_2O$) in the presence of fused cryolite (Na_3AlF_6). Cryolite decreases the melting point of aluminium oxide.

e. Preparation of anodized aluminium

Anodized aluminium is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid which coats a thin layer of oxide on it. The aluminium oxide layer resists attack by corrosive agents. The freshly anodized aluminium is hydrated and can absorb dyes.
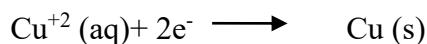
f. Extraction of copper

Electrolytic cell can also be used for purification of copper using $CuSO_4$ as electrolyte. Impure copper as anode and pure copper as cathode. Cu atoms from impure copper are converted to Cu^{+2} and pure copper is deposited on anode. Impurities are left at anode.

At anode:

$$Cu \text{ (s)} \longrightarrow Cu^{+2} \text{ (aq)} + 2e^-$$

At cathode:

$$Cu^{+2} \text{ (aq)} + 2e^- \longrightarrow Cu \text{ (s)}$$

g. Electroplating

Copper, silver, nickel or chromium plating is done by various types of electrolytic cells.

Voltaic or Galvanic Cell

Definition

The electrochemical cell in which a spontaneous oxidation-reduction reaction taking place in solution produces electricity is known as voltaic or galvanic cell.

OR

The electrochemical cell in which chemical energy is converted to electrical energy is known as voltaic or galvanic cell.

Construction

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- Two half cells are electrically connected
- Each half cell is a portion of total cell in which half reaction takes place
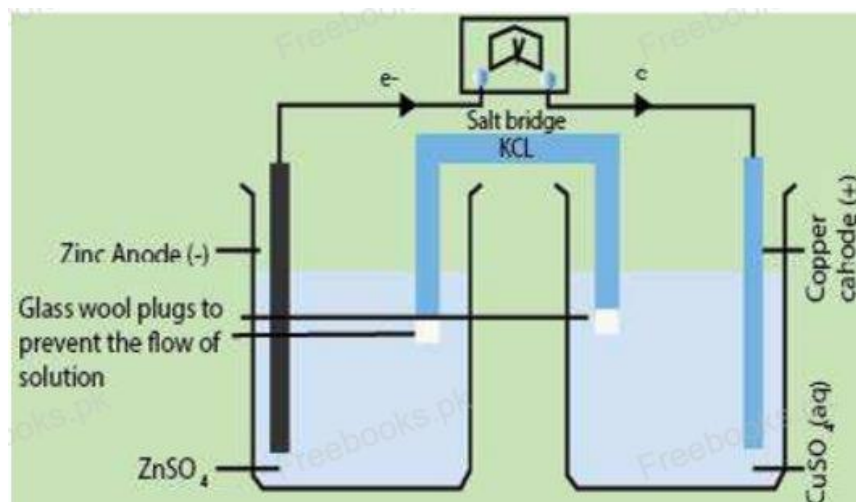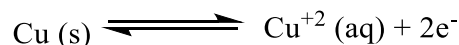

A galvanic cell consisting of Zn and Cu electrodes at 25 ℃ and 1 M electrolyte solution.

Half Cells

Left half cell consists of Zn strip dipped in 1.0 M solution of $ZnSO_4$ giving following equilibrium.

$$Zn\ (s) \rightleftharpoons Zn^{+2}\ (aq) + 2e^-$$

Right half cell consists of Cu strip dipped in 1.0 M solution of $CuSO_4$ giving following equilibrium.

$$Cu\ (s) \rightleftharpoons Cu^{+2}\ (aq) + 2e^-$$

Working

- The half cells are connected electrically by a salt bridge
- Zn tends to lose electrons more rapidly than Cu
- If the external circuit is closed by connecting the two electrodes electrons flow from zinc through external circuit to copper electrode
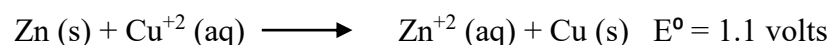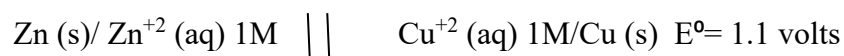
Half Cell reactions

At anode

$$Zn\ (s) \longrightarrow Zn^{+2}\ (aq) + 2e^-\ (oxidation)$$

At cathode

$$Cu^{+2}\ (aq) + 2e^- \longrightarrow Cu\ (s)\ (reduction)$$
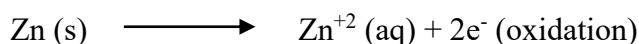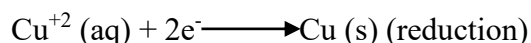
Overall voltaic cell reaction

$$Zn\ (s) + Cu^{+2}\ (aq) \longrightarrow Zn^{+2}\ (aq) + Cu\ (s)\quad E^o = 1.1\ volts$$

Representation of voltaic cell reaction:

$$Zn\ (s)/\ Zn^{+2}\ (aq)\ 1M\ ||\ Cu^{+2}\ (aq)\ 1M/Cu\ (s)\quad E^o= 1.1\ volts$$
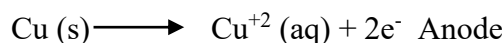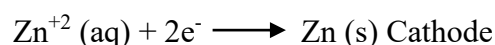
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Sign $||$ shows salt bridge

Function of salt bridge

The purpose of the salt bridge is to prevent any net charge accumulation by allowing negative ions to leave the right beaker, diffuse through the bridge, and enter the left beaker. Otherwise, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and the oxidation-reduction reaction would stop.
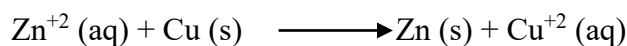
Voltaic Cell is Reversible Cell

If the external source of electricity is applied to voltaic cell then electrode reactions can be reversed. Reverse non-spontaneous reactions occur and cell is called reversible cell.

For Zn-Cu cell

$$Zn^{+2} (aq) + 2e^- \longrightarrow Zn (s)\ Cathode$$

$$Cu (s) \longrightarrow Cu^{+2} (aq) + 2e^-\ Anode$$

Overall Reaction

$$Zn^{+2} (aq) + Cu (s) \longrightarrow Zn (s) + Cu^{+2} (aq)$$

Electrode Potential

Definition

The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element. It is represented as E°.

Method of determination

When a metal strip is placed in a solution of its own ions, there are two tendencies.

1. The metal atoms may dissolve as positive ions. The electrons are deposited on the metal electrode.

2. The metal ions present in solution may take up electrons from the metal and get discharged as atoms. It imparts a positive charge to the metal.

Outcome

In both cases, a potential difference is set up between the metal and the solution which is called single electrode potential.

Determination of electrode potential with reference hydrogen electrode

1. Arbitrary scale

Standard electrode potential of hydrogen has arbitrarily been chosen as zero.

2. Comparison with hydrogen electrode

The standard electrode potentials of other elements are found by comparing them with standard hydrogen electrode potential.

3. Equilibrium between atoms and ions

The electrode potential set up when a metal piece is placed in a solution containing its own ions can be explained in terms of equilibrium between the atoms of the metal and its ions in solution.

4. Formation of positive ions

When a metal is placed in a solution, some of its atoms tend to give electrons to the piece of metal and pass into the solution as positively charged ions.

5. Formation of neutral atoms

The metallic ions already present in solution tend to take up electrons from the piece of metal and deposit themselves as neutral atoms.

6. Factor deciding charge

Whichever tendency is greater determines whether the metal becomes negatively or positively charged.

7. No potential difference change

When equilibrium is attained the two opposing processes continue at the same rate and there is no further change in the potential difference.
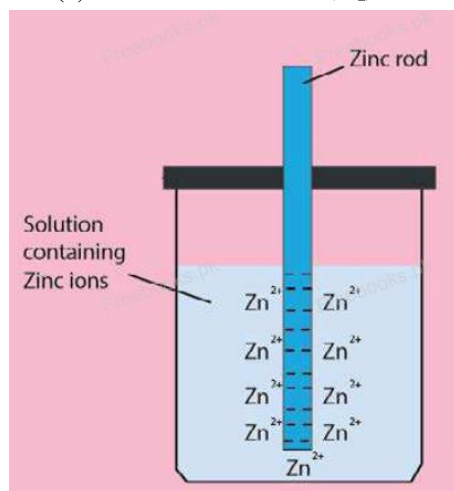
Example

A rod of zinc will bear an accumulation of negative charges. This is due to the net ionization of some of its atoms.

Electrical double layer

The negative charge on the Zn-rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer.

Equation

$$Zn\ (s) \rightleftharpoons Zn^{2+}\ (aq)\ + 2e^-$$

Standard Hydrogen Electrode

Construction

It consists of a piece of platinum foil which is coated electrolytically with finely divided platinum black to give it a large surface area and suspended in one molar solution of HCl.
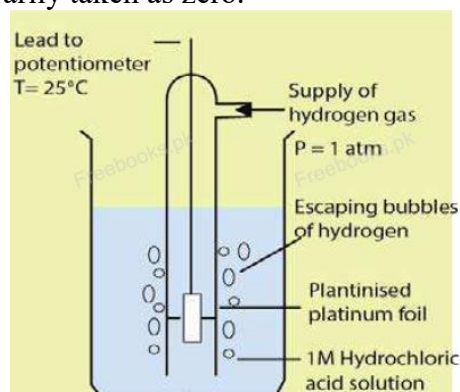
Working

Pure hydrogen gas at one atmosphere pressure is continuously bubbled into 1M HCl solution.

Electrical conductor

The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution.

Electrode potential

The potential of this electrode is arbitrarily taken as zero.

Measurement of Electrode Potential

Establishment of galvanic cell
In any measurement of electrode potential, the concerned electrode is joined electrolytically with the standard hydrogen electrode (SHE) and a galvanic cell is established.

Salt bridge
The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride. The salt bridge is used to provide a highly conducting path between the two electrolytic solutions.

Voltmeter
The potential difference is measured by a voltmeter which gives the potential of the electrode as the potential of SHE is zero.
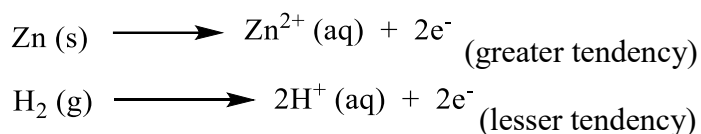
Reaction at SHE
An oxidation or reduction may take place at SHE depending upon the nature of the electrode which is coupled with it.

Example of galvanic cell between zinc and hydrogen
To measure the electrode potential of zinc a galvanic cell is established between zinc electrode dipped in 1 M solution of its ions and standard hydrogen electrode at 25 °C. Under the standard conditions, the voltmeter reads 0.76 volts and the deflection is in such a direction as to indicate that zinc has a greater tendency to give off electrons than hydrogen has.
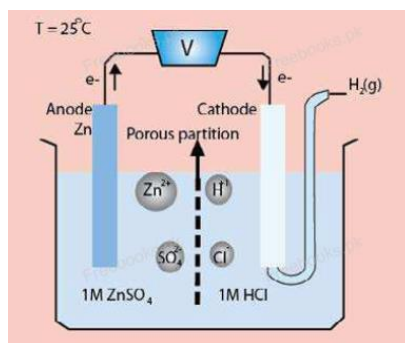The half reaction:

$$Zn\ (s) \longrightarrow Zn^{2+}\ (aq)\ +\ 2e^{-} \quad \text{(greater tendency)}$$

$$H_2\ (g) \longrightarrow 2H^{+}\ (aq)\ +\ 2e^{-} \quad \text{(lesser tendency)}$$

by 0.76 volts.
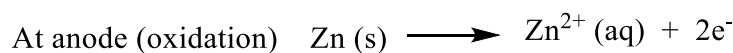
Oxidation potential of zinc
The standard electrode potential of zinc is 0.76 volts. It is called oxidation potential of Zn and is given the positive sign.

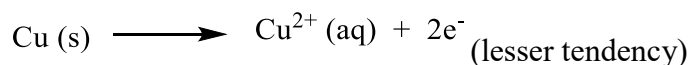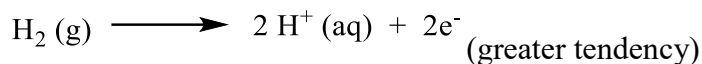The reduction potential Zn-electrode is -0.76 volt.

Electrode Reactions
The electrode reactions are as follows.

$$\text{At anode (oxidation)} \quad Zn\ (s) \longrightarrow Zn^{2+}\ (aq)\ +\ 2e^{-}$$

$$\text{At cathode (reduction)} \quad 2H^{+}\ (aq)\ +\ 2e^{-} \longrightarrow H_2\ (g)$$

Example of galvanic cell between copper and hydrogen
The electrode potential of copper can also be measured using galvanic cell in which copper is an electrode dipped in 1 M solution of its ions and connected with SHE. Under standard conditions, the voltmeter reads 0.34

volts and the deflection is in such a direction as to indicate that hydrogen has a greater tendency to give of electrons than copper has.
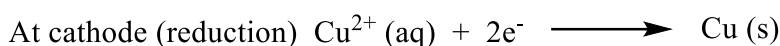
$$H_2 \text{ (g)} \longrightarrow 2 H^+ \text{ (aq)} + 2e^- \quad \text{(greater tendency)}$$

$$Cu \text{ (s)} \longrightarrow Cu^{2+} \text{ (aq)} + 2e^- \quad \text{(lesser tendency)}$$
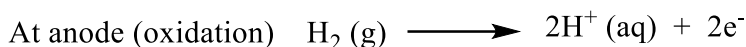
by 0.34 volts.

So the standard electrode potential of Cu is 0.34 volts. It is called reduction potential of Cu.

-0.34 V is called oxidation potential of Cu electrode.

Electrode Reactions

The reactions taking place at two electrodes will be shown as follows.

$$\text{At anode (oxidation)} \quad H_2 \text{ (g)} \longrightarrow 2H^+ \text{ (aq)} + 2e^-$$

$$\text{At cathode (reduction)} \quad Cu^{2+} \text{ (aq)} + 2e^- \longrightarrow Cu \text{ (s)}$$

The Electrochemical Series

Definition

When elements are arranged in the order of their standard electrode potentials on the hydrogen scale the resulting list is known as electrochemical series.

Applications of Electrochemical Series

Following are the applications of electrochemical series:
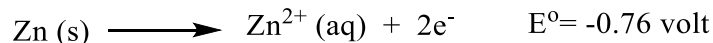
1. Prediction of the Feasibility of a Chemical Reaction

When we look at the electrochemical series it is easy to predict whether a particular reaction will take place or not.
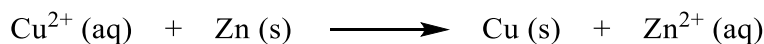
Example

Cu^{2+} (aq) can oxidize solid zinc but Zn^{2+} (aq) cannot oxidize solid copper. Standard reduction potential values of copper and zinc can explain this

$$Cu^{2+} \text{ (aq)} + 2e^- \longrightarrow Cu \text{ (s)} \qquad E^o = +0.34 \text{ volt}$$

$$Zn^{2+} \text{ (aq)} + 2e^- \longrightarrow Zn \text{ (s)} \qquad E^o = -0.76 \text{ volt}$$

Zinc is oxidized

$$Zn \text{ (s)} \longrightarrow Zn^{2+} \text{ (aq)} + 2e^- \qquad E^o = -0.76 \text{ volt}$$

Overall Reaction

$$Cu^{2+} \text{ (aq)} + Zn \text{ (s)} \longrightarrow Cu \text{ (s)} + Zn^{2+} \text{ (aq)}$$
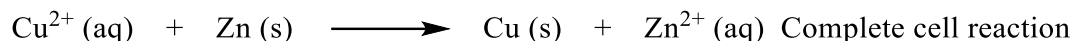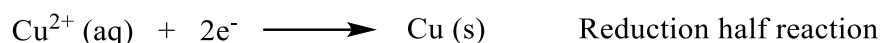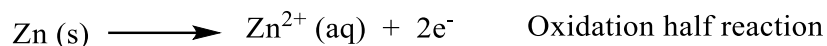
$E^o{}_{cell} = 1.10$ volts

The overall positive value for the reaction potential suggests that the process is energetically feasible.

2. Calculation of the Voltage or Electromotive Force (EMF) of Cells

In a galvanic cell, the electrode occupying a higher position in the electrochemical series, will act as anode and oxidation takes place on it. The electrode occupying the lower position in the series will act as a cathode and reduction will take place.

Example

Let us find out a cell potential or the EMF of the cell. The half cell reactions are:

$$Zn \ (s) \longrightarrow Zn^{2+} \ (aq) \ + \ 2e^- \qquad \text{Oxidation half reaction}$$

$$Cu^{2+} \ (aq) \ + \ 2e^- \longrightarrow Cu \ (s) \qquad \text{Reduction half reaction}$$

$$Cu^{2+} \ (aq) \ + \ Zn \ (s) \longrightarrow Cu \ (s) \ + \ Zn^{2+} \ (aq) \ \text{Complete cell reaction}$$

Calculation of EMF

$$E^o_{cell} = E^o oxi + E^o red$$
$$E^o_{cell} = 0.76 + 0.34$$
$$= 1.10 \ volts$$

The cell voltage or emf measures the force with which electrons move in the external circuit and therefore measures the tendency of the cell reaction to take place.

3. Comparison of Relative Tendency of Metals and Non-Metals to Get Oxidized and Reduced
Reduction Potential Value
Reducing agent
The value of the reduction potential of a metal or a nonmetal tells us the tendency to lose electrons and act as a reducing agent.
Oxidizing agent
It also gives the information about the tendency of a species to gain electrons and act as an oxidizing agent. Greater the value of standard reduction potential of a given species greater is its tendency to accept electrons to undergo reduction and to act as an oxidizing agent.
Example
1. Ions like Au^{3+}, Pt^{2+}, Hg^{2+}, Ag^+, Cu^{2+} and the nonmetal elements like F_2, Cl_2, Br_2 and I_2 which lie below the SHE have a strong tendency to gain electrons and undergo reduction.
2. Strong oxidizing agents like F_2, Cl_2, Br_2, etc. have a large positive value of standard reduction potentials
3. Strong reducing agents have large negative values like Li, K, Ca, Na which lie above SHE.

4. Relative Chemical Reactivity of Metals
Greater the value of standard reduction potential of a metal, smaller is its tendency to lose electrons to change into a positive ion and hence lower will be its reactivity.

Examples
1. Metals like Li, Na, K and Rb are highly reactive.
2. Coinage metals, Cu, Ag, and Au are the least reactive because they have positive reduction potentials.
3. Metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas.
4. Metals like Fe, Cr, Zn, Mn, Al and Mg which have more negative reduction potentials react with steam to produce the metallic oxides and hydrogen gas.

5. Reaction of Metals with Dilute Acids
Greater the value of standard reduction potential of a metal, lesser is its tendency to lose electrons to form metal ions and so weaker is its tendency to displace H^+ ions from acids as H_2 gas.
Examples
1. Metals like Au, Pt, Ag and Cu which have sufficiently high positive values of reduction potentials do not liberate hydrogen gas from acids.
2. Metals like Zn, Mg and Ca which are close to the top of the series and have very low reduction potentials liberate hydrogen gas when they react with acids.

6. Displacement of One Metal by Another from its Solution

One metal will displace another metal from the aqueous solution of its salt if it lies above in the electrochemical series.

Examples

Fe can displace Cu from $CuSO_4$

Zn does not displace Mg from $MgSO_4$

Modern Batteries and Fuel Cells

Lead Accumulator or Lead-Acid Battery

It is commonly used as a car battery. It is secondary or a storage cell.

Principle of working and battery design

Passing a direct current through it must charge it. The charged cell can then produce electric current when required. When the two electrodes are connected through an external circuit, it produces electricity by discharge. A single cell provides around 2 volts. For 12 volts, 6 cells are connected in series. Each cell contains two lead grids packed with the electrode materials. The grid is immersed in an electrolytic solution of $\approx 3.2M$ H_2SO_4 (30%). Fibre glass sheets between the grids prevent shorting by accidental physic al contact.

Cathode

The cathode of a fully charged lead accumulator is lead oxide, PbO_2
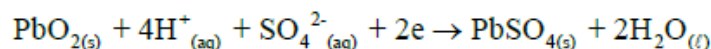
Anode

Anode is metallic lead.

Electrolyte

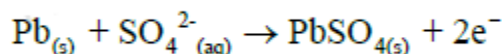The electrolyte is 30% sulphuric acid solution (density 1.25 g cm^{-3}).

Discharging

At the anode the lead atoms release two electrons each to be oxidized to Pb^{2+} ions, which combine with SO_4^{2-} ions present in the electrolyte and get deposited on the anode as $PbSO_4$.

Cathode (reduction)
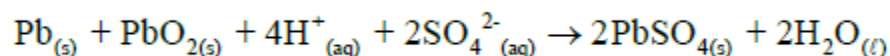
$$PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2e \rightarrow PbSO_{4(s)} + 2H_2O_{(\ell)}$$

Anode (oxidation)

$$Pb_{(s)} + SO_4^{2-}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$$

Overall reaction

$$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{2-}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(\ell)}$$
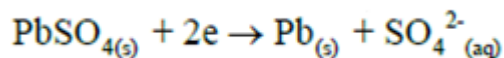
Explanation of discharging

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting up of car lights and so on. At the cathode the electrons from the anode are accepted by PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water. The Pb^{+2} ions then combine with the SO_4^{-2} ions and they both deposit at the cathode as $PbSO_4$. When both electrodes are completely covered with $PbSO_4$ deposits the cell will cease to discharge any more current until it is recharged. When the cell is discharged, it generates electrical energy as a voltaic cell.
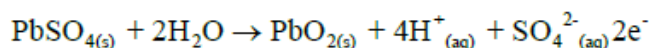
Recharging

During the process of recharging, the anode and the cathode of the external electrical source are connected to the anode and the cathode of the cell respectively. The redox reactions at the respective electrodes are then reversed.
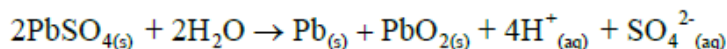
Anode (reduction)

$$PbSO_{4(s)} + 2e \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$$

Cathode (oxidation)

$$PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} 2e^-$$

Overall reaction

$$2PbSO_{4(s)} + 2H_2O \rightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Explanation of recharging

During the process of discharging the concentration of the acid falls decreasing its density to $1.15g \ cm^3$. After recharging the acid is concentrated again bringing its density to its initial value of $1.25g \ cm^3$. The voltage of the battery returns to around 12 volts.
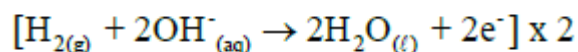
Fuel Cells

Definition

Fuel cells are other means by which chemical energy may be converted into electrical energy. The cell runs continuously till the reactants are supplied. Fuel cells are light, portable and sources of electricity. Many fuel cells do not produce pollutants. Fuel cells are very efficient. They convert about 75% of fuels bond energy into electricity.
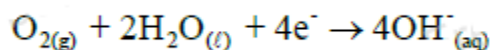
Principle of working

When gaseous fuels, such as hydrogen and oxygen are allowed to undergo a reaction, electrical energy can be obtained. This cell finds importance in space vehicles. The electrodes are hollow tubes made of porous compressed carbon impregnated with platinum, which acts as a catalyst. The electrolyte is KOH. At the electrodes, hydrogen is oxidized to water and oxygen is reduced to hydroxide ions.
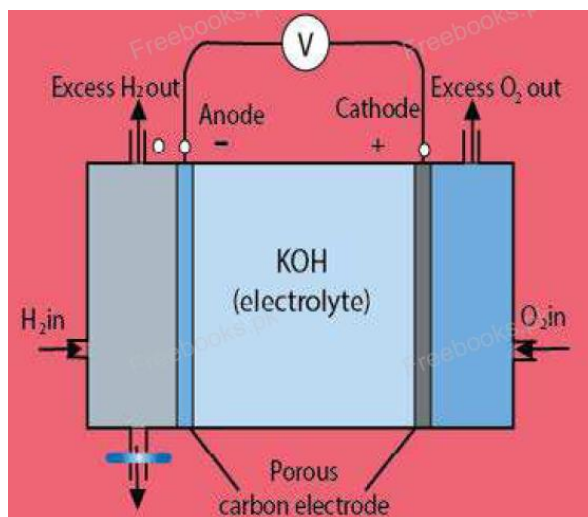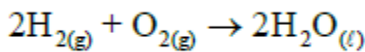
Anode

$$[H_{2(g)} + 2OH^-{}_{(aq)} \rightarrow 2H_2O_{(\ell)} + 2e^-] \ x \ 2$$

Cathode

$$O_{2(g)} + 2H_2O_{(\ell)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$$

Overall reaction

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$$

Water for drinking purpose
This fuel cell is operated at a high temperature so that the water formed as a product of the cell reaction evaporates and may be condensed and used as drinking water for an astronaut.
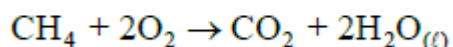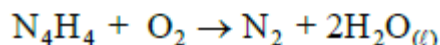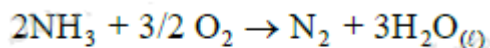**Power generation**
A number of these cells are usually connected together so that several kilowatts of power can be generated.
The fuel cells produce electricity and pure water during space flights.
Other fuel cell reactions
Some other cell reactions in fuel cell are:

$$2NH_3 + 3/2\ O_2 \rightarrow N_2 + 3H_2O_{(\ell)}$$

$$N_4H_4 + O_2 \rightarrow N_2 + 2H_2O_{(\ell)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(\ell)}$$

Important long questions from past papers
33. Define electrochemical series? Explain its any three applications.
34. Explain the structure and function of voltaic or galvanic cell.
35. How can you measure electrode potential of an element using standard hydrogen electrode (SHE)?
36. Describe the construction and working of standard hydrogen electrode?
37. What is standard hydrogen electrode (SHE)? How it is used to measure the electrode potential of Zinc.
38. Describe the electrolysis of molten sodium chloride and a concentrated aqueous solution of sodium chloride.
39. Explain the construction and working of fuel cell.
40. Write a note on fuel cells.
41. Give explanation of discharging and recharging of lead accumulator along with reactions occurring at electrodes.

Chapter 11

Reaction Kinetics

Order of Reaction

Definition

The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised.

OR

The order of reaction may also be defined as the number of reacting molecules, whose concentrations alter as a result of the chemical change.

Importance

1. The order of reaction provides valuable information about the mechanism of a reaction.
2. The order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
3. The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.
4. The chemical reactions are classified as zero, first, second and third order reactions.

Explanation with Examples

For a general reaction between A and B where 'a' moles of A and 'b' moles of B react to form 'c' moles of C and 'd' moles of D.

$$aA + bB \longrightarrow cC + dD$$

We can write the rate equation as:
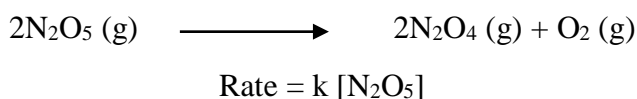
$$R = k[A]^a[B]^b$$

The exponent 'a' or 'b' gives the order of reaction with respect to the individual reactant. Thus the reaction is of order 'a' with respect to A and of order b with respect to B.

The overall order of reaction is:

(a+b)

Decomposition of nitrogen pentoxide
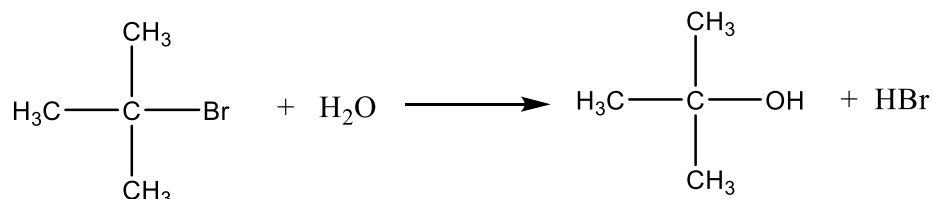
1. Decomposition of nitrogen pentoxide involves the following equation:

$$2N_2O_5 (g) \longrightarrow 2N_2O_4 (g) + O_2 (g)$$

$$Rate = k [N_2O_5]$$

Order of reaction= one

Hydrolysis of tertiary butyl bromide

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$$Rate = k \ [(CH_3)_3CBr]$$

Order of reaction= pseudo first order reaction

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess.

Oxidation of nitric oxide

Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O_3.

$$NO \ (g) + O_3 \ (g) \longrightarrow NO_2 \ (g) + O_2 \ (g)$$

$$Rate = k \ [NO][O_3]$$

Order of reaction= two

Reaction of ferric chloride and potassium iodide

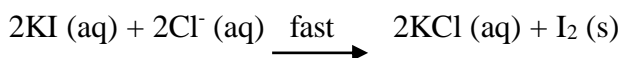$$Rate = k[FeCl_3][KI]^2$$

Order of reaction= third

This rate equation suggests that the reaction is, in fact, taking place in more than one steps.
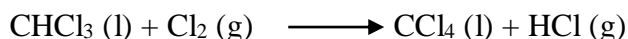
There are two possible steps of the reaction:

Slow step

$$FeCl_3 \ (aq) + 2KI \ (aq) \xrightarrow{\text{slow}} FeI_2 \ (aq) + 2KCl \ (aq) + Cl^- \ (aq)$$

Fast step

$$2KI \ (aq) + 2Cl^- \ (aq) \xrightarrow{\text{fast}} 2KCl \ (aq) + I_2 \ (s)$$

Formation of carbon tetrachloride from chloroform

$$CHCl_3 \ (l) + Cl_2 \ (g) \longrightarrow CCl_4 \ (l) + HCl \ (g)$$

$$Rate = k[CHCl_3][Cl_2]^{1/2}$$

Order of reaction= 1.5

Photochemical reactions

A reaction is said to be zero order if it is entirely independent of the concentration of reactant molecules. Photochemical reactions are usually zero order.

Half Life Period

Definition

Half life period of a reaction is the time required to convert 50% of the reactants into products.

Examples

First Order Reaction

1. Decomposition of N_2O_5 at 45°C takes 24 minutes.

After 24 minutes 0.10 mole dm^{-3} of N_2O_5 decomposes to 0.05 mol dm^{-3}.
After 48 minutes 0.025 (25%) mole dm^{-3} of N_2O_5 will remain unreacted.
After 72 minutes (3 half times) 0.0125 (12.5%) mole dm^{-3} of N_2O_5 will remain unreacted.

First order reaction.

2. The disintegration of radioactive $_{92}U^{235}$ has a half-life of 7.1×10^8 or 710 million years.

1 kg sample disintegrates to 0.5 kg in 710 million years.
0.5 kg disintegrates to 0.25kg in the next 710 million years.

First order reaction.
It is independent of the amount of that substance.

Second Order Reaction

The half-life period is inversely proportional to the initial concentration of the reactants.

Third Order Reaction

The half-life is inversely proportional to the square of the initial concentration of reactants.

Mathematical expression

$$[t_{1/2}]_1 \ \alpha \ \ 1/a^o \ , \ \text{since} \ \ [t_{1/2}] = 0.693/k$$

$$[t_{1/2}]_2 \ \alpha \ \ 1/a^1 \ , \ \text{since} \ \ [t_{1/2}] = 1/ka$$

$$[t_{1/2}]_3 \ \alpha \ \ 1/a^2 \ , \ \text{since} \ \ [t_{1/2}] = 1.5/ka^2$$

$[t_{1/2}]_1$, $[t_{1/2}]_2$, $[t_{1/2}]_3$ = half-life periods of 1st, 2nd and 3rd order reactions

a= initial concentration of reactants

For the reaction of nth order

$$[t_{1/2}]_n \ \alpha \ \ 1/a^{n-1}$$

Determination of the Rate of a Chemical Reaction

The rate of a reaction is expressed in terms of the rates at which the concentrations change.

When the reaction progresses the concentrations of reactants decrease and those of products increase and it is measured at regular time intervals.
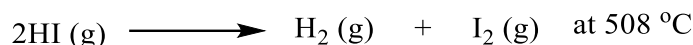
Units

$$\text{Rate of reaction} = \frac{\triangle C}{\triangle t} = \frac{\text{mol } dm^{-3}}{\text{seconds}} = \text{mol } dm^{-3} \ s^{-1}$$

Graphical Explanation

Rate of a chemical reaction always decreases with the passage of time.

To determine the rate of reaction a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained.

$$2HI \ (g) \quad \longrightarrow \quad H_2 \ (g) \quad + \quad I_2 \ (g) \quad \text{at } 508 \ ^oC$$

The change in concentration of HI for first 50 seconds is 0.0284 mol dm^{-3}
Between 300 to 350 sec the decrease is 0.0031 mol dm^{-3}.
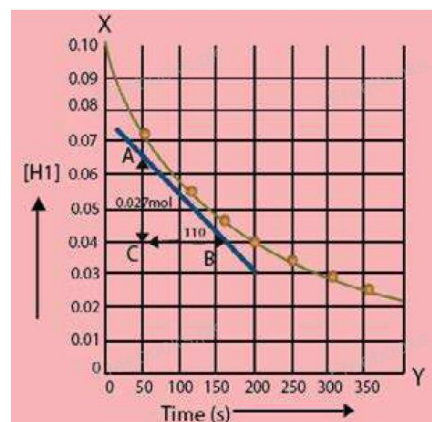
Since HI is a reactant, so it is a falling curve. The steepness of the curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Measurement of Rate of Reaction

In order to measure the rate of reaction, draw a tangent say, at 110 seconds, on the curve and measure the slope of that tangent. A right angled triangle ABC is completed with a tangent as hypotenuse.

$$\text{Slope or rate} = \frac{0.027 \ \text{mol dm}^{-3}}{110 \ \text{sec}}$$

$$= 2.5 \times 10^{-4} \ \text{mol dm}^{-3} \ \text{s}^{-1}$$

In one sec in 1 dm^3 solution, the concentration of HI disappears by 2.5 x 10^{-4} moles, changing into the products. The right angled triangle ABC can be of any size, but the results for the rate of reaction will be the same.

Rising Curve

If we plot a graph between time on x-axis and concentration of any of the products then a rising curve is obtained. The value of the tangent will be the same.

Physical Methods
Following are the physical methods employed for determining the rate of reaction.

1. Spectrometry

If a reactant or a product absorbs ultraviolet, visible or infrared radiation then spectrometry is used. The rate of reaction can be measured by measuring the amount of radiation absorbed.

2. Electrical Conductivity Method

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The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions.

$$\text{Conductivity} \quad \alpha \quad \text{rate of change in the concentration of such ions}$$

3. Dilatometric Method

This method is useful for those reactions which involve small volume changes in solutions.

$$\text{Volume change} \quad \alpha \quad \text{Extent of reaction}$$

4. Refractrometric Method

This method is suitable for reactions in solutions, where change in refractive indices of the substances decides rate of reaction.
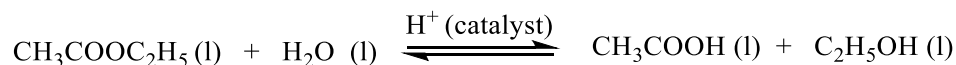
5. Optical Rotation Method

This method is applied to optically active species. The angle through which plane polarized light is rotated is measured by a polarimeter. The extent of rotation determines the concentration of optically active substance in the reaction mixture.

Chemical Method

This is particularly suitable for reactions in solution. Chemical analysis of a reactant or a product is done.

Example

The acid hydrolysis of ethyl acetate, an ester, in the presence of a small amount of an acid.

$$CH_3COOC_2H_5 \text{ (l)} \ + \ H_2O \text{ (l)} \ \underset{}{\overset{H^+ \text{ (catalyst)}}{\rightleftharpoons}} \ CH_3COOH \text{ (l)} \ + \ C_2H_5OH \text{ (l)}$$

The solution of ester in water and the acid acting as a catalyst are allowed to react.

Determination of Rate of Reaction

1. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice cold water.

2. The dilution and chilling stops the reaction.

3. The acid formed is titrated against a standard alkali, say NaOH.

4. Phenolphthalein is used as an indicator.

5. The analysis is repeated at various time intervals after the start of reaction to get information about the change in concentration of acetic acid formed during the reaction at different time intervals.

6. The different concentrations of acetic acid are plotted against the time.

7. A rising curve is obtained.
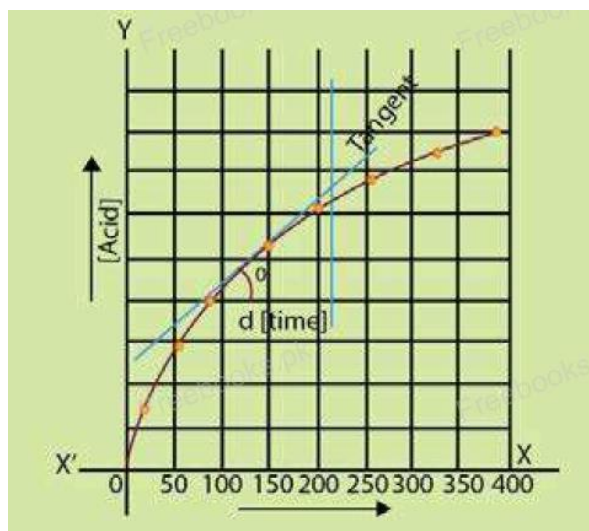
The slope of the curve at any point will give the rate of reaction.
Initially, the rate of reaction is high but it decreases with the passage of time.
When the curve becomes horizontal, the rate becomes zero.

Falling Curves

1. If we plot the graph for decreasing concentrations of $CH_3COOC_2H_5$, then falling curves are obtained.
2. If we have any laboratory technique to record the changing concentration of ester or alcohol, we can measure the rate of the reaction.
3. This is a pseudo first order reaction as water is in large excess.

Finding the Order of Reaction

Following methods are used to determine the order of reaction.

1. Method of hit and trial

2. Graphical method

3. Differential method

4. Half life method

5. Method of large excess

Half Life Method

Half life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

Mathematical Expression

$$(t_{1/2})_n \quad a \quad 1/a^{n-1}$$

Two different initial concentrations 'a$_1$' and 'a$_2$' are taken in a reaction and their half-life periods are found to be t$_1$ and t$_2$, respectively.

$$t_1 \; \alpha \; 1/a_1^{n-1}$$

$$t_2 \; \alpha \; 1/a_2^{n-1}$$

Dividing the two relations

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides

$$\log \frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$

$$n-1 = \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

If we know the two initial concentrations and two half life values we can calculate the order of reaction (n).

Method of Large Excess

One of the reactants is taken in a very small amount.
The active masses of the substances in large excess remain constant throughout.
That substance taken in small amount controls the rate and the order is noted with respect to that.

Reason

A small change in concentration of a substance taken in very small amount affects the value of rate more appreciably.

Example

The hydrolysis of ethyl acetate shows that water being in large excess does not determine the order.

Overall Order Calculation

The reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated.

Factors Affecting Rates of Reactions

Some of the important factors affecting rates of reactions are given below:

1. Nature of Reactants

The rate of reaction depends upon the nature of reacting substances.
Electronic configuration
The chemical reactivity of the substances is controlled by their electronic configuration.
Example
The elements of I-A group have one electron in their outermost s-orbital. They react with water more swiftly than those of II-A group elements having two electrons in their outermost s-orbital.
Type of reactions
The neutralization and double decomposition reactions are very fast as compared to those reactions in which bonds are rearranged. Oxidation-reduction reactions involve the transfer of electrons and are slower than ionic reactions.

2. Concentration of Reactants

An increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate due to more collisions, while a decrease in the concentrations will have a reverse effect.
Example
1. Combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen. 2. Limestone reacts with different concentrations of hydrochloric acid at different rates. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. Increasing the partial pressure of H_2 or Cl_2 from 0.5 to 1.0 atmosphere doubles the rate of reaction in the presence of excess of the other component.
Example for explanation
The effect of change in concentration on the rate of a chemical reaction can be understood from the following gaseous reaction.

$$2NO\ (g)\ +\ 2H_2\ (g)\ \longrightarrow\ 2H_2O\ (g)\ +\ N_2\ (g)$$
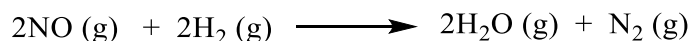
In this reaction, four moles of the reactants form three moles of the products, so the pressure drop takes place during the progress of reaction. The rates of reaction between NO and H_2 at 800°C are studied by noting the change in pressure.

[NO] in (mol dm⁻³)	[H₂] in (mol dm⁻³)	Initial rate (atm min⁻¹)
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

First three experiments

The concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

Next three experiments

The concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. The rate is proportional to the square of concentration of NO.
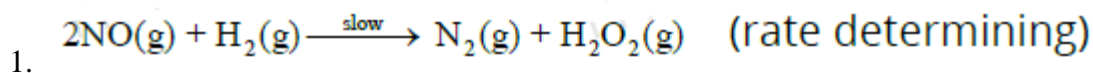
$$\text{Rate} \propto [NO]^2$$
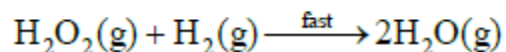
Rate Equation

$$\text{Rate} \propto [H_2][NO]^2$$

$$\text{Rate} = k[H_2]^1[NO]^2$$

Order of reaction: 3rd order reaction

Possible Mechanism

The mechanism has two steps:

1. $2NO(g) + H_2(g) \xrightarrow{\text{slow}} N_2(g) + H_2O_2(g)$ (rate determining)

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$$H_2O_2(g) + H_2(g) \xrightarrow{\text{fast}} 2H_2O(g)$$

2.

3. Surface Area

The increased surface area of reactants increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance.

Examples

1. Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2AI + 2NaOH + 6H_2O \rightarrow 2NaAI(OH)_4 + 3H_2$$
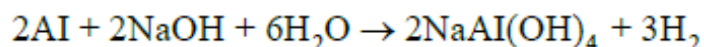
2. $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces.

4. Light

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced.

Examples

1. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight.
2. Light is vital in photosynthesis and the rate is influenced by light.

5. Temperature

Collision theory

The rate of a reaction is proportional to the number of collisions among the reactant molecules.

Effective collisions

The effective collisions are the ones which lead to the formation of product.

Condition for effective collision

For a collision to be effective the molecules must possess the activation energy and they must also be properly oriented. For nearly all chemical reactions the activation energy is quite large and at ordinary temperature very few molecules are moving fast enough to have this minimum energy.

Temperature and activation energy

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded area. As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution of velocities. The curve at higher temperature T2 has flattened. It shows that molecules having higher energies have increased and those with less energies have deceased. So, the number of effective collisions increases and hence the rate increases. When the temperature of the reacting gases is raised by 10K, the fraction of molecule with energy more than Ea roughly doubles and so the reaction rate also doubles.

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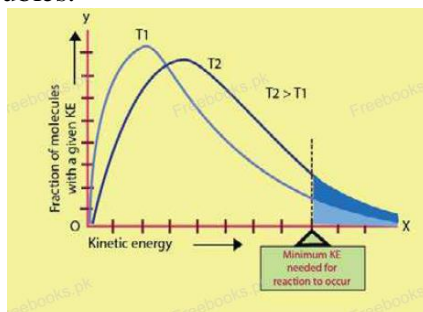
6. Arrhenius Equation
Arrheinus studied the quantitative relationship between temperature, energy of activation and rate constant of a reaction.
Main idea
The rate constant 'k' for many simple reactions is found to vary with temperature.
Arrhenius Equation

$$k=Ae^{-Ea/RT} ..... (1)$$

Ea =activation energy
T =temperature
R =general gas constant
e =base of natural logarithm.
Explanation of equation
The equation shows that the increase in temperature increases the rate constant and the reactions of high activation energy have low 'k' values.
A =Arrhenius constant and it depends upon the collision frequency of the reacting substances.
Determination of energy of activation
We take natural log of Arrhenius equation, which is expressed as n. The base of natural log is e and its value is 2.718281.

$$\ell nk = \ell n(Ae^{-Ea/RT})$$

$$\ell nk = \ell nA + \ell ne^{-Ea/RT}$$

$$\ell nk = \ell nA + \frac{-E}{RT}\ell ne$$

$\ell ne=1$ (log of a quantity with same base is unity)

$$\ell nk= -Ea/RT + \ell nA ..... (2)$$

Calculation of slope
Equation (1) is a straight line equation and from the slope of straight line E_a can be calculated. In order to convert this natural log into common log of base 10, we multiply the ℓn term with 2.303.

$$2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A$$

(The base of common log is 10)

Divide the whole equation by 2.303

$$\log k = \frac{-E_a}{2.303RT} + \log A \quad ....(3)$$

The eq (3) is a straight line equation like $\quad$ y= - mx + c

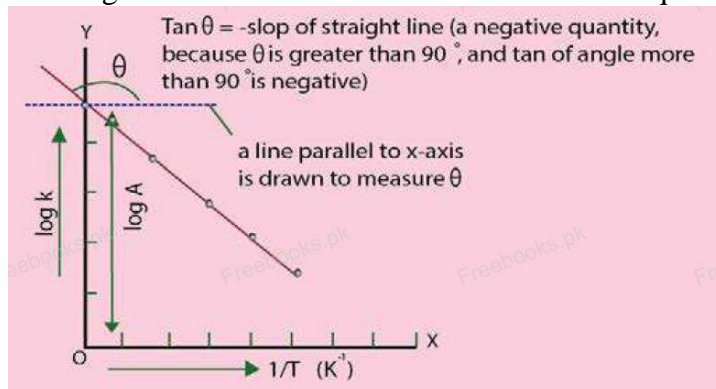m= slope of straight line

c= intercept of straight line

Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like Ea, R and A are constants for a given reaction.

Plotting graph

A graph is plotted between 1/T on x-axis and log k on y-axis. A straight line is obtained with a negative slope. Ea/RT has negative sign so the straight line has two ends in second and fourth quadrants.

Taking slope

The slope of the straight line is measured by taking the tangent of that angle θ which this straight line makes with the x-axis. To measure the slope, draw a line parallel to x-axis and measure angle θ. Take tan θ which is slope. This slope is equal to

$$- \frac{E_a}{2.303\ R}$$

$$\text{Slope} = \frac{-E_a}{2.303\ R}$$

$$E_a = -\ \text{Slope} \times 2.303\ R$$

Units of slope

$$\text{Slope} = \frac{J\ mol^{-1}}{2.303\ JK^{-1}mol^{-1}}$$
$$= K$$

Catalysis

Definition of catalysis

The process which takes place in the presence of a catalyst is called catalysis.

Definition of catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small proportion.

Importance

A catalyst provides a new reaction path with a low activation energy barrier. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

Examples

1. The reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst.

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2. $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2.
3. HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$4HCl + O_2 \xrightarrow{\text{CuCl}_2} 2H_2O + 2Cl_2$$
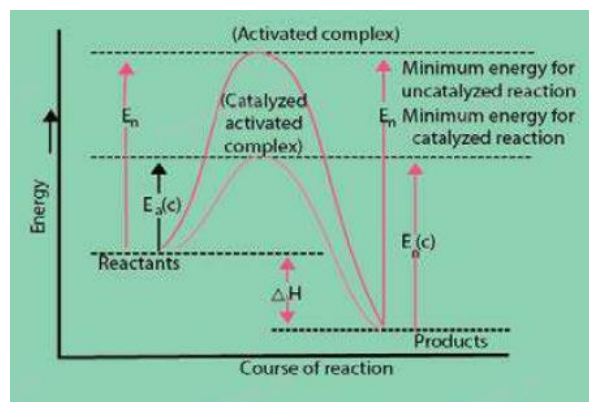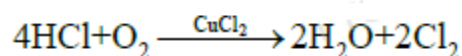
Types of Catalysis

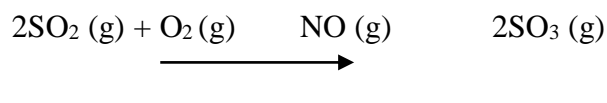Following are the two types of catalysis:
1. Homogeneous catalysis
2. Heterogeneous catalysis
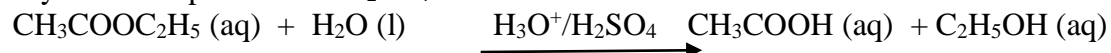
1. Homogeneous Catalysis
The catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system.
Examples
1. The formation of SO_3 (g) from SO_2 (g) and O_2 (g) in the lead chamber process for the manufacture of sulphuric acid needs NO (g) as a catalyst.

$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \xrightarrow{\text{NO (g)}} 2SO_3 \text{ (g)}$$

2. Esters are hydrolyzed in the presence of H_2SO_4.

$$CH_3COOC_2H_5 \text{ (aq)} + H_2O \text{ (l)} \xrightarrow{H_3O^+/H_2SO_4} CH_3COOH \text{ (aq)} + C_2H_5OH \text{ (aq)}$$
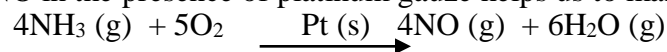
2. Heterogeneous Catalysis

The catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase.

Examples
(i) Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_3 \text{ (g)} + 5O_2 \xrightarrow{\text{Pt (s)}} 4NO \text{ (g)} + 6H_2O \text{ (g)}$$

(ii) Hydrogenation of unsaturated organic compounds is catalyzed by finely divided Ni, Pd or Pt.

$$CH_2{=}CH_2 \text{ (g)} + H_2 \text{ (g)} \xrightarrow{\text{Ni (s)}} CH_3\text{-}CH_3 \text{ (g)}$$

Characteristics of a Catalyst

Following are the characteristics of a catalyst:

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1. Catalyst remains unchanged

A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.

Example

MnO_2 is added as a catalyst for the decomposition of $KClO_3$ in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.

2. Needed in small amounts

We need a trace of a metal catalyst to affect very large amount of reactants.

Example

1. 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.
2. Dry HCl and NH_3 don't combine, but in the presence of trace of moisture they give dense white fumes of NH_4Cl.
3. Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

3. Effectiveness of catalyst

A catalyst is more affective, when it is present in a finely divided form.

Example

A lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used.

4. Establishment of equilibrium

A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.

5. Initiation of reaction

A catalyst cannot start a reaction, which is not thermodynamically feasible. It is now considered that a catalyst can initiate a reaction but the mechanism of it is different.

Enzyme Catalysis

Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells. Many enzymes have been identified and obtained in the pure crystalline state. The first enzyme was prepared in the laboratory in 1969.

Examples

1. Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.

$$NH_2\text{-}CO\text{-}NH_2 + H_2O \xrightarrow{\quad Urease \quad} 2NH_3 + CO_2$$
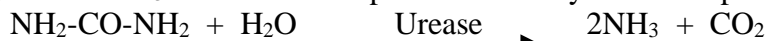
2. Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\quad Invertase \quad} C_6H_{12}O_6 + C_6H_{12}O_6$$
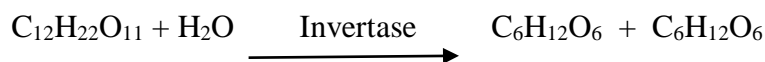
3. Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6 \xrightarrow{\quad Zymase \quad} 2C_2H_5OH + 2CO_2$$
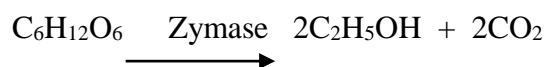
Lock and Key Model

Enzymes have active centres on their surfaces. The molecules of a substrate fit into their cavities just as a key fits into a lock. The substrate molecules enter the cavities, form the complex and reactants and the products get out of the cavity immediately. Michaulis and Menter(1913) proposed the following mechanism for enzyme catalysis.

$$E + S \longrightarrow ES \longrightarrow P + E$$

E = enzyme, S = substrate (reactant)
ES = activated complex, P = product
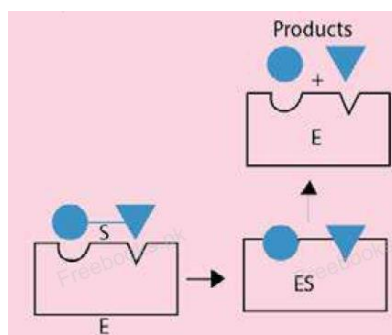
Characteristics of Enzyme Catalysis

Following are the characteristics of enzyme catalysis:
1. Efficiency
Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.
2. Specificity
Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.
3. Optimum temperature
Enzyme catalytic reactions have the maximum rates at an optimum temperature.
4. Optimum pH
The pH of the system also controls the rates of the enzyme catalyzed reaction and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.
5. Co-enzyme or activator
The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.

Important long questions from past papers

1. How does Arrhenius equation help us to calculate the energy of activation of a reaction?
2. How rate of reaction depends on the following factors?
   a. Nature of reactants
   b. Surface area
3. Explain effect of temperature on rate of reaction.
4. What is order of reaction? Describe two methods (half life method and large excess method) for finding the order of reaction.
5. Define half life period. Describe half life method for the determination of order of reaction.
6. Define Order of reaction. Describe it with three examples.
7. Write a brief note on the following:

      a. Homogeneous catalysis
      b. Heterogeneous catalysis

8. What are enzymes? Write any four characteristics of enzyme catalysis.
9. Explain any four characteristics of catalysts**.**

GOOD LUCK
FOR YOUR
Exam
AND
do the best