COMPLETE NOTES

11TH CHEMISTRY FULL BOOK NOTES

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Chapter 1

BASIC CONCEPTS

CHEMISTRY:

"The branch of science which deals with the study of structure of matter, composition of matter, properties of matter, changes in matter and laws and principles which govern these changes is called chemistry."

There are many branches of chemistry like, physical chemistry, organic chemistry, inorganic chemistry biochemistry, analytical chemistry, industrial chemistry etc. The American chemical society (ACS) has divided the chemistry into thirty divisions.

Atom:

"The smallest particle of an element which may or may not exist independently and can take part in chemical reaction is called atom."

For examples: He, Ne, Ar, N, O, S, Fe etc. are all atoms. Atoms of H, O and N do not exist independently but He, Ne and Ar exist independently.

CONCEPT OF ATOM

Long time ago, it was believed that matter is made up of simple, indivisible particle.

In early times, it was thought that matter is made up of tiny particles which cannot be divided. **Greek Philosophers** thought that matter could be divided into smaller and smaller particles to reach basic unit, which could not be further divided. **Democritus** (460 – 370 B.C.) called these particles as atoms, derived from the word "atomos" mean indivisible. The ideas of Greek Philosophers were not based on experimental evidences.

In the late 17th century, the quantitative study of the composition of pure substances disclosed that a few elements are the components of many different substances. It was also investigated that how elements combine to form compounds and how compounds could be broken down into their constituent elements.

In 1808, an English school teacher **John Dalton** recognized that the law of conservation of mater and the law of definite proportions could be explained by the existence of atoms. He developed an atomic theory, the main point of which is that all matter is composed of atoms of different elements, which differ in their properties.

The **modern researches** have clearly shown that an atom is further composed of sub–atomic particles like electron, proton, neutron, hypron, neutrino, anti–neutrino, meson, positron etc. More than 100 fundamental particles are thought to exist in an atom.

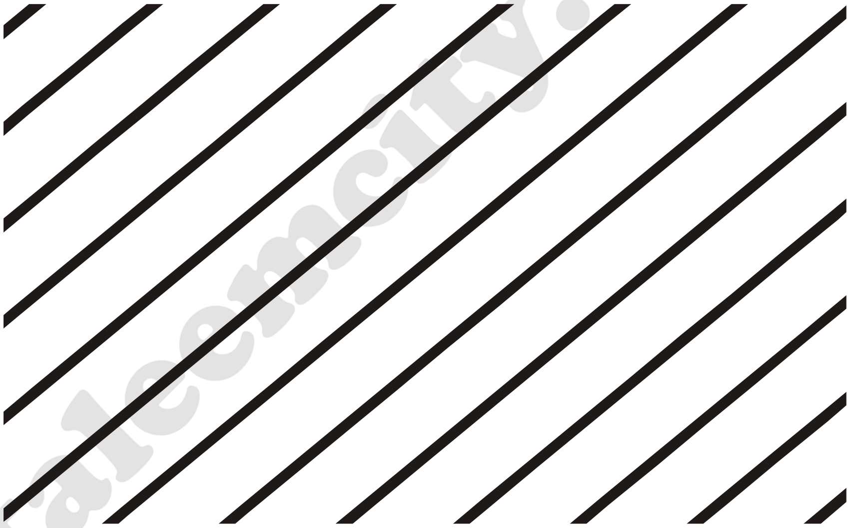
The **Swedish Chemist J. Berzelius** (1779 – 1848) determined the atomic masses of elements. A number of its values are close to the modern values. Berzelius also developed the system of giving element a symbol.

Evidence of Atoms:

Atom is very small particle. It is impossible to see an atom. But the evidence of atom can be seen by the following ways.

(i) Electron microscope:

An ordinary optical microscope can measure the size of an object upto or above 500 nm (1 nm = 10^{-9} m). To see the smaller objects, wavelength should be smaller from the size of an object. However, the objects of size of an atom can be observed in an electron microscope. In electron microscope, a beam of electrons is used instead of visible light. Wavelength of electron is much smaller than visible light. In the figure, a **photograph of piece of graphite** is shown. This photograph is taken by the electron microscope. A piece of graphite have been magnified about 15 million times in this picture. The bright bands in the figure, are layers of carbon atom and dark bands are the spaces between the layers.



Electron Microscope Photograph of Graphite

(ii) X–Rays:

X–rays analysis has shown that diameter of atoms are of the order 2×10^{-10} m which is 0.2 nm (1 nm = 10^{-9} m).

Radius of atoms = 1×10^{-10} m (0.1 nm)

(iii) Atomic masses:

Atomic masses of atoms ranges from 10^{-27} to 10^{-25} kg. They are often expressed in atomic mass units. Where 1 a.m.u = 1.66×10^{-27} kg = 1.66×10^{-24} g = 1.66×10^{-21} mg.

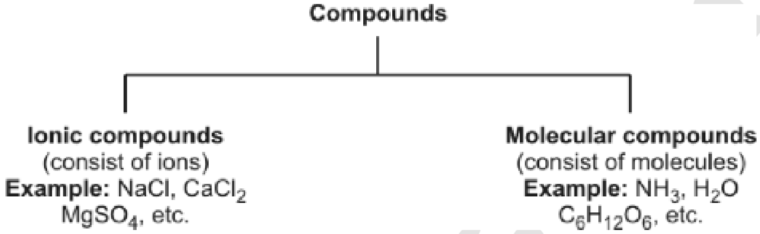
The students can have an idea about the amazingly small size of an atom from the fact that a full stop may have two millions atoms present in it and a colon has four million atoms.

Compound:

"A pure substance which is formed by the chemical combination of two or more that two different elements in a fixed ratio by mass is called compound."

Compound is always homogeneous. Components of a compound cannot be separated easily by physical methods. For example, water is a compound in which hydrogen and oxygen are combined in a fixed ratio (11.19% and 88.81%). Other examples are: NH_3, $NaCl$, H_2SO_4, $NaOH$ etc.

There are two types of compounds.



MOLECULE

"The smallest particle of an element or compound which exist independently is called molecule."

Molecules are classified in different ways; on the basis of size, number of atoms and nature of atoms.

1. Molecule – on the basis of size:

There are two type of molecules on the basis of size.

(i) Macromolecules:

Which have usually large number of atoms of different elements in it. For example, chlorophyll, haemoglobin cholesterol, proteins etc.

One haemoglobin molecule is made nearly 10,000 atoms and is 68,000 times heavier than hydrogen atom. It helps to carry oxygen from lungs and supply to all parts of the body.

(ii) Micromolecules.

Molecules of smaller size and lower molecular mass e.g., H_2SO_4, H_2O, $C_6H_{12}O_6$, CH_4 etc.

2. Molecule – on the basis of nature of atoms:

There are two types of molecules on the basis of nature of atoms.

(i) Homoatomic molecules:

"Those molecules which have same types of atoms are called homoatomic molecules" e.g. H_2, O_2, O_3, N_2, F_2, Cl_2, P_4, S_8 etc.

(ii) Heteroatomic molecules:

"Those molecules which consist of atoms of different elements are called heteroatomic molecules" e.g. CH_4, H_2O, HCl, NH_3, C_6H_6, SO_2 etc.

3. Molecule – on the basis of number of atoms:

(i) Monoatomic molecule:

"The molecule which consist of a single atom is called monoatomic molecule" e.g. He, Ne, Ar, Kr, Xe.

(ii) Diatomic molecule:

"The molecule consisting of two atoms is called diatomic molecule" e.g. H_2, O_2, HCl, CO.

(iii) Polyatomic molecule:

"Molecule consisting of more than two atoms is called polyatomic molecule" e.g. H_2O, NH_3, CCl_4, $C_6H_{12}O_6$.

Atomicity:

"The number of atoms present in a molecule is called atomicity." e.g., Atomicity of $H_2SO_4 = 7$ and that of $C_6H_{12}O_6 = 24$.

ION

The word ion means "wanderer".

"The species which carry either positive or negative charge are called ions."

There are two types of ions on the basis of charge present on them; i.e. cations and anions.

(i) Cations:

When an atom loses electron, it forms cation. Some energy is required to ionize an atom. Formation of cation is an endothermic process.

$$A \xrightarrow{\quad\quad} A^+ + e^-$$

A^+ is called cation. The charge of cation is based upon the number of electrons which an atom loses. If an atom loses one electron or two electron, its charge will be + 1 and +2 e.g. Na^+, Sr^{2+}, Ba^{2+} etc. If an atom loses three electrons, its charge will be + 3 e.g. Al^{3+}, Cr^{3+}, Fe^{3+} etc.

(ii) Anions:

When an atom gains one or more electrons, anion is formed. Some amount of energy is released when an electron is added to an atom. Formation of uni-negative is an exothermic process.

$$B + e^- \xrightarrow{\quad\quad} B^-$$

For example, atoms gaining one electron have – 1 charge on them e.g. F^-, Cl^-, Br^-, I^-. Atom gaining two electrons have – 2 charge e.g. O^{-2}, S^{-2}. (Formation of polynegative ions is endothermic).

Different atoms gain or lose electrons to get stability. Ions are more stable when they have two electrons (Duplet) or eight electrons (Octet) in their outmost shell.

On the basis of number, ions are divided into two classes.

(i) Simple ions (ii) Complex ions

(i) Simple Ion:

"If only a single atom changes to charge species it is called simple ion" e.g. Na^+, k^+, Ca^{2+}, Mg^{2+}, Al^{3+}, F^-, O^{-2} etc.

(ii) Complex Ion:

"If group of atoms have charge on them, they are called complex ions" e.g.

NH_4^+, CH_3^+, OH^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, MnO_4^-, $Cr_2O_7^{2-}$.

Molecular Ion:

"If an electron is removed from a molecule of a substance, it is called molecular ion."

For examples:

CH_4^+, CO^+, CO_2^+, N_2^+, O_2^+ etc. (NH_4^+ is not molecular ion)

If we remove an electron from an atom, it is called cation if we remove electron from a molecule, it is called molecular ion. These ions can be generated by passing high energy electron beam as α–particles or X–rays through a gas. These molecular ions can be used to determine molecular masses of compounds. When a natural product (compound) break down into molecular ions. It gives very important information.

RELATIVE ATOMIC MASS

"The relative atomic mass is the mass of one atom of an element compared with the mass of one atom of carbon taken as 12.000."

It is a relative mass because it is difficult to calculate the mass of an individual atom. Atomic mass is a comparative mass and the element used for comparison has arbitrary value 12.000.

Actual atomic mass explains that how heavy or lighter an element is, from carbon. Carbon is used as reference for comparison due to the following reasons.

(i) It is a stable element.

(ii) Its isotope ${}^{12}_{6}C$ can be found in the purest form.

(iii) It reacts with other elements to form many compounds.

The unit used for the atomic mass is atomic mass unit (a.m.u.).

ATOMIC MASS UNIT

"The mass of 1/12 of an atom of carbon 12 is called atomic mass unit." The relative atomic mass of carbon is 12.000 a.m.u. and relative atomic mass of hydrogen is 1.008 a.m.u.

The masses of the atoms vary from 10^{-27} to 10^{-25} kg. We do not weigh such an extremely small mass that is why we use relative atomic mass. The relative atomic masses and approximate atomic masses of some isotopes are given below in the Table.

Table

Isotope	Relative atomic mass
H^1	1.007825
C^{12}	12.000
O^{16}	15.9994

Ne^{20}	20.1797
Cu^{63}	63.546
U^{235}	235.0289

ISOTOPES

"The atoms of same element having same atomic number but different atomic masses are called isotopes."

Number of protons present in the nucleus of an atom is called atomic number or proton number. The number of protons and neutrons present in the nucleus of an atom is called **mass number**. Mass number is always a whole number.

Isotopes of an element have same chemical properties and same position in the periodic table. Isotopes of same elements have same number of protons and electrons in them. The phenomenon of isotopy was discovered by **Soddy**.

An isotope is represented as
Mass number ⟶ A
Atomic number ⟶ ZX ⟵ symbol of element.

For example, hydrogen has three isotopes ${}_{1}^{1}H$, ${}_{1}^{2}H$, ${}_{1}^{3}H$ naming protium, deuterium and tritium respectively. Carbon has three isotopes ${}_{6}^{12}C$, ${}_{6}^{13}C$ and ${}_{6}^{14}C$.

Chlorine has two isotopes ${}_{17}^{35}Cl$ and ${}_{17}^{37}Cl$. Oxygen has three, nickel has five calcium has six, pladium has six, cadmium has nine, neon has three and **tin** has **eleven** isotopes. Those elements which have only one isotope are called monoisotopic elements **Gold Arsenic, Iodine and fluorine** are monoisotopic elements and the phenomenon is called mono isotopy.

Relative abundance of isotopes:

"The percentage of a particular isotope of an element which exist naturally is called the relative abundance of the isotope."

The isotopes of all the elements have their own natural abundances. The properties, which are mentioned in the literature for a particular element mostly corresponds to the most abundant isotope of that element and their relative abundance can be determined by mass spectrometry. Table shows the natural abundances of some common isotopes.

Table	
Name	**Natural abundance (%)**
Hydrogen	${}_{1}^{1}H = 99.985$, ${}_{1}^{2}H = 0.015$
Carbon	${}_{6}^{12}C = 98.893$, ${}_{6}^{13}C = 1.107$
Nitrogen	${}_{7}^{14}N = 99.634$, ${}_{7}^{15}N = 0.366$
Oxygen	${}_{8}^{16}O = 99.759$, ${}_{8}^{17}O = 0.037$, ${}_{8}^{18}O = 0.204$
Neon	${}_{10}^{20}Ne = 90.51$, ${}_{10}^{21}Ne = 0.27$, ${}_{10}^{22}Ne = 9.22$
Sulphur	${}_{16}^{32}S = 95.0$, ${}_{16}^{33}S = 0.76$, ${}_{16}^{34}S = 4.22$, ${}_{16}^{36}S = 0.014$
Fluorine	${}_{9}^{19}F = 100$

Chlorine	$^{35}_{17}Cl = 75.53$, $^{37}_{17}Cl = 24.47$
Bromine	$^{79}_{35}Br = 50.54$, $^{81}_{35}Br = 49.49$
Iodine	$^{127}_{53}I = 100$

We know at present above 280 different isotopes that occur in nature. They include 40 radioactive isotopes as well. Besides these about 300 unstable radioactive isotopes have been produced through artificial disintegration. The distribution of isotopes among the elements is varied and complex. For example, the elements like arsenic, fluorine, iodine and gold etc have only a single isotope. They are called monoisotopic substances.

In general, the elements of odd atomic number almost never possess more than two stable isotopes. The elements of **even atomic number** usually have much larger number of isotopes. ^{16}O, ^{24}Mg, ^{28}Si, ^{40}Ca and ^{56}Fe form nearly 50% of earth's crust. Out of 280 isotopes that occur in nature, 154 are of even mass number and even atomic number. Isotopes are separated from each other based upon their properties.

MASS SPECTROMETRY

The technique in which atoms or molecules are converted into ions and are separated on the basis of mass to charge (m/e) ratio.

ASTON'S SPECTROMETER

This spectrometer was discovered by Aston in 1927. This spectrometer is used to identity the isotopes of an element on the basis of their atomic masses.

DEMPSTER'S SPECTROMETER

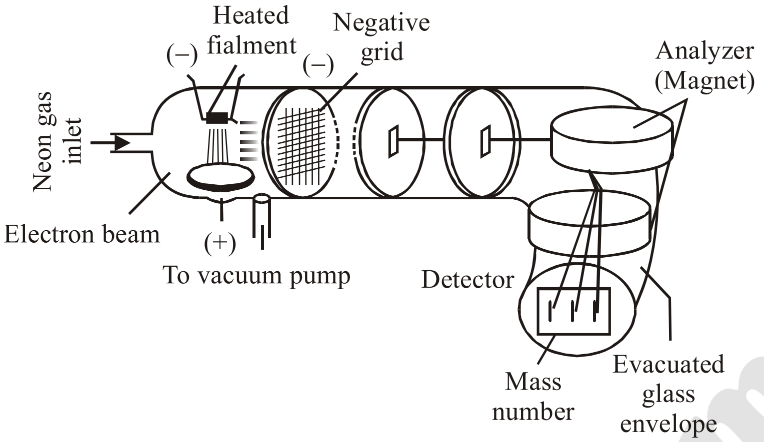
This spectrometer have been designed for the identification of elements which are found in solid state.

DETERMINATION OF RELATIVE ATOMIC MASS OF ISOTOPES BY DEMPSTER MASS SPECTROMETER

Mass spectrometry is used to determine the

- Number of isotopes of an element.
- Relative isotopic masses and relative abundance of isotopes.
- Relative molecular masses and structures of organic compounds.

Mass spectrometer consists of evaporator, ionizing chamber, negatively charged grid, accelerator, variable magnetic field, detector or electrometer, amplifier and recorder.



1. Evaporation and Ionization

The substance whose analysis for the separation of isotopes is required is converted into the vapours state. The **pressure** of these vapours is kept very low that is **10^{-6} to 10^{-7} torr**. These vapours are allowed to enter the ionization chamber where fast moving electrons are thrown upon them. The molecules present in the form of vapours are ionized. These particles may consist of single atoms, bearing the positive charge, but the masses are different depending upon the nature of the isotope of the element. For example neon form $^{20}Ne^+$, $^{21}Ne^+$, $^{22}Ne^+$ ions.

$$\underset{\text{atom}}{x} + \underset{\text{high energy electron}}{\bar{e}} \longrightarrow \underset{\text{positive ion}}{x^+} + \underset{\text{electron knocked out of X}}{\bar{e}} + \underset{\text{High energy electron retreating}}{\bar{e}}$$

$$x + \bar{e} \longrightarrow x^{2+} + \bar{e} + \bar{e} + \bar{e}$$

2 electrons knocked out of X

2. Acceleration and Detection

The positive ion of each isotope has its own mass to charge ratio. When potential difference (E) of 500 – 2000 volts is applied between perforated accelerating plates, these positive ions are strongly attracted towards the negative plate. In this way ions are accelerated. These ions are allowed to pass through the strong magnetic field (H) or analyzer to make the ions to move in circular path. The magnetic field **separates** the ions on the basis of their **m/e ratio**. The ions of definite m/e value move in the form of groups one after another and fall on the detector or electrometer. The mathematical relation for m/e is

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

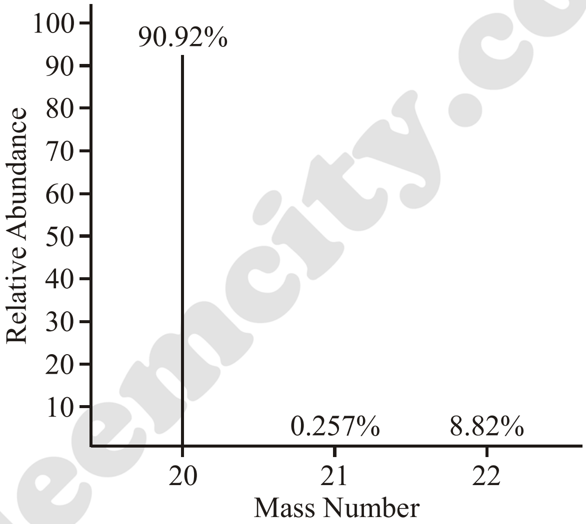
Where H is strength of magnetic field, E is strength of electrical field and r is radius of circular path. If E is increased by keeping H constant, then radius will increase and positive ions of particular m/e will fall at different place as compared to the first place. This can also be done by changing the magnetic field. Each ion set up a minute quantity of electrical current. The strength of current gives the relative abundance of that isotope.

Electrometer is also called ion collector and develops the electrical current. The strength of current thus measures the relative abundance of a particular isotope.

3. Comparison with C – 12:

The same experiment is preformed with C – 12 isotope and current strength is compared. This comparison allows us to measure the exact mass number of each isotope.

However, the current strength of the detector is amplified and recorded on a graph. The recorder graph shows the relative abundance of isotopes plotted against the mass number.



(Computer plotted graph for the isotopes of neon)

Other Methods:

(1) Gaseous diffusion
(2) Thermal diffusion
(3) Distillation
(4) Ultracentrifuge
(5) Electromagnetic separation
(6) Laser separation

Fractional atomic masses:

Atomic mass of an element depends upon the number of isotopes of an element and their natural abundance.

We know that naturally occurring elements have two or more isotopes, so the atomic weight (relative atomic mass) of an element is defined as weighted average of the masses of these isotopes.

$$\text{Average atomic mass} = \frac{\text{Sum of products of masses and natural abundance}}{100}$$

For example, chlorine has two isotopes ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$ having natural abundance 75.53 and 24.47 respectively. The average atomic mass of Cl is

$$\text{Average atomic mass} = \frac{(35 \times 75.53) + (37 \times 24.47)}{100} = 35.5$$

Example (1):

A sample of neon is found to consist of ${}^{20}_{10}Ne$, ${}^{21}_{10}Ne$ and ${}^{22}_{10}Ne$ in the percentage 90.92%, 0.26%, 8.82% respectively. Calculate the fractional atomic mass of Neon.

Solution:

The overall atomic mass of neon, which is an ordinary isotopic mixture, is the average of the determined atomic masses of individual isotopes. Hence

$$\text{Average atomic mass} = \frac{(20 \times 90.92) + (21 \times 0.26) + (22 \times 8.82)}{100} = 20.18$$

Hence the atomic mass of neon is 20.18 a.m.u.

It is important to realize that no individual neon atom in the sample has a mass of 20.18 a.m.u. For most laboratory purposes, however, we consider the sample to consist of atoms with this average mass.

EMPIRICAL FORMULA

"The simplest whole number ratio of atoms of different elements in a compound is called empirical formula."

For example, empirical formula of $C_6H_{12}O_6$ and CH_3COOH is CH_2O, empirical formula of H_2O_2 is HO. Empirical formula of oxalic acid = CHO_2.

For C_6H_6 and C_2H_2, empirical formula is CH empirical formula of oxalic and is CHO_2.

Ionic compounds have only empirical formulas but no molecular formula. For Ex; NaCl, KCl.

The empirical and molecular formula of CH_4, NH_3, H_2O, $C_{12}H_{22}O_{11}$ are same because they cannot be simplified.

MOLECULAR FORMULA

"Actual number of atoms of different elements present in a molecule is called molecular formula."

For example benzene (C_6H_6) ethane (C_2H_6) and glucose ($C_6H_{12}O_6$) have molecular formulas. In all these compounds the molecular formulas are simple multiples of empirical formulas, hence

Molecular formula = n x empirical formula:

Where 'n' is a simple integer. Those compounds whose empirical and molecular formulas are same are numerous. For example, NaCl, H_2O, CO_2, NH_3, SO_2, CH_4, $C_{12}H_{22}O_{11}$ have same empirical and molecular formulas.

Their simple multiple 'n' is unity, 'n' is the ratio of molar mass and empirical formula mass of a substance.

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} \quad (x = 2, 3, 4, \ldots\ldots\ldots)$$

DIFFERENCE BETWEEN MOLECULAR FORMULA AND EMPIRICAL FORMULA STEPS INVOLVED TO DETERMINE THE EMPIRICAL AND MOLECULAR FORMULAS OF A COMPOUND

Followings steps are involved to determine the empirical and molecular formulas of the compounds.

(1) Qualitative analysis:

Qualitative analysis means which elements are present in the given compound.

(2) Quantitative analysis:

The analysis in which mass of an element present in a compound is determined and % of each element is calculated.

(3) Determination of empirical formula:

Empirical formulas can be calculated from the given percentage composition of the compounds by the following procedure.

(i) Divide the mass of each element (% of an element) by its atomic mass to get the number of moles.

(ii) Divide each number of moles by smallest number of moles to get the mole ratio of elements.

(iii) If ratio is simple whole number, then it gives empirical formula, otherwise multiply with a suitable digit to get the whole number ratio.

(4) Determination of value of n:

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

n is simple integer, n may be 1, 2, 3, 4, 5, 6 etc.

(5) Determination of molecular formula:

Molecular formula = n x Empirical formula.

Percentage of an Element in a Compound:

Percentage of an element in a compound is the number of gram of that element present in 100 grams of the compound.

$$\text{Percentage of an element} = \frac{\text{Mass of element}}{\text{Mass of compound}} \times 100$$

Example (2):

8.657 g of a compound were decomposed into its elements and gave 5.217 g of carbon, 0.962 g of hydrogen, 2.478 g of oxygen. Calculate the percentage composition of the compound under study.

Solution:

Applying the formula:

$$\text{Percentage of element} = \frac{\text{Mass of element}}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of carbon} = \frac{\text{Mass of carbon}}{\text{Mass of compound}} \times 100$$

$$= \frac{5.217\text{ g}}{8.657\text{ g}} \times 100 = 60.26\%$$

$$\text{Percentage of hydrogen} = \frac{\text{Mass of hydrogen}}{\text{Mass of compound}} \times 100$$

$$= \frac{0.962\text{ g}}{8.657\text{ g}} \times 100 = 11.11\%$$

$$\text{Percentage of oxygen} = \frac{\text{Mass of oxygen}}{\text{Mass of compound}} \times 100$$

$$= \frac{2.478\text{ g}}{8.657\text{ g}} \times 100 = 28.62\%$$

The above results tell us that in one hundred grams of the given compound, there are 60.26 grams of carbon, 11.11 grams of hydrogen and 28.62 grams of oxygen.

Percentage composition of a compound can also be determined theoretically if we know the formula mass of the compound. The following equation can be used for this purpose.

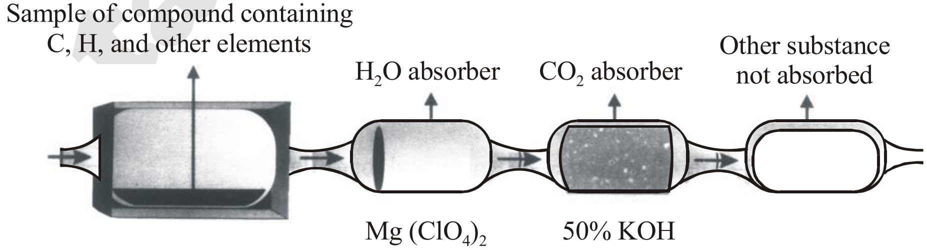
$$\text{Mass \% of an element} = \frac{\text{Mass of the element}}{\text{Formula mass of the compound}} \times 100$$

COMBUSTION ANALYSIS – PERCENTAGE COMPOSITION OF AN ORGANIC COMPOUND

Those compounds which simply consist of carbon hydrogen and oxygen can be analyzed very easily by combustion analysis. The product of combustion is H_2O and CO_2. These two products are collected separately and weighed.

Experiment:

A weighed quantity of sample is placed in the dish of the combustion tube. Excess oxygen is supplied to burn the compound.



The carbon and hydrogen present in the compound reacts with oxygen in the presence of cupric oxide and change to CO_2 and H_2O respectively. These gases are passed first through **water absorber** like **Mg $(ClO_4)_2$** magnesium per–chlorate and than through **CO_2 absorber**, which is **50% KOH** solution.

The increase in mass of these absorbers corresponds to the mass of water and carbon dioxide produced in the combustion of organic compound. From the mass of water and carbon dioxide produced in an organic compound, we can calculate the percentage of hydrogen and carbon respectively. Percentage of oxygen is determined indirectly.

Percentage of Hydrogen:

$$\% \text{ H} = \frac{2.016}{18.00} \times \frac{\text{Mass of } H_2O}{\text{Mass of organic compound}} \times 100$$

Percentage of Carbon:

$$\% \text{ C} = \frac{12.00}{44.00} \times \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times 100$$

Percentage of Oxygen:

If the sum of percentages of all elements in a compound is 100, it means oxygen in not present. If sum of percentages of elements is not 100, the difference of sum and 100 is percentage of oxygen.

% O = 100 – (sum of percentage of all other elements in a compound).

% 0 = 100 – (% C + % H).

Example (3):

Ascorbic acid (vitamin C) contains 40.92% carbon, 4.58% hydrogen and 54.5% of oxygen by mass. What is the empirical formula of the ascorbic acid? Its molecular mass is 176. Find the molecular formula.

Solution:

From the percentages of these elements, we believe that in 100 grams of ascorbic acid, there are 40.92 grams of carbon, 4.58 grams of hydrogen and 54.5 grams of oxygen.

Divide these masses of the elements (or percentages) by their atomic masses to get the number of gram atoms.

$$\text{No. of gram atoms of carbon} = \frac{40.92 \text{ g}}{12.0 \text{ g mole}^{-1}} = 3.41 \text{ gram atoms}$$

$$\text{No. of gram atoms of hydrogen} = \frac{4.58 \text{ g}}{1.008 \text{ g mole}^{-1}} = 4.54 \text{ gram atoms}$$

$$\text{No. of gram atoms of oxygen} = \frac{54.5 \text{ g}}{16 \text{ g mole}^{-1}} = 3.41 \text{ gram atoms}$$

Atomic ratio is obtained by dividing the gram atoms with 3.41, which is the smallest number.

$$\text{C : H : O} = \frac{3.41}{3.41} : \frac{4.54}{3.41} : \frac{4.54}{3.41}$$

$$\text{C : H : O} = 1 : 1.33 : 1$$

To convert them into whole numbers, multiply with three

C : H : O = 3 (1 : 1.33 : 1) = 3 : 4 : 3.

This whole number ratio gives us the subscripts for the empirical formula of the compound i.e. $C_3H_4O_3$.

Empirical formula = mass = 36 + 4 + 48 = 88

Molar mass = 176

$$n = \frac{176}{88} = 2$$

Molecular formula = n × (Empirical formula)

$= 2 \times C_3H_4O_3$

$= C_6H_8O_6$

Example (4):

A sample of liquid consisting of carbon, hydrogen and oxygen was subjected to combustion analysis. 0.5439 g of the compound gave 1.039 g of CO_2, 0.6369 g of H_2O. Calculate empirical formula of the compound.

Solution:

Mass of organic compound = 0.5439 g

Mass of carbon dioxide = 1.039 g

Mass of water = 0.6369 g

$$\text{Percentage of carbon} = \frac{1.039\text{ g}}{0.5439\text{ g}} \times \frac{12.00}{44.00} \times 100 = 52.10\%$$

$$\text{Percentage of hydrogen} = \frac{0.6369\text{ g}}{0.5439\text{ g}} \times \frac{2.016}{18} \times 100 = 13.11\%$$

Percentage of oxygen = 100 – (52.10 + 13.11) = 34.79%

Element	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	52.10	$\frac{52.10}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	C_2H_6O
H	13.11	$\frac{13.11}{1.008} = 13.01$	$\frac{13.01}{2.17} = 6$	
O	34.77	$\frac{34.79}{16.00} = 2.17$	$\frac{2.17}{2.17} = 1$	

Example (5):

The combustion analysis of an organic compound shows that it contains 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is the empirical formula of the compound? If the molecular mass of this compound is 110.15. Calculate the molecular formula of the compound.

Solution:

First of all divide the percentage of each element by its atomic mass to get the number of gram atoms or moles.

$$\text{No. of gram atoms of carbon} = \frac{65.44\text{ g of C}}{12\text{ g/mole}} = 5.45\text{ g atoms of C}$$

$$\text{No. of gram atoms of hydrogen} = \frac{5.50\text{ g of H}}{1.008\text{ g/mole}} = 5.45\text{ g atoms of H}$$

$$\text{No. of gram atoms of oxygen} = \frac{29.06\text{ g of O}}{16.00\text{ g/mole}} = 1.82\text{ g atoms of O}$$

Molar Ratio	C	:	H	:	O
	5.45	:	5.45	:	1.82

Divide the number of gram atoms by the smallest number i.e. 1.82.

C : H : O

$$\frac{5.45}{1.82} : \frac{5.45}{1.82} : \frac{1.82}{1.82}$$

3 : 3 : 1

Carbon, hydrogen and oxygen are present in the given organic compound in the ratio of 3 : 3 : 1. so the empirical formula is C_3H_3O.

In order to determine the molecular formula, first calculate the empirical formula mass.

Empirical formula mass = 12 x 3 + 1.008 x 3 + 16 x 1 = 55.05 g/mole

Molar mass of the compound = 110.15

$$n = \frac{\text{Molar mass of the compound}}{\text{Empirical formula mass}} = \frac{110.15}{55.05} = 2$$

Molecular formula = n (Empirical formula)

$= 2\,(C_3H_3O) = C_6H_6O_2$

Example (6):

An organic compound contains 26.4% carbon, 2.2% hydrogen and 71.4% oxygen.

Molar mass of the compound is 90. find its molecular formula?

Solution:

(i) Dividing by the respectively atomic masses.

$$\text{No. of gram – atoms of carbon} = \frac{26.4}{12} = 2.2$$

$$\text{No. of gram – atoms of hydrogen} = \frac{2.2}{1} = 2.2$$

$$\text{No. of gram – atoms of oxygen} = \frac{71.4}{16} = 4.4$$

Molar Ratio C : H : O

2.2 : 2.2 : 4.4

(ii) Dividing by the least number.

C : H : O

$$\frac{2.2}{2.2} : \frac{2.2}{2.2} : \frac{4.4}{2.2}$$

1 : 1 : 2

The empirical formula = $C_1H_1O_2$ = CHO_2

Empirical formula mass = 12 + 1 + 32 = 45

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{90}{45} = 2$$

Molecular formula = n x (empirical formula)

= 2 x CHO_2

= $C_2H_2O_4$ (oxalic acid)

CONCEPT OF MOLE

In chemistry we deals with the atoms, ions or molecules which are very small particles. It is not easy to weigh one atom or one molecule.

On the other hand due to extremely smaller size, they cannot be counted in dozen. So concept of mole is used. The "mole" is a Latin word meaning a "**huge mass**".

The mole is the unit of counting as well as the unit of measurement used in chemistry.

(1) MOLE

"The atomic mass, formula mass or molecular mass of a substance expressed in grams is called mole."

(i) Gram atom (mole):

"When a substance is in atomic state, its atomic mass expressed in grams is called gram atom."

No. of gram atoms or moles of an element.

For example:

1 gram atom of hydrogen = 1.008 g

1 gram atom of carbon = 12.00 g

and 1 gram atom of uranium = 238.0 g

It means that one gram atoms of different elements have different masses in them. One mole of carbon is 12 g, while 1 mole of magnesium is 24 g. It also shows that one atom of magnesium is twice as heavy as an atom of carbon.

(ii) Gram – molecule (mole):

"The molecular mass of a substance expressed in gram is called gram molecule or gram mole or simply the mole of a substance."

No. of gram molecules or

$$\text{Moles of molecular substance} = \frac{\text{Mass of the molecular subtance in grams}}{\text{Molar mass of the substance}}$$

For example:

1 gram molecule of water (mole) = 18.0 g

1 gram molecule of H_2SO_4 (mole) = 98.0 g

and 1 gram molecule of glucose = 180 g

It means that the one gram molecules of different molecular substances have different masses.

(iii) Gram formula (mole):

"The formula unit mass of an ionic compound expressed in grams is called gram formula of the substance." Since ionic compounds do not exist in molecular form therefore the sum of atomic masses of individual ions gives the formula mass. The gram formula is also referred to as gram mole or simply a mole.

$$\text{No. of gram formulas} = \frac{\text{Mass of the ionic substance in grams}}{\text{Formula mass of the ionic substance}}$$

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

(iv) Gram – ion (mole):

The ionic mass of an ionic specie expressed in grams is called one gram ion or one mole of ions.

$$\text{No. of gram ions} = \frac{\text{Mass of the ionic specie in grams}}{\text{Formula mass of the ionic specie}}$$

Moles of ionic specie

For example:

1 gram ions of OH^- = 17 g

1 gram ions of SO_3^{2-} = 80 g

1 gram ions of CO_3^{2-} = 60 g

So, the atomic mass, molecular mass, formula mass or ionic mass of the substance expressed in gram is called moles of those substances.

or $$\text{Mole} = \frac{\text{Mass of substance in grams}}{\text{Atomic mass/molecular mass/formula mass/ionic mass}}$$

Example (7):

Calculate the gram atoms (moles) in

(a) 0.1 g of sodium

(b) 0.1 kg of silicon

Solution:

(a) $$\text{No. of gram atoms} = \frac{\text{Mass of element in gram}}{\text{Atomic mass of element}}$$

Mass of sodium = 0.1 g

Atomic mass of sodium = 23 g/mole

$$\text{No. of gram atoms of sodium} = \frac{0.1 \text{ g}}{23 \text{ g mole}^{-1}}$$

$$= 0.0043 = 4.3 \times 10^{-3} \text{ mole}$$

(b) First of all convert the mass of silicon into grams.

Mass of silicon = 0.1 kg = 100 g

Atomic mass of silicon = 28 g mole^{-1}

$$\text{No. of gram atoms of silicon} = \frac{100\text{ g}}{28\text{ g mole}^{-1}} = 3.57\text{ moles.}$$

Example (8):

Calculate the mass of 10^{-3} moles of $MgSO_4$

Solution:

$MgSO_4$ is an ionic compound. We will consider its formula mass in place of molecular mass.

$$\text{No. of gram formula} = \frac{\text{Mass of ionic substance}}{\text{Formula mass of ionic substance}}$$

Formula mass $MgSO_4$ = 24 + 96 = 120 g/mole

No. of moles of $MgSO_4$ = 10^{-3} moles

$$\text{Applying the formula } 10^{-3} = \frac{\text{Mass of } MgSO_4}{120\text{ g mole}^{-1}}$$

$$\text{Mass of } MgSO_4 = 10^{-3}\text{ moles} \times 120\text{ g/mole}$$
$$= 120 \times 10^{-3} = 0.12\text{ g}$$

(2) (AVOGADRO'S NUMBER) N_A

The number of atoms, ions or molecules and formula units which are present in one gram atom of an element, one gram molecule of a compound or one gram ion and 1 gram-formula mass of a substance is also called Avogadro's number. It is denoted by N_A.

Its value is 6.022×10^{23}

To understand Avogadro's number let us consider the following quantities of substances.

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.

This number, 6.02×10^{23} is the number of atoms in one mole of the element. It is interesting to know that different masses of elements have the same number of atoms. An atom of sodium is 23 times heavier than an atom of hydrogen. In order to have equal number of atoms sodium should be taken 23 times greater in mass than hydrogen. Magnesium atom is twice heavier than carbon; i.e. 10 g of Mg and 5 g of C contain the same number of atoms.

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.

Hence, one mole of different compounds has different masses but has the same number of molecules.

In case of ions

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^-

58.5 g of NaCl = 6.02×10^{23} formula units

From the above discussion, we reach the conclusion that the number 6.02×10^{23} is closely related with one mole of a substance. This number is called as Avogadro's number and it is denoted by N_A.

(i) Number of atoms of an element $= \dfrac{\text{Mass of the element} \times N_A}{\text{Atomic mass}}$

(ii) No. of molecules $= \dfrac{\text{Mass}}{\text{Molecular mass}} \times N_A$

(iii) No. of ions $= \dfrac{\text{Mas}}{\text{Ionic mass}} \times N_A$

(iv) No. of formula units $= \dfrac{\text{Mass}}{\text{Formula mass}} \times N_A$

When we have compounds of known mass we can calculate the number of atoms from their formulas.

In 18 g of water there are present 6.02×10^{23} molecule of H_2O, $2 \times 6.02 \times 10^{23}$ atoms of hydrogen and 6.02×10^{23} atoms of oxygen. Similarly, in 98 g 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 atom.

Some substances ionize in suitable solvents to yield cations and anions. The number of such ions, their masses, number of positive and negative charges can be easily calculated from the known amount of the substance dissolved. Let us dissolve 9.8 g of H_2SO_4, in sufficient quantity of H_2O to get it completely ionized. It has 0.1 mole of H_2SO_4. It will yield 0.2 mole or $2 \times 6.02 \times 10^{23}$ H^+ and 0.1 mole or $1 \times 6.02 \times 10^{23}$ SO_4^{2-} ions.

$$\begin{array}{lclcl}
H_2SO_4 & \longrightarrow & 2H^+ & + & SO_4^{2-} \\
0.1\ M & & 0.2\ M & & 0.1\ M \\
6.02 \times 10^{23} & & 12.04 \times 10^{23} & & 6.02 \times 10^{23}
\end{array}$$

Total positive charges will be $2 \times 6.02 \times 10^{23}$ and the total negative charges will be $2 \times 6.02 \times 10^{23}$ (because each SO_4^{2-} has two negative charges). The total mass of H^+ is (0.2×1.008) g and that of SO_4^{2-} is (0.1×98) g.

Example (9):

How many molecules of water are there in 10.0 g of ice? Also calculate the number of atoms of hydrogen and oxygen separately, the total number of atoms and the covalent bonds present in the sample.

Solution:

Mass of ice (water) = 10.0 g

Molar mass of water = 18 g/mole

$$\text{No. of molecules of water} = \frac{\text{Mass of water in g} \times N_A}{\text{Molar mass of water in g mole}^{-1}}$$

$$= \frac{10\ \text{g}}{18\ \text{g mole}^{-1}} \times 6.02 \times 10^{23}$$

No. of molecules of water = 3.34×10^{23}

One molecule of water contains hydrogen atoms = 2

3.34×10^{23} molecules of water contain H atoms = $2 \times 3.34 \times 10^{23}$

= 6.68×10^{23}

One molecule of water contains oxygen atom = 1.

3.34×10^{23} molecules of water contains O atoms = 3.34×10^{23}

One molecules of water contains number of covalent bonds = 2.

3.34×10^{23} molecules of water contain number of covalent bonds = $2 \times 3.34 \times 10^{23}$

= 6.68×10^{23}

Total number of atoms of hydrogen and oxygen = $3.34 \times 10^{23} \times 3$

= 1.003×10^{24}

Example (10):

10.0 g of H_3PO_4 have been dissolved in excess of water to dissociate it complete into ions. Calculate,

(a) No. of molecules in 10.0 g of H_3PO_4.

(b) No. of positive and negative ions in case of complete dissociation in water.

(c) Masses of individual ions.

(d) No. of positive and negative charges dispersed in the solution.

Solution:

(a) Mass of H_3PO_4 = 10 g

Molar mass of H_3PO_4 = 3 + 31 + 64 = 98 g/mole

$$\text{No. of molecules of } H_3PO_4 = \frac{\text{Mass of } H_3PO_4}{\text{Molar mass of } H_3PO_4} \times 6.02 \times 10^{23}$$

$$= \frac{10\ \text{g}}{98\ \text{g mole}^{-1}} \times 6.02 \times 10^{23}$$

$$= 6.14 \times 10^{22}$$

(b) H_3PO_4 dissolves in water and ionized as follows.

$$H_3PO_4 \longrightarrow 3H^+ + PO_4^{-3}$$

According to the balanced chemical equation

$H_3PO_4 : H^+$

$1 : 3$

$6.14 \times 10^{22} : 3 \times 6.14 \times 10^{22}$

$: 1.842 \times 10^{23}$

Hence, the number of H^+ will be 1.842×10^{23}

$H_3PO_4 : PO_4^{3-}$

$1 : 1$

$6.14 \times 10^{22} : 6.14 \times 10^{22}$

Hence, the number of PO_4^{3-} will be 6.14×10^{22}

(c) In order to calculate the mass of the ions, use the formulas.

$$\text{Total mass of } H^+ = \frac{1.842 \times 10^{23} \times 1.008}{6.02 \times 10^{23}}$$

$$\text{Total mass of } PO_4^{3-} = \frac{6.14 \times 10^{22} \times 95}{6.02 \times 10^{23}}$$

$$= 9.689 \text{ g}$$

(d) One molecule of H_3PO_4 gives three positive charges in the solution.

6.14×10^{22} molecules of H_3PO_4 will give $= 3 \times 6.14 \times 10^{22}$

$= 1.842 \times 10^{23}$ positive charges

Number of positive and negative charges are always equal. So the number of negative charges dispersed in the solution $= 1.842 \times 10^{23}$.

Example (11):

A puff of smoke weighs 0.1 grams. How many atoms are present (smoke is assumed to be pure carbon).

$$\text{No. of atoms} = \frac{\text{Mass}}{\text{At. mass}} \times N_A$$

$$= \frac{0.1}{12} \times 6.02 \times 10^{23}$$

$$= 0.5 \times 10^{22} \text{ atoms}$$

Example (12):

A ring is studded with 6 grams of diamond. How many atoms are present?

$$\text{No. of atoms} = \frac{\text{Mass}}{\text{At. mass}} \times N_A$$

$$= \frac{6}{12} \times 6.02 \times 10^{23}$$

$$= 3.01 \times 10^{23}$$

Molar Volume (V_m):

"One mole of an ideal gas at standard temperature and pressure occupies 22.414 dm^3, which is called molar volume."

With the help of this information, we can convert the mass of a gas at STP into its volume and vice versa.

Hence we can say that

2.016 g of H_2 = 1 mole of H_2 = 6.02×10^{23} molecules of H_2 = 22.414 dm^3 of H_2 at STP.

16 g of CH_4 = 1 mole of CH_4 = 6.02×10^{23} molecules of CH_4 = 22.414 dm^3 of CH_4 at STP.

It is very interesting to know from the above data that 22.414 dm^3 of each gas has a different mass but the same number of molecules. The reason is that the masses and the sizes of the molecules don't affect the volumes. Normally it is known that in the gaseous state the distance between molecules is 300 times greater than their diameters.

Example (13):

A well known ideal gas is enclosed in a container having volume 500 cm^3 at STP. Its mass comes out to be 0.72 g. What is the molar mass of this gas.

Solution:

We can calculate the number of moles of the ideal gas at STP from the given volume.

22.414 dm^3 or 22414 cm^3 of the ideal gas at STP = 1 mole

$$1\ cm^3 \text{ of the ideal gas at STP} = \frac{1}{22414} \text{ mole}$$

$$500\ cm^3 \text{ of the ideal gas at STP} = \frac{1}{22414} \times 500 = 0.0223 \text{ mole}$$

We know that

$$\text{No. of moles of the gas} = \frac{\text{Mass of the gas}}{\text{Molar mass of the gas}}$$

$$\text{Molar mass of the gas} = \frac{\text{Mass of the gas}}{\text{No. of moles of the gas}}$$

$$\text{Molar mass of the gas} = \frac{0.72\ g}{0.0223\ \text{mole}} = 32\ \text{mole}^{-1}$$

Law of Conservation of Mass:

“This law states “Mass can neither be created nor destroyed in a chemical reaction.”

But as matter is atomic in nature, we can say: “Atoms can neither be created nor destroyed in a chemical reaction.”

Law of Definite Proportions:

It is stated as “The different samples of same compound will contain the number of atoms of different elements in the same fixed ratio by mass.

For example, water collected from any source contain two atoms of hydrogen and one atom of oxygen. We can say that ratio of H_2 and O_2 is fixed by mass i.e. 1 : 8. (11.19 : 88.81)

CALCULATIONS BASED ON CHEMICAL EQUATION (STIOCHIOMETRY)

“The branch of chemistry which deals with the quantitative relationship between reactants and products in a balanced chemical equation is called Stiochiometry.”

Chemical equations have certain limitations as well. They do not tell about the conditions, and the rate of reaction. Chemical equation can even be written to describe a chemical change that do not occur. So, when stiochiometric calculations are performed, we have to assume the following conditions.

1. All reactants are completely converted into the products.
2. No side reactions occurs.
3. While doing calculations, law of conservation of mass and law of definite proportions are obeyed.

Stiochiometric Amounts:

“The amount of reactants and products in a balanced chemical equations are called Stiochiometric amounts”, e.g.

$$2H_2 + O_2 \xrightarrow{\qquad} 2H_2O$$

In above equation 4 g of H_2, 32 g of O_2 and 36 g of H_2O are called Stiochiometric amounts.

The following type of relationship can be studied with the help of a balanced chemical equation.

(1) Mass – mass relationship:

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

(2) Mass – mole relationship or mole – mass relationship:

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

(3) Mass – volume relationship:

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

Example (14):

Calculate the number of grams of K_2SO_4 and water produced when 14 g of KOH are reacted with excess of H_2SO_4. Also calculate the number of molecules of water produced.

Solution:

For doing such calculations, first of all convert the given mass of KOH into moles and then compare these moles with those of K_2SO_4 with the help of the balanced chemical equation.

Mass of KOH = 14.0 g

Molar mass of KOH = 39 + 16 + 1 = 56 g/mole

No. of moles of KOH = $\frac{14.0\text{ g}}{56\text{ g mole}^{-1}}$ = 0.25 mole

Equation:

$$2KOH\,(aq) + H_2SO_4\,(aq) \longrightarrow K_2SO_4\,(aq) + 2H_2O\,(l)$$

To get the number of moles of K_2SO_4 compare the moles of KOH with the those of K_2SO_4.

2 moles of KOH produces K_2SO_4 = 1 mole

0.25 moles of KOH produces K_2SO_4 = $\frac{1}{2}$ x 0.25 mole

= 0.125 mole K_2SO_4

Molar mass of K_2SO_4 = 2 x 39 + 96 = 174 g/mole

Mass of K_2SO_4 produced = No. of moles x molar mass

= 0.125 moles x 174 g mole^{-1}

= 21.75 g

To get the number of moles of H_2O, compare the moles of KOH with those of water.

KOH : H_2O

2 : 2

1 : 1

0.25 : 0.25

So, the number of moles of water produced = 0.25.

Mass of water produced = 0.25 moles x 18 g mole^{-1}

= 4.5 g

No. of molecules of water = No. of moles x 6.02×10^{23}

= 0.25 moles x 6.02×10^{23} molecules/mole

= 1.505×10^{23} molecules

Example (15):

Mg metal reacts with HCl to give hydrogen gas. What is the minimum volume of HCl solution (27% by weight) required to produce 12.1 g of H_2. The density of HCl solution is 1.14 g/cm^3.

$$Mg\,(s) + 2\,HCl\,(aq) \xrightarrow{\qquad} MgCl_2\,(aq) + H_2\,(g)$$

Solution:

Mass of H_2 produced = 12.1 g

Molar mass of H_2 = 2.016 g mole^{-1}

$$\text{Moles of } H_2 = \frac{\text{Mass of } H_2}{\text{Molar mass of } H_2}$$

$$= \frac{12.1\text{ g}}{2.016\text{ g mole}^{-1}} = 6.0\text{ moles}$$

To calculate the number of moles of HCl, compare the moles of H_2 with those of HCl.

H_2 : HCl

1 : 2

12 moles of HCl are being consumed to produce to moles of H_2.

$$\text{Mass of HCl} = \text{Moles of HCl} \times \text{Molar mass of HCl}$$

$$= 12\text{ moles} \times 36.5\text{ g mole}^{-1}$$

$$= 438\text{ g}$$

We know that HCl solution is 27% by weight.

27 g of pure HCl are present in impure HCl solution = 100 g.

$$\text{1 g is present in HCl solution} = \frac{100}{27}$$

$$\text{438 g are present in how much of HCl solution} = \frac{100}{27} \times 438 = 1622.2\text{ g}$$

Density of HCl of solution = 1.14 g/cm^3

$$\text{Volume of HCl} = \frac{\text{Mass of HCl solution}}{\text{Density of HCl}}$$

$$= \frac{1622.2\text{ g}}{1.14\text{ cm}^3} = 1423\text{ cm}^3$$

LIMITING REACTANT

Often reactants are added to a reaction vessel in amounts different from the molar proportions given by the balanced chemical equation. In that case only one of the reactants is completely consumed in the reaction. This reactants which consumes earlier, control the amount of product.

"The reactant which is consumed earlier during a chemical reaction and gives the least moles of the product is called limiting reactant."

Once this reactant is consumed, the reaction stops and no further product is formed. The reactant which is in excess cannot control the amount of product. The moles of products are always determined by the moles of limiting reactant.

The concept of limiting reactant is analogous to the relationship between the number of "kababs" and the "slices" to prepare "sandwiches". If we have 30 "kababs" and five breads "having 58 slices", then we can only prepare 29 "sandwiches". One "kababs" will be extra (excess reactant) and "slices" will be the limiting reactant. It is a practical problem that we can not purchase exactly sixty "slices" for 30 "kababs" to prepare 30 "sandwiches".

To understand the concept of limiting reactant consider the reaction between hydrogen and oxygen to form water.

Experiment 1:

In first experiment 4 g of H_2 was reacted with 32 g of O_2 and 36 g of H_2O was formed.

$$2H_2 \quad + \quad O_2 \quad \xrightarrow{\qquad\qquad} \quad 2H_2O$$
$$4\text{ g } H_2 \qquad 32\text{ g } O_2 \qquad\qquad\qquad 36\text{ g } H_2O$$

In this experiment all quantities of H_2 and O_2 are consumed because they have Stiochiometric ratio in them.

Experiment 2:

In second experiment 6 g of H_2 was reacted with 32 g of O_2 and 36 g of H_2O was produced.

$$2H_2 \quad + \quad O_2 \quad \xrightarrow{\qquad\qquad} \quad 2H_2O$$
$$6\text{ g } H_2 \qquad 32\text{ g } O_2 \qquad\qquad\qquad 36\text{ g } H_2O$$

In this experiment, formation of H_2O is limited by O_2 reactant. 2g H_2 remains un–reactive therefore in excess or non–limiting reactant.

Experiment 3:

In third experiment 4 g of H_2 was reacted with 40 g of O_2 and 36 g of H_2O was produced.

$$2H_2 \quad + \quad O_2 \quad \xrightarrow{\qquad\qquad} \quad 2H_2O$$
$$4\text{ g } H_2 \qquad 40\text{ g } O_2 \qquad\qquad\qquad 36\text{ g } H_2O$$

In this experiment, formation of H_2O is limited by H_2 and O_2 is in excess 8 g of O_2 remains un–reactive so H_2 is 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.

Example (16):

NH_3 gas can be prepared by heating together two solids NH_4Cl and $Ca(OH)_2$. If a mixture containing 100 g of each solid is heated then.

(a) Calculate the number of grams of NH_3 produced.

(b) Calculate the excess amount of reagent left un–reacted.

$$2NH_4Cl\,(s) + Ca(OH)_2\,(s) \xrightarrow{\qquad} CaCl_2\,(s) + 2NH_3\,(g) + 2H_2O\,(l)$$

Solution:

(a) (i) Convert the given amounts of both reactants into their number of moles.

Mass of NH_4Cl = 100 g

Molar mass of NH_4Cl = 53.5 g/mole

$$\text{Moles of } NH_4Cl = \frac{100\text{ g}}{53.5\text{ g mole}^{-1}} = 1.87\text{ moles}$$

Mass of $Ca(OH)_2$ = 100 g

Molar mass of $Ca(OH)_2$ = 74 g mole^{-1}

$$\text{Moles of } Ca(OH)_2 = \frac{100\text{ g}}{74\text{ g mole}^{-1}} = 1.35\text{ moles}$$

(ii) Compare the number of moles of NH_4Cl with those of NH_3.

NH_4Cl : NH_3
2 : 2
1 : 1
1.87 : 1.87

Similarly compare the number of moles of $Ca(OH)_2$ with those of NH_3.

$Ca(OH)_2$: NH_3
1 : 2
1.35 : 2.70

Since the number of moles of NH_3 produced by 100 g or 1.87 moles of NH_4Cl are less, so NH_4Cl is the limiting reactant. The other reactant, $Ca(OH)_2$ is present in excess. Hence

Mass of NH_3 produced = 1.87 moles x 17 g/mole = 31.179 g

(b) Amount of the reagent present in excess.

Let us calculate the number of moles of $Ca(OH)_2$ which will completely react with 1.87 moles of NH_4Cl with the help of equation.

NH_4Cl : $Ca(OH)_2$
2 : 1
1 : $\frac{1}{2}$
1.87 : 0.935

Hence the number of moles of $Ca(OH)_2$ which completely react with 1.87 moles of NH_4Cl is 0.935 moles.

No. of moles of $Ca(OH)_2$ taken = 1.35 mole.

No. of moles of $Ca(OH)_2$ used = 0.935 mole.

No. of moles of $Ca(OH)_2$ left behind = 1.35 – 0.935 = 0.415 mole.

Mass of non–reactive $Ca(OH)_2$ = 0.415 x 74 = 30.71 g.

It means we should have mixed 100 g of NH_4Cl with 69.3 g of $Ca(OH)_2$ to get 1.87 mole NH_3.

YIELD

"The amount of product obtained as a result of chemical reaction is called yield."

Theoretical Yield:

"The amount of product calculated from balanced chemical equations, is called theoretical yield", e.g.

$$\begin{array}{lclcl} CaCO_3 & \longrightarrow & CaO & + & CO_2 \\ 1 \text{ mole} & & 1 \text{ mole} & & 1 \text{ mole} \\ 100 \text{ g} & & 56 \text{ g} & & 44 \text{ g} \\ 50 \text{ g} & \longrightarrow & 28 \text{ g} & & 22 \text{ g} \end{array}$$

Actual Yield:

"The amount of product that is actually obtained experimentally in a chemical reaction is called actual yield."

Many chemical reactions do not produce the amount of products expected theoretically. The reasons are:

(a) Side reaction produces by – products.

(b) Reactions are reversible.

(c) Mechanical loss of product during separation by filtrations, separation by distillation, separation by a separating funnel, washing, drying and crystallization is not properly carried out decreases the yield.

PERCENT YIELD (EFFICIENCY OF REACTION)

"Actual yield divided by the theoretical yield and answer is multiplied by 100 is called percent yield."

$$\text{Efficiency of Reaction} = \%\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Example (17):

When lime stone ($CaCO_3$) is roasted, quicklime (CaO) is produced according to the following equation. The actual yield of CaO is 2.5 kg, when 4.5 kg of lime stone is roasted. What is the percentage yield of this reaction.

$$CaCO_3\,(g) \xrightarrow{\quad\quad} CaO\,(g) + CO_2\,(g)$$

Solution:

Mass of lime stone roasted = 4.5 kg = 4500 g

Mass of quicklime produced (actual yield) = 2.5 kg = 2500 g

Molar mass of $CaCO_3$ = 100 g/mole

Molar mass of CaO = 56 g/mole

According to the balanced chemical equation.

100 g of $CaCO_3$ should give CaO = 56 g

1 g of $CaCO_3$ should give CaO = $\frac{56}{100}$

4500 g of $CaCO_3$ should give CaO = $\frac{56}{100} \times 4500$ = 2520 g

Theoretical yield of CaO = 2520 g

Actual yield of CaO = 2500 g

$$\%\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \frac{2500\text{ g}}{2520} \times 100 = 99.2\%$$

Significance:

% yield indicates the efficiency of the reaction.

Greater the % yield, greater the efficiency.

Actual Yield	**Theoretical Yield**
(1) Amount of the product actually obtained.	(1) Amount of the product obtained from the balanced chemical equation.
(2) It is always less than the theoretical yield.	(2) It is greater than the actual yield.
(3) It is not calculated from the limiting reactant.	(3) It is calculated from the limiting reactant.

EXERCISE

Q.1 Select the most suitable answer from the given ones in each questions.

(i) Isotopes differ in:
- (a) Properties which depend upon mass
- (b) Arrangement of electrons in orbitals
- (c) Chemical properties
- (d) The extent to which they may be affected in electromagnetic field

(ii) Which of the following statement is true?
- (a) Isotopes with even atomic masses are comparatively abundant
- (b) Isotopes with odd atomic masses are comparatively abundant
- (c) Isotopes with even atomic masses and even atomic numbers are comparatively abundant
- (d) Isotopes with even atomic masses and odd atomic numbers are comparatively abundant

(iii) Many elements have fractional atomic masses. This is because:
- (a) The mass of the atom is itself fractional
- (b) Atomic masses are average masses of isobars
- (c) Atomic masses are average masses of isotopes
- (d) Atomic masses are average masses of isotopes proportional to their relative abundance

(iv) The mass of one mole of electron is:
- (a) 1.008 mg (b) 0.184 mg
- (c) 1.673 mg (d) 0.55 mg

(v) 27 g of Al will react completely with how much mass of O_2 to produce Al_2O_3?
- (a) 8 g of oxygen (b) 16 g of oxygen
- (c) 32 g of oxygen (d) 24 g of oxygen

(vi) The number of moles of CO_2, which contain 8.0 g of oxygen:
- (a) 0.25 (b) 0.50
- (c) 1.0 (d) 1.50

(vii) The largest number of molecules are present in:
- (a) 3.6 g of H_2O (b) 4.8 g of C_2H_5OH
- (c) 2.8 g of CO (d) 5.4 g of N_2O_5

(viii) One mole of SO_2 contains:

(a) 6.023×10^{23} atoms of oxygen (b) 18.1×10^{23} molecules of SO_2

(c) 6.023×10^{23} atoms of sulphur (d) 4 g atom of SO_2

(ix) The volume occupied by 1.4 g of N_2 at S.T.P. is:

(a) 2.24 dm^3 (b) 22.4 dm^3

(c) 1.12 dm^3 (d) 112 dm^3

(x) A limiting reactant is the one which:

(a) is taken in lesser quantity in grams as compared to other reactants

(b) is taken in lesser quantity in volume as compared to the other

(c) carries the maximum amount of the product which is required

(d) gives the minimum amount of the product under consideration

ANSWERS

Answers	Reasons
(i) (a)	Isotopes have same chemical properties but have different physical properties, these depend upon their different masses.
(ii) (c)	
(iii) (d)	The atomic mass depends upon number of isotopes and their relative percentage abundance. Its formula is: Average atomic mass $= \sum \frac{\text{Mass} \times \text{Natural abundance}}{100}$ That's why many elements have fractional atomic masses usually.
(iv) (d)	Mass of one electron $= 9.1 \times 10^{-31}$ kg $= 9.1 \times 10^{-31} \times 10^{6}$ $= 9.1 \times 10^{-25}$ mg Mass of one mole of electrons $= 6.02 \times 10^{23} \times 9.1 \times 10^{-25}$ $= 0.55$ mg
(v) (d)	$4Al + 3O_2 \longrightarrow 2Al_2O_3$ 1 mole of Al = 27 g ⇒ 4 moles of Al react with = 3 moles of O_2 1 moles of Al react with $= \frac{3}{4} = 0.75$ moles Mass of 0.75 moles of 'O_2' $= 0.75 \times 32 = 24$ g

(vi)	(a)	Molecular mass of CO_2 = 44 g 32g of ‘O’ = 1 mole of CO_2 1 g ‘O’ = $\frac{1}{32}$ 8 g ‘O’ = $\frac{1}{32} \times 8$ = 0.25 moles of CO_2
(vii)	(a)	Moles = $\frac{\text{Mass in grams}}{\text{Molar mass}}$ Moles of H_2O = $\frac{3.6}{18}$ = 0.2 moles Moles of C_2H_5OH = $\frac{4.8}{46}$ = 0.1 mole Moles of CO = $\frac{2.8}{28}$ = 0.1 mole Moles of N_2O_5 = $\frac{5.4}{108}$ = 0.05 mole No. of molecules = No. of moles × N_A Larger the no. of moles, larger will be the no. of molecules.
(viii)	(c)	One mole of SO_2 contain ‘O’ = 2 moles Atoms of ‘O’ = $2 \times 6.02 \times 10^{23}$ atoms One mole of SO_2 contain molecules = 6.02×10^{23} One mole of SO_2 contain = 6.02×10^{23} atoms of S
(ix)	(c)	1 mole of N_2 = 28 g molar mass 28 g N_2 occupy volume at S.T.P = 22.414 dm^3 1 g N_2 occupy volume at S.T.P = $\frac{22.414}{28}$ 1.4 g N_2 occupy volume at S.T.P = $\frac{22.414}{28} \times 1.4$ = 1.12 dm^3
(x)	(d)	A reactant which is consumed earlier and limitise the amount of products is called limiting reactant.

Q.2 Fill in the blanks.

(i) The unit of relative atomic mass is ————.

(ii) The exact masses of isotopes can be determined by ———— spectrography.

(iii) The phenomenon of isotopy was first discovered by ————.

(iv) Empirical formula can be determined by combustion analysis for those compounds which have ———— and ———— in them.

(v) A limiting reagent is that which controls the quantities of ————.

(vi) A mole of glucose has ———— atoms of carbon, ———— of oxygen and ———— of hydrogen.

(vii) 4 g of CH_4 at 0°C and 1 atm. pressure has ———— molecules of CH_4.

(viii) Stoichiometric calculations can be performed only when ———— is obeyed.

ANSWERS

Answers		**Explanation**
(i)	a.m.u (atomic mass unit	
(ii)	Mass	
(iii)	Soddy	
(iv)	Carbon, hydrogen	
(v)	Products	
(vi)	$6N_A$, $6N_A$, $12N_A$	6 N_A atoms or 6 gram atoms or 3.612×10^{24} atoms 6 N_A atoms or 6 gram atoms or 3.612×10^{24} atoms 12 N_A atoms or 12 gram atoms 7.224×10^{24} atoms Molecular formula of glucose = $C_6H_{12}O_6$ Which shows that 1 mole of glucose has 6 moles of carbon, 6 moles of oxygen and 12 moles of hydrogen. No. of atoms = No of moles × N_A No. of C-atoms = $6 \times N_A$ = 3.612×10^{24} No. of O-atoms = $6 \times N_A$ = 3.612×10^{24} No. of H-atoms = $12 \times N_A$ = 7.22×10^{24} Note: 6 N_A and 12 N_A can be written as 6 gram atoms and 12 grams atoms respectively.

(vii) $N_A / 4$	Molecular mass of CH_4 = 16 g = 1 mole 1 mole = $N_A = 6.02 \times 10^{23}$ 16 g of CH_4 contain molecules = N_A 1 g of CH_4 contain molecules = $\frac{N_A}{16}$ 4 g of CH_4 contain molecules = $\frac{N_A}{16} \times 4$ $= \frac{N_A}{4}$ $= \frac{6.02 \times 10^{23}}{4}$ $= 1.505 \times 10^{23}$
(viii) Law of conservation of mass	

Q.3 Indicate true or false as the case may be.

(i) Neon has three isotopes and the fourth one with atomic mass 20.18 a.m.u.

(ii) Empirical formula gives the information about the total number of atoms present in the molecule.

(iii) During combustion analysis $Mg(ClO_4)_2$ is employed to absorb water vapours.

(iv) Molecular formula is the integral multiple of empirical formula and the integral multiple can never be unity.

(v) The number of atoms in 1.79 g of gold and 0.023 of sodium are equal.

(vi) The number of electron in the molecules of CO and N_2 are 14 each, so 1 mg of each gas will have same number of electrons.

(vii) Avogadro's hypothesis is applicable to all types of gases i.e., ideal and non–ideal.

(viii) Actual yield of a chemical reaction may be greater than the theoretical yield.

ANSWERS

Answers	Correct Statement
(i) False	Neon has three isotopes and 20.18 a.m.u. is the average atomic mass of three isotopes of neon.
(ii) False	Empirical formula gives the information about the simplest ratio among the atoms present in a molecule.
(iii) True	
(iv) False	Molecular formula is the integral multiple of empirical formula and the integral multiple can be unity.
(v) False	23 g of Na contain atoms = 1 mole = 6.02×10^{23} 1 g of Na contain atoms = $\frac{6.02 \times 10^{23}}{23}$ 0.023g of Na contains = $\frac{6.02 \times 10^{23}}{23} \times 0.023$ = 6.02×10^{20} atoms 179 g of gold contain atoms = 1 mole = 6.02×10^{23} 1 g of gold contain atoms = $\frac{6.02 \times 10^{23}}{179} \times 1.79$ = 6.02×10^{21} atoms
(vi) True	1 mole of carbon (12 g) = 6 moles of electrons 1 mole of oxygen(16 g) = 8 moles of electrons 1 mole of 'CO' (28 g) = 14 moles of electrons 1 mole of 'N' (14 g) = 7 moles of electrons 1 mole of 'N' (14 g) = 7 moles of electrons 1 mole of N_2' (28 g) = 14 moles of electrons So, any equal mass of these two substances have equal number of electrons.
(vii) False	Avogadro's hypothesis is applicable to ideal gas only.
(viii) False	Due to (i) mechanical loss (ii) reaction reversibility and (iii) side reactions. The actual yield is always lesser than theoretical yield.

Q.4 What are ions? Under what conditions are they produced.

Ans. Ion: Charge carrying species are called ions.

Conditions for Ion Formation:

1. Positively charged ions called cations are formed by loss of electrons e.g., Na^+, Mg^{++}. Atoms of elements in gaseous state lose electrons under the following condition:
   - (a) When they are heated sufficiently.
   - (b) When a beam of fast moving electrons or α-particles or X-rays is passed through the gas.

   Molecular cations are also formed under the above mentioned condition 'b'.
2. Negatively charged ions called anions are formed by gain of electrons. Atoms of highly electronegative elements gain electrons when they are placed in a medium having a source of electrons. Molecular anions are very rare.

Q.5 (a) What are isotopes? How do you deduce the fractional atomic masses of elements from the relative isotopic abundance? Give two examples in support of your answer.

(b) How does a mass spectrograph show the relative abundance of isotopes of an element?

(c) What is the justification of two strong peaks in the mass spectrum for bromine; while for iodine only one peak at 127 amu, is indicated?

Ans.

(a) **Isotopes:** "Atoms of the same element which have different atomic masses but same atomic numbers. Such atoms of an element are called isotopes".

Fractional Atomic Mass: Fractional atomic mass is the average of the atomic masses of all isotopes and their relative abundance.

Example:

(i) Fractional atomic mass of neon $= \dfrac{(20 \times 90.92) + (21 \times 0.26) + (22 \times 8.82)}{100}$

$= 20.18$ g/mol

(ii) Average atomic mass of silver $= \dfrac{(106.90509)(51.84) + (108.9476)(48.16)}{100}$

$= 107.86$ g/mol

(b) Relative abundance of isotopes is equal to the current strength produced. When cations of respective isotopes fall on ion collector.

Finally, graph is plotted between mass no. and relative abundance. The height of the peak in the graph against specific mass no. shows the relative abundance of respective isotopes.

(c) Bromine has two stronger peaks in the mass spectrograph because it has two isotopes. Whereas iodine has only one peak at 127 a.m.u because it has only one isotope with 100% relative abundance.

Q.6 Silver has atomic number 47 and has 16 known isotopes, but two occur naturally i.e., Ag-107 and Ag-109. Given the following mass spectrometric data, calculate the average atomic mass of silver.

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

Ans. Average atomic mass $= \dfrac{(106.90509)(51.84) + (108.90476)(48.16)}{100}$

$= \dfrac{5541.959 + 5244.853}{100}$

$= \dfrac{10786.81}{100}$

$=$ 107.86 g/mol.

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

Average atomic mass of boron = 10.81 amu
Isotopic mass of ^{10}B = 10.0129 amu
Isotopic mass of ^{11}B = 11.0093 amu.

Ans. Average atomic mass of boron = 10.81 amu.
Isotopic mass of ^{10}B = 10.0129 amu.
Isotopic mass of ^{11}B = 11.0093 amu.
Relative abundance of ^{10}B = x
Relative abundance of ^{11}B = 100 – x

Average atomic mass $= \dfrac{(10.0129)\,x + (11.0093)(100 - x)}{100}$

$10.81 = \dfrac{10.0129\,x + 1100.93 - 11.0093\,x}{100}$

$10.81 \times 100 = -0.9964\,x + 1100.93$

$-0.9964\,x = 1081 - 1100.93 = -19.93$

$x = \dfrac{19.93}{0.9964}$

$x = 20\%$

Relative abundance of ^{10}B = 20%
Relative abundance of ^{11}B = 100 – 20
= 80%

Q.8 Define the following terms and give three examples of each.

(i) Gram atom
(ii) Gram molecular mass
(iii) Gram formula
(iv) Gram ion
(v) Molar volume
(vi) Avogadro's number
(vii) Stoichiometry
(viii) Percentage yield

Ans.

(i) Gram Atom: The atomic mass of an element expressed in grams is called gram atom. It is also known as gram mole or simply mole.

Examples:

1. 1 gram atom of hydrogen = 1.008 g = 1 mole
2. 1 gram atom of carbon = 12.0 g = 1 mole
3. 1 gram atom of oxygen = 16.0 g = 1 mole

(ii) Gram Molecular Mass: The molecular mass of a molecular substance expressed in grams is called gram molecular mass, gram mole or simply mole of a substance.

Examples:

1. 1 gram mole of H_2 = 2 g = 1 mole
2. 1 gram mole of O_2 = 32 g = 1 mole
3. 1 gram mole of H_2O = 18 g = 1 mole

(iii) Gram Formula: The formula mass of an ionic compound expressed in grams is called gram formula or mole.

Examples:

1. 1 gram formula of NaCl = 58.5 g = 1 mole
2. 1 gram formula of $AgNO_3$ = 170 g = 1 mole
3. 1 gram formula of Na_2CO_3 = 106 g = 1 mole

(iv) Gram Ion: The ionic mass of an ionic species expressed in grams is known as on gram ion or one mole of ions.

Examples:

1. 17 gram of OH^- = 1 mole of OH^-
2. 60 gram of CO_3^{-2} = 1 mole of CO_3^{-2}
3. 96 gram of SO_4^{-2} = 1 mole of SO_4^{-2}

(v) **Molar – Volume:** One mole of any gas at STP occupies 22.414 dm^3. It is called molar volume.

For Example;

44g of CO_2 at STP occupies = 22.414 dm^3

17g of NH_3 at STP occupies = 22.414 dm^3

64g of SO_2 at STP occupies = 22.414 dm^3

(vi) **Avogadro's Number:** The number of atoms, ions, molecules in one mole of a substance (1 gram – atom, 1 gram molecule, 1 gram ion) is called Avogadro's number. It is constant denoted by N_A and is equal to 6.022×10^{23}.

For Example;

23g of Na contains = 6.02×10^{23} atoms

44g of CO_2 contains = 6.02×10^{23} molecules

17g of OH^- contains = 6.02×10^{23} ions

(vii) **Stoichiometry:** The study of quantitative relationship between reactants and the products in a balanced chemical equation is called stoichiometry.

Stoichiometric calculations are based upon two laws of chemical combination.

(i) Law of conservation of mass.

(ii) Law of definite proportions.

The following assumptions must be obeyed when stoichiometric calculations are performed.

(a) All reactants are completely converted into products.

(b) No side reaction occur.

(c) Two laws of chemical combination must be obeyed.

(viii) **Percentage Yield:**

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

% age yield shows the efficiency of the reaction.

Factors Responsible for Low Yield:

(i) Side reaction produced by products.

(ii) Sometimes the reaction is reversible.

(iii) Mechanical loss of product during filtration, distillation, washing, drying and crystallization.

Q.9 Justify the following statements:

Ans.

(a) 23 g of sodium and 238 g of uranium have equal numbers of atoms in them.

23 g of Na and 238 g of U is equal to their one mole. We know that 1 mole of all elements contain equal no. of atoms i.e., 6.02×10^{23} atoms.

(b) Mg atom is twice heavier than that of carbon.

Atomic mass of C is 12 and of Mg is 24. 6.02×10^{23} atoms of Mg weight 24 grams and 6.02×10^{23} atoms of carbon which 12 grams. It shows that Mg is twice havier than C.

(c) 180 g of glucose and 342 g of sucrose have the same number of molecules but different number of atoms present in them.

180 g of glucose and 342 g of sucrose is equal to their one mole. 1 mole of every molecular substance contain equal no. of molecules (6.02×10^{23}). 1 molecule of glucose contain 24 atoms and 1 molecule of sucrose contain 45 atoms. Hence they have same no. of molecules but different no. of atoms.

(d) 4.9 g of H_2SO_4 when completely ionized in water have equal number of positive and negative charges but the number of positively charged ions are twice the number of negatively charged ions.

$$\text{Moles of } H_2SO_4 = \frac{4.9}{98} = \frac{1}{20} = 0.05 \text{ moles}$$

$$\begin{array}{cccc} H_2SO_4 & \rightleftharpoons \; 2H^+ & + & SO_4^{-2} \\ 4.9\text{ g} & 2 \times 0.05 & & 0.05 \\ (0.05\text{ moles}) & \text{moles} & & \text{moles} \end{array}$$

4.9 g of H_2SO_4 (0.05 moles) when ionized completely produces 0.1 moles of positive charges and 0.1 moles of negative charges. Hence no. of positive and negative charges are same. 4.9 g of H_2SO_4 (0.05 moles) produces 0.1 moles of H^+ ions and 0.05 moles of SO_4^{-2} ions. Hence, no. of positively charged ions is twice than the no. 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.

$$K_2CrO_4 \overset{H_2O}{\rightleftharpoons} 2K^+ + CrO_4^{-2}$$

This equation shows that 1 mg formula unit of K_2CrO_4 ionizes into three ions ($2K^+$ and 1 CrO_4^{-2}) hence the no. of ions is thrice the no. of formula units of K_2CrO_4. One mg will have same values.

(f) Two grams of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3, although the sizes and masses of molecules of three gases are very different from each other.

The sizes and masses do not affect the occupied volume at S.T.P. Since, distance between gas molecules is 300 times of their diameter. Hence, if no. of molecules of different gases are same at S.T.P, the occupied volume, will also be same.

Q.10 Calculate each of the following quantities:

Ans.

(a) Mass in grams of 2.74 moles of $KMnO_4$

Mass of $KMnO_4$ = m = ?

No. of moles of $KMnO_4$ = n = 2.74 moles

Molecular mass = 39 + 55 + 64 = 158 g

m = n(M) = 2.74(158)= 432.92 g

(b) Moles of oxygen atoms in 9 g of $Mg(NO_3)_2$

Mass of $Mg(NO_3)_2$ = m = 9 g

$$n = \frac{m}{M} = \frac{9}{148} = 0.06 \text{ moles}$$

1 mole of $Mg(NO_3)_2$ = 6 moles of O-atoms

0.06 mole of $Mg(NO_3)_2$ = 6(0.06) moles of O-atoms

= 0.36 moles

(c) No. of oxygen atoms in 10.037 g of $CuSO_4 . 5H_2O$

Mass of $CuSO_4 . 5H_2O$ = 10.037 g

Molar mass = 63.5 + 32 + 64 + (5 × 18)

= 249.5

$$n = \frac{m}{M} = \frac{10.037}{249.5} = 0.04 \text{ moles}$$

1 mole of $CuSO_4 . 5H_2O$ = 9 moles of O-atoms

0.04 moles of $CuSO_4 . 5H_2O$ = 0.04 × 9 = 0.362 moles

1 mole of oxygen atom = 6.02×10^{23} = atoms

0.36 mole of oxygen atom = $0.36 \times 6.02 \times 10^{23}$

= 2.18×10^{23} atoms

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

$N = 2.6 \times 10^{20}$ molecules

Molecular mass of $SO_2 = 32 + 16 \times 2 = 64$

Mass in kg = ?

$$N = \frac{m}{M} \times N_A$$

$$m = \frac{NM}{N_A}$$

$$= \frac{(2.6 \times 10^{20})(64)}{6.02 \times 10^{23} \times 1000}$$

$$= 27.64 \times 10^{20-23-3}$$

$$= 27.64 \times 10^{-6}$$

$$m = 27.64 \times 10^{-6} \text{ kg}$$

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

$m = 0.822$ g

Cl-atoms = ?

Molecular mass of $C_2H_4Cl_2 = 12 \times 2 + 1 \times 4 + 35.5 \times 2$

$= 99$

No. of mole of $C_2H_4Cl_2 = n = \dfrac{m}{M}$

$= \dfrac{0.822}{99} = 8.30 \times 10^{-3}$ moles

1 mole of $C_2H_4Cl_2$ = 2 moles of Cl-atoms

8.30×10^{-3} moles of $C_2H_4Cl_2 = 2 \times 10^{-3} \times 8.30$

= 0.017 moles of Cl-atoms

(f) Mass in grams of 5.136 moles of Ag_2CO_3

$n = 5.136$ moles

$m = ?$

Molecular mass of $Ag_2CO_3 = (108 \times 2) + 12 + (16 \times 3)$

$= 276$

$m = nM$

$= (5.136)(276)$

$m = 1417.53$ g

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

$$m = ?$$

$$N = 2.78 \times 10^{21} \text{ molecules}$$

Molecular mass of CrO_2Cl_2 = $52 + 16 \times 2 + 35.5 \times 2$

$$= 155$$

No. of molecules $= N = \frac{m}{M} \times N_A$

$$m = \frac{NM}{N_A}$$

$$= \frac{(2.78 \times 10^{21})(155)}{6.02 \times 10^{23}}$$

$$= 71.57 \times 10^{-2}$$

$$m = 0.7157 \text{ g}$$

(h) No. of moles and formula units in 100 g of $KClO_3$

Molecular mass of $KClO_3$ = $39 + 35.5 + 16 \times 3$

$$M = 122.5$$

$$n = ?$$

$$N = ?$$

$$m = 100 \text{ g}$$

$$n = \frac{m}{M} = \frac{100}{122.5} = 0.816 \text{ moles}$$

No. of formula units (N) = $n \times N_A$

$$= (0.816)(6.02 \times 10^{23})$$

$$= 4.91 \times 10^{23} \text{ formula units}$$

(i) No. of K^+ ions, ClO_3^- ions, Cl-atoms and O-atoms in (h).

1 formula units of $KClO_3$ = 1 K^+ ion

4.91×10^{23} formula units of $KClO_3$ = 4.91×10^{23} K^+ ions

1 formula unit of $KClO_3$ = 1 ClO_3^- ions

4.91×10^{23} formula units of $KClO_3$ = 4.91×10^{23} ClO_3^- ions

1 formula unit of $KClO_3$ = 1 Cl-atom

4.91×10^{23} formula unit of $KClO_3$ = 4.91×10^{23} Cl-atoms

1 formula unit of $KClO_3$ = 3 oxygen atoms

4.91×10^{23} formula unit of $KClO_3$ = $3(4.91 \times 10^{23})$

= 14.73×10^{23}

= 1.473×10^{24}-atoms

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

Ans.

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

Mass of one mole of aspartame $C_{14}H_{18}N_2O_5$

Mass of one mole of aspartame $C_{14}H_{18}N_2O_5$ = $12 \times 14 + 1 \times 18 + 14 \times 2 + 16 \times 5$

= $168 + 18 + 28 + 80$

M = 294 g/mole

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

m = 52 g

M = 294 g/mole

n = ?

$$n = \frac{52}{294} = 0.177 \text{ moles}$$

(c) What is mass in grams of 10.122 mole of aspartame?

n = 10.122 moles

M = 294 g/mole

m = ?

$m = n \times M$

$= 10.122 \times 294$

$= 2975.88$ g

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

m = 2.43 g

M = 294 g/mole

No. of H-atoms = ?

$$\text{No. of molecules (N)} = \frac{m}{M} \times N_A$$

$$= \frac{2.43}{294} \times 6.02 \times 10^{23}$$

$= 4.975 \times 10^{21}$ molecules

1 molecule of aspartame = 18 H-atoms

4.975×10^{21} molecules of aspartame = $18 \times 4.975 \times 10^{21}$

= 8.955×10^{22} H-atoms

Q.12 A sample of 0.6 moles of a metal M reacts completely with excess of fluorine to form 46.8 g of MF_2.

Ans.

(a) How many moles of F are present in sample?

No. of moles of 'M' = 0.6 moles

$$\underset{0.6\text{ moles}}{M + F_2} \longrightarrow \underset{46.8\text{ g}}{MF_2}$$

No. of moles of F = ?

1 mole of M = 1 mole of MF_2

0.6 mole of M = 0.6 moles of MF_2

1 mole of MF_2 = 2 moles of F-atom

0.6 moles of MF_2 = 2(0.6) moles of F-atoms

= 1.2 moles of F-atoms

(b) Which element is represented by "M"?

$$M = ?$$

$$n = \frac{m}{M}$$

$$M = \frac{m}{n}$$

$$= \frac{46.8}{0.6} = 78\text{ g}$$

$$MF_2 = 78\text{ g}$$

$$M + 38 = 78\text{ g}$$

$$M = 78 - 38$$

$$= 40\text{ g} = \text{Calcium} = \text{Ca}$$

$$MF_2 = CaF_2$$

Q.13 In each pair, choose larger of indicated quantity or state if samples are equal.

Ans.

(a) Individual particles: 0.4 moles of oxygen molecules or 0.4 moles of oxygen atoms.

0.4 moles of O_2 = 0.4 × N_A molecules

0.4 moles of O = 0.4 × N_A atoms

0.4 moles of O-atoms and 0.4 moles of O-molecules have equal no. of particles.

(b) Mass: 0.4 moles of ozone molecules or 0.4 mole of oxygen atoms.

Mass of ozone = 0.4×48

= 19.2 g

Mass of oxygen atom = 0.4×16

= 6.4 g

0.4 moles of ozone is larger than 0.4 moles of oxygen atoms.

(c) Mass: 0.6 mole of C_2H_4 or 0.6 mole of I_2.

Mass = nM

Mass of C_2H_4 = (0.6)(28)

= 16.8 g

Mass of I_2 = (0.6)(254)

= 152.4 g

0.6 moles of I_2 is larger than the 0.6 moles of C_2H_4.

(d) Individual particles: 4 g of N_2O_4 or 3.3 g of SO_2

$$\text{No. of molecules} = \frac{m}{M} \times N_A$$

$$= \frac{4}{92} \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 0.26 \times 10^{23} \text{ molecules}$$

$$\text{No. of molecules of } SO_2 = \frac{m}{M} \times N_A$$

$$= \frac{3.3}{64} \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 0.31 \times 10^{23} \text{ molecules}$$

3.3 g of SO_2 (0.31×10^{23} molecules) contain larger no. of molecules than 4 g (0.26×10^{23} molecules) of N_2O_4.

(e) Total ions: 2.3 moles of $NaClO_3$ or 2.0 moles of $MgCl_2$.

$$NaClO_3 \rightleftharpoons Na^{+1} + ClO_3^{-1}$$

$NaClO_3$ ionizes into two ions Na^+ and ClO_3^{-1}.

1 mole of $NaClO_3$ = 2 moles of ions

2.3 moles of $NaClO_3$ = 2(2.3)

= 4.6 moles of ions

4.6 moles of ions = $4.6 \times 6.02 \times 10^{23}$ ions

= 27.692×10^{23} ions

$MgCl_2 \rightleftharpoons Mg^{+2} + 2Cl^-$

$MgCl_2$ ionizes into three ions Mg^{+2} and $2Cl^-$

1 mole of $MgCl_2$ = 3 moles of ions

2 moles of ions = 3(2)

= 6 moles of ions

6 moles of ions = $6 \times 6.02 \times 10^{23}$ ions

= 36.12×10^{23} ions

2 moles of $MgCl_2$ contains larger no. of ions than 2.3 moles of ions than 2.3 moles of $NaClO_3$.

(f) Molecules: 11.0 g H_2O or 11.0 g H_2O_2

$$\text{No. of molecules of } H_2O = \frac{m}{M} \times N_A$$

$$= \frac{11}{18} \times 6.02 \times 10^{23}$$

$$= 3.67 \times 10^{23} \text{ molecules}$$

$$\text{No. of molecules of } H_2O_2 = \frac{m}{M} \times N_A$$

$$= \frac{11}{34} \times 6.02 \times 10^{23}$$

$$= 1.94 \times 10^{23} \text{ molecules}$$

11 g of water contains larger no. of molecules than H_2O_2.

(g) Na^+ ion: 0.500 moles of NaBr or 0.0145 kg of NaCl.

$0.0145 \times 1000 = 14.5$ g NaCl

$$\text{No. of moles of NaCl} = \frac{m}{M}$$

$$= \frac{14.5}{58.5} = 0.25 \text{ moles}$$

$NaBr \rightleftharpoons Na^+ + Br^-$

0.500 moles 0.500 moles 0.500 moles

$NaCl \rightleftharpoons Na^+ + Cl^-$

0.25 moles 0.25 moles 0.25 moles

No. of ions in 0.500 moles of NaBr is larger.

(h) Mass: 6.02×10^{23} atoms of ^{235}U or 6.02×10^{23} atoms of ^{238}U.

6.02×10^{23} atoms of ^{235}U = 235 g

6.02×10^{23} atoms of ^{238}U = 238 g

6.02×10^{23} atoms of ^{238}U have larger mass.

Q.14 (a) Calculate the percentage of nitrogen in the four important fertilizers i.e.,

(i) NH_3 (ii) NH_2CONH_2 (urea)

(iii) $(NH_4)_2SO_4$ (iv) NH_4NO_3

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

(i) $NH_4H_2PO_4$ (ii) $(NH_4)_2HPO_4$

(iii) $(NH_4)_3PO_4$

Ans.

(a) (i) NH_3 molar mass of compound $= 14 + 1 \times 3 = 17$ g/mol

% age of nitrogen = ?

% age of nitrogen $= \frac{14}{17} \times 100 = 82.351\%$

(ii) NH_2CONH_2 molar mass of the compound $= 14 + 2 + 12 + 16 + 14 + 2$

$= 60$ g/mol

% age of nitrogen $= \frac{28}{60} \times 100 = 46.67\%$

(iii) $(NH_4)_2SO_4$ molar mass of compound $= (14 + 4) \times 2 + 32 + 64 = 132$

$= 132$ g/mol

% age of nitrogen $= \frac{28}{132} \times 100 = 21.21\%$

(iv) NH_4NO_3 molar mass of the compound $= 14 + 4 + 14 + 16 \times 3 = 80$ g/mol

% age of nitrogen $= \frac{28}{80} \times 100 = 35\%$

(b) (i) $NH_4H_2PO_4$ molar mass of compound $= 14 + 4 + 2 + 31 \times 16 \times 4$

$= 115$ g/mol

% age of nitrogen $= \frac{14}{115} \times 100 = 12.17\%$

% age of phosphorus $= \frac{31}{115} \times 100 = 26.96\%$

(ii) $(NH_4)_2HPO_4$ molar mass of compound $= 28 + 8 + 1 + 31 + 16 \times 4$

$= 132$ g/mol

% age of nitrogen $= \frac{28}{132} \times 100 = 21.21\%$

% age of phosphorus $= \frac{31}{132} \times 100 = 23.48\%$

(iii) $(NH_4)_3PO_4$ molar mass of compound $= 42 + 12 + 31 + 64 = 149$ g/mol

% age of nitrogen $= \frac{42}{149} \times 100 = 28.18\%$

% age of phosphorus $= \frac{31}{149} \times 100 = 20.8\%$

Q.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.

Ans. Molar mass of $C_6H_{12}O_6 = 12 \times 6 + 12 + 16 \times 6 = 180$ g/mol

% age of carbon $= \frac{72}{180} \times 100 = 40\%$

% age of hydrogen $= \frac{12}{180} \times 100 = 6.67\%$

% age of oxygen $= \frac{96}{180} \times 100 = 53.3\%$

$C_6H_{12}O_6 = 10.5$ g

No. of moles of $C_6H_{12}O_6 = \frac{10.5}{180} = 0.06$ moles

1 mole of $C_6H_{12}O_6$ = 6 moles of C-atoms

0.06 moles of $C_6H_{12}O_6 = (0.06)(6) = 0.36$ moles

No. of carbon atoms $= (0.36)(6.02 \times 10^{23}) = 2.167 \times 10^{23}$

1 mole of $C_6H_{12}O_6$ = 12 moles of H-atoms

0.06 moles of $C_6H_{12}O_6 = (0.06)(12) = 0.72$ moles of H

No. of hydrogen atoms $= 0.72 \times 6.02 \times 10^{23} = 4.33 \times 10^{23}$ atoms

1 mole of $C_6H_{12}O_6$ = 6 moles of O-atoms

0.06 moles of $C_6H_{12}O_6 = (0.06)(6) = 0.36$ moles

No. of oxygen atoms $= 0.36 \times 6.02 \times 10^{23} = 2.167 \times 10^{23}$ atoms

Q.16 Ethylene glycol is used to as automobile antifreeze. It has 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. Its molar mass is 62.1 grams mol^{-1}. Determine its empirical formula.

Ans.

(i) % age of C = 38.7%

% age of H = 9.7%

% age of O = 51.6%

(ii) No. of gram atoms of C $= \dfrac{38.7}{12} = 3.225$

No. of gram atoms of H $= \dfrac{9.7}{1.008} = 9.62$

No. of gram atoms of O $= \dfrac{51.6}{16} = 3.225$

(iii) Atomic ratio:

$$\begin{array}{ccccc} C & : & H & : & O \\ \dfrac{3.225}{3.225} & : & \dfrac{9.62}{3.225} & : & \dfrac{3.225}{3.225} \\ 1 & : & 3 & : & 1 \end{array}$$

(iv) Empirical formula = CH_3O

(v) For molecular formula:

Molar mass = 62.1 g / mole

Formula mass $= 12 + 3 \times 1.008 + 16 = 31.024$ g/mole

Molecular mass = n × Formula mass

$$n = \frac{\text{Molar mass}}{\text{Formula mass}} = \frac{62.1}{31.024} = 2.001$$

n = 2

Molecular formula = n × Emp. formula

Molecular formula $= 2 \times CH_3O$

$= C_2H_6O_2$

Q.17 Serotenin (Molecular mass = 176 g mol^{-1}) is a compound that conducts nerve impulses in brain and muscles. It contains 68.2% C, 6.86% H, 15.09% N and 9.08% O. What is its molecular formula?

Ans. Molecular mass = 176 g / mole

(i) % age of C = 68.2%

% age of H = 6.86%

% age of O = 9.08%

% age of N = 15.09%

(ii) No. of gram atoms of C $= \dfrac{68.2}{12} = 5.68$

No. of gram atoms of H $= \dfrac{6.86}{1.008} = 6.80$

No. of gram atoms of O $= \dfrac{9.08}{16} = 0.57$

No. of gram atoms of N $= \dfrac{15.09}{14} = 1.07$

(iii) Atom ratio

$$\begin{array}{ccccccc} C & : & H & : & N & : & O \\ \frac{5.68}{0.57} & : & \frac{6.80}{0.57} & : & \frac{1.07}{0.57} & : & \frac{0.57}{0.57} \\ 10 & : & 12 & : & 2 & : & 1 \end{array}$$

(iv) Empirical formulas= $C_{10}H_{12}N_2O$

Formula mass = $C_{10}H_{12}N_2O$ = $12 \times 10 + 12 \times 1.008 + 14 \times 2 + 16$

= 176.096 g/mole

Molecular formula = n × Empirical formula mass

$$n = \frac{\text{Molecular mass}}{\text{Formula mass}}$$

$$n = \frac{176}{176.096} = 0.999 = 1$$

Molecular formula = n × Empirical formula

$C_{10}H_{12}N_2O = 1 \times C_{10}H_{12}N_2O$

Molecular formula = $C_{10}H_{12}N_2O$

Q.18 An unknown metal M reacts with S to form a compound with a formula M_2S_3. If 3.12 g of M reacts with exactly 2.88 g of sulphur, what are the names of metal M and the compound M_2S_3?

Ans. $2M + 3S \longrightarrow M_2S_3$

Mass of "M" = 3.12 g

Mass of "S" = 2.88 g

No. of moles of 'S'= $n = \frac{2.88}{32} = 0.09$ moles

According to balanced equation:

3 moles of "S' = 2 moles of "M"

1 mole of "S" = $\frac{2}{3}$ moles of "M"

0.09 moles of "S" = $\frac{2}{3} \times 0.09 =$ 0.06 moles of "M"

$$n = \frac{m}{M}$$

$$\left(\begin{array}{c}\text{At. wt of} \\ \text{metal M}\end{array}\right) M = \frac{m}{n} = \frac{3.12}{0.06} = 52$$

M = Cr. (Atomic mass = 52)

$M_2S_3 = Cr_2S_3$

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

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

Ans.

(a) How many moles of O_2 are needed to react fully with 4 moles of octane?

According to balanced equation:

2 moles of octane = 25 moles of O_2

4 moles of octane = 50 moles of O_2

(b) How many moles of CO_2 can be produced from one mole of octane?

According to balanced equation:

2 moles of octane = 16 moles of CO_2

1 mole of octane = $\frac{16}{2}$ = 8 moles of CO_2

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

According to balanced equation:

2 moles of octane = 18 moles of H_2O

6 moles of octane = 18 × 3 = 54 moles H_2O

(d) If this reaction 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?

According to balanced equation:

16 moles of CO_2 = 25 moles of O_2

1 moles of CO_2 = $\frac{25}{16}$ moles of O_2

8 moles of CO_2 = $\frac{25}{16} \times 8$ = 12.5 moles

m = n(M) = 12.5 × 32 = 400 g of O_2

16 moles of CO_2 = 2 moles of octane

1 mole of CO_2 = $\frac{2}{16}$ moles of octane

8 moles of CO_2 = $\frac{2}{16} \times 8$ = 1 mole of octane

m = n(M) = 1 × 114

= 114 g of octane

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

Ans. $2Al + 3S \longrightarrow Al_2S_3$

Mass of Al = 20 g

Mass of S = 30 g

No. of moles of "Al" $= n = \frac{m}{N} = \frac{20}{27} = 0.74$ moles

No. of moles of "S" $= n = \frac{m}{M} = \frac{30}{32} = 0.93$ moles

According to balanced equation:

2 moles of Al = 1 mole of Al_2S_3

1 mole of Al $= \frac{1}{2}$ mole of Al_2S_3

0.74 mole of Al $= \frac{1}{2} \times 0.74 = 0.37$ moles of Al_2S_3

3 moles of S = 1 mole of Al_2S_3

1 moles of S $= \frac{1}{3}$ mole of Al_2S_3

0.9 moles of S $= \frac{1}{3} \times 0.93 = 0.31$ moles of Al_2S_3

Limiting reactant = "S"

Mass of Al_2S_3 $= n \times M = 0.31 \times 150 = 46.5$ g

Mass of reactant left in excess:

3 moles of "S" = 2 moles of "Al"

1 moles of "S" $= \frac{2}{3}$ moles of "Al"

0.93 moles of "S" $= \frac{2}{3} \times 0.93 = 0.62$ moles of "Al"

Moles of "Al" left $= 0.74 - 0.62 = 0.12$ moles

$m = n(M) = 0.12 \times 27 = 3.24$ g

Q.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 vapours. How many grams of N_2 gas will be formed by reacting 100 g of N_2H_4 and 200 g of N_2O_4.

$$2\,N_2H_4 + N_2O_4 \longrightarrow 3\,N_2 + 4\,H_2O$$

Ans.

Mass of N_2H_4 = 100 g

Mass of N_2O_4 = 200 g

No. of moles of $N_2H_4 = \frac{100}{32} = 3.125$ moles

No. of moles of $N_2O_4 = \frac{200}{92} = 2.17$ moles

2 moles of N_2H_4 = 3 moles of N_2

1 mole of $N_2H_4 = \frac{3}{2}$ moles of N_2

3.125 moles of $N_2H_4 = \frac{3}{2} \text{ x } 3.125 = 4.68$ moles of "N_2"

1 mole of N_2O_4 = 3 moles of N

2.17 mole of N_2O_4 = (2.17) (3) = 6.5 moles of "N"

Limiting reactant = N_2H_4

Mass of nitrogen (N_2) = m = n M = (4.68) (28) = 131 g

Q.22 Silicon carbide (SiC) is an important ceramic material. It is produced by allowing sand (SiO_2) to react with carbon at high temperature.

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

When 100 kg sand is reacted with excess of carbon, 51.4 kg of SiC is produced. What is the percentage yield of SiC?

Ans.

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

Mass of S and (SiO_2) = 100 kg = 10^5 g

Mass of SiC = 51.4 kg = 51.4 x 1000 = 51400 g

Molar mass of SiO_2 = 28 + 16 x 2 = 60 g

Molar mass of SiC = 28 + 12 = 40 g

60 g of SiO_2 = 40 g of SiC

1 g of $SiO_2 = \frac{40}{60}$ g of SiC

10^5 g of $SiO_2 = \frac{40}{60} \text{ x } 10^5 = 66666.67$ g

Theoretical yield = 66666.67 g

Actual yield = 51400

$$\%\text{ age yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \text{ x } 100$$

$$= \frac{51400}{66666.67} \text{ x } 100 = 77.1\%$$

Q.23 (a) What is the Stiochiometry? Give its assumptions. Mention two important laws, which help to perform the Stiochiometric calculations.

(b) What is a limiting reactant? How does it control the quantity of the product formed? Explain with three examples.

Ans.

(a) Stiochiometry:

The branch of chemistry which deals with the study of quantitative relationship between the reactants and the products in a balanced chemical equation.

Assumptions of Stiochiometry:

1. All the reactants must be converted into products.
2. No side reaction should occur.
3. In Stiochiometric calculations law of conservation of mass and law of definite proportions are obeyed.

Law of conservation of mass and law of definite proportions help to perform Stiochiometric calculations.

(b) Limiting reactant:

A reactant that controls the amount of product formed in a chemical reaction due to its smaller amount than required.

It controls the amount of product formed by being consumed earlier than the other reactant. It produces the least moles of the product.

Examples:

1. Burning of coal:

$$C + O_2 \xrightarrow{\qquad} CO_2$$

In this reaction O_2 is in excess and carbon is the limiting reactant.

2. Burning of natural gas:

$$CH_4 + 2O_2 \xrightarrow{\qquad} CO_2 + 2H_2O$$

In this reaction, O_2 is in excess and natural gas is the limiting reactant.

3. Combustion (burning) of gasoline (petrol):

$$C_8H_{18} + \frac{25}{2} O_2 \xrightarrow{\qquad} 8CO_2 + 9H_2O$$

In this reaction O_2 is in excess and petrol is the limiting reactant.

Q.24 (a) Define yield. How do we calculate the percentage yield of a chemical reaction?

(b) What are the factors which are mostly responsible for the low yield of the products in chemical reaction?

Ans.

(a) Yield:

The amount of product obtained as a result of chemical reaction is called yield.

Percentage yield:

Let us calculate the percentage yield with the help of example. 2500 g CaO is formed according to following equation when 4500 g of $CaCO_3$ is roasted.

$$CaCO_3 \longrightarrow CaO + CO_2$$

So calculate percentage yield, we require actual yield which is 2500 g and theoretical yield which is 2500 g and theoretical yield which is to be calculated through balanced equation.

$$\begin{array}{lll} CaCO_3 & \longrightarrow & CaO + CO_2 \\ 100\text{ g} & & 56\text{ g} \quad 44\text{ g} \end{array}$$

According to balanced chemical equation:

$$100\text{ g of } CaCO_3 \text{ gives } = 56\text{ g of } CaO$$

$$1\text{ g of } CaCO_3 \text{ gives } = \frac{56}{100}\text{ g of } CaO$$

$$4500\text{ g of } CaCO_3 \text{ gives } = \frac{56}{100} \times 4500\text{ g of } CaO$$

$$= 2520\text{ g}$$

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

$$= \frac{2500}{2520} \times 100 = 99.2\%$$

(b) There are various factors responsible for low yield (actual yield) of a product in a chemical reaction.

1. Side reaction produces by products.
2. Sometimes reaction is reversible.
3. Mechanical loss of product during separation by filtration, distillation, separating funnel, washing, drying and crystallization.

Q.25 Explain the following with reasons.

(i) Law of conservation of mass has to be obeyed during Stiochiometric calculations.

(ii) Many chemical reactions taking place in our surrounding involve the limiting reactants.

(iii) No individual neon atom in the sample of the element has a mass of 20.18 a.m.u.

(iv) One mole of H_2SO_4 should completely react with two moles of NaOH. How does Avogadro's number help to explain it?

(v) One mole of H_2O has two moles of bonds, three moles of atoms, ten moles of electrons and twenty–eight moles of the total fundamental particles present in it.

(vi) N_2 and CO have the same number of electrons protons and neutrons.

Ans.

(i) Law of conservation of mass is stated as, "mass can neither be created nor destroyed but it can be transformed from one form to other.

Stiochiometric calculations are based on balanced chemical equation, so number of moles atoms in reactants and product are equal. As number of moles atoms are equal hence their masses should also be equal in reactants and products which is according to law of conservation of mass.

(ii) Many chemical reactions taking place in our surrounding involve the limiting reactants. If it is not so, the reaction will go on continuously and would not stop. But due to this limiting reactants, the reaction stops after some time after the complete consumption of limiting reactant.

For example, when wood burns, it reacts with the oxygen of air which is in excess in nature. But after the complete consumption of wood, the fire extinguishes.

(iii) Neon has three isotopes which have atomic masses Ne^{20}, Ne^{21} and Ne^{22}. The relative abundance of these isotopes in nature is 92.92%, 0.26% and 8.82%, respectively and 20.18 is the relative atomic mass of neon, i.e., the average atomic mass of all the three isotopes of neon. This is the reason that no individual neon atom in the sample of the element has a mass of 20.18 a.m.u. exactly.

(iv) When one mole of H_2SO_4 ionizes, it gives 2 moles of positively charged H^+ ions which in turn needs 2 moles of negatively charged OH^- ions. These OH^- ions are given by two moles of NaOH ions. According to Avogadro's rule, one mole of any substance contain 6.02×10^{23} atoms, ions or molecules. So the yield of H^+ ions from one mole of H_2SO_4 is $2 \times 6.02 \times 10^{23}$ ions and the yield of OH^- ions from two moles of NaOH is $2 \times 6.02 \times 10^{23}$ ions. So Avogadro's number explain that equal number of positive ions react with equal number of negative ions, i.e., one mole of H_2SO_4 should completely react with two moles of NaOH.

(v) (i) The molecular structure of water is:

As one molecule of water has two bonds. So one mole of water contain two moles of bonds as follow:

$H_2O \longrightarrow$ 2 bonds
1 mole $\longrightarrow$ 2 moles

(ii) $H_2O \longrightarrow 2H + O$
1 mole $\longrightarrow$ 2 moles + 1 mole

As, 1 molecule of H_2O contain 3 atoms, i.e., two hydrogen atoms and one oxygen atom each.

So 1 mole of H_2O contain 3 moles of atom.

(iii) $H_2O \longrightarrow 8e^- \text{ of } O + 2\,(1\,e^- \text{ of } H)$

$1 \text{ mole} \longrightarrow 8 \text{ moles of} + 2 \text{ moles}$

As 1 molecule of H_2O contain 10 electrons i.e., 8 electrons of oxygen and 1 electron of 2 hydrogen atoms.

So, 1 mole of H_2O contain 10 moles of electrons.

(iv) $H_2O \longrightarrow 2H + O$

$2H \longrightarrow 2 \text{ x } [1\,e^- + 1\,p^+] = 4$

$O \longrightarrow 8e^- + 8p^+ + 8n = 24$

As, 1 molecule of H_2O contain 24 fundamental particles i.e., one electrons and one proton in two hydrogen atoms and 8 electrons, 8 protons and 8 neutrons in one oxygen atom.

So, 1 mole of H_2O contain 28 moles of fundamental particles.

(vi) No. of Electrons:

$N_2 \longrightarrow N + N \longrightarrow 7e^- + 7e^- = 14 \text{ electrons}$

$CO \longrightarrow C + O \longrightarrow 6e^- + 8e^- = 14 \text{ electrons}$

No. of Protons:

$N_2 \longrightarrow N + N \longrightarrow 7p + 7p = 14 \text{ protons}$

$CO \longrightarrow C + O \longrightarrow 6p + 8p = 14 \text{ protons}$

No. of Neutrons:

$N_2 \longrightarrow N + N \longrightarrow 7n + 7n = 14 \text{ neutrons}$

$CO \longrightarrow C + O \longrightarrow 6n + 8n = 14 \text{ neutrons}$

So, N_2 and CO have the same number of electrons, protons and neutrons.

(vii) How many protons, neutrons and electrons are present in H_2SO_4.

$2H_1^1 \quad S_{16}^{32} \quad 4O_8^{16}$

$P = 2 + 16 + 32 = 50$

$E = 2 + 16 + 32 = 50$

$N = 0 + 16 + 32 = 48$

IMPORTANT FORMULAE

Hydrazine (rocket fuel)	N_2H_4
Ascorbic acid (vit – C)	$C_6H_8O_6$
Aspartame (artificial sweetener)	$C_{14}H_{18}N_2O_5$
Serotenin conducts nerve impulses in brain and muscles	$C_{10}H_{12}N_2O$

Silicon carbide (carborundum)	SiC
Urea (fertilizer)	$CO\ (NH_2)_2$
(Urea contain 46.6% N)	
Chromyl chloride	CrO_2Cl_2
Blue vitriol	$CuSO_4 . 5H_2O$
Green vitriol	$FeSO_4 . 7H_2O$
White vitriol	$ZnSO_4 . 7H_2O$
Laughing gas (nitrous oxide)	N_2O
Artificial milk	$BiOCl$
Sucrose (sugar)	$C_{12}H_{12}O_{11}$
Ethylene glycol (glycol)] antifreezes	$\begin{array}{l} CH_2 - OH \\ \vert \\ CH_2 - OH \end{array} \rightarrow C_2H_6O_2$
Caustic soda	$NaOH$
Caustic potash	KOH
Washing soda	$Na_2CO_3 . 10H_2O$
Soda ash	Na_2CO_3
Pearl ash	K_2CO_3
Soda lime	$NaOH + CaO$
Quicklime	CaO
Lime water	$Ca\ (OH)_2$
Baking soda	$NaHCO_3$

DO YOU KNOW?

1. ACS (American Chemical Society) has divided chemistry into thirty branches.
2. Swedish Chemist J. Berzelius (1779 – 1848) determined the atomic masses of elements.
3. Atomic masses of atoms range from $10^{-27} - 10^{-25}$ kg.
4. X–ray analysis has shown that diameter of atoms are of the order 2×10^{-10} m (0.2 nm).
5. NH_4^+ is not molecular ion.
6. The word ion means wanderer.
7. Atomicity of haemoglobin molecule is equal to 10,000 and it is 68,00 times heavier than hydrogen atom.
8. 1 a.m.u. = 1.66×10^{-24} grams.
   1 a.m.u. = 1.66×10^{-27} kg.
9. Cadmium has nine isotopes.
10. Empirical formula of glucose and acetic acid is same (CH_2O).
11. Empirical formula of acetylene (ethyne) and benzene is same (CH).
12. Formula of artificial milk is BiOCl.
13. Aspartame ($C_{14}H_{18}N_2O_5$) is artificial sweetener.
14. Hydrazine (N_2H_4) is used an rocket fuel.
15. Formula of chromyl chloride is CrO_2Cl_2.
16. $C_2H_4Cl_2$ is called Dutch liquid.
17. $KMnO_4$ is called “pinky”.
18. Urea $CO(NH_2)_2$ is fertilizer and it contains 46.6% nitrogen.
19. Gasoline (C_8H_{18}) is petrol.
20. Tetra ethyl lead is anti–knocking agent.
21. Ethylene glycol ($C_2H_6O_2$) is used as antifreeze.
22. Serotenin ($C_{10}H_{12}N_2O$) conducts nerve impulses in brain and muscles.
23. H_2SO_4 has 48 neutrons but 50 electrons.
24. Molar mass of H_2SO_4 and H_3PO_4 is equal (98).
25. Molecular mass of NaCl is 58.5 is false statement. (58.5 is formula mass of NaCl).
26. Molecular mass of $K_2Cr_2O_7$ and aspartame is equal (294).
27. A colon (:) may have four million atoms.
28. Radius of atoms is of the order 1×10^{-10}m (0.1nm).

Chapter 2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY

ANALYTICAL CHEMISTRY

“The branch of chemistry which provides a complete characterization of a substance. A complete characterization means, the qualitative and quantitative analysis of the substance.”

Qualitative analysis:

“The detection and identification of elements in a compound is called **qualitative analysis**.”

Quantitative analysis:

“The determination of amount or percentage of different elements in a compound is called **quantitative analysis**.”

A complete quantitative determination generally consists of four major steps.

(1) Obtaining a sample for analysis.
(2) Separation of desired constituents.
(3) Measurement and calculation of the results.
(4) Drawing conclusion from that analysis.

Filtration:

“The process by which insoluble particles are separated from a liquid is called **filtration**.”

Filtrate:

“The liquid which is obtained after passing through the filter medium is called **filtrate**.”

Residue:

“The solid substance which is present at the filter paper during filtration is called **residue**.”

Filter medium:

The porous substance used for filtration is called **filter medium**. Filter paper, Gooch crucible, sintered crucible are different filter mediums.

Selection of filter medium depends upon the size of precipitates or solid particles which are being separated.

Filtration Process (by Filter paper):

1. Select the suitable filter paper for filtration. Pour the mixture on the filter paper. Solvent passes through the filter paper and residue is left over the filter paper.
2. The filter paper should be large enough so that it is $\frac{1}{4}$ th to $\frac{1}{2}$ th of precipitate at the end of filtration.
3. Filter paper should properly be fitted in funnel.
4. The size of the funnel should be so large that its rim extend 1 to 2 cm above the circumference of the filter papers.
5. To run the process smoothly, the stem of the funnel should remain continuously full of liquid, as long as liquid remains in conical portion.
6. The stem of the funnel should be several inches long so that distance of receiving beaker increases.
7. The tip of funnel should touch the side of beaker. In this way, filtrate runs down the side of beaker without splashing.
8. Filtration rate is slow with cone filter paper, it can be increased by using fluted filter paper.

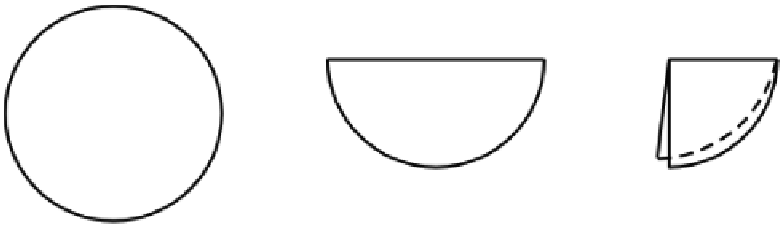
Folding of Filter Paper:

Folding of filter is done by two ways:

(i) Cone filter paper (ii) Fluted filter papers.

(i) Cone filter paper:

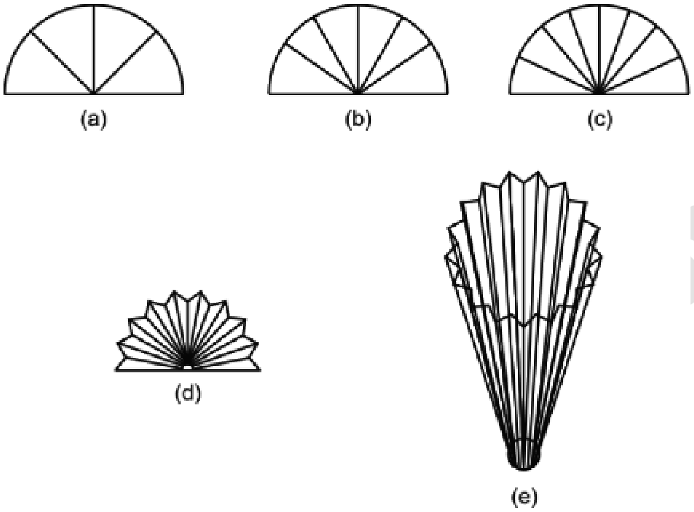
The paper should be folded twice. The first fold should be along the diameter of the paper, the second fold should be such that edges do not quite match. The paper should be opened on the slightly larger section. This provides a cone with three fold thickness halfway around and one thickness the other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



Cone filter papers

(ii) Fluted filter paper:

The rate of filtration through conical funnel can be considerably increased by using a Fluted Filter Paper. For preparation of such a 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. In fluted filter paper **surface area increases** at which filtration occurs so the rate of filtration increases.



Fluted filter paper

Filter Crucibles:

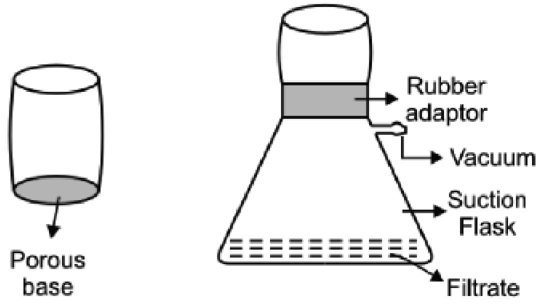
Another way of filtration is by crucible. Two types of crucibles are generally used.

(a) Gooch crucible (b) Sintered glass crucible

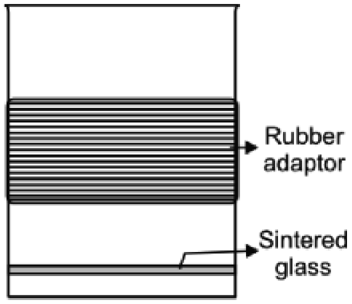
(a) Gooch Crucible:

This crucible is made up of **porcelain**. Its base has number of small holes or perforations. The holes at the bottom are covered with mat of wood pulp or filter paper or asbestos. **Asbestos** mat is used when filter solution reacts with paper. For example, filtration of strong acidic solutions like HCl, H_2SO_4 or some oxidizing agents like $KMnO_4$ which are not feasible with filter paper. Gooch crucible is also useful for filtration of precipitates, which need to be ignited at high temperature.

This filtration process can be speeded up by placing the Gooch crucible in the suction filtering apparatus as shown in the figure.



Gooch Crucible with filtering apparatus



Sintered glass Crucible

(b) Sintered Glass Crucible:

Sintered glass crucible is made of **glass**, have porous glass disc sealed at the bottom. No further filter paper is required and strongly acidic solution can be filtered easily. This crucible is convenient to use than the Gooch crucible because no preparation of filter medium is needed like Gooch Crucible.

Use of Filtration in Industry:

Many industries use filtration to remove solid particles from their liquid components. In many countries rivers and lakes water is used for drinking purpose and purified by filtration. For filtration, the beds of gavels, sands and charcoal are used.

CRYSTALLIZATION

"Separation of excess solid at low temperature in the form of crystals from a saturated solution prepared at high temperature is called **crystallization**."

Principle:

The basic principle of crystallization is that solute should be soluble in suitable solvent at high temperature and when solution is cooled down, the excess amount of solute comes out of the solution in the form of crystals.

This technique is used for the separation of different substances on the basis of their solubilities. The process of crystallization involves the following steps.

1. Choice of Solvent:

The solvent is chosen on hit and trial basis and it is necessary to try a number of solvents before arriving a conclusion. An ideal solvent should have the following characteristics.

(i) It should dissolve a large amount of the solute at its boiling point and only a small amount of solute 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.

The solvents which are mostly used for crystallization are, (1) water, (2) rectified spirit (95% ethanol), (3) absolute ethanol (100%), (4) diethyl ether, (5) acetone, (6) chloroform, (7) carbon tetrachloride (8) acetic acid (9) petroleum ether. If none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be employed. If the solvent is inflammable then precaution should be taken while heating the solution so that it does not catch fire. In such cases, water bath or sand bath is used for heating purpose.

2. Preparation of the Saturated Solution:

After selecting a suitable solvent, the substance is then dissolved in a minimum amount of solvent and is heated directly or on a water bath with constant stirring. Add more solvent to the boiling solution if necessary until all the solutes has dissolved.

3. Filtration:

The insoluble impurities in the saturated solution are then removed by filtering the hot saturated solution, through a normal or a fluted filter paper. This avoids the premature crystallization of the solute on the filter paper or in the funnel stem. If necessary, hot water funnel should be used for this purpose.

4. Cooling:

The hot filtered solution is then cooled at a moderate rate so that medium size crystals are formed. In slow cooling bigger crystals are obtained but have considerable amount of solvent carrying impurities in it.

5. Collecting the Crystals:

When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a filter paper or Gooch crucible using a vacuum pump. The solution remaining after formation of crystals is called **mother liquor**. Full suction is applied in the order to drain the mother – liquor from the crystals as effectively as possible. When the filter cake is rigid enough it is pressed firmly with cork to drain the left – over liquid. The crystals are then washed with a small portion of cold solvent and the process is repeated several times. The mother liquor is quite often concentrated by evaporation and cooled to obtained a fresh crop of crystals. The process of crystallization appears to be very simple yet the success of operation lies in the amount or the percentage of crystallized product obtained from the crude substance.

6. Drying of the Crystallized Substance:

Drying of crystals can be done by three ways.

(1) Pressing it between several folds of filter papers and repeating the process several times dries the crystallized substance. This process has the disadvantage that the crystals are crushed to a fine powder and sometimes the fibers of filter paper contaminate the product.

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

(3) A **safe and reliable** method of drying crystals is through a **vacuum desiccators**. In this process the crystals are spread over a watch glass and kept in a vacuum desiccators for

several hours. The drying agents usually used in a desiccators are $CaCl_2$, silica gel or phosphorous penta – oxide P_2O_5.

7. Decolourization of Undesirable Colours:

Sometimes during the preparation of a crude substance, the colouring matter or resinous products affect the appearance of product and it may appear coloured. Such impurities are conveniently removed by boiling the substance in the solvent with the sufficient quantity of finely powdered **animal charcoal** and then filtering the hot solution. The coloured impurities are absorbed by animal charcoal and the pure decolourized substance crystallizes out from the filtrate on cooling.

Industrial Uses of Crystallization:

It is extensively used in sugar industries. The solution left over is called **molasses** and it still contains a small percentage of sugar.

SUBLIMATION

"The process in which a solid, when heated, directly changes into vapours, without changing into liquid state is called **sublimation**."

The substance which shows such properties are called **sublime substance**. For example (1) naphthalene, (2) iodine, (3) ammonium chloride, (4) benzoic acid, (5) dry ice, (6) camphor, (7) anthracene, (8) hexachloroethane, etc are sublime substances. This technique is used to separate volatile substance from the mixture of volatile and non–volatile substances. The solids, which have high vapour pressure, sublime easily.

Sublimand:

The solid substance that is sublimed is called "**sublimand**."

Sublimate:

The pure solid obtained after sublimation in called "**sublimate**."

Processes:

The given sample of impure substance is taken in a china dish. China dish is placed over the tripod stand in a sand bath. The china dish is covered with the inverted funnel. Funnel opening is plugged with cotton. Some wet cotton or wet paper is wrapped around the funnel to keep it cool. The substance is heated. The pure solid gets deposited in the inner side of the funnel. When whole of the substance is removed, stop heating. Now pure crystals of a substance are scratched from the funnel. In a better method, process is carried out in a cold finger (name of an apparatus).

SOLVENT EXTRACTION

Principle (Distribution law)

It is a separation technique. When a solute is soluble in two immiscible liquids, the solute distribute itself between two liquids. The ratio in which it is distributed is governed by the distribution law.

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

This is also called **partition law**.

Mathematically $K_D = \frac{C_m}{C_s}$

Where K_D is called **partition coefficient or partition ratio**. C_s is the total concentration of solute in stationary phase. C_m is the concentration of solute in mobile phase. In solvent extraction, there is an equilibrium between solute concentrations in mobile and stationary phase.

Conc. of solute in mobile phase $\rightleftharpoons$ Conc. of solute in stationary phase.

Process:

According to this technique 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. Usually it is done by placing the solution and the second liquid into a separating funnel. The funnel is stoppered and the two liquids are shaken together and separated.

Ether Extraction:

The most common laboratory example of solvent extraction is ether extraction. This is used to separate the products of organic synthesis from water. In a typical organic synthesis, the aqueous solution containing the organic product is shaken up with ether in a separating funnel and allowed to separate. The inorganic impurities remain in aqueous phase whereas the organic compound goes to the ether layer. The ether layer is separated and the organic product is obtained by evaporating the ether. Repeated extractions using small portions of solvent (ether) are more efficient than using a single but larger volume of solvent. The technique is particularly useful when the product is volatile or thermally unstable.

Extraction of I_2 from Water:

Consider, 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. The following dynamic equilibrium is established.

$$I_2 + I^-_{(aq)} \rightleftharpoons I^-_{3(aq)}$$

Soluble in CCl_4 Soluble in water

At this point the rate at which iodine passes from CCl_4 to water equals the rate at which it passes from water to CCl_4.

So 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. As a result, the brown colour of the tri–iodide ions fades and the purple colour or free iodine molecules appears in organic phase. To achieve a good separation, the two liquids are gently shaken to increase their area of contact and improve the chances of transferring iodine molecules. 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

$$K = \frac{[I_2\ (CCl_4)]}{[I_2 \text{ as } I_3^-\ (H_2O)]}$$

At 25^oC value of K for equilibrium is 85. This means that concentration of I_2 in CCl_4 is 85 times higher than water. This is because I_2 is a non polar solute and it is more soluble in non polar solvent (CCl_4) than in water which is polar solvent.

CHROMATOGRAPHY

Introduction:

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

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. The **stationary phase** may be a solid or a liquid supported as a thin film on the surface of an inert solid. The **mobile phase** flowing over the surface of the stationary phase may be a gas or a liquid. The phase over which mobile phase flow is called **stationary phase** and solvent used to separate the components is called **mobile phase**.

Principle:

In chromatography, substances are separated due to their relative affinities for the stationary and mobile phases. The distribution of the components of a mixture between the two phases is governed by distribution coefficient K_D.

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

The component of a mixture with a small value of K_D mostly remains in the stationary phase as the moving phase flows over it. The component with a greater value of K_D remains largely dissolved in the mobile phase and passes over the stationary phase quickly.

On the basis of mechanism, there are two types of chromatography.

(i) Adsorption Chromatography:

Chromatography in which the **stationary phase** is a **solid**, is classified as adsorption chromatography. In this type, a substance leaves the mobile phase which may be liquid or gas to become absorbed on the surface of the solid phase, e.g., column chromatography.

(ii) Partition Chromatography:

Chromatography in which the stationary phase is a liquid is called **partition chromatography**. In this type, separation involve distribution of components between stationary phase and mobile phase. Distribution is based upon the solubility, e.g., paper chromatography.

There are various techniques of chromatography.

(i) Paper chromatography (ii) Thin layer chromatography (TLC) (iii) Column chromatography (iv) Gas–liquid chromatography (GLC) (v) High performance liquid chromatography (HPLC) (vi) Paper chromatography.

Paper Chromatography:

It is a technique of partition chromatography. Paper is made up of cellulose. The stationary phase in paper chromatography is the moisture or water which is present in the paper. Mobile phase is the solvent used in chromatographic tank. Solvent or mobile phase is also called **Eluent**. Solvent may be a single substance or the mixture of many substances.

There are three ways of papers chromatography (a) ascending (b) descending (c) radial or circular.

In ascending chromatography, solvent move upward, and in descending chromatography solvent move downward. In radial chromatography, circular paper is taken with a wick but parallel to radius from edge to center. The sample is applied at the center of the paper and solvent is supplied through the wick. The solvent ascends the wick an then goes radically through the paper.

Ascending Paper Chromatography:

In ascending paper chromatography, solvent moves upward. Solvent is taken in the chromatographic tank. Solvent travel upward in paper through capillary action. (Rising of solvent is small bore tube is called **capillary action**).

A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatography tank. Cover the tank to homogenize its inner atmosphere. Take about 20 cm strip of Whattman's chromatographic paper No. 1 and draw on it a thin line about 2.5 cm from one end with lead pencil. This line is called **base line**.

Apply the mixture sample on base line with the help of capillary jet. To facilitate identification of the components of the mixture, spots of the known compounds may also be placed alongside.

When the spots have dried, suspend the paper with clips so that the base line end dips into solvent mixture to a depth of 5 – 6 mm. Base line should not dip in mobile phase. Cover the tank with lid. As the solvent front passes the spots, the solutes begin to move upward. The rate at which they move depends on their distribution coefficients. When the solvent front has risen to about $\frac{3}{4}$ th of the length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry.

The dried paper at which various components have been separated is called **chromatogram**.

The different components of the mixture, if coloured, can visually be identified. If colourless, the chromatogram has to be developed by chemical methods (locating agents) or physical techniques used to identify the spots. Each component has a specific retardation factor called $\mathbf{R_f}$ **value**. The R_f value is related to its distribution coefficient and is given by:

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

Uses of Chromatography:

(1) The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products.

(2) They are equally important in qualitative and quantitative analysis and for determination of the purity of a substance.

EXERCISE

Q.1 Multiple choice questions:

(i) A filtration process could be very time consuming if it was not aided by a gentle suction which is developed:

(a) If the paper covers the funnel up to its circumference.

(b) If the paper has got small sized pores in it.

(c) If the stem of the funnel is larger so that it dips into the filtrate.

(d) If the paper fits tightly.

(ii) During the process of crystallization, the hot saturated solution:

(a) Is cooled very slowly to get larger sized crystals.

(b) Is cooled at a moderate rate to get medium sized crystals.

(c) Is evaporated to get the crystals of the product.

(d) Is mixed with an immiscible liquid to get the pure crystals of the products.

(iii) Solvent extraction is an equilibrium process and it is controlled by:

(a) Law of mass action

(b) The amount of solvent used

(c) Distribution law

(d) The amount of solute

(iv) Solvent extraction method is a particularly useful technique for separation when the product to be separated is:

(a) Non–volatile or thermally unstable

(b) Volatile or thermally stable

(c) Non–volatile or thermally stable

(d) Volatile or thermally unstable

(v) The comparative rates at which the solute move in paper chromatography depend on:

(a) The size of paper used

(b) R_f values of solutes

(c) Temperature of the experiment

(d) Size of the chromatographic tank used

ANSWERS

Answers		Reasons
(i)	(d)	When filtration paper is inserted into moistened funnel, paper fits tightly to its circumstance and gentle suction is developed. In this case filtration is faster, otherwise slow and time consuming.
(ii)	(b)	Slow cooling produces big crystals which has following disadvantages: (i) Crystals include large amount of solvent making the drying process difficult. (ii) Crystals may include impurities hindering the process of purification. Fast (rapid) cooling leads to improper crystallization. Hence, cooling is done at moderate rate to get medium sized crystals.
(iii)	(c)	According to distribution law, solute distributes itself between two immiscible solvents in constant ratio of concentration irrespective of the amount of solute added. In a single extraction amount of solute extracted cannot exceed constant ratio. Hence, controlled by distribution law.
(iv)	(d)	For separation of volatile or thermally unstable product solvent extraction is employed, since no other technique involving heat is useful. Because on heating volatile product evaporates and thermally unstable product decomposes.
(v)	(b)	R_f stands for retardation factor or retention factor. The rate at which a solute moves in chromatography depends upon the fact that how much solute is retarded on stationary phase. Different solutes have different retardation factor in a specific solvent.

Q.2 Fill in the blanks.

(i) A complete chemical characterization of a compound must include __________.

(ii) During filtration the tip of the stem of the funnel should touch the side of the beaker to avoid __________.

(iii) A fluted filter paper is used to __________the process of filtration.

(iv) A solvent used for crystallization is required to dissolve __________ of the substance at its boiling point and __________ at the room temperature.

(v) Repeated solvent extractions used small portions of solvent are __________ than using a single extraction with larger volume of the solvent.

ANSWERS

(i)	Quantitative and qualitative analysis	**(ii)**	Splashing	**(iii)**	Speed up
(iv)	Large amount, small amount	**(v)**	Efficient		

Q.3 Tick the correct sentences. If the sentence is incorrect, write the correct statement:

(i) A qualitative analysis involves the identification of elements present in a compound.

(ii) If the process of filtration is to run smoothly, the stem of the funnel should remain empty.

(iii) If none of the solvents is found suitable for crystallization, a combination of two or more immiscible solvents may be used.

(iv) A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added.

(v) Paper chromatography is a technique of partition chromatography.

ANSWERS

Answers		Correct Statement
(i)	True	
(ii)	False	If the process of filtration is to run smoothly, the stem of the funnel should be continuously full of liquid.
(iii)	False	If none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be used.
(iv)	False	A solute distributes itself between two immiscible liquids in a constant ratio of concentration independent of amount of solvent added.
(v)	True	

Q.4 Why is there a need to crystallize the crude product?

Ans. The crude product have soluble and insoluble impurities. The insoluble impurities are removed by filtration. The soluble impurities are removed by crystallization. The actual product is crystallized out and impurities remain soluble, and crystals of the product are separated by filtration and dried.

Q.5 A water insoluble organic compound aspirin is prepared by the reaction of salicylic acid with a mixture of acetic acid and acetic anhydride. How will you separate the product from the reaction mixture?

Ans. Aspirin being water insoluble can be separated by filtration.

The reaction mixture is added to cold water, aspirin crystallizes out, while other products remain soluble. Aspirin is filtered from water by using sintered glass crucible or filter paper.

Q.6 A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe the method to obtain it from this layer.

Ans. Solvent extraction technique is used to obtain the compound from aqueous layer. Chloroform is added to aqueous layer, the organic compound distributes itself between two layers which are separated by separating funnel. The extraction is separated using small volumes of chloroform for maximum efficiency. The chloroform layer is evaporated to get pure compound.

Q.7 The following figure shows a developed chromatogram on paper with five spots.

(i) Unknown mixture X **(ii) Sample A**
(iii) Sample B **(iv) Sample C**
(v) Sample D

Find out (i) the composition of unknown mixture (ii) which sample is impure and what is its composition.

Ans.(i) The composition of unknown mixture X is B + C i.e. it is a mixture of a sample B and C. Since, the R_f value of two spots of mixture 'X' matches with R_f values of two spots of pure samples B and C.

$X = B + C$

(ii) Sample D is impure since it has two spots on chromatogram. A pure sample always have one spot on chromatogram. Its composition is A and C since, R_f values of its spots matches with R_f values of two spots of pure sample 'A' and 'C'.

Q.8 In solvent extraction technique, why repeated extraction using small portions of solvent are more efficient than using a single extraction but larger volume of solvent.

Ans. For example, we want to separate a solute from aqueous layer by using another immiscible organic solvent. Place the aqueous layer containing solute in separating funnel followed by organic solvent. Shake the mixture well and allow it to stand. The solute will distribute itself in constant ratio of concentration between two solvents and equilibrium is reached. At this stage, the value of distribution co–efficient will be

$$K = \frac{\text{Concentration of solute in organic solvent}}{\text{Concentration of solute in aqueous layer}}$$

Then separate the layer and add small portion of fresh organic solvent in separating funnel containing aqueous layer. The solute starts moving towards fresh organic layer. Since it has no concentration of solute before, and equilibrium is reached. Repeat the process. Every time more and more solute is extracted and finally we have maximum amount of solute extracted.

Q.9 Write down the main characteristics of a solvent selected for crystallization of a compound.

Ans. The main characteristics are:

1. It should dissolve large amount of solute at its boiling point and small amount at its room temperature.
2. It should not chemically react will the solute.
3. It should either not dissolve impurities or impurities should not crystallize out from it along with the solute.
4. It should be cheaper / inexpensive.
5. On cooling, it should deposit well formed crystals of a pure compound.
6. It should be safe to use and easily removable.

Q.10 You have been provided with a mixture containing three inks of different colours. Write down the procedure to separate the mixture using paper chromatography.

Ans. The following steps are involved to separate the mixture of inks.

(1) Cut the strips of Whattman's filter paper.

(2) Mark base line one inch above the bottom with the lead pencil.

(3) Apply mixture of inks on the base line.

(4) Put some solvent (eluent) in the chromatographic tank and cover it for some time.

(5) Dip the paper in the solvent in such a way that base line should not dip in the solvent.

(6) Cover the chromatographic tank and wait for about 30 minutes so that the solvent moves upward.

(7) Put out the paper from the tank and mark the solvent front with the pencil.

(8) Find out R_f value of each spot of ink.

$$R_f = \frac{\text{Distance travelled by solute from base line}}{\text{Distance travelled by the solvent front}}$$

(The paper at which mixture of ink have been separated is called **chromatogram**).

Q.11 Why fluted filter paper is more effective?

Ans. The filter paper folded in such a way that fan like arrangement with alternate elevation and depression at various folds is formed. It increases the surface area and the rate of evaporation in enhanced.

DO YOU KNOW?

1. The rate of filtration through conical funnel can be increased by using a fluted filter paper.
2. In the fluted filter paper, the surface area increases and rate of filtration also increases.
3. Silica gel, $CaCl_2$ and P_2O_5 are important desiccating agents.
4. The solvent used in the chromatographic tank is called "**Eluent**".
5. The concentration of I_2 in CCl_4 is 85 times more than in H_2O.
6. Naphthalene is also called **moth–balls**.
7. The chromatography in which stationary phase is solid is called adsorption chromatography.
8. The chromatography in which stationary phase in liquid is called partition chromatography.
9. Gooch crucible is made of porcelain.
10. Sintered glass crucible is made of glass having porous glass disc sealed at the bottom.

Chapter 3

GASES

MATTER

"Any thing which occupies space and has mass is called **matter**."

There are four states of matter Gas, liquid, solid and plasma state.

Liquids are less common than solids, gases and plasmas. The reason is that the liquid state of any substance can exist only within a relatively narrow range of temperature and pressure.

PROPERTIES OF GASES

1.	**Volume**	Gases don't have a definite volume and occupy all the available space. The volume of a gas is the volume of the container.
2.	**Shape**	They don't have a definite shape and take the shape of the container just like liquids.
3.	**Density**	Due to low densities of gases as compared to those of liquids solids, the gases bubble through liquids and tend to rise up.
4.	**Pressure**	Molecules of gases are in a constant state of random motion. They can exert a certain pressure on the walls of the container and this pressure is due to the number of collisions.
5.	**Expansion**	Gases can expand on heating or by increasing the available volume. Liquids and solids, on the other hand, do not show an appreciable increase in volume when they are heated.
6.	**Diffusion**	Gases can diffuse and effuse. This property is negligible in solids but operates in liquids as well.
7.	**Compressibility**	Gases can compressed by applying a pressure because there are large empty spaces between their molecules.
8.	**Intermolecular force**	The intermolecular forces in gases are very weak.
9.	**Joule–Thomson effect**	When sudden expansion of compressed gases take place from a very small hole, it cause cooling. It is called Joule Thomson effect.

Properties of Liquids:

1.	**Shape volume**	Liquids don't have a definite shape but have a definite volume. Unlike solids they adopt the shape of the container.
2.	**Diffusion and evaporation**	Molecules of liquids are in a constant state of motion. The

	evaporation and diffusion of liquid molecules is due to this motion.
3. Empty space	The spaces among the molecules of liquids are negligible just like solids.
4. Density	The densities of liquids are much greater than those of gases but are close to those of solids.
5. Kinetic energy	Molecules of liquid possess kinetic energy due to their motion. Liquids can be converted into solids on cooling i.e., by decreasing their kinetic energy. Molecules of liquids collide among themselves and exchange energy but those of solids can not do so.
6. Intermolecular force	The intermolecular attractive forces in liquids are intermediate between gases and solids. The melting and boiling points of gases, liquids and solids depend upon the strength of such forces.

Properties of Solids:

1. Shape and volume	There are strong attractive forces in solids which hold the particles together firmly and for this reason solids have definite shape and volume.
2. Diffusion	The particles present in solid substances are very close to each other and they are tightly packed. Due to this reason solids are non–compressible and they cannot diffuse into each other.
3. Vibrational motion	The solid particles possess vibrational motion only.

Units of Pressure:

The atmosphere of earth is a mixture of gases and that exerts pressure called **atmospheric pressure**. Atmosphere pressure is measured with barometer. The standard atmospheric pressure is defined as:

"The force exerted by 76 cm long column of Hg on the area of 1 cm^2 at 0^oC at sea level is called **standard atmospheric pressure**."

At sea level atmospheric pressure is 76 cm Hg or 760 mm Hg or 1 atmosphere.

1 atmosphere = 76 cm Hg
= 760 mm Hg
= 760 torr
= 101325 Nm^{-2} (SI units)
= 101325 Pascal (SI units)
= 101.325 Kilo Pascal
= 14.7 PSi (Pounds per $inch^{-2}$)
= 1.01325 bar
= 1013.25 millibar

where 1 mm Hg = 1 torr,

1 bar = 100,000 Pascal (Pa)

1 Pascal = 1 Nm^{-2}

The unit pound per square inch (PSi) is used most commonly in engineering work. The unit millibar is commonly used by meteorologists.

Atmospheric pressure decreases as we go at higher altitude due to decrease in the concentration of air.

SCALES OF THERMOMETRY

Three scales of temperature are commonly used.

(a) Celsius or Centigrade Scale (^oC):

In this scale, freezing point of water at 1 atmospheric pressure is 0^oC and boiling point is 100^oC.

Space between the two marks of temperature is equally divided into 100 parts. Each part is equal to 1^oC.

(b) Fahrenheit Scale (^oF):

In this scale freezing point of water at 1 atmospheric pressure is 32^oF and boiling point is 212^oF. The space between the two marks of temperature is divided into 180 parts and one part is equal to 1^oF.

(c) Absolute Scale or Kelvin Scale (K):

In this scale, the melting point of ice or freezing point of water at one atmospheric pressure is 273 K and boiling point of water is 373 K. Centigrade can be change into Kelvin scale as

$$K = {}^oC + 273$$

Celsius scale and Fahrenheit are inter convertible

$$\frac{^oC}{5} = \frac{^oF - 32}{9}$$

$$^oC = \frac{5}{9}[^oF - 32]$$

$$F^\circ = \frac{9}{5}(^oC) + 32$$

$$(-40^oC = -40F^\circ]$$

Example: Convert 50°C into F°.

$$F^\circ = \left(50 \times \frac{9}{5}\right) + 32$$

$$= 90 + 32 = 122^\circ F$$

Gas Laws:

"The uniform change in the behaviour of different gases by changing the condition of temperature, pressure and volume are called **gas law**."

BOYLE'S LAW

Robert Boyle's gave this law in 1662. This law states that

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

Mathematically $V \propto \frac{1}{P}$

or $V = \frac{k}{P}$

$PV = k$ (when T and n are constant) (1)

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

According to the Equation (1) Boyle's law can also be defined as

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

We can write this as

$P_1 V_1 = k$ and $P_2 V_2 = k$

Hence $P_1 V_1 = P_2 V_2$

$P_1 V_1$ are the initial values of pressure and volume, while, $P_2 V_2$ are the final values of pressure and volume.

Experimental Verification of Boyle's Law:

The following diagram indicates that at constant temperature say to 25°C, the volume of a given quantity of a gas is reduced in proportion to the increase in pressure. Let us take a gas in a cylinder having a moveable piston. The cylinder is also attached with a manometer (a pressure measuring device) to read the pressure of the gas directly. Let the initial volume of gas is 1 dm^3 and its pressure is 2 atmospheres when the piston has one weight out it. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres. Similarly when the pistons is loaded with a mass three times greater, then the pressure becomes six atmospheres. The initial volume of the gas at two atmospheres is 1 dm^3, it is reduced to $\frac{1}{2}$ dm^3 and then $\frac{1}{3}$ dm^3 with increase of weights, respectively

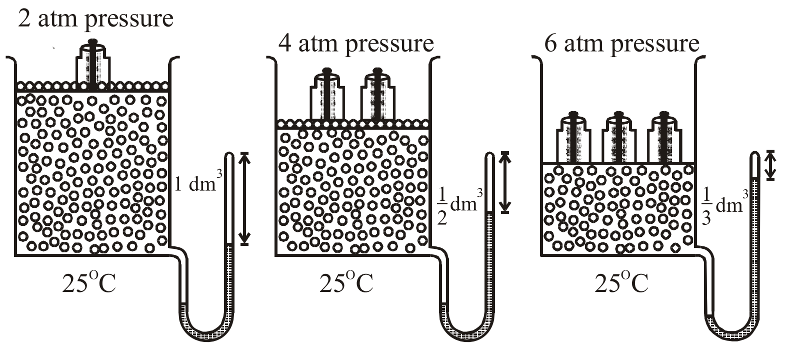
$P_1 V_1 = 2 \text{ atmosphere} \times dm^3 = 2 \text{ dm}^3 \text{ atmosphere} = k$

$P_2 V_2 = 4 \text{ atmosphere} \times \frac{1}{2} \text{ dm}^3 = 2 \text{ dm}^3 \text{ atmosphere} = k$

$P_1 V_1 = 6 \text{ atmosphere} \times \frac{1}{3} \text{ dm}^3 = 2 \text{ dm}^3 \text{ atmosphere} = k$

Hence Boyle's law is verified.

The value of k will remain the same for the same quantity of a gas at the same temperature.



Verification of Boyle's Law

Example 1:

As gas having a volume of 10 dm^3 is enclosed in a vessel to 0^oC and the pressure is 2.5 atmospheres. This gas is allowed to expand until the new pressure is 2 atmospheres. What will be the new volume of this gas, if the temperature is maintained at 273 K.

Solution:

Initial volume of gas (V_1) = 10 dm^3

Initial temperature (T_1) = 0^oC + 273 K = 273 K

Initial pressure (P_1) = 2.5 atmosphere

Final pressure (P_2) = 2 atmosphere

Final temperature (T_2) = 273 K

Final volume (V_2) = ?

Since the temperature is constant ($T_1 = T_2$) Boyle's law is applicable $P_1 V_1 = P_2 V_2$ (when T and n are constant).

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

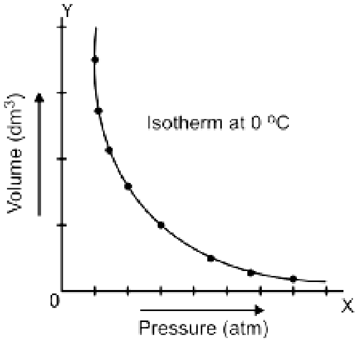
$$V_2 = \frac{2.5 \text{ atm} \times 10 \text{ dm}^3}{2 \text{ atm}} = 12.5 \text{ dm}^3$$

Graphical Explanation of the Boyle's Law:

(a) Pressure volume isotherm:

Let us take a particular amount of a gas at constant temperature say 0^oC and enclose it in a cylinder having a piston in it. When the pressure of the gas is varied, its volume changes. Increase in pressure decreases the volume. If a graph is plotted between pressure on the x–axis (abscissa) and volume on the y–axis (ordinate), then a curve is obtained as shown in the figure.

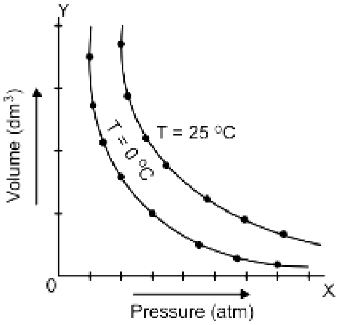
This curve is called **isotherm** ("iso" means same, "therm" means heat).



Isotherm at 0 °C

(b) Isotherm at different temperatures:

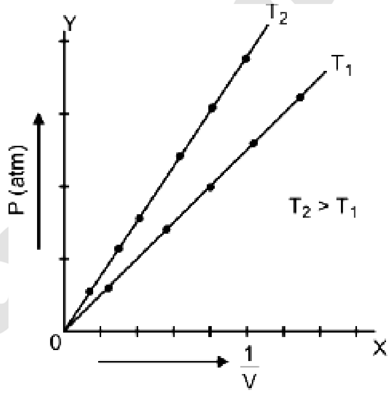
Now increase the temperature of the gas to $25^{o}C$. Keep this temperature constant and again vary the pressure and volume. Again plot the isotherm, which goes away from the both the axes as shown in figure. The reason is that, at higher temperature, the volume of the gas has increased. Similarly, if we increase the temperature further, make it constant and plot another isotherm, it further goes away from the axes.



A plot between pressure and volume of gas at different temperature.

(c) Graph between P and $\frac{1}{V}$ at different temperature:

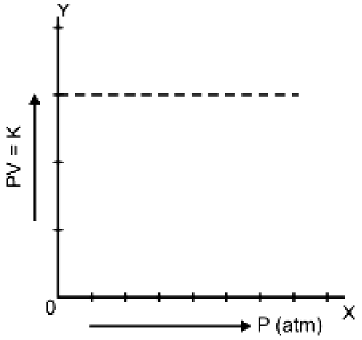
If a graph is plotted between $\frac{1}{V}$ on x–axis and the pressure P on the y–axis then a straight lines is obtained as shown in the figure. This shows that the pressure and inverse of volume are directly proportional to each other. This straight line will meet at the origin which means that when 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 $\frac{1}{V}$ will give another straight line. This straight line at T_2 will be closer to the y–axis.



A plot between P and 1/V

(d) Graph between PV and P:

Again if we plot a graph between pressure on x–axis and the product PV on y–axis, then 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 increases, but PV remains constant and a straight line parallel to the pressure axis is obtained. This type of straight line will help us to understand the non–ideal behaviour of gases. Boyle's law is applicable only to ideal gases.



A plot between pressure and product of PV

CHARLES'S LAW

This law was given by **French Scientist J. Charles in 1787**.

This law state as:

"Volume of the given mass of a gas is directly proportional to the absolute temperature at constant pressure."

Mathematically

$V \alpha T$ (when pressure and number of moles are constant).

$$V = kT$$

$$\frac{V}{T} = k$$

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

$$\frac{V_1}{T_1} = k \text{ and } \frac{V_2}{T_2} = k$$

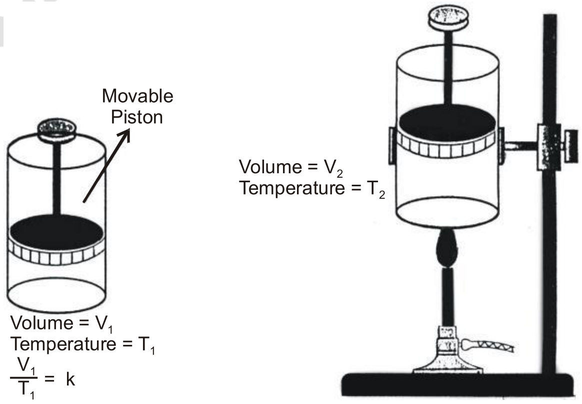
So $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

We can say that "for the given mass of gas, the ratio of volume and temperature remains constant at constant pressure."

Experimental Verification of Charles's Law:

Let us consider some amount of gas is present in cylinder. The piston of cylinder is moveable and frictionless. The volume of the gas is V_1 and its temperature is T_1. When we heat the gas, the average kinetic energy of the molecules increases, as the result, the force of collision per unit area also increases. By increasing the force of collision at unit area, pressure increase. When piston moves upward, due to pressure, the volume of the gas increases. By increasing volume, the pressure of gas reduces and remains constant. Hence

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



Verification of Charle's Law

Example 2:

250 cm^3 of hydrogen is cooled from 127^oC to -27^oC by maintaining the pressure constant. Calculate the new volume of the gas at low temperature.

Solution:

Pressure has been kept constant so this gas is obeying the Charles's law.

Initial volume (V_1) = 250 cm^3 = 0.25 dm^3

Initial temperature (T_1) = $127^oC + 273$ = 400 K

Final temperature (T_2) = $-27^oC + 273$ = 246 K

Final volume (V_2) = ?

According to Charles's law

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

(when pressure and number of moles are constant).

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

$$V_2 = \frac{0.25\ dm^3 \times 246\ K}{400\ K} = 0.153\ dm^3 = 153\ cm^3$$

Derivation of absolute zero:

Concept of absolute zero is derived from the quantitative definition of Charles's law.

"At constant pressure, the volume of the given mass of a gas increases or decreases by $\frac{1}{273}$ of its original volume at 0^oC for every 1^oC rise or fall in temperature, respectively.

Original volume is the volume of gas at 0^oC:

In order to understand the above statement, look at the Table of temperature volume data of a hypothetical gas. At 0^oC the volume of the gas taken is 546 cm^3. At 273^oC the volume of the gas has doubled (1092 cm^3) and it should become practically zero at -273^oC.

The general equation to know the volumes of the gas at various temperatures is

$$V_T = V_0 + \frac{V_0 t}{273}$$

$$V_T = V_0\left(1 + \frac{t}{273}\right) \qquad (3)$$

where V_T = Volume of gas at temperature t

V_0 = Volume of gas at 0^oC

t = Temperature on centigrade or Celsius scale.

If a gas is warmed by 1^oC, expands by $\frac{1}{273}$ of its original volume at 0^oC. Since original volume is 546 cm^3, so for 1^oC rise in temperature 2 cm^3 increase in volume will take place. Similarly, for 100^oC rise in temperature, a change of 200 cm^3 will take place.

By decreasing temperature of 1^oC, the decrease in original volume is $\frac{1}{273}$ of original volume, which is 2 cm^3 or $\frac{1}{273} \times 546$.

The quantitative change in volume by changing temperature is shown in the Table.

TABLE

Volume (cm^3)	Temperature ^oC	Kelvin temperature K
1092	273	546
946	200	473
746	100	373
566	10	283
548	1	274
546	0	273
544	– 1	272
526	– 10	262
346	– 100	173
146	– 200	73
0	– 273	0

The ratio of $\frac{V}{T}$ remains same for an ideal gas.

If we plot a graph with temperature at x–axis and volume at y–axis, a straight line is obtained. The slope of this straight line is different for different masses of the same gas. The slope is also different for different gases.

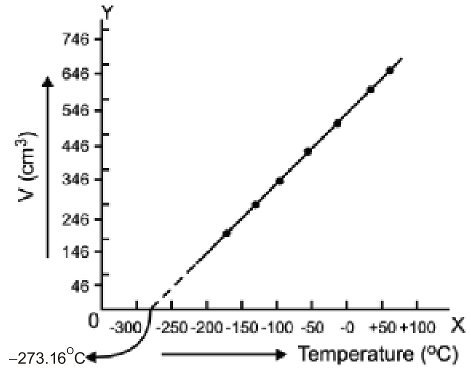
When we reduce the temperature of a gas. Its volume reduces and distances between molecules also decreases. Intermolecular forces become more prominent at low temperature. By decreasing temperature a stage will reach that all gases becomes liquids or solid and do not obey the Charles's law. If we extrapolate this line of V – T, it touches the x–axis at – 273.15^{o}C. This – 273.15^{o}C is called **absolute temperature**. It is defined as

"The hypothetical temperature (–273.16°C) at which volume of the gases become zero is called **absolute zero**."

or "The temperature at which motion of molecules ceases is called **absolute zero**."

The difference between the 0^{o}C and OK is of 273, so when we change Celsius scale to Kelvin scale we add 273 in it.

$^oC + 273 = K$



Can we use ^{o}C Temperature in Charles's Law?

Celsius temperature cannot be used in Charles's law or general gas equation or combined gas law. For example, in Charles's law ratio of $\frac{V}{T}$ will be in minus if the Celsius scale is used below 0^{o}C. Consider a gas has a volume 400 cm^3 at – 73^{o}C. The ratio of $\frac{V}{T}$ will be – 5.479

which is incorrect. If this temperature is taken in Kelvin scale (– 73 + 273 = 200 K), the ratio of $\frac{V}{T}$ will be 2.

GENERAL OR IDEAL GAS EQUATION

This equation has a relationship between temperature, volume, pressure and moles of the gases.

According to Boyle's law

$V \propto \frac{1}{P}$ (when n and T are constant)

According to Charles's law

$V \propto T$ (when n and P constant)

It is a well known fact that volume of the given gas at constant temperature and pressure is directly proportional to the number of moles (Avogadro's law).

$V \propto n$ (when P and T are held constant)

If we think for a moment that none of the variables are to be kept constant then all the above three relationships can be joined together.

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

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

The constant suggested is R which is called **general gas constant**.

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

$$PV = nRT \qquad (1)$$

The Equation (2) is called an **ideal gas equation**. It is also known as general gas equation.

This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature. This equation is reduced to Boyle's law, Charles's law and Avogadro's law, when appropriate variables are held constant.

$PV = nRT$, when T and n are held constant, $PV = k$ (Boyle's law).

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

Combined gas law:

For one mole of a gas, the general gas equation is

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

$$\text{Hence } \frac{P_1 V_1}{T_1} = R \quad \frac{P_2 V_2}{T_2} = R$$

$$\text{Therefore } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad (2)$$

This Equation (2) is called **combined gas law**.

DENSITY OF AN IDEAL GAS

For calculating the density of an **ideal gas**, we substitute the value of number of moles (n) of the gas in terms of the mass (m), and the molar mass (M) of the gas.

$$n = \frac{m}{M} = \frac{\text{mass}}{\text{molar mass}}$$

$$PV = \frac{m}{M} RT \qquad (3)$$

Equation (3) may be employed to calculate the mass of a gas whose P, T, V and molar mass are known. Rearranging Equation (3).

$$PM = \frac{m}{V} RT$$

$$PM = d\,RT \qquad \left(d = \frac{m}{V}\right)$$

$$d = \frac{PM}{RT} \qquad (4)$$

Hence the density of an ideal gas is directly proportional to its molar mass. Greater the pressure on the gas, closer will be the molecules and greater the density. Higher temperature makes the gases to expand, hence density falls with the increase in temperature.

Significance of Density Equation:

If we determine the pressure, density and temperature, the molecular mass of the gas can be calculated.

$$PM = d\,RT$$

$$M = d\frac{RT}{P}$$

Units of Gas Density:

If pressure is taken in atmosphere, M in g mole^{-1} T in Kelvin and R in dm^3 atmosphere K^{-1} mole^{-1} the unit of d will be

$$d = \frac{PM}{RT} = \frac{\text{atm} \times \text{g mole}^{-1}}{\text{dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1} \times \text{K}}$$

$d = g/dm^3$

IDEAL GAS CONSTANT R

The value of R depends upon the units chosen for pressure, volume and temperature.

(a) When P is in atmosphere and V in dm^3:

$n = 1$ mole $\quad T = 273.15$ K

$V = 22.414\ dm^3 \quad P = 1$ atmosphere

[Values of molar volume]

$$R = \frac{PV}{nT}$$

$$R = \frac{1\ atm \times 22.414\ dm^3}{1\ mole \times 273.15\ K}$$

$$R = 0.0821\ dm^3\ atmosphere\ K^{-1}\ mole^{-1}$$

The physical meanings of this value is that if we have one mole of an ideal gas at 273.15 K and one atmospheric pressure and its temperatures is increased by 1 K then it will absorb 0.0821 dm^3 atmosphere of energy, dm^3 atmosphere being the unit of energy. Hence the value of R is a universal parameter for all the gases. It tells us that the Avogadro's number of molecules of all the ideal gases have the same demand of energy.

(b) When P is in mm Hg torr and V in dm^3:

$n = 1$ mole $\quad T = 273.15$ K

$V = 22.414\ dm^3 \quad P = 760$ mm Hg

$$R = \frac{PV}{nT}$$

$$R = \frac{760\ mm\ Hg \times 22.414\ dm^3}{1\ mol \times 273.15\ K}$$

$$R = 62.4\ dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$$

or $$R = 62400\ cm^3\ torr\ K^{-1}\ mol^{-1}$$

(c) When P is in Nm^{-2} and V in m^3 (SI units):

$n = 1$ mole $\quad T = 273.15$ K

$P = 101325\ Nm^{-2} \quad V = 22.414\ dm^3 = 0.022414\ m^3$

$$R = \frac{PV}{nT}$$

$$R = \frac{101325\ Nm^{-2} \times 0.022414\ m^3}{1\ mole \times 273.15\ K}$$

$$R = 8.3143\ Nm\ K^{-1}\ mol^{-1}$$

$1\ Nm = 1\ J$

So $R = 8.3143\ J\ K^{-1}\ mol^{-1}$

$R = 8.3143 \times 10^{7}\ erg\ K^{-1}\ mol^{-1}$ (where $1\ J = 10^{7}\ erg$)

$1\ cal = 4.184\ J$

So $\frac{8.313}{4.184} = 1.987\ cal\ K^{-1}\ mol^{-1}$

Example 3:

A sample of nitrogen gas is enclosed in a vessel of volume 380 cm^3 at 120^oC and pressure of 101325 Nm^{-2}. This gas is transferred to a 10 dm^3 flask and cooled to 27^oC. Calculate the pressure in Nm^{-2} exerted by the gas at 27^oC.

Solution:

All the three parameters of this gas have been changed, so we can solve this problem by using the general gas equation.

Initial volume of the gas (V_1) = 380 cm^3 = 0.38 dm^3

Initial temperature (T_1) = $120^oC + 273$ = 393 K

Initial pressure (P_1) = 101325 Nm^{-2}

Final volume (V_2) = 10 dm^3

Final temperature (T_2) = $27^oC + 273$ = 300 K

Final pressure (P_2) = ?

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

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

$$P_2 = \frac{101325\ Nm^{-2} \times 0.38\ dm^3 \times 300\ K}{393\ K \times 10\ dm^3}$$

$$P_2 = 2939.1\ Nm^{-2}$$

Example 4:

Calculate the density of CH_4 (g) at 0^oC and 1 atmospheric pressure. What will happen to the density if (a) temperature is increased to 27^oC, (b) the pressure is increased to 2 atmospheres at 0^oC.

Solution:

Formula for density of a gas at any temperature and pressure.

$$d = \frac{PM}{RT}$$

Nature of the gas = CH_4

Temperature of the gas = $0^oC + 273 = 273\ K$

Pressure of the gas = 1 atmosphere

Molecular mass of the gas = $16\ g\ mole^{-1}$

Gas constant (R) = $0.0821\ dm^3$ atmosphere $K^{-1}\ mole^{-1}$

$$d = \frac{PM}{RT}$$

$$d = \frac{1\ atm \times 16\ g\ mole^{-1}}{0.0821\ dm^3\ atm\ K^{-1}\ mole^{-1} \times 273\ K}$$

$$d = \frac{16}{0.0821 \times 273}\ g\ dm^{-3}$$

$$d = 0.7138\ g\ dm^{-3}$$

So under the conditions $1\ dm^3$ of CH_4 has a mass of 0.7138 g.

Density at 27^oC:

Temperature = $27 + 273 = 300\ K$

$$d = \frac{PM}{RT}$$

$$d = \frac{1\ atm \times 16\ g\ mole^{-1}}{0.0821\ dm^3\ atm\ K^{-1}\ mole^{-1} \times 300\ K}$$

$$d = 0.649\ g\ dm^{-3}$$

So, by increasing the temperature from 0^oC to 27^oC the density of gas has decreased from 0.7138 to 0.649 $g\ dm^{-3}$.

Density at 2 atmospheric pressure and 0^oC:

$T = 0^oC + 273 = 273\ K$

P = 2 atmosphere

$$d = \frac{PM}{RT}$$

$$d = \frac{2\ atm \times 16\ g\ mole^{-1}}{0.0821\ dm^3\ atm\ K^{-1}\ mole^{-1} \times 273\ K}$$

$$d = 1.427\ g\ dm^{-3}$$

The increase of pressure has increased the density of CH_4. The density has almost doubled by doubling the pressure.

Example 5:

Calculate the mass of 1 dm^3 of NH_3 gas at 30^oC and 1000 mm Hg pressure, considering that NH_3 is behaving ideally.

Solution:

General gas equation $PV = \frac{m}{M}RT$ can be used to calculate the mass (m) of the gas.

Pressure of the gas = 1000 mm Hg = 1.315 atmosphere

Volume of the gas = 1 dm^3

Temperature of the gas = $30^oC + 273 = 303$ K

Molecular mass of the gas = 17 g $mole^{-1}$

$$PV = \frac{m}{M}RT$$

$$m = \frac{PVM}{RT}$$

$$m = \frac{1.315 \text{ atm} \times 1 \text{ dm}^3 \times 17 \text{ g mole}^{-1}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1} \times 303 \text{ K}}$$

$$m = \frac{1.315 \times 1 \times 17 \text{ g}}{0.0821 \times 303} = 0.896 \text{ g}$$

This is the mass of 1 dm^3 of NH_3 under the given conditions. In other words, it is the density of NH_3, if it is acting as an ideal gas.

AVOGADRO'S LAW

"Equal volume of ideal gases at the same temperature and pressure contain equal number of molecules."

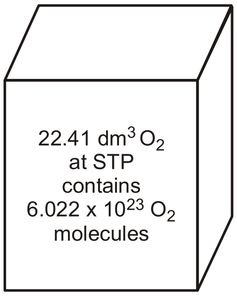
This statement is indirectly the same as has been used for evaluating the general constant R i.e. one mole of an ideal gas at 273.15 K and one atmosphere pressure has a volume of 22.414 dm^3. Since one mole of gas have Avogadro's number of particles, so 22.414 dm^3 of various ideal gases as STP will have Avogadro's number of molecules i.e. 6.02×10^{23}.

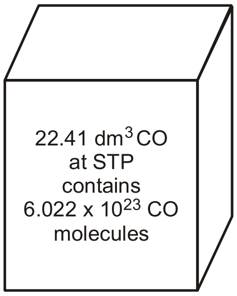
22.414 dm^3 of a gas at 273.15 K and one atmosphere pressure has number of molecules = 6.02×10^{23}.

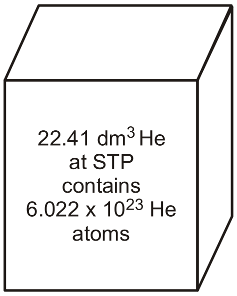
22.414 dm^3 of O_2 at STP has molecules = 6.02×10^{23}.

22.414 dm^3 of CO at STP has molecules = 6.02×10^{23}.

22.414 dm^3 of He at STP has molecules = 6.02×10^{23}.







In other words if we have one dm^3 of each of H_2, O_2, N_2 and CH_4 in separate vessels at STP, then the number of molecules in each will be 2.68×10^{22} (Divide N_A by 22.414).

$$\frac{6.02 \times 10^{23}}{22.414} = 2.68 \times 10^{22}$$

similarly when the temperature or pressure are equally changed for these four gases, then the new equal volumes will have the same 2.68×10^{22} number of molecules.

No doubt, one dm^3 of H_2 at STP weighs approximately 0.0899 grams and one dm^3 of O_2 at STP weighs 1.4384 g, but their number of molecules are the same. Although, oxygen molecule is 16 times heavier then hydrogen but this does not disturb the volume occupied, because molecules of the gases are widely separated from each other at STP. One molecule is approximately at a distance of 300 times its own diameter from its neighbour at room temperature.

DALTON'S LAW OF PARTIAL PRESSURE

"Total pressure exerted by the mixture of non–reacting gases is equal to the sum of their individual partial pressures."

Let a mixture consist of three gases 1, 2, and 3 and have partial pressures P_1, P_2 and P_3 respectively. Total pressure will be

$$P_1 = P_1 + P_2 + P_3$$

Partial Pressure:

"The pressure of an individual gas in the mixture of gases is called **partial pressure**."

Experimental Verification of Dalton's Law:

Let us have cylinders of same volume, i.e., 10 dm^3 each and three gases H_2, CH_4 and O_2 are separately enclosed in each of them at the same temperature. Let their partial pressures be 400 torr, 500 torr and 100 torr respectively. They are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law

$$P_1 = p_{H_2} + p_{CH_4} + p_{O_2} = (400 + 500 + 100) \text{ torr}$$

$$P_1 = 1000 \text{ torr}$$

Partial pressure of each gas depends upon the number of molecules of each case. **Gases having greater number of moles and molecules have greater partial pressure**.

Molecules of each gas move independently, so the general gas equation (PV = n RT) can be applied to the individual gases in the gaseous mixture.

$p_{H_2}\ V = n_{H_2}\ RT \qquad p_{H_2} = n_{H_2}\frac{RT}{V}$ or $p_{H_2} \propto n_{H_2}$

$p_{CH_4}\ V = n_{CH_4}\ RT \qquad p_{CH_4} = n_{CH_4}\frac{RT}{V}$ or $p_{CH_4} \propto n_{CH_4}$

$p_{O_2}\ V = n_{O_2}\ RT \qquad p_{O_2} = n_{O_2}\frac{RT}{V}$ or $p_{O_2} \propto n_{O_2}$

Adding three equations

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

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

Where $n_t = n_{H_2} + n_{CH_4} + n_{O_2}$

$$P_t V = n_t RT$$

According to above equation, total pressure of the mixture of gases depends upon the total number of molecules.

Calculations of Partial Pressure:

Suppose we have three gases A, B, C we know that

$$PV = n RT$$

$$P = \frac{n RT}{V}$$

$$P_{(A)} = n_A\frac{RT}{V} \qquad (1)$$

$$P_{(B)} = n_B\frac{RT}{V} \qquad (2)$$

$$P_{(C)} = n_C\frac{RT}{V} \qquad (3)$$

$$\begin{aligned} P_{(total)} &= P_A + P_B + P_C \\ &= n_A\frac{RT}{V} + n_B\frac{RT}{V} + n_C\frac{RT}{V} \\ &= (n_A + n_B + n_C)\frac{RT}{V} \qquad (4) \end{aligned}$$

Dividing Equation (1) by Equation (4).

$$\frac{P_{(A)}}{P_{(Total)}} = \frac{n_A\ RT/V}{(n_A + n_B + n_C)\ RT/V} = \frac{n_A}{n_A + n_B + n_C}$$

Similarly

$$\frac{P_{(B)}}{P_{(Total)}} = \frac{n_B\ RT/V}{(n_A + n_B + n_C)\ RT/V} = \frac{n_B}{n_A + n_B + n_C}$$

and $$\frac{P_{(C)}}{P_{(Total)}} = \frac{n_C\ RT/V}{(n_A + n_B + n_C)\ RT/V} = \frac{n_C}{n_A + n_B + n_C}$$

$$\therefore \quad \frac{P_{(gas)}}{P_{(Total)}} = \frac{\text{Moles of a gas}}{\text{Total moles of all gases}}$$

$$P_{(gas)} = \frac{\text{Moles of a gas}}{\text{Total moles of all gases}} \times P_{(total)}$$

$$P_{(gas)} = \text{Mole fraction of a gas} \times P_{(total)}$$

$$P_{(gas)} = X_{gas} \times P_{(total)}$$

Example 6:

There is a mixture of hydrogen, helium and methane occupying a vessel of volume 13 dm^3 at 37^oC and pressure of 1 atmosphere. The masses of H_2 and He are 0.8 g and 0.12 respectively. Calculate the partial pressure in mm Hg of each gas in the mixture.

Solution:

Volume of the mixture of gases = 13 dm^3

Temperature of the mixture = $37^oC + 273 = 310$ K

Pressure of the mixture = 1 atmosphere

Calculate the total number of moles present in the mixture of gases by applying the general gas equations.

$$P_t V = n_t RT$$

$$n_t = \frac{PV}{RT}$$

$$n_t = \frac{1 \text{ atm} \times 13 \text{ dm}^3}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1} \times 310 \text{ K}}$$

$$n_t = 0.51 \text{ moles}$$

So, the total number of moles H_2, He and CH_4 = 0.51 moles.

$$\text{No. of moles of } H_2 = \frac{0.8 \text{ g}}{2.0 \text{ g mole}^{-1}} = 0.4 \text{ mole}$$

$$\text{No. of moles of He} = \frac{0.12 \text{ g}}{4 \text{ g mole}^{-1}} = 0.03 \text{ mole}$$

$$\begin{aligned} \text{No. of moles of } CH_4 &= \text{Total moles} - \text{mole of } H_2 - \text{mole of He} \\ &= 0.51 - 0.4 - 0.03 \\ &= 0.08 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of } H_2\ (p_{H_2}) &= \frac{n_{H_2}}{n_t} \times 760 \\ &= \frac{0.4}{0.51} \times 760 \\ &= 596.08 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of He } (p_{He}) &= \frac{n_{He}}{n_t} \times 760 \\ &= \frac{0.03}{0.51} \times 760 \end{aligned}$$

$$= 44.70 \text{ mm Hg}$$

$$\text{Partial pressure of } CH_4\ (p_{CH_4}) = \frac{n_{CH_4}}{n_t} \times 760$$

$$= \frac{0.08}{0.51} \times 760$$

$$= 119.22 \text{ mm Hg}$$

The sum of individual pressures is almost equal to 760 mm Hg or one atmosphere i.e., total pressure of the mixture.

APPLICATIONS OF DALTON'S LAW OF PARTIAL PRESSURE

Following are the four important 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, therefore, the sum of the partial pressures of the dry gas and that of water vapours. The partial pressure exerted by the water vapour is called **aqueous tension**.

$P_{moist} = P_{dry} + P_{H_2O}$

$P_{moist} = P_{dry} + \text{Aqueous tension}$

$P_{dry} = P_{moist} - \text{Aqueous tension}$

While solving the numerical the aqueous tension is subtracted from the total pressure (P_{moist}).

2. Respiration Process:

Dalton's law finds its applications during the process of respiration. The process of respiration depends upon the difference in partial pressures. When animals inhale air, 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 116 torr. CO_2 produced during respiration moves out in the opposite direction, as its partial pressure is greater in blood than in air.

3. Higher Altitude:

At higher altitudes, the pilots feel uncomfortable in breathing because the partial pressure of oxygen in the un–pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing. Therefore their cabin is pressurized to 159 torr or they are provided oxygen masks.

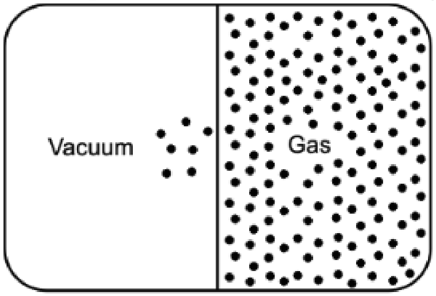
4. Divers:

In the sea, atmospheric pressure increases 3 atm at a depth of every 100 feet. Normal air cannot be breathed because partial pressure of oxygen increases. On the other hand, pressure of N_2 also increases and diffuses in the blood. At ordinary condition nitrogen gas does not diffuses in the lungs. So deep sea divers take **oxygen mixed** with an **inert gas helium** and adjust the partial pressure of oxygen according to the requirement. Sea divers are provided a mixture of 80% He and 20% oxygen.

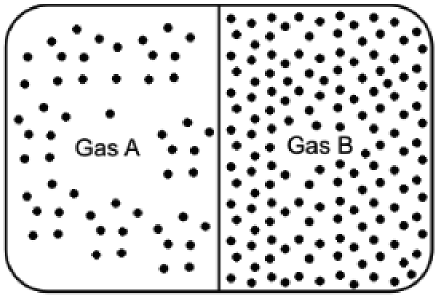
DIFFUSION

"Spontaneous mixing of gases by their random motion and collision is called **diffusion**."

This diffusion of the gas is due to movement of the molecules. Lighter gases has greater velocities and greater rate of diffusion. For example, spreading of fragrance of rose or a perfume is due to diffusion. When gases are mixed together, they have same partial pressure in every part the container. Suppose NO_2, a brown coloured gas and O_2 (colourless) are separated by a partition. If that partition is removed, a homogeneous brown coloured is formed.



(Effusion of gases)



(Diffusion of gases)

EFFUSION

"The escape of gas molecules to low pressure region one by one without collisions through a tiny hole of molecular dimension is called **effusion**."

The effusion of a gas is due to its movement through an extremely tiny opening into a region of lower pressure as shown in the figure. Where as diffusion is an intermixing of one substance with another.

GRAHAM'S LAW OF DIFFUSION

"The rate of diffusion of two gases is inversely proportional to the square root of their molecular masses or densities at constant temperature and pressure."

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

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

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

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

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

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

According to Graham's law

$$r_1 \times \sqrt{d_1} = k \qquad (1)$$

$$r_2 \times \sqrt{d_2} = k \qquad (2)$$

Divide the two equations and rearrange

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \qquad (3)$$

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

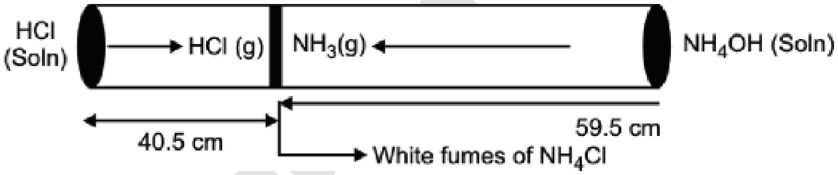
$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \qquad (4)$$

Where M_1 and M_2 are the molecular masses of gases.

Experimental Verification of Graham's Law:

This law can be verified in the laboratory by noting the rates of diffusion of two gases in a glass tube when they are allowed to move from opposite ends. Two cotton plugs soaked in HCl and NH_4OH solutions are introduced in the open ends of 100 cm long tube simultaneously. HCl molecules travel a distance of 40.5 cm when NH_3 molecules cover 59.5 cm in the same time duration. They produced dense white fumes of ammonium chloride at the point of junction.

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(s)}$$



The ratio of velocities (rate) of two gases depends on their distance traveled by the respective gases at the same time is as follow:

$$\frac{\text{Velocity of } NH_3}{\text{Velocity of } HCl} = \frac{\text{Distance travelled by } NH_3}{\text{Distance travelled by } HCl}$$

$$\frac{NH_3}{HCl} = \frac{59.5}{40.5} = 1.46$$

This means NH_3 gas diffuses 1.46 times faster than $HCl_{(g)}$ because NH_3 is lighter gas.

Same result is obtained on the basis of Graham's law of diffusion while considering their densities.

Density of HCl $= 1.66 \text{ g dm}^{-3}$

Density of NH_3 $= 0.76 \text{ g dm}^{-3}$

According to Graham's law

$$\frac{r\,NH_3}{r\,HCl} = \sqrt{\frac{\text{density of } HCl}{\text{density of } NH_3}}$$

$$\frac{r\ NH_3}{r\ HCl} = \sqrt{\frac{1.66}{0.76}} = 1.47$$

3. The same result is obtained by calculating their rates while considering molecular masses of NH_3 and HCl.

Molecular mass of HCl = 36.5

Molecular mass of NH_3 = 17

$$\frac{r\ NH_3}{r\ HCl} = \sqrt{\frac{\text{Molecular mass of HCl}}{\text{Molecular mass of } NH_3}}$$

$$\frac{r\ NH_3}{r\ HCl} = \sqrt{\frac{36.5}{17}} = 1.46$$

These results verify Graham's law of diffusion.

Example 7:

250 cm^3 of the sample of hydrogen effuse four times as rapidly as 250 cm^3 of an unknown gas. Calculate the molar mass of unknown gas.

Solution:

Let the unknown gas is given the symbol X.

Rate of effusion of unknown gas (r_x) = 1

Rate of effusion of hydrogen gas (r_{H_2}) = 4

Molar mass of H_2 gas (M_{H_2}) = 2 g $mole^{-1}$

Molar mass of unknown gas (M_x) = ?

$$\frac{r_{H_2}}{r_x} = \sqrt{\frac{M_x}{M_{H_2}}}$$

$$\frac{4}{1} = \sqrt{\frac{M_x}{2}}$$

Taking square on both sides

$$\frac{M_x}{2} = \frac{16}{1}$$

M_x = 16 x 2 = 32 g $mole^{-1}$

KINETIC MOLECULAR THEORY OF GASES

Physical theories are often given in the form of postulates.

"A set of postulates which explain the behaviour of gases is called **kinetic molecular theory**."

Many scientists contribute to explain the different behaviour of gases, e.g.,

Bernoulli (1738):

Gave kinetic molecular theory.

Clausius (1857):

Formed kinetic equation and deduced gas laws from it.

Maxwell:

He gave the law of distribution of velocities of gases. According to this law molecules are in the form of groups having definite velocity ranges.

Boltzman:

He studied the distribution of energies among the gas molecules.

Vander Waal:

He studied non-ideal behaviour of gases in 1873.

FUNDAMENTAL POSTULATES OF THIS THEORY ARE GIVEN BELOW

(1) Every gas consists of large number of smaller molecules. Gases like He, Ne, Ar are monatomic molecules.

(2) Molecules move randomly in linear motion. They move in straight line, and their path changes only when they collide with one another or with the wall of the container.

(3) When gas molecules collide with one another, they have elastic collision in them.

(4) Pressure exerted by the gas molecules is due to the force of collision at unit area of the container, $P = \frac{F}{A}$

(5) The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.

(6) The molecules of a gas have no forces of attraction for each other.

(7) The actual volume of molecules of a gas is negligible as compared to the volume of the gas.

(8) The force of gravity has almost no influence on the movement of the molecules of a gas.

(9) The kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

KINETIC EQUATION FOR GASES

This is the fundamental equation of the kinetic molecular theory of gases. R.J. Clausius deduced an expression for pressure of an ideal gas.

When molecules move, they collide themselves and they collide with the walls of the container. The force of collisions of molecules at unit area is called **pressure**.

$$\text{Pressure} = \frac{\text{force of collision}}{\text{area}}$$

The kinetic equation which have been derived from the kinetic gas model is given below:

$$PV = \frac{1}{3} m N\bar{C^2}$$

Where P = pressure of the gas

V = volume of the gas

m = mass of one molecules of gas

N = number of molecules of the gas

$\bar{C^2}$ = mean square velocity.

This expression of kinetic equation relates the pressure of gas with number of molecules of the gases, masses of gas molecules, velocities of the molecules and the volume of the molecules.

$$P = \frac{m\,N\bar{C^2}}{3V}$$

MEAN SQUARE VELOCITY

"The average of square of all possible velocities of molecules is called **mean square velocity**."

It is denoted by $\bar{C^2}$.

All molecules of a gas under same conditions have different velocities. Velocity of a molecule at a particular time changes million times per second due to collisions. Different velocities are distributed among the molecules. If n_1 molecule has velocity c_1 and n_2 molecule has velocity c_2 and so on then

$$N = n_1 + n_2 + n_3 + \ldots\ldots\ldots \qquad \text{(i)}$$

Total KE = number of molecules x kinetic energy

or $N \times \frac{1}{2} m\bar{C^2}$

The total kinetic energy of N gas molecules is the sum of kinetic energies of the individual molecules. Thus

$$KE = n_1 \times \frac{1}{2} mc_1^2 + n_2 \times \frac{1}{2} mc_2^2 + n_3 \times \frac{1}{2} mc_3^2 + \ldots\ldots\ldots \qquad \text{(ii)}$$

or $N \times \frac{1}{2} m\bar{c}^2 = n_1 \times \frac{1}{2} mc_1^2 + n_2 \times \frac{1}{2} mc_2^2 + n_3 \times \frac{1}{2} mc_3^2 + \ldots\ldots\ldots$

or $N\bar{c}^2 = n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \ldots\ldots\ldots$

$$\bar{c}^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \ldots\ldots}{N}$$

$$\bar{c}^2 = \frac{(n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \ldots\ldots)}{n_1 + n_2 + n_3 + \ldots\ldots}$$

ROOT MEAN SQUARE VELOCITY

The under–root of mean square velocity is called **root mean square velocity**. It is denoted by c_{rms}.

$$c_{rms} = \sqrt{C^{\bar{2}}} = \sqrt{\frac{(n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \ldots\ldots)}{n_1 + n_2 + n_3 + \ldots\ldots}}$$

According to kinetic equation $PV = \frac{1}{3} m Nc^{-2}$

For one mole of gas $N = N_A$

So $PV = \frac{1}{3} m N_A C^{\bar{2}}$

$PV = \frac{1}{3} M C^{\bar{2}}$ where $m N_A = M$

$C^{\bar{2}} = \frac{3PV}{M} = \frac{3RT}{M}$ (where $PV = RT$)

$$C^{\bar{2}} = \frac{3RT}{M}$$

$$\sqrt{C^{\bar{2}}} = \sqrt{\frac{3RT}{M}}$$

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

Root mean square velocity is directly proportional to absolute temperature and inversely proportional to molecular masses of the gases.

Similarly;

Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

Most probable velocity $= \sqrt{\frac{2RT}{M}}$

EXPLANATION OF GAS LAWS FROM KINETIC MOLECULAR THEORY

(a) BOYLE'S LAW

Statement:

"Volume of the given mass of a gas is inversely proportional to its pressure at constant temperature."

According to the kinetic theory of gases, the kinetic energy is directly proportional to the absolute temperature of the gas. The kinetic energy of a n molecules in $\frac{1}{2}\,m\,NC^{\bar{2}}$.

So $\quad \frac{1}{2}mNC^{\bar{2}} \propto T$

$$\frac{1}{2}mNC^{\bar{2}} = KT = \frac{3}{2}\times\frac{1}{3}mNC^{\bar{2}} = KT$$

$$= \frac{1}{3}m\,NC^{\bar{2}} = \frac{2}{3}KT$$

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

$$PV = \frac{1}{3}m\,NC^{\bar{2}}$$

or $\quad PV = \frac{2}{3}\left(\frac{1}{2}\;m\,NC^{\bar{2}}\right) \qquad (2)$

As we know $\frac{1}{2}mNC^{\bar{2}} = KT \qquad (1)$

Putting Equation (1) into Equation (2).

$$PV = \frac{2}{3}k\,T \qquad (3)$$

If the temperature (T) is constant then right hand side of Equation (3) is constant.

So $\quad PV = k'$ (which is Boyle's law).

(b) CHARLES'S LAW

Statement:

"Volume of given mass of a gas is directly proportional to its absolute temperature at constant pressure."

Consider the equation.

$$PV = \frac{2}{3}k\,T$$

or $\quad V = \frac{2}{3}\,\frac{k\,T}{P}$

At constant pressure,

$$\frac{2}{3}\,\frac{K}{P} = k'$$

Therefore,

$$V = k' T$$

or $$V \propto T$$

Which is Charles's law.

(c) AVOGADRO'S LAW

"Equal volume of different gases at same temperature and pressure contains equal number of molecules."

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 $\overline{c_1^2}$ and $\overline{c_2^2}$ respectively. Their kinetic equations can be written as follows:

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

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

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

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

$$\frac{1}{2} m_1 \overline{c_1^2} = \frac{1}{2} m_2 \overline{c_2^2} \qquad \text{Hence} \qquad m_1\overline{c_1^2} = m_2\overline{c_2^2} \qquad (2)$$

Divide Equation (2) by Equation (1).

$$N_1 = N_2$$

Hence 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

Statement:

The rate of diffusion of two gases is inversely proportional to the square root of their molecular masses or densities."

Applying the kinetic equation

$$PV = \frac{1}{3} m N\overline{C^2} \qquad (1)$$

If we take one mole of a gas having Avogadro's number of molecules N_A then the Equation (1) can be written as:

$$PV = \frac{1}{3} M\overline{C^2} \qquad (M = m N_A) \qquad (2)$$

M is the molecular mass of the gas.

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

We know that

$$d = \frac{M}{V} \text{ and } \frac{1}{d} = \frac{V}{M}$$

Put this value of $\frac{V}{M}$ in Equation (3).

$$C^{\bar{2}} = \frac{3P}{d}$$

$$\sqrt{C^{\bar{2}}} = \sqrt{\frac{3P}{d}}$$

Since root mean square velocity of gases is proportional to the rate of diffusion of gases.

So $$\sqrt{C^{\bar{2}}} \propto r$$

$$C_{rms} = \sqrt{\frac{3P}{d}}$$

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

Which is called **Graham's law**.

KINETIC INTERPRETATION OF TEMPERATURE

According to kinetic molecular theory of gases the molecules of a gas move randomly, they collide among themselves and with the walls of the vessels and change their directions. The collisions are elastic and the pressure of the gas is the result of these collisions with the walls of the container.

Let us write the kinetic equation.

$$PV = \frac{1}{3} m N C^{\bar{2}} \qquad (1)$$

m is the mass of one molecule of the gas, N is the total number of molecules in the vessel, and $C^{\bar{2}}$ is their mean square velocity. The kinetic energy associated with one molecule of a gas due to its translation motion is given be the following equation.

$$E_k = \frac{1}{2} m C^{\bar{2}} \qquad (2)$$

E_k is the average translation kinetic energy of a gas.

Equation (1) can be rewritten as:

$$PV = \frac{2}{3} N \left(\frac{1}{2} m C^{\bar{2}}\right) \qquad (3)$$

Putting Equation (2) into Equation (3).

So $$PV = \frac{2}{3} N E_k \qquad (4)$$

Equation (4) gives an important insight into the meaning of temperature. To understand it, consider one mole of a gas.

So $N = N_A$

$$PV = \frac{2}{3} N_A E_k \qquad (5)$$

According to the general gas Equation for 1 mole of a gas.

$$PV = RT \qquad (6)$$

Comparing Equation (5) and Equation (6).

$$\frac{2}{3} N_A E_k = RT \qquad (7)$$

$$E_k = \frac{3R}{2N_A} T \quad \left[\text{For one mole of a gas } E_k = \frac{3RT}{2}\right] \qquad (8)$$

The Equation (8) gives a new definition of temperature. The Kelvin temperature of a gas is directly proportional to the average translation kinetic energy of its molecules.

$$E_k \ \alpha \ T$$

Interpretation of Heat Flow:

Change in temperature means change in the intensity of molecular motion. When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to molecules in the colder body. this process of flow of heat continues until the average translational kinetic energy of all the molecules become equal. This equalizes the temperature of both bodies.

Interpretation of Physical State:

In gases and liquids, temperature is the measure of average translational kinetic energies of molecules. In solids, where molecules cannot move freely temperature becomes a measure of vibrational kinetic energy.

Interpretation of Absolute Zero:

Keeping in view this kinetic interpretation of temperature, we can explain absolute zero of temperature. It is that temperature at which the molecular motion ceases. The absolute zero is unattainable. Any how, current attempts have resulted in temperature as low as 10^{-5} K.

CRITICAL TEMPERATURE AND CRITICAL PRESSURE

"The temperature below which the continuous increase of pressure on a gas bring about liquefaction and above which no liquefaction takes place.

or "The temperature above which the liquid state of a substance no longer exists is called **critical temperature**."

The pressure at critical temperature is called **critical pressure**. Critical temperature is denoted as T_c and critical pressure as P_c. Critical temperatures and critical pressure of some gases are given below.

TABLE

Substance	Critical Temperature T (K)	Critical Pressure P (atmosphere)
Ammonia, NH_3	405.6 (132.44°C)	111.5
Argon, Ar	150.9 (– 122.26°C)	48
Carbon dioxide, CO_2	304.3 (31.142°C)	73.0
Nitrogen, N_2	126.1 (– 147.06°C)	33.5
Oxygen, O_2	154.4 (– 118.75°C)	49.7
Freon–12, $CCl_2 F_2$	384.7 (111.54°C)	39.6
Water vapours, H_2O	647.6 (374.44°C)	217.0

Non–polar gases of low polarizeability like Ar have a very low critical temperature. Polar gases have greater intermolecular forces in them and have high critical temperatures. The substances like H_2O vapours and NH_3 gas are among the polar gases and they have better tendencies to be liquids. CO_2 cannot be liquefied above 31.1^{o}C, no matter how much pressure is applied. Anyhow, if temperature of CO_2 is maintained below 31.1^{o}C, then lower pressure than critical pressure is required to liquefied it. The value of the critical temperature of a gas, depend upon its size, shape and intermolecular forces present in it.

When a gas is measured at its critical temperature and pressure, the volume of one mole of gas at that stage is called **critical volume V_c**. The critical volume of O_2 is 74.42 $cm^3\ mole^{-1}$, CO_2 is 95.65 $cm^3\ mole^{-1}$ and H_2 is 64.51 $cm^3\ mole^{-1}$.

LIQUEFACTION OF GASES

Principle:

The conversion of gas into liquid requires high pressure and low temperature. High pressure brings the molecules close to each other. Low temperature reduces the kinetic energy of the molecules and as a result attractive forces between the molecules increases.

"The temperature below which a gas can be liquefied by increasing pressure but above this temperature no liquefaction takes place."

or "The temperature above which liquid state of a substance no longer exists is called **critical temperature**."

These properties provides us information about the conditions under which gases liquefy. For example, the critical temperature of oxygen is 154.4 K or – 118.75^{o}C. It must be below this temperature, before it can be liquefied by applying high pressure. Ammonia is a polar gas. Its critical temperature is 405.6 K or 132.4^{o}C, so it an be liquefied by applying sufficient pressure close to room temperature.

METHODS OF LIQUEFACTION OF GASES

There are three methods of for the liquefaction of gases:

(1) Claud's Method:

In this method, gas is allowed to do some mechanical work.

(2) Faraday's Method:

In this method, cooling is done with the freezing mixture.

JOULE THOMSON EFFECT

"When highly compressed gas is allowed to expand in low pressure region, it cause cooling. It is called **Joule – Thomson effect**."

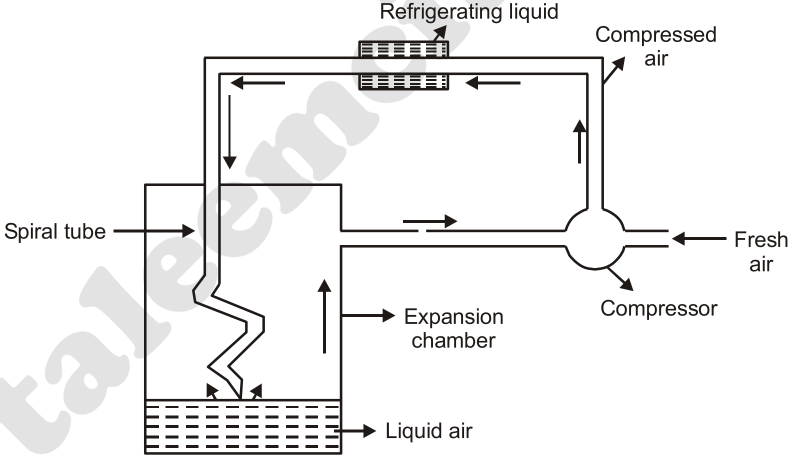
The molecules of the compressed gas are very close to each other and appreciable attractive forces are present among them. When a gas is allowed to undergo sudden expansion through the nozzle of a jet, then the molecules move apart. In this way energy is needed to overcome the intermolecular attraction. This energy is taken from the gas itself which is cooled.

This method is used for cooling in refrigerators, ice factories, air conditioners etc.

(3) LIND'S METHOD OF LIQUEFACTION OF GASES

In Lind's process Joule Thomson effect principle is used for cooling. Diagram of the process is shown below.

For the liquefaction of air, it is compressed to about **200 atmosphere** and then passed though a water cooled pipe where the heat of compression is removed. It is then allowed to pass through spiral pipe having a jet at the end. When the air comes out of the jet, the expansion takes place from **200 atmosphere to 1 atmosphere**. In this way considerable fall of temperature occurs. This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber. All gases except **H_2 and He** can be liquefied by this process. H_2 and He gases have very low critical temperatures.



Lind's Method of Liquification of air

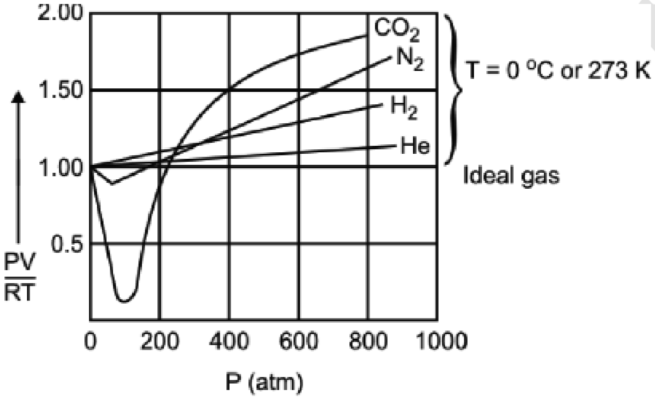
NON IDEAL BEHAVIOURS OF GASES

"The gas which obeys the gas laws at all conditions of temperature and pressure is called an **ideal gas**."

All the real gases like H_2, N_2, O_2, CO_2, CO. He, Ne etc, show non ideal behaviour at low temperature and high pressure. Ideal behaviour of a gas gave equation PV = n RT.

For an ideal gas $\frac{PV}{RT}$ has a straight line for one mole of a gas. $\frac{PV}{RT}$ is called the **compressibility factor** of the gas. It we plot a graph between pressure at x–axis compressibility factor at the y-axis are get a straight line and compressibility factor for an ideal gas is **unity** for all conditions of temperature and pressure. It is shown in the graph. All the real gases have been found to show marked deviations from this behaviours. It is observed that He goes along with the expected horizontal dotted line to some extent but goes above this line at very high pressure. It means that at very high pressure, the decrease in volume is not according to general gas equation and the value of the product $\frac{PV}{RT}$ has increased from the expected value. With this type of behaviour, we would say that the gas is non–ideal.

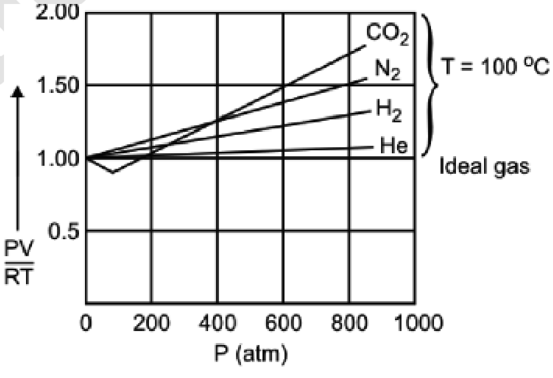
In the case of H_2 the deviation starts even at low pressure in comparison to He. N_2 shows a decrease in $\frac{PV}{RT}$ value at the beginning and shows marked deviation than H_2. CO_2 has a very strange behaviour as it is evident from the graph.



Non ideal behaviour of gases at 0 °C

The extent of deviation of these four gases show that these gases have their own limitations for obeying general gas equation. It depends upon the nature of that gas.

When we study the behaviour of four gases at high temperature i.e., **100°C** then the graphs come closer to the expected straight line and the deviations are shifted towards higher pressure. This means that the increase in temperature makes the gases more ideal.



Non ideal behaviour of gases at 100 °C

This discussion on the basis of experimental observations, convinces us that;

1. Gases are ideal at low pressure and non–ideal at high pressure.
2. Gases are ideal at high temperature and non–ideal at low temperature.

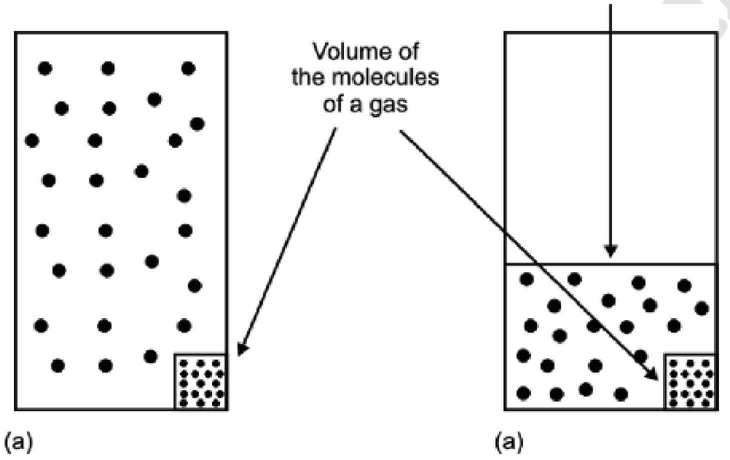
Causes of Deviation:

Real gases deviate form ideal behaviour in these two conditions;

1. When temperature is very low.
2. When pressure is very high.

Vander Waal studied in 1873 this non ideal behaviour of gases. According to him, non–ideality in real gases is due to two wrong postulates of the kinetic molecular theory. These postulates are given below.

1. There are no forces of attraction among the molecules of a gas.
2. The actual volume of gas molecules is negligible as compared to the volume of the vessel.



(a) A gas at low pressure (b) A gas at high pressure

When the pressure on a gas is high and the temperature is low then the attractive forces among the molecules become significant, so the ideal gas equation $PV = nRT$ does not hold. Actually, under these conditions the gas does not remain ideal.

The actual volume of the molecules of a gas is usually very small as compared to the volume of the vessel and hence it can be neglected. This volume, however, does not remain negligible when the gas is subjected to high pressure. This can be understood from the following figure.

Vander Waal Equation for Real Gases:

Real gases deviate from ideal behaviour at low temperature and high pressure. The pressure and volume factor of the ideal gas equation $PV = nRT$ needs some correction in it in order to make it applicable for the real gases.

Vander Waal's Equation for Real Gases:

Keeping in view the above discussion, Vander Waal pointed out that both pressure and volume factors in ideal gas equation needed correction in order to make it applicable to the real gases.

Volume Correction:

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them. When pressure is increased further it is opposed by the molecules themselves, because molecules have definite volume. No doubt very small as compared to the vessel, but it is not negligible. Vander Waal postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas. If the **effective volume** of the molecules per mole of a gas is represented by **b**, then the volume available to gas molecules is the volume of the vessel minus the volume of gas molecules.

$$V_{\text{free}} = V_{\text{vessel}} - V_{\text{molecules}}$$

$$V_{\text{free}} = V_{\text{vessel}} - b \qquad (1)$$

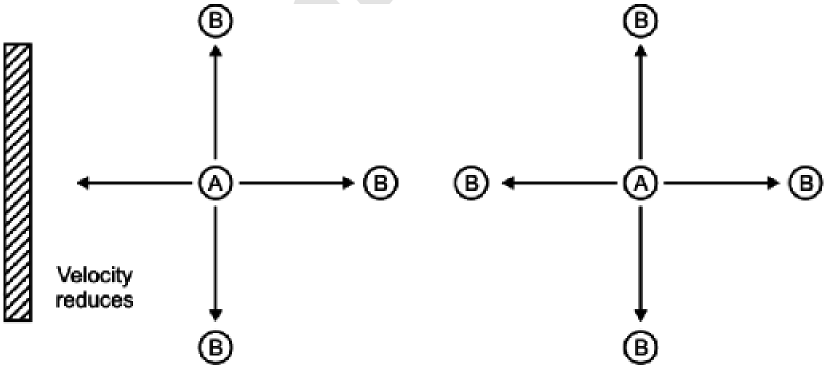
V_{free} is that volume which is available to gas molecules. The factor b is termed as the **excluded volume** which is constant and characteristic of a gas. It’s value depends upon the size of gas molecules. Table (3.3) shows the b values for some important gases. it is interesting to know that the excluded volume b is not equal to the actual volume of gas molecules. In fact, it is four times the actual volume of molecules.

$$b = 4\,V_m$$

Where V_m is the actual volume of one mole of a gas molecules. “b” is the effective volume or excluded volume of one mole of a gas. It is that volume of gas which is occupied by 1 mole of gas molecules in highly compressed state and not in the liquid state.

Pressure Correction:

At low temperature and high pressure, the force of attraction increases among the gas molecules. Consider a molecule A in the interior of the container. It has equal force of attraction on every side and there is no net attraction on the molecule A. Force is a vector quantity and opposite force with same magnitude cancel to each other.



Pressure correction

On the other hand, when such molecules strike with the wall of the container it has inward pull or drag due to the unbalance force of attraction between gas molecules. When this molecules A strikes at the wall, the other molecules prevent it from doing so. As a result that molecule A exert **less force on a unit area**. So observed pressure is less than the actual pressure.

$$P = P_i - P'$$

Where P is observed pressure, P_i is ideal pressure and P' is decrease in ideal pressure.

$$P_i = P + P'$$

Vander Waal suggested that part of pressure used up against intermolecular forces should decrease as the volume of container increase. He suggested the following expression to calculate the intermolecular forces.

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

Decrease in pressure P' depends upon concentration of hitting and dragging molecules.

$P' \alpha$ concentration of A molecules x concentration of B molecules.

Where A are hitting and B are dragging molecules.

$$P' \alpha \frac{n}{V} \times \frac{n}{V}$$

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

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

$$P' = \frac{a}{V^2} \quad (\text{where } n = 1)$$

Where a is called **coefficient of attraction or attraction per unit volume**. It has a constant volume for particular real gas. The effective kinetic pressure of gas is given by equation.

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

Put value of Equation (1) and Equation (2) in general equation we get

$$PV = RT$$

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

Observed pressure Observed volume

For n mole of gas

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

This equation is called **Vander Waal equation**. 'a' and 'b' are called **Vander Waal's constants**.

Units of 'a':

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

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

$$a = \frac{\text{atm} \times (\text{dm}^3)^2}{(\text{mole})^2} = \text{atmosphere dm}^6\ \text{mole}^{-2}$$

In SI unit

$$\frac{\text{Nm}^{-2} \times (\text{m}^3)^2}{(\text{mole})^2} = \text{Nm}^{+4}\ \text{mole}^{-2}$$

Unit of 'b':

"b" is called **excluded or incompressible** volume/mole of gas. Hence its unit is dm^3 mole^{-1} or m^3 mole^{-1}.

TABLE

Vander Waal's Constant for Some Common Gases

Gas	**a (atmosphere dm^6 mole^{-2})**	**b (dm^3 mole^{-1})**
Hydrogen	0.245	0.0266
Oxygen	1.360	0.0318
Nitrogen	1.390	0.0391
Chlorine	6.493	0.0562
Carbon dioxide	3.590	0.0428
Ammonia	4.17	0.0371
Sulphur dioxide	6.170	0.0564

The presence of intermolecular forces in gases like Cl_2 and SO_2 increases their 'a' factor. Value of "a" depends upon intermolecular forces and value of "b" depends upon the size of gas molecules. H_2 has less value of "a" than SO_2 or Cl_2 due to greater non–polar characters. The "b" value of H_2 is 0.0266 dm^3 mole^{-1}. It means that if 2.016 g (1 mole) of H_2 is taken, it will occupy 0.0266 dm^3 or 26.6 cm^3 of at closest approach in the gaseous state.

Example 8:

One mole of methane gas is maintained at 300 K. Its volume is 250 cm^3. Calculate the pressure exerted by the gas under the following conditions.

(i) When the gas is ideal.

(ii) When the gas is non–ideal.

$a = 2.253$ atmosphere dm^6 mole^{-2},

$b = 0.0428$ dm^3 mole^{-1}

Solution:

(a) When the gas is ideal, general gas equation is applied i.e.

PV = n RT

$V = 250\ \text{cm}^3 = 0.25\ \text{dm}^3$

$n = 1$ mole

$T = 300$ K

$R = 0.0821\ \text{dm}^3$ atmosphere K^{-1} mole^{-1}

$$P = \frac{n\,RT}{V}$$

$$P = \frac{1\ \text{mole} \times 0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mole}^{-1} \times 300\ \text{K}}{0.25\ \text{dm}^3}$$

$P = 98.5$ atmosphere

(b) When the gas is behaving as non–ideal, we should use the Vander Waal's equation.

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

by rearranging the equation

$$P = \frac{n RT}{V - n b} - \frac{n^2 a}{V^2}$$

Substituting the following values

$n = 1$ mole, $R = 0.0821$ dm^3 atmosphere K^{-1} mole^{-1},

$V = 0.25$ dm^3, $T = 300$ K,

$a = 2.253$ dm^3 atmosphere mole^{-2},

$b = 0.0428$ dm^3 mole^{-1}

$$P = \frac{1 \text{ x } 0.0821 \text{ x } 300}{0.25 - 1\,(0.0428)} - \frac{1 \text{ x } 2.253}{(0.25)^2}$$

$P = 82.8$ atmosphere

Conclusion:

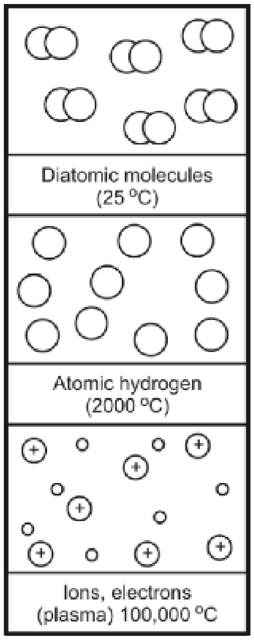
The difference of these two pressures shows that this gas is non–ideal. Actually CH_4 is thought to be ideal near 1 atmosphere, but around 100 atmospheres, it develops non–ideal attitude.

PLASMA STATE

"An electrically neutral mixture of electrons, ions and atoms is called **plasma**."

It is fourth state of matter. Plasma was identified in 1879 by William Crook. **99% of the universe is plasma** state and solid, liquid and gases are only 1%.

Although, naturally occurring plasma is rare on earth, there are many man made examples. Inventors have used plasma to conduct electricity in neon signs and fluorescent bulbs. Scientists have constructed special chambers to experiment with plasma in laboratories. It occurs only in lightning discharges and in artificial devices like fluorescent lights, neon signs, etc. It is everywhere in our space environment.



- **How is Plasma formed?**

When more heat is applied, the atoms or molecules may be ionized. An electron may gain enough energy to escape from its atom. This atoms 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. However, all the atoms are not necessarily ionized, and some of them may remain completely intact with no net charge. This **ionized gas mixture, consisting of ions, electrons and neutral atoms,** is called **plasma**.

$$\text{Molecule} \xrightarrow{\text{heat}} \text{Atomic gas}$$

$$\text{Atomic gas} \xrightarrow{\text{heat}} \text{positive ions + electrons}$$

It means that a plasma is a distinct state of matter containing a significant number of electrically charged particles, number sufficient to affect its electrical properties and behaviour.

- **What Plasma can Potentially do?**

Plasma can generate explosions, carry electrical currents and support magnetic fields within themselves. Space plasmas can contain enough heat to melt the earth thousands of times over. Crystal plasmas can freeze the earth at least a hundred times, one after the other.

- **Natural and Artificial Plasma:**

Artificial plasma can be created by using electrical charges on a gas, as in neon signs. Plasma at low temperatures is hard to maintain outside a vacuum.

Natural plasma exist only at very high temperatures, or low temperatures vacuums. Natural plasma on the other hand do not breakdown or react rapidly, but are extremely hot (over 20,000^{o}C minimum). Their energy is so high that they vaporize any material they touch.

- **Characteristic of Plasma:**

1. A plasma must have sufficient numbers of charged particles so as whole, it exhibits a collective response to electric and magnetic fields. The motions of the particles in the plasma generate 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. Although plasma includes electrons and ions conducts electricity, it is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.

- **Where is Plasma found?**

Entire universe is almost made of plasma. It existed before any other forms of matter came into being. Plasma are found in everything from the sun to quarks, the smallest particles in the universe.

As stated earlier, plasma is the most abundant form of matter in the universe. It is the stuff of stars. A majority of the matter in inner–stellar space is plasma. All the starts that shine are all plasma. The sun is a 1.5 million kilometer ball of plasma, heated by nuclear fusion.

On earth it only occurs in a few limited places, like lighting bolts, flames, auroras and fluorescent lights. When an electric current is passed through neon gas, it produces both plasma and light.

APPLICATIONS OF PLASMA

Plasmas have many important technological applications. It is present in many devices. It help us to understand much of the universe around us. Because plasmas are conductive respond to electric and magnetic fields and can be used in innumerable applications where such control is needed or when special sources of energy or radiation are required.

(i) **A fluorescent light bulb** is not like regular light bulbs. Inside the long tube is a gas. When the light is turned on, electricity flows through the tube. This electricity acts as that special energy and charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.

(ii) **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, possibly neon and creates a plasma inside the tube. The plasma glows special colour depending on what kind of gas is inside.

(iii) 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.

(iv) They also provide the foundation for important potential applications such as the generation of electrical energy from fusion pollution control and removal of hazardous chemicals.

(v) They drive lasers, help to clean up the environment, pasteurize foods and make tools corrosion–resistant.

Future Horizon:

Scientists are working on putting plasma to effective use. Plasma would have to be low energy and should be able to survive without instantly reacting and degenerating. The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which create molecules that are in what scientist call a meta–stable state. The magnetic fields used to create the low temperature plasma give the plasma molecules electrons, which do not react until they collide with another molecule with just the right energy. This enables these meta–stable molecules to survive long enough to react with a designated molecule.

These meta–stable particle are selective in their reactivity. It make them a potentially unique solution to problems like radioactive contamination.

Scientist are currently experimenting with mixtures of gases to work as meta–stable agents on plutonium and uranium and this is just the beginning.

EXERCISE

Q.1 Select the correct answer out of the following alternative suggestions:

(i) Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C.

(a) 546°C (b) 200°C

(c) 546 K (d) 273 K

(ii) Number of molecules in one dm^3 of water is close to:

(a) $\frac{6.02}{22.4} \times 10^{23}$ (b) $\frac{12.04}{22.04} \times 10^{23}$

(c) $\frac{18}{22.4} \times 10^{23}$ (d) $55.6 \times 6.02 \times 10^{23}$

(iii) Which of the following will have the same number of molecules at STP?

(a) 280 cm^3 of CO_2 and 280 cm^3 of N_2O

(b) 11.2 dm^3 of O_2 and 32 g of O_2

(c) 44 g of CO_2 and 11.2 dm^3 of CO

(d) 28 g of N_2 and 5.6 dm^3 of oxygen

(iv) If absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of the gas will:

(a) Remain unchanged (b) Increase four times

(c) Reduce to 1/4 (d) Be doubled

(v) How should the conditions be changed to prevent the volume of a given gas from expanding when its mass is increased?

(a) Temperature is lowered and pressure is increased.

(b) Temperature is increased and pressure is lowered.

(c) Temperature and pressure both are lowered.

(d) Temperature and pressure both are increased.

(vi) The molar volume of CO_2 is maximum at:

(a) STP (b) 127°C and 1 atm.

(c) 0°C and 2 atm. (d) 273°C and 2 atm.

(vii) The order of the rate of diffusion of gases NH_3, SO_2, Cl_2 and CO_2 is:

(a) $NH_3 > SO_2 > Cl_2 > CO_2$ (b) $NH_3 > CO_2 > SO_2 > Cl_2$

(c) $Cl_2 > SO_2 > CO_2 > NH_3$ (d) $NH_3 > CO_2 > Cl_2 > SO_2$

(viii) Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is:

(a) $\frac{1}{3}$ (b) $\frac{8}{9}$

(c) $\frac{1}{9}$ (d) $\frac{16}{17}$

(ix) Gases deviate from ideal behaviour at high pressure. Which of the following is correct for non-ideality?

(a) At high pressure, the gas molecules move in one direction only.
(b) At high pressure, the collisions between the gas molecules are increased manifold.
(c) At high pressure, the volume of the gas becomes insignificant.
(d) At high pressure, the intermolecular attractions become significant.

(x) The deviation of a gas from ideal behaviour is maximum at:

(a) −10°C and 5.0 atm. (b) −10°C and 2.0 atm.
(c) 100°C and 2.0 atm. (d) 0°C and 2.0 atm.

(xi) A real gas obeying van der waal's equation will resemble ideal gas, if:

(a) both 'a' and 'b' are large (b) both 'a' and 'b' are small
(c) 'a' is small and 'b' is large (d) 'a' is large and 'b' is small

ANSWERS

Answers		Reasons
(i)	(c)	$T_1 = 0°C$ or $T_1 = 0 + 273 = 273\text{ K}$ $T_2 = ?$ Consider any value of initial volume $V_1 = 8\text{ dm}^3$ and twice of it as final volume $V_2 = 16\text{ dm}^3$ of it as final volume $V_2 = 16\text{ dm}^3$. $V_1 = 8\text{ dm}^3$, $V_2 = 16\text{ dm}^3$ At constant pressure, we know from Charles law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ $T_2 = \frac{V_2}{V_1} \times T_1$ $= \frac{16\text{ dm}^3}{8\text{ dm}^3} \times 273\text{ K}$ $T_2 = 2 \times 273 = 546\text{ K}$ Under these conditions, the answer of $\frac{V_2}{V_1}$ will be 2 when multiplied with 273 will give 546.
(ii)	(d)	Density of water is 1 g/cm^3 means $1\text{g} = 1\text{ cm}^3$ and 1000 m^3 (1 dm^3) = 1000 g mass of 1 dm^3 of water = 1000 g. No. of moles of 1 dm^3 of water (n) $= \frac{m}{M} = \frac{1000}{18} = 55.5$ moles No. of molecules is 1 dm^3 of water (N) $= n \times N_A$ $= 55.5 \times 6.02 \times 10^{23}$ molecules

(iii)	(a)	We know that same volumes of all different gases at STP have equal no. of molecules. So, in (a) both gases CO_2 and N_2O have same volume at STP and hence have same no. of molecules.
(iv)	(b)	Since $PV = nRT$ $V = \frac{nRT}{P}$ FirstlyP_1 , V_1 and T_1 So, $V_1 = \frac{nRT_1}{P_1}$ The temperature of gas becomes double ($2T_1$) and pressure reduces to one half $\left(\frac{P_1}{2}\right)$ $V_2 = \frac{nRT_2}{P_2}$ or $V_2 = \frac{nR(2T_1)}{\frac{P_1}{2}}$ $V_2 = \frac{4nRT_1}{P_1}$ Result shows that final volume is 4 times larger than initial volume.
(v)	(a)	Increase in mass increases the no. of moles (n) and volume is volume is directly proportional to no. of molecules or moles $V \propto n$. It means volume will increase with increasing the no. of molecules. We can maintain the volume by increasing the pressure and decreasing the temperature.
(vi)	(b)	(a) At STP: Molar volume of $CO_2 = 22.414\ dm^3$ (b) $n = 1$ mole, $R = 0.821\ dm^3\ atm\ K^{-1}\ mol^{-1}$, $P = 1$ atm $T = 127°C = 127 + 273 = 400\ K$, $V = ?$ $PV = nRT$, $V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 400}{1} = 32.84\ dm^3$ (c) $T = 0°C = 273 + 0 = 273\ K$, $P = 2$ atm. $n = 1$ mole, $R = 0.082\ dm^3\ atm\ K^{-1}\ mol^{-1}$, $V = ?$ $PV = nRT$, $V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 273}{2} = 11.2\ dm^3$ (d) $T = 273°C = 273 + 273 = 546\ K$, $P = 2$ atm, $n = 1$ moles $R = 0.0821\ atm\ dm^3\ K^{-1}\ mol^{-1}$, $V = ?$ $PV = nRT$, $V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 546}{2} = 22.413\ dm^3$ Thus molar volume of CO_2 is maximum at 127°C and 1 atm.

(vii)	(b)	Molar mass of NH_3 = 17 g/mole Molar mass of SO_2 = 64 g/mole Molar mass of Cl_2 = 71 g/mole Molar mass of CO_2 = 44 g/mole According to Graham's law rate $\propto \frac{1}{\sqrt{M}}$ Mean, lesser the molar mass, greater will be the rate. The correct order of rate of diffusion is: $NH_3 > CO_2 > SO_2 > Cl_2$ 17 g/mol 44 g/mol 64 g/mol 71 g/mol
(viii)	(a)	The fraction of total pressure exerted by a gas (say O_2) in a mixture of gases (say O_2 and CH_4) is equal to its mole fraction in the mixture. Equal mass of O_2 and CH_4 is 32 g $n_{O2} = \frac{32}{32} = 1$ mole and $n_{CH4} = \frac{32}{16} = 2$ moles and Mole fraction (X_{O2} and X_{CH4}) are $X_{O2} = \frac{n_{O2}}{n_{O2} + n_{CH4}} = \frac{1}{1+2} = \frac{1}{3}$ $X_{CH4} = \frac{n_{CH4}}{n_{O2} + n_{CH4}} = \frac{2}{1+2} = \frac{2}{3}$ Hence fraction of total pressure exerted by O_2 is $\frac{1}{3}$.
(ix)	(d)	Any change that can bring gas molecules closer, will help attractive forces to dominate and gases deviate from ideality. At higher pressure, molecules come closer and attractions become significant responsible for non-ideality.
(x)	(a)	Deviation of a gas from ideal behaviour is maximum at highest pressure and lowest temperature. Because under these conditions attractions are maximum.
(xi)	(b)	Small value of factor "a" and "b" shows that weak forces and small value of excluded volume. Means lesser deviation resemble ideal gas.

Q.2 Fill in the blanks:

(i) The product PV has the S.I. unit of —————.

(ii) Eight grams each of O_2 and H_2 at 27°C will have total K.E. in the ratio of —————.

(iii) Smell of the cooking gas during leakage from a gas cylinder is due to the property of ————— of gases.

(iv) Equal ―――――― of ideal gases at the same temperature and pressure contain ―――――― number of molecules.

(v) The temperature above which a substance exists only as a gas is called ――――――.

ANSWERS

Answers	Explanation
(i) Nm	
(ii) 1 : 16	The ratio of kinetic energy of gases in a mixture is equal to ratio of their no of moles in the mixture. No. of moles in 8g of $O_2 = \frac{8}{32} = \frac{1}{4} = 0.25$ moles No. of moles in 8g of $H_2 = \frac{8}{2} = 4$ moles $O_2 : H_2$ $0.25 : 4$ $1 : 16$
(iii) Diffusion	
(iv) Volume, equal	
(v) Critical temperature	

Q.3 Label the following sentences as true or false:

(i) K.E. of molecules of a gas is zero at 0°C.

(ii) A gas in a closed container will exert much higher pressure at the bottom due to gravity than at the top.

(iii) Real gases show ideal gas behaviour at low pressure and high temperature.

(iv) Liquefaction of gases involves decrease in intermolecular spaces.

(v) An ideal gas on expansion will show Joule-Thomson effect.

ANSWERS

Answers	Correct Statement
(i) False	The temperature at which molecular motion ceases (zero K.E) is absolute zero (–273.16°C) which is not attainable.
(ii) False	According to kinetic molecular theory the gravitational force does not affect the motion of gas molecules. So gas in closed container will exert same pressure at top, bottom and on sides.
(iii) True	
(iv) True	
(v) True	

Q.4 (a) What is Boyle's law of gases? Give its experimental verification.

(b) What are isotherms? What happens to the position of the isotherms when they are plotted at high temperature for a particular gas?

(c) Why do we get a straight line when pressures exerted on a gas are plotted against inverse of volumes. This straight line change its position in the graph by varying the temperature. Justify it.

(d) How will you explain that the value of the constant K in the equation PV = K depends upon:

(i) the temperature of a gas.

(ii) the quantity of a gas.

Ans.

(a) Boyle's Law: "The volume of given amount of gas is inversely proportional to the pressure at constant temperature".

$$V \propto \frac{1}{P} \quad \text{or} \quad V = K \times \frac{1}{P} \text{ or } \quad PV = K$$

When n and T are constant and K in the above equation is a proportionality constant. It depends upon:

(i) nature of gas

(ii) pressure of gas

(iii) quantity of gas

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

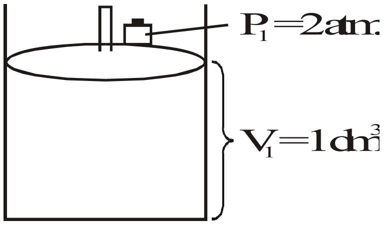
For initial pressure and volume $P_1V_1 = K$.

For final pressure and volume $P_2V_2 = K$.

Also, $P_1V_1 = P_2V_2$

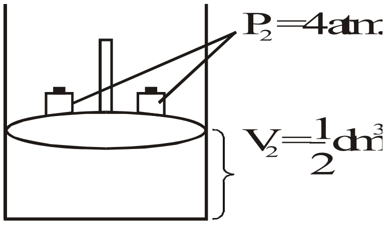
Experimental Verification: Consider initial pressure (P_1) and volume (V_1) of a gas is 2 atm and 1 dm^3 respectively

$$P_1V_1 = K$$
$$2 \times 1 = K$$
$$\boxed{K = 2}$$



When pressure of the gas is increased to 4 atm (P_2), then volume becomes $\frac{1}{2}$ dm^3 (V_2). And product will remain same.

$$P_2V_2 = K$$
$$4 \times \frac{1}{2} = K$$
$$\boxed{K = 2}$$

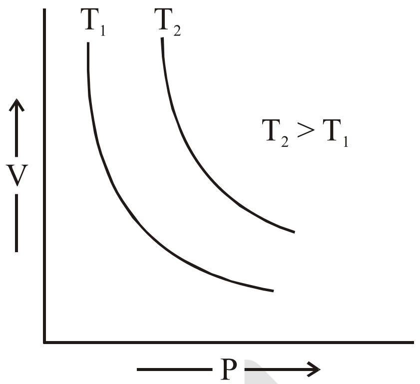


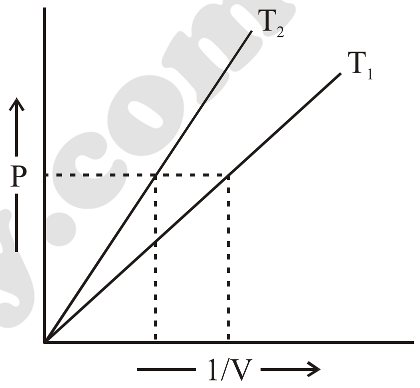
And, $P_1V_1 = P_2V_2 = K = 2$

Hence, Boyle's law is verified.

(b) Isotherm: "The curve obtained by plotting a graph between pressure on x-axis and volume on y-axis at constant temperature is called isotherm".

At high temperature, the isotherm moves away from both axis because at higher temperature volume of gas increases at the same value of pressure and vice versa.





(c) When we increase the pressure on a gas, its volume (V) decreases and its inverse (1/V) increases. Hence, there is a direct relation between pressure and inverse of volume. Increase of pressure increases the value of inverse of volume and straight-line is obtained. At higher temperature, volume increases and value of inverse of volume decreases at the same value of pressure and vice versa. And resultantly straight line move closer to pressure axis (y-axis).

(d) The value of K in the above equation depends on temperature and quantity of gas. If these two factors are kept constant, the value of K is constant (Boyle's law) otherwise as explained below:

- (i) If we increase the temperature and keep the volume constant then pressure of same amount of gas, increases and vice versa. Hence PV also increases.
- (ii) At constant temperature if we increase the quantity of gas and keep the pressure constant, then volume increases and vice versa. Hence the PV product also increases.

Q.5 (a) What is the Charles's law? Which scale of temperature is used to verify that V/T = k (Pressure and no. of moles are constant).

(b) A sample of carbon monoxide gas occupies 150.0 Cm^3 at 25°C. It is then cooled at constant pressure until it occupies 100 Cm^3. What is the new temperature?

(c) Do you think that the volume of any quantity of a gas becomes zero at −273°C, Is it not against the law of conservation of mass? How do you deduce the idea of absolute zero from this information?

Ans.

(a) **Charle's Law:** "The volume of given amount of gas is directly proportional to absolute temperature under constant pressure".

$$V \propto T$$
$$V = KT$$
$$\frac{V}{T} = K$$

The ratio of volume and temperature for fixed amount of gas at constant pressure is constant.

For initial volume (V_1) and temperature (T_1) $\Rightarrow \quad \frac{V_1}{T_1} = K$

For final volume (V_2) and temperature (T_2) $\Rightarrow \quad \frac{V_2}{T_2} = K$

Hence, $\quad \frac{V_1}{T_1} = \frac{V_2}{T_2} = K$

Kelvin scale is used to verify Charle's law because it gives the constant ratio of volume and temperature with the variation of temperature.

(b) $V_1 = 150$ ml , $T_1 = 25°C$ or $25 + 273 = 298$ K

$V_2 = 100$ ml , $T_2 = ?$

Applying Charle's law:

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

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

$$T_2 = \frac{100 \times 298}{150} = 198.6 \text{ K}$$

$$\boxed{T_2 = 198.6 \text{ K}}$$

(c) Let calculate the volume of gas at –273°C by using the following equation:

$$V_T = V_o\left(1 + \frac{T}{273}\right)$$

$$V_{-273} = V_o\left(1 + \frac{-273}{273}\right)$$

$$= V_o\left(1 - \frac{273}{273}\right)$$

$$= V_o\left(\frac{273 - 273}{273}\right)$$

$$= V_o\left(\frac{0}{273}\right)$$

$$= V_o\,(0)$$

$$\boxed{V_{-273} = 0}$$

The solution of this equation shows that volume of given mass of gas becomes equal to zero at –273°C. When gases are cooled, they are liquefied well before reaching this temperature.

When gases are converted into liquids, the concept of zero volume does not hold for liquids i.e., volume of liquids does not become zero. Hence law of conservation of mass is conserved.

From the above information, it is deduced that absolute zero is hypothetical temperature at which volume of gas is supposed to become equal to zero, if it remains in the gaseous state.

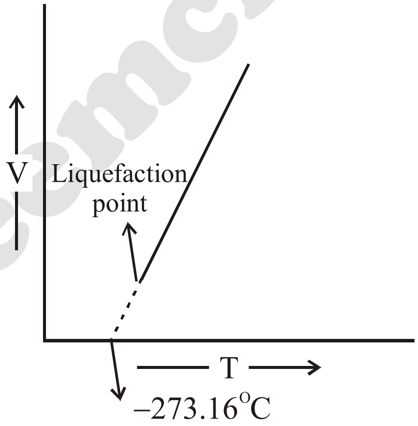
Q.6 (a) What is Kelvin scale of temperature? Plot a graph for one mole of an ideal gas to prove that a gas becomes liquid, earlier than –273.16°C.

(b) Throw some light on the factor 1/273 in Charles's law.

Ans.

(a) **Kelvin Scale:** "The temperature scale at which melting point of water is 273K and boiling point of water is 373K at 1 atm".

In the graph, continuous straight line shows the behaviour of a real gas. At the end of continuous straight line, the gas is converted into liquids earlier than –273.16°C. After this dotted line shows hypothetical behaviour of real gas.



(b) The value of volume calculated by multiplying $\frac{1}{273}$ with original volume of gas at 0°C is the volume that will increase or decrease for every degree rise or fall in temperature and it is called $\frac{1}{273}$ of original volume of gas at 0°C. Consider a gas at 0°C with volume (V_o) = 546 cm^3. Its $\frac{1}{273}$ will be $\frac{1}{273} \times 546 = 2\ cm^3$. For this gas 2 cm^3 volume will increase for every degree rise in temperature and vice versa.

Q.7 (a) What is the general gas equation? Derive it in various forms.

(b) Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of that gas.

(c) How do you justify from general gas equation that increase in temperature or decrease of pressure decreases density of the gases?

(d) Why do we feel comfortable in expressing the densities of gases in the units of gdm^{-3} or g/dm^3 rather than g/cm^3 or gcm^{-3} a unit which is used to express the densities of liquids and solids.

Ans.

(a) **General Gas Equation:** It is the combined mathematical relationship of volume in the three variables temperature, pressure and no. of moles.

OR

It is the combined mathematical relationship of gas laws i.e., Boyle's, Charles's law and Avagadro's law.

$$V \propto \frac{1}{P} \quad \text{(when n and T = constant) Boyle's law}$$

$$V \propto T \quad \text{(when n and P = constant) Charles's law}$$

$$V \propto n \quad \text{(when T and P = constant) Avogadro's law}$$

By combing the three laws:

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

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

$$\boxed{PV = nRT}$$

$$\downarrow$$

General gas equation

or

Ideal gas equation

R = General / Ideal gas constant

(A) For 1 mole of gas:

$$PV = nRT$$

When n = 1 mole

$$\frac{PV}{T} = R$$

$$\frac{P_1V_1}{T_1} = R \quad \text{or} \quad \frac{P_2V_2}{T_2} = R$$

Hence,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

(B) Verification of gas laws from general gas equation by applying respective conditions.

(1) $PV = nRT$ when n and T = constant then

$\boxed{PV = R}$ (Boyle's law)

(2) $PV = nRT$ when n and T = constant then

$V = \frac{nRT}{P}$ and $\boxed{V = KT}$ (Charles's low)

(3) $V = \frac{nRT}{P}$ when P and T are constant then

$\boxed{V = Kn}$ (Avogadro's law)

(C) General gas equation for general gas constant

$$PV = nRT$$

$$\boxed{R = \frac{PV}{nT}}$$

General gas constant for density of ideal gas:

$$PV = nRT$$

$$PV = \frac{m}{M}RT \quad \left(n = \frac{m}{M}\right)$$

$$PM = \frac{m}{V}RT$$

$$PM = dRT \quad \left(d = \frac{m}{V}\right)$$

$\boxed{d = \frac{PM}{RT}}$ units = g/dm^3

(b) By using general gas equation:

$$PV = nRT$$

or $PV = \frac{m}{M}RT$ since $n = \frac{m}{M}$

or $\boxed{M = \frac{mRT}{PV}}$

This form of general gas equation can be used to determine the molar mass of unknown gas if we known P, V, T and m of gas.

(c) From general gas equation, we have:

$$PV = nRT$$

$$PV = \frac{m}{M}RT \qquad \text{since } n = \frac{m}{M}$$

$$PM = \frac{m}{V}RT$$

$$PM = dRT$$

$$\boxed{d = \frac{PM}{RT}} \qquad \text{units} = g/dm^3$$

From this form of general gas equation we can infer that:

$$d \propto P$$

$$d \propto \frac{1}{T}$$

It is clear from this conclusion that decrease of pressure will decrease the density and increase of temperature will decrease the density as well.

(d) The densities of gases are very low as compared to liquids and solids. If we express densities in gcm^{-3}, the answer will be very small i.e., mass of gases in unit volume (1 cm^3) is very much less.

When we express the densities in bigger units (g/dm^3) the mass of gases in 1 dm^3 are more and values of densities are reasonable to be expressed. e.g., density of methane (CH_4) at 0°C and 1 atm is 0.71 g/dm^3 but if is expressed in g/cm^3, then it is $0.00071 = 7.1 \times 10^{-4}$ g/cm^3.

Q.8 Derive the units for gas constant R in general gas equation:

(a) When the pressure is in atmosphere and volume in dm^3.

(b) When the pressure is in Nm^{-2} and volume in m^3.

(c) When energy is expressed in ergs.

Ans.

(a) Unit of R:

When $P = \text{atm}$ and $V = dm^3$ units

$PV = nRT$ Since $P = 1\text{ atm}$, $V = 22.414\ dm^3$

$n = 1\text{ mole}$, $T = 273.16\ K$

$$R = \frac{PV}{nT}$$

$$R = \frac{1\text{ atm} \times 22.414\ dm^3}{1\text{ mole} \times 273.16\ K}$$

$$\boxed{R = 0.0821\ \text{atm.dm}^3.\text{mol}^{-1}K^{-1}}$$

$$= 62.4\ \text{mm Hg dm}^3\ K^{-1}\ \text{mol}^{-1}$$

$$= 62400\ \text{mm Hg cm}^3\ K^{-1}\ \text{mol}^{-1}$$

(b) When $P = Nm^{-2}$ and $V = m^{-3}$ units

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

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

$n = 1\text{ mole}$, $T = 273.16\text{ K}$

$$R = \frac{PV}{nT}$$

$$R = \frac{101325\text{ Nm}^{-2} \times 0.022414\text{ m}^3}{1\text{ mole} \times 273.16\text{ K}}$$

$$\boxed{R = 8.314\text{ Nm.mol}^{-1}\text{K}^{-1}}$$

OR

$$\boxed{R = 8.314\text{ Jmol}^{-1}\text{K}^{-1}} \quad (1\text{ Nm} = 1\text{ J})$$

$1\text{ cal} = 4.184\text{ J}$

$$R = \frac{8.314}{4.184} = 1.987\text{ cal K}^{-1}\text{mol}^{-1}$$

(c) When energy is in ergs units.

As the value of R in SI units is:

$R = 8.314\text{ Nm.mol}^{-1}\text{K}^{-1}$

$R = 8.314\text{ J mol}^{-1}\text{K}^{-1}$ (1 Nm = 1 J)

$$\boxed{R = 8.314 \times 10^7\text{ ergs mol}^{-1}\text{K}^{-1}} \quad (1\text{ J} = 10^7\text{ ergs})$$

Q.9 (a) What is Avogadro's law of gases?

(b) Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0°C and 1 atm. pressure will have Avogadro's number of particles. If not, why?

(c) Justify that 1 cm^3 of H_2 and 1 cm^3 of CH_4 at STP will have same number of molecules, when one molecule of CH_4 is 8 times heavier than that of hydrogen.

Ans.

(a) **Avogadro's Law:** "Equal volumes of all the ideal gases at the same temperature and pressure have equal no. of molecules".

22.414 dm^3 of all the ideal gases at STP have 6.02×10^{23} molecules. Also, 1 dm^3 of all the ideal gases have equal no. of molecules $\frac{6.02 \times 10^{23}}{22.414}$.

Although the sizes and masses of different gases molecules are different. But sizes and masses of the gases molecules do not affect the occupied volume. Since distance between molecules of gases are 300 times of their diameter in gaseous state.

(b) At 0°C and 1 atm pressure which are the standard conditions, 1 mole of every gas occupies volume 22.414 dm^3 and have 6.02×10^{23} i.e., Avogadro's no. of particles (molecules).

Means:

1 mole = 22.414 dm^3 = 6.02×10^{23} (Avogadro's no. of particles (molecules)

So, both 1 mole of the H_2 1 mole NH_3 will have Avogadro's no. of particles separately.

(c) According to Avogadro's law, equal volumes of different gases have equal no. of molecules at STP. Hence, 1 cm^3 of H_2 and CH_4 will have same no. of molecules separately at S.T.P.

Although CH_4 molecules is 8 times havier than H_2, but masses and sizes of gas molecules do not affect occupied volume. The reason is that the distance between gas molecules is 300 times of their diameter at STP.

Q.10 (a) Dalton's law of partial pressure is only obeyed by those gases which don't have attractive forces among their molecules. Explain it.

(b) Derive an equation to find out the partial pressure of a gas knowing the individual moles of component gases and the total pressure of the mixture.

(c) Explain that the process of respiration obeys the Dalton's Law of Partial Pressure.

(d) How do you differentiate between diffusion and effusion? Explain Graham's Law of Diffusion.

Ans.

(a) We know that partial pressure of gases depends upon the no. of collisions of gas molecules per unit area. If there are attractive forces between gas molecules, then gas molecules will start holding each other by attractive forces. As a result of that no. of collisions per unit area will be reduced, consequently partial pressure of gases in the mixture will also be reduced. Hence Dalton's law of partial pressure will not be obeyed.

Dalton's law is only applicable to the mixture of those gases in which molecules of different gases do not affect each other either by attraction or by reacting together.

(b) Consider the mixture of two gases A and B. General gas equation for the individual pressures (when they are separate) and for total pressure of the mixture is as:

(i) $P_AV = n_ART$ for gas "A" (no. of moles of gas "A" = n_A)

(ii) $P_BV = n_BRT$ for gas "B" (no. of moles of gas "B" = n_B)

(iii) $P_tV = n_tRT$ for gas mixture (total no. of moles = n_t)

Dividing eq. (i) by (iii)

$$\frac{P_AV}{P_tV} = \frac{n_ART}{n_tRT}$$

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

$$\frac{P_A}{P_t} = X_A\left(X_A = \frac{n_A}{n_t}\right)$$

$$\boxed{P_A = X_AP_t}$$

X_A is the mole fraction of gas "A" in the mixture and it is the ratio of no. of moles of gas "A" to total no. of moles.

This is the equation used to calculate the partial pressure of gas "A" in the mixture if we know the no. of moles of each component and total pressure of the mixture. Similarly, for gas B.

$$\boxed{P_B = X_B P_t}$$

(c) Partial pressure of O_2 in air is 159 torr and that of in lungs is 116 torr. Due to difference of partial pressure O_2 moves from atmosphere (high partial pressure region) to lungs (low partial pressure region). Similarly CO_2 moves out of the lungs due to difference of partial pressure i.e., higher in the lungs than atmosphere. This is how respiration occurs obeying Dalton's law of partial pressure.

(d)

Diffusion	Effusion
(i) The spontaneous mixing of molecules of different gases by random motion and collision to form homogeneous mixture is called diffusion.	(i) Escape of gas molecules to a low pressure region one by one without collision through a tiny hole is called effusion.
(ii) Collision is necessary for diffusion.	(ii) Collisions are not necessary for effusion.
(iii) It takes place through open surface.	(iii) It takes place through tiny hole.
(iv) Example: Spreading of fragrance of perfumes.	(iv) Example: Escape of air through the tiny holes of tyres and Balloons.

Graham's Law of Diffusion: The rate of diffusion and effusion of gasses is inversely proportional to the square root of density (or molar mass) of gas at constant temperature and pressure.

$$\text{Rate} \propto \frac{1}{\sqrt{d}}$$

$$r = K\frac{1}{\sqrt{d}}$$

$$r\sqrt{d} = K \qquad \ldots\ldots (1)$$

For two gases:

$$r_1\sqrt{d_1} = K \text{ gas} \qquad \ldots\ldots \text{I}$$

$$r_2\sqrt{d_2} = K \text{ gas} \qquad \ldots\ldots \text{II}$$

Divide I by II

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

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \qquad \ldots\ldots (2)$$

$$\text{Rate} \propto \frac{1}{\sqrt{M}}$$

$$r = K\frac{1}{\sqrt{M}}$$

$$r\sqrt{M} = K \qquad \ldots\ldots (1)$$

For two gases:

$$r_1\sqrt{M_1} = K \text{ gas} \qquad \ldots\ldots \text{I}$$

$$r_2\sqrt{M_2} = K \text{ gas} \qquad \ldots\ldots \text{II}$$

Divide I by II

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

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \qquad \ldots\ldots (2)$$

For eq. (1) the product of rate of diffusion of a gas and its density is constant under constant temperature and pressure. For eq. (2). The ratio of rate of diffusion of two gases is equal to the ratio of square root of their densities or molar masses.

Q.11 (a) What is critical temperature of a gas? What is its importance for liquefaction of gases? Discuss Lind's method of liquefaction of gases.

(b) What is Joule-Thomson Effect? Explain its importance in Lind's method of liquefaction of gases.

Ans.

(a) **Critical Temperature of a Gas:** The highest temperature at which a substance can exist as a liquid is called its critical temperature. It is denoted by (T_C).

Importance of Critical Temperature for the Liquefaction of Gases: The value of critical temperature for any gas tells us the value of highest temperature at which or below with continuous increase of pressure will bring about liquefaction. Above critical temperature gas cannot be liquefied how much pressure may be applied. It means for the liquefaction of gases, at least minimum of critical temperature will have to be maintained, otherwise liquefaction is not possible.

Lind's Method for Liquifaction of Gases: Descriptive question see the article in text book.

(b) **Joule Thomson Effect:** "When highly compressed gas is allowed to expand in a region of low pressure it produces cooling".

Importance of Joule Thomson Effect in Lind's Method: In Lind's method, gases are compressed by a compressor to develop very high pressure of 200 atm. When this highly compressed gas is allowed to expand through the opening of nozzel, sudden expansion takes place and gas is cooled. This sample of gas is re-circulated again and again. Every time gas is cooled and temperature is lowered, A temperature reaches at which gas is liquefied. Hence, Lind's method is based on Joule-Thomson effect.

Q.12 (a) What is the kinetic molecular theory of gas? Give its postulates.

(b) How does kinetic molecular theory of gases explain the following gas laws?

(i) Boyle's law (ii) Charles's law

(iii) Avogadro's law (iv) Graham's law of diffusion

Ans.

(a) Descriptive question, for answer see the article in text book.

(b) Descriptive question, for answer see the article in text book.

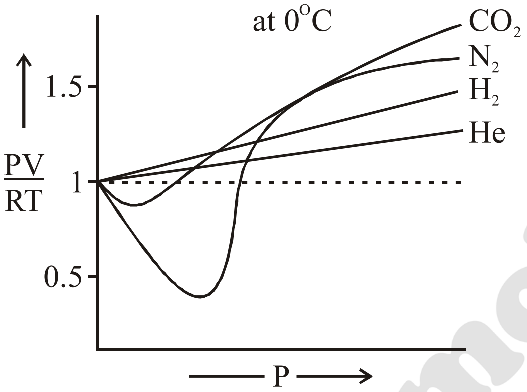
Q.13 (a) Gases show non-ideal behaviour at low temperature and high pressure. Explain this with the help of a graph.

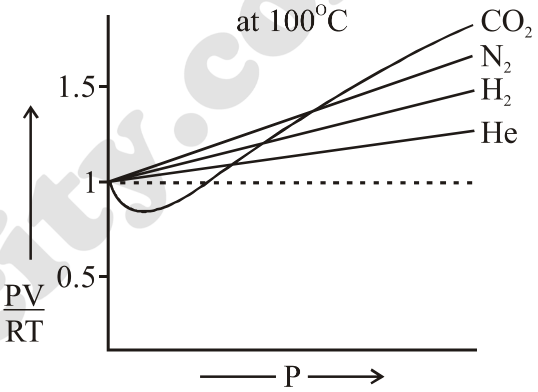
(b) Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.

(c) Hydrogen and helium are ideal at room temperature, but SO_2 and Cl_2 are non-ideal. How will you explain this?

Ans.

(a) Any condition under which attractive forces between gas molecules dominate, they show non-ideal behaviour. As high pressure bring gas molecules closer and low temperature deprive molecules of their kinetic energy, under these conditions, attractive forces are stronger and gases show non-ideal behaviour.





If we observe to right of each graph (high pressure region). There are greater deviations that than to left of each graph (low pressure region).

If we compare both the graphs as whole, the graph at low temperature (0°C) show more deviation than at high temperature (100°C).

Gases are non-ideal at low temperature and high pressure.

(b) According to Vander Waal, there are two faulty postulates of kinetic theory of gases, appreciately observed under low temperature and high pressure. These are:

(i) There are no forces of attraction between gas molecules.

(ii) The actual volume of gas molecules is negligible as compared to occupied volume.

(c) Both SO_2 and Cl_2 have strong intermolecular forces between their molecules at room temperature due to greater size and greater polarizability. Factor "b" (excluded volume) for both the gases is also very high due to their large size. That's why SO_2 and Cl_2 are non-ideal.

H_2 and He both have small sizes and lesser polarizability. Due to which they have very weak forces and hence are ideal at room temperature.

Q.14 (a) Derive Van der Waal's equation of real gases.

(b) What is the physical significance of Van der Waal's constants, 'a' and 'b'. Give their units.

Ans.

(a) Descriptive question consult the chapter.

(b) **Vander Waal's Constant "a":** "a" is the attraction per unit volume and is called co-efficient of attraction for a gas. Its value depends upon the strength of intermolecular forces.

Vander Waal's Constant "b": "b" is effective volume per mole and is also called as excluded or incompressible volume. Its value depends upon the size of gas molecules. Greater sized gas molecules will have greater value of "b".

Physical Significance of "a" and "b": The values of Vander Waal's constant "a" and "b" measures the non-ideality of a gas. Greater is the value of "a" and "b" for any gas, greater is its non-ideality. The values of "a" and "b" are index to non-ideality of a gas.

Units of "a":

$$P = \frac{an^2}{V^2}$$

$$a = \frac{PV^2}{n^2} = \frac{\text{atm}\,(\text{dm}^3)^2}{(\text{mol})^2}$$

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

SI Units of "a":

$$a = \frac{PV^2}{n^2} = \frac{\text{Nm}^{-2}\,(\text{m}^3)^2}{(\text{mol})^2}$$

$$= \text{Nm}^{-2}.\text{m}^6.\text{mol}^{-2}$$

$$= \boxed{\text{Nm}^4\ \text{mol}^{-2}}$$

Units of "b":

"b" is effective volume per mole.

$$b = \frac{V}{n}$$

$$b = \frac{\text{dm}^3}{\text{mol}}$$

$$b = \text{dm}^3.\text{mol}^{-1}$$

$$\boxed{b = \text{dm}^3.\text{mol}^{-1}}$$

SI Units of "b":

$$b = \frac{V}{n} = \frac{\text{m}^3}{\text{mol}}$$

$$\boxed{b = \text{m}^3.\text{mol}^{-1}}$$

Q.15 Explain the following facts:

(a) The plot of PV versus P is a straight line at constant temperature and with a fixed number of moles of an ideal gas.

(b) The straight line in (a) is parallel to x-axis and goes away from the pressure axis at higher pressure for many gases.

(c) The Van der Waal's constant 'b' of a gas is four times the molar volume of that gas.

(d) Pressure of NH_3 gas at given conditions (Say 1 atm. pressure and room temp.) is less as calculated by Van der Waal's equation than that calculated by general gas equation.

(e) Water vapours do not behave ideally at 273°C.

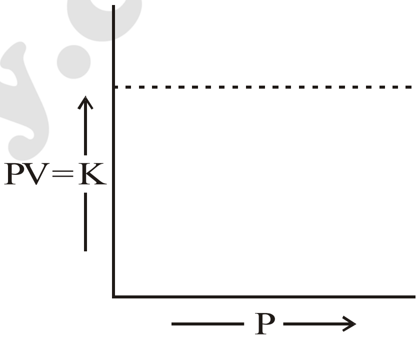
(f) SO_2 is comparatively non-ideal at 273 K but behaves ideally at 327°C.

Ans.

(a) When graph is plotted between PV along y-axis and P along x-axis, a straight line parallel to x-axis is obtained as follows:

This straight line in the graph is according to Boyle's law which states that:

"The product of pressure and volume at a constant quantity at constant temperature and for fixed no. of moles of gas".



$$PV = K$$

This straight-line also shows the ideal behaviour.

(b) At high pressure, gases deviate from gas laws and straight line moves away from pressure axis. It is due to fact that value of PV increases (because under high pressure, there is very small decrease of volume against greater increase of pressure).

This shows that gases are less compressible under high pressure.

(c) If r is the radius of a molecule, then the volume of a molecule is $\frac{4}{3}\pi r^3$. If two molecules come close to each other, the radius is 2r and excluded volume by two molecules is $\frac{4}{3}\pi(2r)^3$ or $8 \times \frac{4}{3}\pi r^3$.

Volume excluded by two molecules $= 8 \times \frac{4}{3}\pi r^3$

Volume excluded by one molecules $= 4 \times \frac{4}{3}\pi r^3$

Volume excluded by Avodagro's numbers of molecules $= N_A \times 4 \times \frac{4}{3}\pi r^3$

$$b = 4\,N_A\left(\frac{4}{3}\pi r^3\right)$$

$$b = 4\,V_m$$

where $V_m = N_A\left[\frac{4}{3}\pi r^3\right]$

(d) NH_3 gas is polar gas and at 20 atm pressure, there will be strong attractive forces between its molecules. These attractive forces decreases the no. of collisions of gas molecules. Due to these attractive forces, observed pressure will be less as calculated by Vander Waal's equation for real gases.

General gas equation treats NH_3 as ideal gas having no. forces of attraction. If we neglect the forces between NH_3 molecules then the calculated pressure will be high, as forces of attraction decreases the pressure.

Hence, pressure of NH_3 calculated by general gas equation is greater than that calculated by Van der Waal's equation.

(e) Water vapours do not behave ideally at 273°C. This temperature is below the critical temperature of water (374°C). By applying the pressure, these vapours can be converted into liquid below critical temperature because they have sufficient inter-molecular forces between them.

(f) At 273 K (0°C), being very low temperature attractive forces between SO_2 molecules are very strong and it behaves non-ideally. By increasing temperature, intermolecular forces are decreased. Hence, at 327°C, forces are very weak and SO_2 behaves ideally at this temperature.

Q.16 Helium gas in a 100 cm^3 container at a pressure of 500 torr is transferred to a container with a volume of 250 cm^3. What will be the new pressure?

(a) If no change in temperature occurs?

(b) If its temperature changes from 20°C to 15°C?

Sol.

(a)

$$V_1 = 100\ cm^3$$

$$V_2 = 250\ cm^3$$

$$P_1 = 500\ \text{torr or mm Hg}$$

$$P_2 = ?$$

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

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

$$\boxed{P_2 = 200\ \text{torr}}$$

(b)

$V_1 = 100\ cm^3$

$V_2 = 250\ cm^3$

$T_1 = 20°C = 20 + 273 = 293\ K$

$T_2 = 15°C = 15 + 273 = 288\ K$

$P_1 = 500\ torr$

$P_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2}$$

$$= \frac{500\ torr \times 100\ cm^3 \times 288\ K}{293\ K \times 250\ cm^3}$$

$$\boxed{P_2 = 196.5\ torr}$$

Q.17 (a) What are the densities in kg/m^3 of the following gases at STP (P = 101325 Nm^{-2}, T = 273 K, molecular mass is in kg mol^{-1})

(i) Methane (ii) Oxygen (iii) Hydrogen

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

(c) How do you justify that increase of volume upto 100 dm^3 at 27°C of 2 moles of NH_3 will allow the gas behave ideally, as compared to S.T.P. conditions.

Sol.

(a)

$T = 273\ K$

$P = 101325\ Nm^{-2}$

Molecular mass of CH_4 = 16 g/mol or 0.016 kg.mol^{-1}

Molecular mass of O_2 = 32 g/mol or 0.032 kg.mol^{-1}

Molecular mass of H_2 = 2 g/mol = 0.002 kg.mol^{-1}

$$d = \frac{PM}{RT}$$

$$d_{CH4} = \frac{101325\ Nm^{-2} \times 0.016\ kg.mol^{-1}}{8.313\ Nm.K^{-1}.mol^{-1} \times 273\ K}$$

$$\boxed{d_{CH4} = 0.714\ kgm^{-3}}$$

$$d_{O2} = \frac{101325\ Nm^{-2} \times 0.032\ kg.mol^{-1}}{8.313\ Nm.K^{-1}.mol^{-1} \times 273\ K}$$

$$\boxed{d_{O2} = 1.428\ kgm^{-3}}$$

$$d_{H2} = \frac{101325\ Nm^{-2} \times 0.002\ kg.mol^{-1}}{8.313\ Nm.K^{-1}\ mol^{-1} \times 273\ K}$$

$$\boxed{d_{H2} = 0.089\ kgm^{-3}}$$

(b) $H_2 \quad CH_4 \quad O_2$

Molar masses $2 < 16 < 32$

Densities $0.089 < 0.714 < 1.428$

The order of densities of all three gases is same as the order of their molar masses. Heavier gases with greater molar masses have greater density.

(c) At S.T.P volume is 22.414 dm^3 and temperature is 0°C, conditions favourable for attractive forces and gas is non-ideal. When temperature is raised to 27°C and volume is increased to 100 dm^3 (i.e., distances between gas molecules are increased). At this high temperature and greater volume, the forces are weaker and NH_3 behaves ideally.

Q.18 A sample of krypton with a volume of 6.25 dm^3, a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be its final temperature (in °C)?

Sol.

$$\begin{aligned}
V_1 &= 6.25\ dm^3 \\
V_2 &= 9.55\ dm^3 \\
P_1 &= 765\ torr \\
P_2 &= 375\ torr \\
T_1 &= 20°C + 273 \quad = \quad 293\ K \\
T_2 &= ? \\
\frac{P_1V_1}{T_1} &= \frac{P_2V_2}{T_2} \\
T_2 &= \frac{T_1}{P_1V_1} \times P_2V_2 \\
&= \frac{293\ K \times 375\ torr \times 9.55\ dm^3}{765\ torr \times 6.25\ dm^3} \\
&\boxed{T_2 = 219\ K}
\end{aligned}$$

$$\begin{aligned}
\text{Temperature in °C} &= K - 273 \\
&= 219 - 273 \\
&\boxed{T_2 = -54°C}
\end{aligned}$$

Q.19 Working at a vacuum line, a chemist isolated a gas in a weighing bulb with a volume of 255 cm^3, at a temperature of 25°C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. What is the molecular mass of this gas?

Ans.

$$\begin{aligned}
V &= 255\ cm^3 = 0.255\ dm^3 \\
T &= 25°C + 273 = 298\ K \\
P &= \frac{10}{760}\ torr = 0.0131\ atm. \\
\text{Mass} &= 12.1\ mg = 0.0121\ g \\
R &= 0.0821\ dm^3.atm.K^{-1}.mol^{-1} \\
M &= ?
\end{aligned}$$

$$PV = nRT$$

$$PV = \frac{W}{M}RT$$

$$M = \frac{WRT}{PV}$$

$$M = \frac{0.0121\ g \times 0.0821\ dm^3.atm.K^{-1}.mol^{-1} \times 298\ K}{0.0131\ atm. \times 0.255\ dm^3}$$

$$\boxed{M = 88.6\ g/mol}$$

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

Sol.

$T = 273K$

$V = 10\ dm^3$

Mol Mass of H_2 $= \frac{2g}{2g\ mol^{-1}} = 1\ mol$

Mol of N_2 $= \frac{8g}{28g\ mol^{-1}} = 0.285\ mol$

$R = 0.0821\ dm^3.atm.K^{-1}.mol^{-1}$

$PV = nRT$

$$P_{H2} = \frac{n_{H2}RT}{V}$$

$$= \frac{1\ mol \times 0.0821\ dm^3.atm.K^{-1}.mol^{-1} \times 273\ K}{10\ dm^3}$$

$P_{H2} = 2.241\ atm.$

$$P_{N2} = \frac{n_{N2}RT}{V}$$

$$= \frac{0.285\ mol \times 0.0821\ dm^3.atm.K^{-1}.mol^{-1} \times 273\ K}{10\ dm^3}$$

$P_{N2} = 0.638\ atm.$

$P_t = P_{H2} + P_{N2}$

$= 2.241\ atm. + 0.638\ atm.$

$$\boxed{P_t = 2.88\ atm.}$$

Q.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 dm^3 of A will diffuse.

(b) Hydrogen (H_2) diffuses through a porous plate at a rate of 500 cm^3 per minute at 0°C. What is the rate of diffusion of oxygen through the same porous plate at 0°C?

(c) The rate of effusion of an unknown gas A through a pinhole is find to be 0.279 times the rate of effusion of H_2 gas through the same pinhole. Calculate the molecular mass of the unknown gas at STP.

Ans. Density of gas A = 1

Density of gas B = 1.5

Volume of A diffuses = 150 dm^3

Volume of B diffuses = ?

Diffusion of volume depends upon the rates of the gas. Those gases which have greater rate of diffusion will diffuse more in volume.

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

or

$$\frac{V_A}{V_B} = \sqrt{\frac{d_B}{d_A}}$$

$$\frac{150}{V_B} = \sqrt{\frac{1.15}{1}}$$

$$\frac{150}{V_B} = 1.224$$

$$V_B = \frac{150}{1.224}$$

$$\boxed{V_B = 122.5\ dm^3}$$

(b) Rate of diffusion of oxygen = ?

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

Molecular mass of O_2 = 32g mol^{-1}

$$\frac{r_{H2}}{r_{O2}} = \sqrt{\frac{M_{O2}}{M_{H2}}}$$

$$\frac{500}{r_{O2}} = \sqrt{\frac{32}{2}}$$

$$\frac{500}{r_{O2}} = 4$$

$$r_{O2} = \frac{500}{4}$$

$$\boxed{r_{O2} = 125\ cm^3 \text{ per mixture}}$$

(c) Rate of effusion of H_2 = 1

Rate of effusion of unknown gas = 0.279

Molecular mass of unknown gas = ?

Molecular mass H_2 = $2\ g/mol^{-2}$

$$\frac{r_{H2}}{r_{unknown}} = \sqrt{\frac{M_{unknown}}{M_{H2}}}$$

$$\frac{1}{0.279} = \sqrt{\frac{M_{unknown}}{2}}$$

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

$$12.84 = \frac{M_{unknown}}{2}$$

$$M_{unknown} = 2 \times 12.84$$

$$\boxed{M_{unknown} = 25.7\ g.mol^{-1}}$$

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

(a) $20\ cm^3$ of CH_4 at 0°C and pressure of 700 mm of mercury.

(b) $1\ cm^3$ of NH_3 at 100°C and pressure of 1.5 atm.

Sol.

(a)

$V = 20\ cm^3$ or $0.02\ dm^3$

$T = 0°C$ or $0°C + 273\ K = 273\ K$

$P = \frac{700}{760}$ mm Hg or 0.92 atm.

$n = ?$

$R = 0.0821\ atm.\ dm^3.K^{-1}.mol^{-1}$

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$= \frac{0.929\ atm. \times 0.02\ dm^3}{0.0821\ atm.dm^3.K^{-1}.mol^{-1} \times 273\ K}$$

$$= 8.2 \times 10^{-4}\ mol$$

Number of molecules $= mol \times 6.02 \times 10^{23}$

$$= 8.2 \times 10^{-4} \times 6.02 \times 10^{23}$$

$$= 4.9364 \times 10^{20}\ molecules$$

Each molecule of CH_4 contain 5 atoms. So total atoms will be

$$4.9364 \times 10^{26} \times 5 = 2.4682 \times 10^{21}\ atoms$$

(b) $V = 1\ \text{cm}^3 = 0.001\ \text{dm}^3$

$T = 100°\text{C} + 273 = 373\ \text{K}$

$P = 1.5\ \text{atm.}$

$n = ?$

$R = 0.0821\ \text{atm.dm}^3.\text{K}^{-1}.\text{mol.}$

$$n = \frac{PV}{RT}$$

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

$n = 4.8982 \times 10^{-5}$ mol

No. of molecules $= \text{mol.} \times 6.02 \times 10^{23}$

$= 4.8982 \times 10^{-5} \times 6.02 \times 10^{23}$

$= 2.948 \times 10^{19}$ molecules

Each NH_3 molecule consist of 4 atoms so total atoms will be

$= 2.948 \times 10^{19} \times 4$

$= 1.179 \times 10^{20}$ atoms.

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

Ans. No. of molecule of H_2 $= 10^{20}$

Molecular mass of H_2 $= 2$ g/mol.

6.02×10^{23} molecules have mass $= 2$g

1×10^{20} molecules of H_2 have mass $= \dfrac{2 \times 1 \times 10^{20}}{6.02 \times 10^{23}} = 3.32 \times 10^{-4}$ g

6.02×10^{23} molecules of O_2 have mass $= 32$ g

1×10^{20} molecules of O_2 have mass $= \dfrac{32 \times 1 \times 10^{20}}{6.02 \times 10^{23}} = 5.31 \times 10^{-3}$ g

6.02×10^{23} molecules of CO_2 have mass $= 44$ g

1×10^{20} molecules of CO_2 have mass $= \dfrac{44 \times 10^{20}}{6.02 \times 10^{23}} = 7.30 \times 10^{-3}$ g

There will be no change in masses by increasing temperature and decreasing pressure.

Q.24 (a) Two moles of NH_3 are enclosed in a 5 dm^3 flask at 27°C. Calculate the pressure exerted by the gas assuming that:

(i) Gas behaves like an ideal gas.

(ii) Gas behaves like a real gas.

$a = 4.17 \text{ atm. dm}^3 \text{ . mol}^{-2}$

$b = 0.0371 \text{ dm}^3 \text{ . mol}^{-1}$

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

(c) Do you expect the same decrease in the pressure of 2 moles of NH_3 having a volume of 40 dm^3 and at temperature of 27°C.

Ans.

(a) Gas is NH_3:

No. of moles of NH_3 = 2.00

Volume of NH_3 = 5.00 dm^3

Temperature of NH_3 = 27°C + 273 = 300 K

P = ?

(i) Using general gas equation PV= nRT

$$P = \frac{nRT}{V}$$

$$P = \frac{2.00 \text{ moles} \times 0.0821 \text{ dm}^3\text{.atm.K}^{-1}\text{.mol}^{-1} \times 300 \text{ K}}{5.00 \text{ dm}^3}$$

$$P = \frac{2.00 \times 0.0821 \times 300}{5.00} \text{ atm.}$$

$$P = \frac{49.26}{5.00}$$

$$\boxed{P = 9.85 \text{ atm.}}$$

(ii) Using Vander Waal's equation:

$b = 0.0371 \text{ dm}^3\text{.mol}^{-1}$

Formula used:

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

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

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

$$= \frac{2 \times 0.0821 \times 300}{(5 - (2 \times 0.0371))} - \frac{2^2 \times 4.17}{(5.0)^2}$$

$$= \frac{49.26}{5 - 0.0742} - \frac{16.68}{25}$$

$$= \frac{49.26}{4.92} - \frac{16.68}{25}$$

$$\boxed{P = 9.34 \text{ atm.}}$$

(b) Amount of pressure lessened = 9.85 – 9.34

$$= \boxed{0.51 \text{ atm.}}$$

(c) When two moles of NH_3 at 27°C is allowed to occupy 40 dm^3 of volume instead of 5 dm^3, the pressure will be less as compared to the above calculations in part 'a'. Due to greater volume, the forces of attractions has decreased. So, gas has not remained as much non-ideal and amount of pressure lessened is small.

$$P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300 \text{ K}}{40} = 1.238 \text{ atm.}$$

[illegible] KNOW?

1. S.I units of pressure = Pascal
1 Pascal = 1 Nm^{-2}
1 atmospheric pressure = 76 cm Hg
= 760 mm Hg
= 760 torr
= 101325 Pascal
= 101325 Nm^{-2}
= 101.325 K. Pascal
= 1.01325 bar (1 bar = 100,000 Pascal)
= 14.7 lbs per sq. inch (lbs / □″) / psi

2. 1 kg = 2.2046 lbs (Pounds)

3. A liquid other than Hg can also be used in the Barometer. Hg is preferred due to its density.

4. Charles's low is obeyed in the Kelvin scale and not in the centrigrade scale.

5. The unit millibar is used by meterologists.

6. At –40° centigrade scale = Fahrenheit scale. For example: –40°C = –40°F.

7. The amount of heat required to raise the temperature of one gram of water through 1°C is called is equal to 1 calorie.

8. The amount of heat required to raise the temperature of one pound of water through 1°F is equal to 1 BTU (British thermal Unit).

9. Water boil at 69°C at Mount Evrest where atmospheric pressure = 323 mm Hg (323 torr).

10. Joule is defined as the energy expended when a force of 1 Newton moves an object 1 meter in the direction of the force.

1 J = 1 N × 1 m

11. 1 J = 10^7 ergs

12. Bernouli (1738) gave the kinetic molecular theory of gases.

13. Clausius (1857) formed kinetic equation of gases.

14. Maxwell gave the law of distribution of velocities of gases.

15. Boltzman studied the distribution of energies among the gas molecules.

16. Vander Waal studied the non-ideal behaviour of gases.

17. $C_{rms} = \sqrt{\frac{3RT}{M}}$

18. Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

19. Most probable velocity $= \sqrt{\frac{2RT}{M}}$

20. Non-polar gases have low polarizability and low critical temperature.

21. Polar gases have high critical temperature and non-polar gases have low critical temperature.

22. Ideal gases do not obey Joule-Thomson's effect.

23. $\frac{PV}{RT}$ is called compressibility factor.

24. The compressibility factor for an ideal gas is unity for all conditions of temperature and pressure.

25. H_2 and He cannot be liquefied by the Lind's method.

26. Plasma was identified by William Crooks in 1879.

27. The sun is a 1.5 million kilometer ball of Plasma.

28. The ionized gas mixture consisting of ions, electrons and neutral atoms is called plasma.

29. Absolute zero = $-273.16°C = 0K$
$= -459°F$

30. B.P of H_2O is 200°C at 11664 mm Hg.

Chapter 4

LIQUID AND SOLIDS

INTRAMOLECULAR FORCES

"The force of attraction between the atoms within a molecule are called **intramolecular forces**." Intramolecular forces are stronger than the intermolecular forces.

INTERMOLECULAR FORCES

"The weak forces which are present between the molecules are called **intermolecular forces**."

"Inter" is a "Latin" word means "between". These forces are mostly present in liquids and solids. These forces are present when atoms or molecules are present very close together. These forces includes;

(1) Dipole – dipole forces.
(2) Ion – dipole forces.
(3) Dipole – induced dipole forces.
(4) Induced dipole – induced dipole forces or London dispersion forces.
(5) Hydrogen bonding.

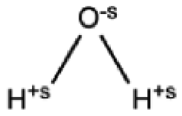
Except hydrogen bonding, all these forces are also called **Vander Waals forces**. Physical state of matter depends upon intermolecular forces present between its molecules.

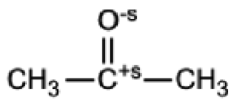
(1) DIPOLE – DIPOLE FORCES

"The force which is present between positive pole of a molecule and the negative pole of other polar molecule."

For example, HCl is a polar molecule, due to greater electronegative of chlorine.

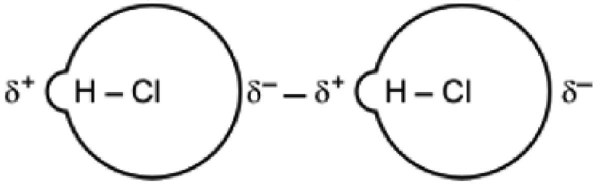
$H^{\delta+} - Cl^{\delta-}$





(Acetone)

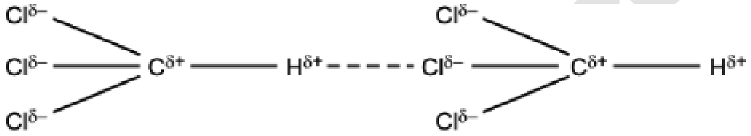
Chlorine being more electronegative, develops the partial negative charge and hydrogen develops the partial positive charge. So, whenever the molecules are close to each other, they tend to line up. The positive end of one molecule attracts the negative end of the other molecule. However, due to greater kinetic energy, these molecules do not have **permanent** perfect **alignment**.



There is net attraction between polar molecules. These forces are approximately one percent as effective as covalent bond.

Strength of Dipole – Dipole Attraction:

The strength of dipole – dipole attraction depends upon the difference of electronegative between bonded atoms and the distances between them. Dipole attraction between HCl molecules is greater than HBr molecules, due the greater electronegative of chlorine. Gas molecules have greater distance than liquids and solids and have very small forces of attraction between them. Dipole – dipole attraction between $CHCl_3$ (chloroform) molecules are shown below.



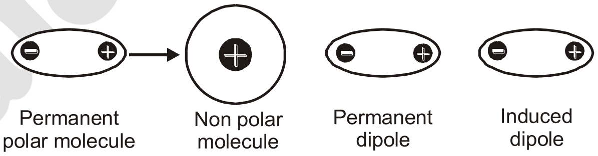
(Dipole-dipole forces in chloroform)

Effect of Dipole – Dipole Forces:

Melting point, boiling point, heat of vaporization and heat of sublimation of different substances are based upon their intermolecular forces. Greater is the strength of these forces; greater will be the properties like M.P, B.P, heat of vaporization and heat of sublimation.

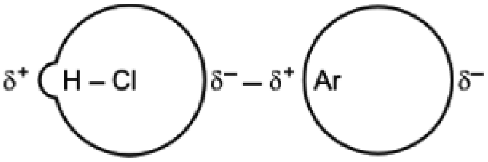
(2) DIPOLE – INDUCED DIPOLE FORCES (DEBYE FORCES)

"The forces which are present between polar and non-polar molecules are called **dipole – induced dipole forces**."



(Dipole Induced dipole ineteractions)

Sometimes, we have a mixture of substances containing polar and non-polar molecules. The positive end of polar molecule attracts the mobile electrons of the nearby non-polar molecule. In this way, polarity is induced in non–polar molecule, and both molecules become dipolar.



For example, when HCl (a polar molecule) and argon (non–polar molecule) are mixed together, they attract each other with these forces. When an argon atom comes close to a polar HCl molecule, the electron can shift to one side of the nucleus to produce a very small dipole for an instant. By distorting the distribution of electrons around the argon atom, induced dipole is formed. Force of attraction between polar HCl and induced dipole of argon is called **dipole – included dipole attraction**. This force is very weak, with a bond energy of **1 kJ / mole**.

(3) INSTANTANEOUS DIPOLE – INDUCED DIPOLE FORCES OR (LONDON DISPERSION FORCES)

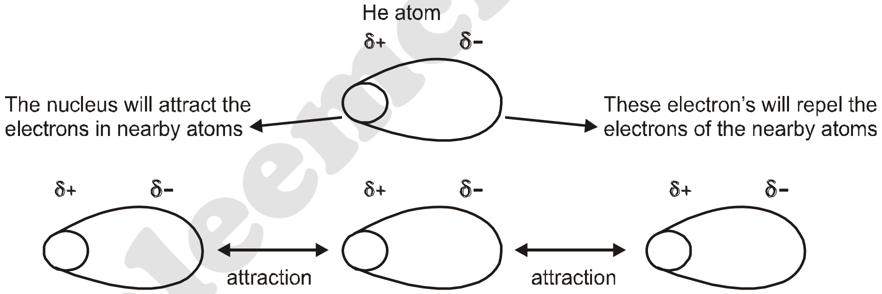
Neither dipole – dipole nor dipole induced dipole forces can explain the fact that helium becomes a liquid at temperature below 4.2K. Non-polar gases like noble gases (He, Ne, Ar, Kr, Xe), methane, chlorine etc, becomes liquid at low temperature and high pressure.

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

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 move nearer to the electron of other atom, they are pushed away from each other. In this way a temporary dipole is created in the atom as shown in the figure.

The result is that, at any moment, the electron density of the atom is no more symmetrical. It has more negative charge on one side than one the other. At that particular instant, the atom becomes a dipole. This is called **instantaneous dipole**. This instantaneous dipole then disturbs the electronic could of other molecule and forms induced dipole.

"The momentary force of attraction created between instantaneous dipole and the induced dipole is called **Instantaneous dipole – induced dipole interaction or London dispersion forces**."



(Instantaneous dipole-induced dipole attractions)

It is a very short-lived attraction because the electrons keep moving. This movement of electrons cause the dipoles to vanish as quickly as they are formed. Anyhow, a moment later, the dipoles will appear in different orientation and again weak attractions are developed.

London force are present in all types of molecules whether polar non–polar but they are very significant for non–polar molecules like Cl_2, H_2 and noble gases.

POLARIZABILITY

"The distortion of electronic could of an atom or molecule is called **polarizability**."

Polarizability of atoms depend upon the size and atomic number. In a group of the periodic table, size of atom increases and polarize ability increases. I_2 has more polarizability than Cl_2 and Br_2.

By increasing atomic number in a group, the polarizability increases.

FACTORS AFFECTING THE LONDON DISPERSION FORCES

(i) Boiling points and physical state of noble gases and halogens.

London forces are weaker than dipole – dipole interactions. The strength of these forces depend upon the size of the electronic could of the atom or molecules. When the **size of the atom** or molecule is **large** then the dispersion becomes easy and these **force become** more prominent. The elements of the zero group in the periodic table are all **mono–atomic** gases. They don't make covalent bonds with other atoms because their outermost shells are complete. Their boiling points increase down in the group from helium to radon. The following graph shows the increase in their boiling points. Boiling points of noble gases are given in Table.

The atomic number increase 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 polarize ability of these atoms go on increasing.

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

Similarly, the boiling points of halogens in group VII – A also increase from fluorine to iodine. All the halogens are non–polar diatomic molecules, but there is a big difference in their physical states at room temperature. Fluorine is a gas and boils at – 188.1^{o}C. While iodine is a solid at room temperature which boils at + 184.4^{o}C. The polarizability of iodine molecule is much greater than that of fluorine.

TABLE

Boiling Points of Halogens and Noble Gases.

Group VII A	B.P (^{o}C)	Zero Group	B.P (^{o}C)
F_2	– 188.1	He	– 268.6
Cl_2	– 34.6	Ne	– 245.9
Br_2	58.8	Ar	– 185.7
I_2	184.4	Kr	– 152.3
		Xe	– 107.1
		Rn	– 61.8

(ii) Physical states and boiling points of hydrocarbon molecules.

Another important factor that affects the strength of London forces is the number of atoms in a non–polar molecule. **Greater the number of atoms** in a molecule, **greater is its polarizability**. Let us discuss the boiling points of saturated hydrocarbons. These hydrocarbons have chain of C–atoms linked with hydrogen atoms. Compare the length of the chain for C_2H_6

and C_6H_{14}. They have the boiling points – 88.6°C and 68.7°C respectively. This means that the molecule with a large chain length experiences stronger attractive forces. The reason is that longer molecules have more places along its length where they can be attracted to other molecules. It is very interesting to know that with the increasing molecular mass of these hydrocarbons, they change from gaseous to liquid and then finally become solids. The following Table gives the boiling points and the physical states of some hydrocarbons.

TABLE

Boiling Points and Physical States of Some Hydrocarbons.

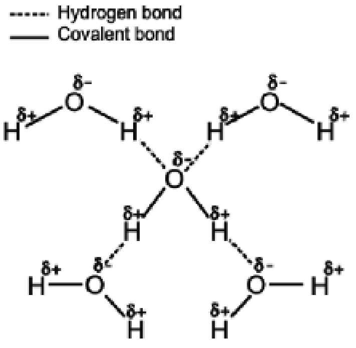
Molecular formula	B.P (^{o}C at 1 atmosphere)	Physical state at STP
CH_4	– 161.5	Gas
C_2H_6	– 88.6	Gas
C_3H_8	– 42.1	Gas
C_4H_{10}	– 0.5	Gas
C_5H_{12}	36.1	Liquid
C_6H_{14}	68.7	Liquid
$C_{10}H_{22}$	174.1	Liquid
Iso-decane	327°	Liquid

(4) HYDROGEN BONDING

"An intermolecular attraction between covalently bonded polar hydrogen and lone pair of highly electronegative atoms like N, O or F, is called **hydrogen bonding**."

Examples:

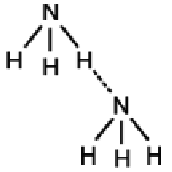
(1) To understand hydrogen bonding, let us consider the molecule of water. Oxygen is more electronegative element as compared to hydrogen, so water is a polar molecule. Hence there will be dipole – dipole interactions between partial positively charged hydrogen atom and partial negatively charged oxygen atom. Actually hydrogen bonding is something more than simple dipole – dipole interaction. Firstly, oxygen atom has two lone pairs. Secondly, hydrogen has sufficient partial positive charge. Both the hydrogen atom of water molecule create strong electrical field due to their small size. The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons.



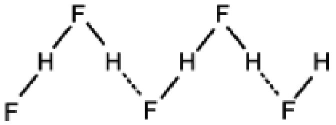
Hydrogen bonding in water

H_2O is liquid at room temperature due to hydrogen bonding, while other hydrides of group VI (H_2S, H_2Se, H_2Te) are gases are room temperature.

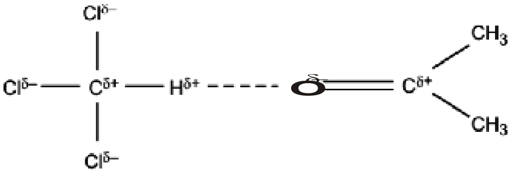
(2) NH_3 is an example of N – H……N type of hydrogen bond. This hydrogen bond is only about half as strong as O – H……O bond in water, because of the smaller electronegative of nitrogen than oxygen.



(3) There is strong hydrogen bonding in HF.
HF has zigzag arrangement hydrogen bonding.
HF is **liquid** at room temperature due to hydrogen bond.
HF molecule has low acidic strength than HCl, and HI.
HF is weakest acidic in halogen acids. In HF, partial positive hydrogen is entrapped between two highly electronegative atom.



(4) **Acetone and chloroform** are miscible liquids due to hydrogen bonding. In this case partial positive hydrogen of $CHCl_3$ attract the lone pair of oxygen present in acetone as shown in diagram.



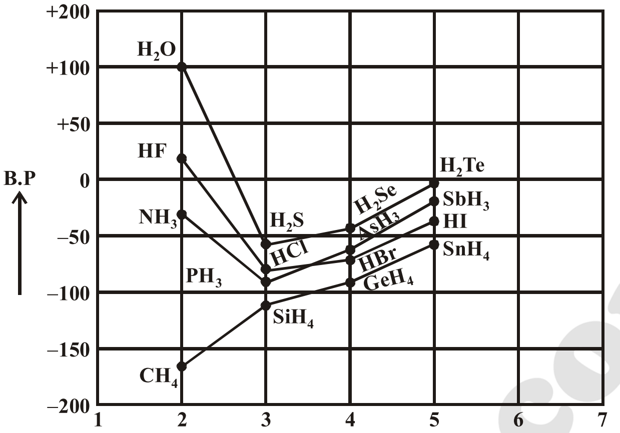
Hydrogen bonding between chloroform and Acetone

PROPERTIES OF COMPOUNDS CONTAINING HYDROGEN – BONDING

1. Thermodynamic Properties of Covalent Hydrides:

Hydrogen bonding exists in compounds having partial positively charged hydrogen and highly electronegative atoms bearing partial negative charge. Obviously such intermolecular attractions will influence the physical properties like **melting and boiling points**. Let us compare the physical properties of hydrides of group IV – A, V – A, VI – A and VII A. The graphs are plotted between the period number of the periodic Table on x–axis and boiling points in Kelvin on y–axis as shown in figure.

A look at the boiling points of hydrides of group IV – A convinces us that they have low boiling points as compared to those of group V – A, VI – A, VII – A. The reason is that these elements are least electronegative. CH_4 has the lowest boiling points because it is a very small molecule and its polarize ability is the least.



Graph between period number and boiling point

Hydrides	B.P (^{o}C)
CH_4	– 164
SiH_4	– 112
GeH_4	– 88
SnH_4	– 52
NH_3	– 36.5
PH_3	– 88
AsH_3	– 55
SbH_3	– 17
H_2O	100
H_2 S	– 61
H_2 Se	– 42
H_2 Te	– 2
HF	19.9
HCl	– 85
HBr	– 67
HI	– 36

When we consider the hydrides of group V – A, VI – A, VII – A then NH_3, HF and H_2O show maximum boiling points in the respective series. The reason is, the enhanced electronegative character of N, O and F. That is why, water is liquid at room temperature, but H_2S and H_2Se are gases.

Boiling point of water seems to be more affected by hydrogen bonding than that of HF. Fluorine is more electronegative than oxygen. So, we should expect H – bonding in HF to be stronger than that in water and as a result the boiling point of HF should be higher than that of H_2O. However it is lower and the reason is that the fluorine atom can make only one hydrogen bond with electropositive hydrogen of a neighbouring molecule but 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.

HF is liquid due to hydrogen bonding and other hydrogen halides are gases due to lack of hydrogen bonding. Almost no hydrogen bonding exist in HCl and none in HBr or HI. Boiling point of HCl is less than HBr. Hydrides of fourth period of GeH_4, AsH_3, H_2S and HBr show greater boiling points than those of third period due to greater size and greater polarize ability.

2. Solubility of Hydrogen – Bonded Molecules:

Water is the best example of H – bonded system. Similarly ethyl alcohol (C_2H_5OH) also has the tendency to form hydrogen bonds. So, ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other. Similarly carboxylic acids are also soluble in water, if their sizes are small. Hydrocarbons not soluble in water at all, because they are non–polar compounds and there are no chances of hydrogen bonding between water and hydrocarbon molecules.

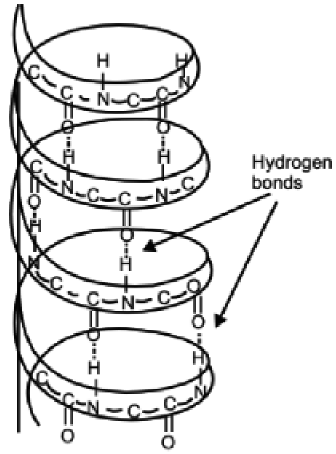
3. Cleansing Action:

Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen – bonding and the non–polar parts remain outside water.

4. APPLICATION OF HYDROGEN BONDING IN BIOLOGICAL COMPOUNDS

(a) Proteins:

Hydrogen bonding exists in the molecules of living system. amino acids combine through peptide bond and form proteins. Many fibrous proteins like hair, nail, horn, skin, feather, etc, are composed of secondary structure pattern of proteins. These long chains are coiled about one another into a spiral. This spiral is called a **helix**. Such a helix may either be right handed or left – handed. In the case of right – handed helix the groups like > C = O are vertically adjacent to one another and they are linked together by hydrogen bonds. These H – bonds links one spiral to the other. X–ray analysis has shown that one the average there are 27 amino acid units for each turn of the helix.

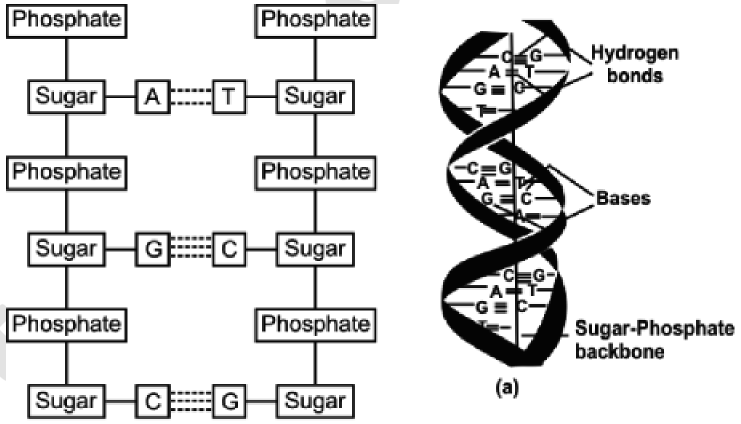


Hydrogen bonding in α-helix of proteins

(b) Deoxyribonucleic acid DNA:

DNA is a heredity material and it is double helix of nucleotide. Each nucleotides consists of 5 carbon sugar, phosphate and a base molecule. There are two types of base molecules purines and pyrimidines. Purine consists of adenine and guanine while pyrimidines consist of thymine, and cytosine. Complementary bases are attached through hydrogen bonding. Adenine form double hydrogen bond with thymine. Guanine form triple hydrogen bond with cytosine.

These nucleotide chains folds to form the double helix like spiral staircase. Diameter of helix is 18 – 20 °A.



Hydrogen bonding in DNA double helix.

5. Hydrogen Bonding in Paints and Dyes:

One of the most important properties of paints and dyes is their adhesive action. This property is developed due to hydrogen bonding. Similar type of hydrogen bonding makes glue and honey sticky substances.

6. Clothing:

We use cotton, silk or synthetic fibers for clothing. Hydrogen bonding is of vital importance in these thread making materials. This hydrogen bonding is responsible for their rigidity and the tensile strength.

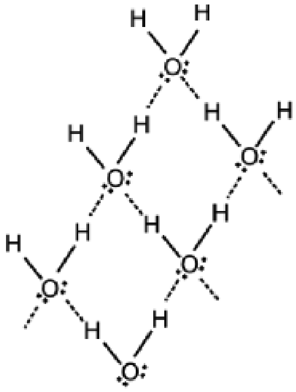
7. Food Materials:

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.

8. Structure of Ice:

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. 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. 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. Hexagonal empty spaces are created in the structure as shown in the following Figure.

That is why when water freezes it **occupies 9% more space** and its density decreases. The result is that ice floats on water. The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the center of tetrahedron just like the oxygen of water molecule in ice.



(a) (Structure of liquid water)

The lower density of ice than liquid water at $0^{\circ}C$ compels water in ponds and lakes to freeze from surface to the downward direction. Water attains the temperature of $4^{\circ}C$ by the fall of temperature in the surrounding. As the outer atmosphere becomes further cold, the water at the surface becomes less dense. This less dense water below $4^{\circ}C$ stays on the top of slightly warm water underneath. A stage reaches when it freezes. This layer of ice insulates water underneath for further heat loss. Fish and plants survive under this thick blanket of ice for months.

Keeping the whole discussion in view we are forced to believe that the pattern of life for the plants and animals would have been totally different in the absence of H – bonding in water.

EVAPORATION

"The conversion of a liquid into vapours in an open container at all temperatures is called **evaporation**."

In order to understand evaporation, we have to examine the movement of molecules in liquids. The molecules of a liquid are not motionless. The energy of molecules is not equally distributed. The molecules which have low kinetic energy move slowly, while others with high kinetic energy move faster. If one of the higher speed molecules reaches the surface, it may escape the attractions of neighbouring molecules and leaves the bulk of the liquid. This spontaneous change of a liquid into its vapours is called evaporation and its continues at all temperatures.

Evaporation Causes Cooling:

Temperature is a measure of average kinetic energy of all the molecules of a liquid. As the liquid evaporates, the escape of high energy molecules from the liquid **lowers the average kinetic energy of the remaining molecules** in the liquid. As a result, the temperature of the liquid falls down. Thus evaporation will cause cooling. As the evaporation process proceeds it absorbs more and more heat from the surrounding therefore, temperature of the surrounding also decreases.

FACTORS AFFECTING EVAPORATION

1. Intermolecular Forces:

The liquids with greater intermolecular forces have less evaporation. The escaping tendency of molecules depend upon attractive forces between molecules. Water has greater intermolecular force than gasoline and has less evaporation rate. Ether evaporates faster than ethyl alcohol.

2. Temperature:

Evaporation occurs at all temperatures. Rate of evaporation is however, affected by the change in temperature. On increasing temperature, the number of molecules having high kinetic energy increases and such molecules escape more readily from the surface of the liquid. Therefore, the rate of evaporation increases by increasing temperature.

3. Surface Area:

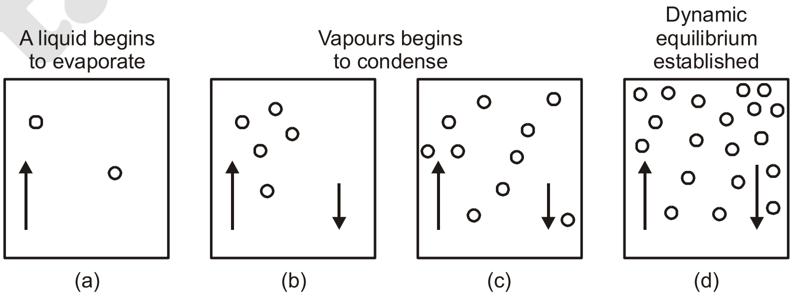
Evaporation of a liquid takes place at the surface. If surface area is increased, more molecules are able to escape from the surface quickly.

VAPOUR PRESSURE

"The pressure exerted by vapours in equilibrium with its pure liquid at given temperature is called **vapour pressure**."

When the molecules of a liquid leave the open surface, they mixed up with air above the liquid. If the vessel is open these molecules go on leaving the surface. But if we close the system the molecules of liquid start gathering above the surface. These molecules not only collide with the walls of the container but also with the surface of the liquid as well and there are chances that these molecules are recaptured by the surface of liquid. This process is called **condensation**. The two–processes i.e., evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation. This is called the state of **dynamic equilibrium**. At this state the pressure exerted by the vapour on the surface of liquid is called its vapour pressure at that temperature.

$$\text{Liquid} \rightleftharpoons \text{Vapours}$$



Evaporation of a liquid and establishment of dynamic equilibrium between liquid and its vapours

The number of molecules leaving the surface is just equal to the number of molecules coming back into it, at a constant temperature. The molecules which are in the liquid state at any moment may be in vapour state in the next moment.

The magnitude of vapour pressure does not depend upon the amount of liquid in the container or the volume of container. It also does not depend on surface area of a liquid. The larger surface area also presents a larger target for returning the molecules, so the rate of condensation also increases.

FACTORS AFFECTING THE VAPOUR PRESSURE

1. Intermolecular Forces:

Vapour pressure depends upon the extent of intermolecular attractive forces. Those liquids which have greater intermolecular forces have less evaporation. For example, at same temperature, vapour pressure of water is less than ether due to greater intermolecular forces.

Name of compound	Formula	Vapour pressure at 20°C [mn Hg (torr)]
Isopentane	$CH_3 - CH_2 - CH\ (CH_3) - CH_3$	580
Diethyl ether	$C_2H_5 - O - C_2H_5$	442.2
Chloroform	$CHCl_3$	170
Carbon tetrachloride	CCl_4	87
Water	H_2O	17.54
Mercury	Hg	0.012
Glycerol	$C_3H_8O_3$	0.00016

2. Temperature:

Vapour pressure of a liquid increases with the increase of temperature. This is because the average kinetic energy of the molecules increases with the increase in temperature, which causes an increase in vapour pressure. Capability of the molecules to leave the surface of the liquid at high temperature increases. The increase of vapour pressure goes on increasing with the same difference of temperature. For example, when temperature of water increase from 0°C to 10°C, the increase of vapour pressure is of 4.63 torr (9.209 – 4.579). When temperature of water is changes from 90°C to 100°C, the increase of vapour pressure is 232.2 torr (760 – 572.8).

Vapour pressure of water at different temperature is shown in the given Tables.

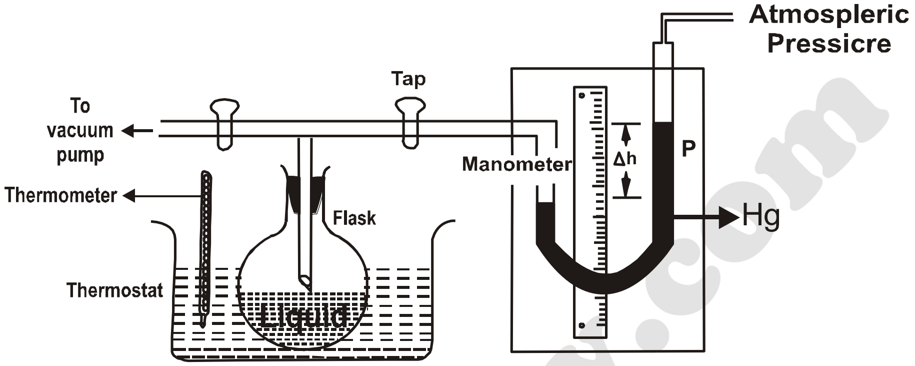
Temperature	Vapour Pressure (torr)	Temperature (°C)	Vapour Pressure (torr)
0	4.579	50	92.51
10	9.209	60	149.4
20	17.54	70	233.7
30	31.82	80	355.1
37	47.07	90	527.8
40	55.32	100	760.0

MEASUREMENT OF VAPOUR PRESSURE

There are many methods for the measurement of vapour pressure. One important method is described in the following paragraph.

Manometric Method:

Manometric method is comparatively an accurate method. The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat, as shown in the Figure.



One end of the tube of the flask is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid along with the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and released air is evacuated. This process is repeated many times till almost all the air is removed.

Now the liquid is warmed in the thermostat to that temperature at which is vapour pressure is to be determined. Difference in the heights of the columns of Hg in the two limbs of the manometer determines the vapour pressure of the liquid. The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, 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, and it is given by the following equation.

$P = P_a + \Delta h$

Where P = Vapour pressure of the liquid at 1 atmosphere pressure.

P_a = Atmospheric pressure

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer.

BOILING POINT

"The temperature to which vapour pressure of a liquid becomes equal to the atmospheric pressure or to any other external pressure to which the liquid is subjected is called **boiling point**."

The boiling point which is noted at sea level is called **normal boiling point**.

When a liquid is heated, the vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the external atmospheric pressure. This temperature is called the boiling point of that liquid. The reason for this is that the bubbles of vapour which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This makes the bubble to come out of the liquid and burst upon the surface. Thus a constant steam of bubbles comes out at the boiling point.

TABLE

Boiling Point of Some Common Liquids

Liquid	B.P (^{o}C)
Acetic acid	118.50
Acetone	56.00
Aniline	184.4
Benzene	80.15
Carbon disulphide	46.30
Carbon tetrachloride	76.50
Ethanol	78.28
Naphthalene	218.00
Phenol	181.80
Water	100.00

Molar Heat of Vapourization:

“The amount of heat required to vapourize one mole of a liquid at its boiling point is called **molar heat of vapourization**.”

The molar heat of vapourization of water is 40.6 kJ per mole.

When a liquid is heated, the kinetic energy of its molecules increases and hence the temperature also increases. At the boiling point, the kinetic energy of the molecules becomes maximum and any further heating at this stage will not increase the temperature rather this heat will only be utilized to break the intermolecular forces and convert the liquid into its vapours.

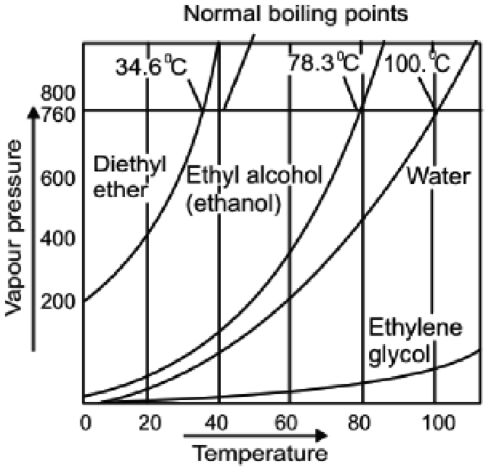
FACTORS AFFECTING THE BOILING POINT

(a) Intermolecular Forces:

Those molecules which have **greater intermolecular forces**, have **less vapour pressure**. So the molecules with stronger intermolecular forces have high boiling point. For example, boiling point of water is greater than ether, due to greater vapour pressure and less attractive forces.

The following figure show the normal boiling points of diethyl ether, ethyl alcohol and water.

It shows that the liquids reach upto their boiling points when their vapour pressures are equal to 760 torr at sea level. The start of these curves at 0^{o}C is interesting. Water takes start at 4.8 torr while diethyl ether at around 200 torr. This is due to difference in the strengths of their intermolecular forces. The curve for water goes along with temperature axis to a greater extent at the beginning as compared to ether. It means that water can hardly overcome its intermolecular forces at low temperatures. It is clear from the curves that the vapour pressure increases very rapidly when the liquids are closer to their boiling points.



Vapour pressure of four common liquids as a faction of temperature

(b) Boiling Point and External Pressure:

The boiling point of a liquid depends upon the external pressure. It increases with the increase in external pressure and decreases with the decrease in external pressure.

As we know that boiling of a liquid is that point where vapour pressure of the liquid become equal to the external pressure. If external pressure is increased, the vapour pressure of liquid becomes equal to the **increased external pressure**, at a certain higher temperature. This results an **increase in boiling point** of the liquid. On the other hand if external pressure is decreased, the vapour pressure become rather readily equal to lower external pressure at lower temperature and boiling point of the liquid decreases. Thus water boils at temperature lower than 100°C at higher altitude. Water would boil at about 98°C at Murree hills because atmospheric pressure is 700 torr. Boiling point of water at Mount Everest is 69°C because atmosphere pressure is 323 torr. At 23.7 torr water boils at 25°C and at 1489 torr water boils at 120°C.

(i) Vacuum Distillation: (Reduced Pressure Distillation):

"The distillation process that is carried out under reduced pressure or in vacuum is called the "**Vacuum Distillation**."

Vacuum distillation is based on the principle that boiling points are lowered at lower external pressures. Some liquids with high boiling point can decompose if distilled. In order to boil or distil them at lower temperature, pressure is lowered or distillation is carried out under vacuum. For example Glycerin boils at 290°C under normal atmospheric pressure (760 torr) but on lowering pressure to 50 torr it can be distilled at 210°C without decomposition.

(ii) Pressure Cooker:

The working principle of a pressure cooker is "**the boiling point of a liquid increase with external pressure**." When a liquid is heated in a pressure cooker which is a closed container, more and more vapours are accumulated over the surface of the liquid, exerting more pressure. Therefore boiling point of the liquid (say water) in pressure cooker is increased and energy supplied is conserved in it. This pressure cooker helps in cooking the meat and vegetables quickly even at high altitudes.

Temperature Remains Constant During Boiling:

The heat energy supplied to a liquid, is mostly consumed in increasing the average kinetic energy of the molecules or simply the **temperature** of the liquid. This also increase the rate of evaporation and vapour pressure of liquid go on increasing till the liquid starts boiling. Any more heat supplied is now used to **overcome the intermolecular attractive forces** and excessive energy is carried away by the molecules into their vapour state. Thus the average kinetic energy or temperature of liquid remains constant. Amount of energy which is utilized to change phase of a liquid is **latent heat of vapourization**.

ENERGETIC OF PHASE CHANGE

Different phases of a substance have different energies. When a phase change to another phase some energy is evolved. The change in energy is mostly in the form of heat.

Enthalpy Change:

"If physical or a chemical change takes place at a constant pressure, then the heat change during this process is also called **enthalpy change**."

This is denoted by ΔH. These enthalpy changes are usually expressed per mole of the substances. Three types of enthalpy changes are associated with usual physical changes.

Molar Heat of Fusion (ΔH_{fus}):

"The conversion of solid into its liquid is called **fusion or melting**."

The amount of heat required to convert one mole of solid into liquid at constant pressure is called **heat of fusion**.

MOLAR HEAT OF VAPOURIZATION (ΔH_{vap})

"The conversion of a liquid into vapour is called **evaporation**."

The amount of heat required to convert one mole of liquid into vapours at constant pressure is called molar heat of vapourization.

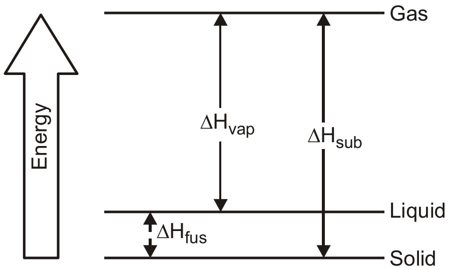
MOLAR HEAT OF SUBLIMATION (ΔH_{sub})

"The conversion of a solid into its vapours without changing into liquid state is called **sublimation**."

The amount of heat required to convent one mole of solid into its vapours without changing into liquid at constant pressure is called molar heat of sublimation.

All–these enthalpy changes are positive because they are endothermic processes.

$$\Delta H_{(sub)} = \Delta H_{(fus)} + \Delta H_{(vap)}$$



Relative energies of the solid, liquid, and gases states of at typical substance, at constant pressure

ENERGY CHANGES AND INTERMOLECULAR ATTRACTION

Strength of intermolecular forces are related to the force of attraction between the particles:

Solid $\longrightarrow$ liquid $\Delta H_{(fus)}$ (i)

Liquid $\longrightarrow$ vapour $\Delta H_{(vap)}$ (ii)

When solid melts $\Delta H_{(fus)}$ is small and less amount of energy is required to break the attraction between atoms and molecules. But the $\Delta H_{(vap)}$ has always high value than $\Delta H_{(fus)}$, because very large amount of energy is required to separate the molecules.

$\Delta H_{(sub)}$ of substance is always greater than $\Delta H_{(vap)}$ because solids have greater attraction than the liquids, $\Delta H_{(vap)}$ based upon;

1. Polarity:

Polar molecules have greater $\Delta H_{(vap)}$ than non polar molecules due to greater intermolecular forces. SO_2, H_2O and NH_3 are polar and have greater $\Delta H_{(vap)}$ than non polar molecules like F_2, Cl_2 and Br_2.

2. Polarize ability:

In halogens the $\Delta H_{(vap)}$ of I_2 is greater than all its family members due to the greater polarize ability.

3. Size of Molecule:

Molecules with greater size have greater $\Delta H_{(vap)}$. For example, hexane (C_6H_{14}) has greater $\Delta H_{(vap)}$ than methane (CH_4). Ethane C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}. Actually London dispersion forces are stronger in bigger size molecules.

Molar heat of vapourization of some liquids are given below in the Table.

TABLE

Heat of Vapourization of Some Substances.

Substance	**$\Delta H_{(vap)}$ (Kj/mole)**
H_2O	+ 40.6
NH_3	+ 21.7
HCl	+ 15.6
SO_2	+ 24.3
F_2	+ 5.9
Cl_2	+ 10.00
Br_2	+ 15.00
I_2	+ 22.00
CH_4	+ 8.60
C_2H_6	+ 15.1

C_3H_8	+ 16.9
C_6H_{14}	+ 30.1

CHANGE OF STATE AND DYNAMIC EQUILIBRIUM

Whenever, a change of state occurs the system moves towards the condition of dynamic equilibrium. Dynamic equilibrium is a situation when two opposing changes occur at equal rates. Being a chemist, we should know that the concept of dynamic equilibrium is the fate or a ultimate goal of all the reversible chemical reactions and all the physical changes.

At $0^{o}C$ solid water (ice) exist in dynamic equilibrium with liquid water.

$$\text{Ice} \overset{0°\text{C}}{\rightleftharpoons} \text{Water}$$

At $100^{o}C$ liquid water and water vapours have dynamic equilibrium.

$$\text{Liquid water} \overset{100°\text{C}}{\rightleftharpoons} \text{Water vapours.}$$

LIQUID CRYSTALS (MESOMORPHS) / DOUBLE MELTING POINT PHENOMENON

"The liquid crystals state is intermediate state between solids and liquids. The substances which have arrangement like solids but freedom of motion like liquids are called **liquid crystals**."

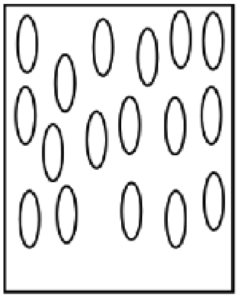
Solids have sharp melting points. The temperature remains constant at the melting point until all the solid melts. In **1888, Frederick Reinitzer**, an Austrian botanist discovered an universal property. He was studying an organic compound cholesterol benzoate. The compound turned milky liquid at $145^{o}C$ and become clear liquid at $179^{o}C$. When the substance was cooled the reverse process taken place. This turbid liquid phase was called **liquid crystal (mesomorphic form)**. Up till now, there are many crystal like solids which melt to turbid liquid phase, before finally melting to a clear liquid. These turbid liquid phases are called **liquid crystals** because they can **flow like liquids**. They have the properties like liquids as surface tension, viscosity, etc, but it is very interesting to know that the molecules of such turbid liquids possess some **degree of orderness** as well. It means that these turbid liquids resemble crystals in certain properties and the most important properties are optical properties. These turbid liquids are hence called **liquid crystals**. A liquid crystalline state exists between two temperatures i.e., melting temperature and clearing temperature.

$$\text{Crystal} \rightleftharpoons \text{Liquid crystals} \rightleftharpoons \text{Liquid (double melting – phenomenon)}$$

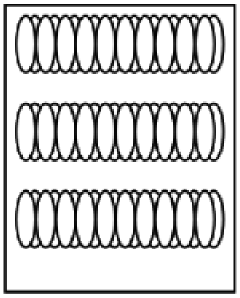
From 1888 to until about 30 years ago, liquid crystal were largely a laboratory curiosity. But now they have found large number of applications.

Properties of Liquid Crystals:

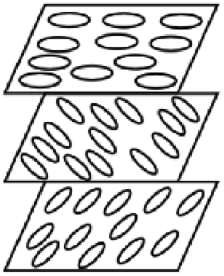
Those substance which make the liquid crystals are often composed of long rod like molecules. In the normal liquid phase, these molecules are oriented in random direction but in liquid crystals they have some orderly arrangement. Depending upon the nature of ordering, liquid crystals can be divided into three classes **nematic**, **smectic** and **cholesteric**.



Nematic



Smectic



Cholesteric

Properties of liquid crystals are intermediate between crystals and isotropic liquids. They have fluidity of liquid and the optical properties of crystals.

USES OF LIQUID CRYSTALS

Due to the remarkable optical and electrical properties, liquid crystals find many practical application. Many organic compounds and biological tissues behave as liquid crystals. Some of their important uses are as follows.

1. Temperature Sensor:

Like solid crystals, liquid crystals can diffract light. When one of the wavelengths of white light is reflected from a liquid crystal it appears coloured. As the temperature changes, the distance between the layers of the molecules of liquid crystals changes. Therefore, the colour of the reflected light changes accordingly. Thus liquid crystals can be used as temperature sensors.

2. Potential Failure:

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

3. Thermometer:

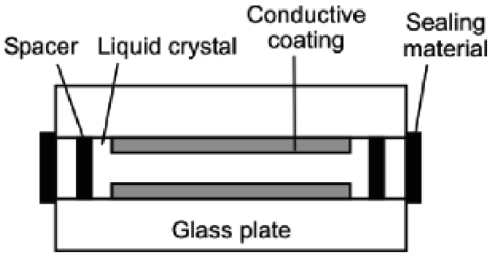
Room thermometer also contain liquid crystal with a suitable temperature range. As the temperature changes, figures show up in different colours.

4. Diagnosis:

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. 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.

5. Liquid Crystal Display (LCD):

Liquid crystal are used in the display of electrical devices such as calculators, digital watches, pH meters, laptop computers and many other electronic devices. The optical characters of liquid crystals are changed by the electrical field. In this case a thin film of liquid crystal is sandwiched between transparent electrodes arranged on glass in special patterns. When the particular segment of



A liquid crystal display device

electrode is energized, the orientation in the molecules of liquid crystal are changed. In this way, various numbers or letters are formed.

6. In the **chromatographic** separation, liquid crystals are used as **solvents**.
7. **Oscillographic and TV displays** are also use liquid crystal screens.

SOLIDS

"The substance which is rigid, hard, has definite volume and shape is called a **solid**."

In solid, atoms, ions or molecules are closely packed. They cannot move from one place to another place, but can only vibrate at their positions. They have strong cohesive forces in them. The force of attraction between similar particles is called **cohesive force**.

TYPE OF SOLIDS

On the basis of arrangement of atoms, ions or molecules, solids are classified as

(i) Crystalline solids (ii) Amorphous solids.

(i) Crystalline Solids:

"The solids in which atoms, ions or molecules have three dimensional regular arrangement, are called **crystalline solids**."

A definite geometrical shape in which atoms, ions or molecules have repeated three dimensional arrangement is called **crystals**. All crystalline substances consist of crystals. For example, diamond, sodium chloride, ice, sugar, copper, silver are crystalline solid's.

(ii) Amorphous Solids:

"The solids in which atoms, ions or molecules have irregular arrangement, are called **amorphous solids**."

The amorphous means shapeless. For example, glass, plastic, rubber and glue are amorphous solids.

Amorphous solids or **pseudo solids** have diffused melting points (not sharp).

Many crystalline solids can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way the constituent particles do not find time to arrange themselves.

A long range regularity does not exist in amorphous solids but they can possess **small regions of orderly arrangements**. These crystalline parts of otherwise amorphous solids are known as crystallites.

PROPERTIES OF CRYSTALLINE SOLIDS

1. Geometrical Shape:

All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three–dimensional space. For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown. The faces and angles remain characteristic even when the material is ground to a fine power.

2. Melting Points:

Crystalline solids have sharp melting points and can be identified from their definite melting points.

3. Cleavage Plane:

"The conversion of a bigger crystal into smaller identical crystals by applying pressure is called **cleavage**."

The plane at which pressure is applied to do so, is called **cleavage plane**. These planes are inclined to one another at a particular angle for a given crystalline solid. The value of this angle varies from one solid to another solid.

4. Anisotropy:

"The variation in the intensity of property, by changing the direction is called anisotropic property and the substance which shows such behaviour is called **anisotropic**."

The physical properties of crystalline solids like refractive index, coefficient of thermal expansion. Electrical and thermal conductivities are sometimes an isotropic in nature for some crystals. The variation in these properties with direction is due to fact that the orderly arrangement of the particles in crystalline solids is different in different directions. For example, **electrical conductivity of graphite** is greater in one direction than in another. Actually electrons in graphite are mobile for electrical conduction parallel to the layers only. Therefore, its conductivity in this direction is far better than perpendicular to the layers. Similarly cleavage is an isotropic behaviour.

5. Symmetry:

"The repetition of face, angles or edges when a crystal is rotated by 360^o along its axis is called **symmetry**."

This an important property of the crystal and there are various types of symmetrical elements found in crystals like, center of symmetry, plane of symmetry and axis of symmetry.

6. Habit of a Crystal:

"The shape of a crystal in which it usually grows is called **habit of a crystal**."

Crystals are usually obtained by cooling the saturated solution or by slow cooling of the liquid substances. If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same. If the conditions are changed the shape of the crystal may change. For example, a cubic crystal of $NaCl$ becomes needle like (octahedral having 8 faces) when 10% urea is present in its solution as an impurity. This property of crystal is called **change of habit**.

7. ISOMORPHISM

"Iso" means same "morph" means "structure".

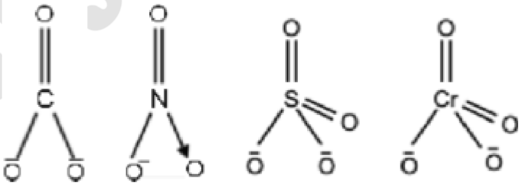
“The phenomenon in which two different substances are found in same crystalline form is called **isomorphism**. The substances which show such behaviour are called isomorphs to each other.”

Physical and chemical properties of the substances are also different from each other. Isomorphism substances crystallize together in all proportions in homogeneous mixture.

Isomorphs	Crystalline Form	Atomic Ratio
$NaNO_3$, $CaCO_3$	Rhombohedral	1 : 1 : 3
K_2SO_4, K_2CrO_4	Orthorhombic	2 : 1 : 4
$ZnSO_4$, $NiSO_4$	Orthorhombic	1 : 1 : 4
NaF, MgO	Cubic	1 : 1
Cu, Ag	Cubic	1 : 1
Zn, Cd	Hexagonal	1 : 1

In some of the isomorphic compounds, the cations have same ionic radii and anions have identical shapes. For example; in $CaCO_3$ and $NaNO_3$ ionic radius of Ca^{++} = 0.99A° and Na^+ = 0.95°A and shapes of CO_3^{2-} and NO_3^{1-} are identical.

The structure of the negatively charged ions like NO_3^{1-} and CO_3^{2-} are the same. Similarly shapes of SO_4^{2-} and CrO_4^{2-} are also alike. CO_3^{2-} and NO_3^{1-} are triangular planar, while SO_4^{2-} . CrO_4^{2-} are both tetrahedral.



8. POLYMORPHISM

“Poly” means “many” and “morph” means “structure”.

“The phenomenon in which same substance is present in more than one crystalline form is called polymorphism and the different crystalline forms are called polymorph to each other.”

Polymorphs have same chemical properties but they differ in the physical properties. The difference in physical properties is due to different structural arrangement of their particles.

Substance	Crystalline Forms
Ag NO_3	Rhombohedral, orthorhombic
$CaCO_3$	Calcite (Trigonal)
$CaCO_3$	Aragonite (Orthorhombic)

9. ALLOTROPY

"The existence of an element in more than one crystalline forms is known as allotropy and these forms of the element are called **allotropes or allotropic forms**."

Sulphur, phosphorus, carbon and tin are some important examples of elements which show allotropy:

Element	**Crystalline Forms**
Sulphur, S	Rhombic, Monoclinic
Carbon, C	Cubic (Diamond)
	Hexagonal (graphite)

Allotropy is for elements while polymorphism is for compounds.

10. TRANSITION TEMPERATURE

"The temperature at which two crystalline forms of a substance can coexist at equilibrium is called **transition temperature**."

At this temperature, one crystalline form of a substance changes to another. Above and below this temperature only one form exists. Transition temperature of some substances are given below.

(i) Grey tin (cubic) $\overset{13.2^\circ\text{C}}{\rightleftharpoons}$ White tin (Tetragonal)

(ii) Sulphur, S (rhombic) $\overset{95.5^\circ\text{C}}{\rightleftharpoons}$ Sulphur (Monoclinic)

(iii) KNO_3 (Orthorhombic) $\overset{128^\circ\text{C}}{\rightleftharpoons}$ KNO_3 (rhombohedral)

(iv) $Na_2SO_4 \cdot 10H_2O$ (hydrated form) $\overset{32.38^\circ\text{C}}{\rightleftharpoons}$ Na_2SO_4 (anhydrous form) + $10H_2O$

(v) $Na_2CO_3 \cdot 10H_2O$ (higher hydrated form) $\overset{32.02^\circ\text{C}}{\rightleftharpoons}$ $Na_2CO_3 \cdot 7H_2O$ (lower hydrated form) + $3H_2O$

It has been noticed that the transition temperature of the allotropic forms of an element is always less than its melting point.

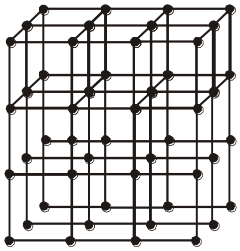
Lattice:

"The location of position of atoms, ions or molecules in solids is called **lattice**."

CRYSTAL LATTICE

“The location of the arrangement of atoms, ions or molecules in a crystal three dimensionally is called **crystal lattice or space lattice**.”

A crystal lattice is always formed by the three dimensional arrangement of particles. In a crystalline solid, atoms, ions or molecules are located at definite positions. These positions are represented by points in a crystal. These points are called **lattice points or lattice sites**. This arrangement of points is called **crystal lattice**.



Cubic crystal lattice

UNIT CELL

“The smallest part of the crystal lattice that has all the characteristic features of the entire crystal is called **unit cell**.”

For example, cubic crystal lattice is actually composed of many small parts. The smaller part – of that cubic crystal is also a cube as shown in diagram.

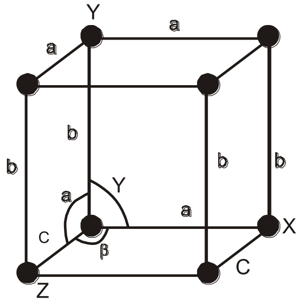
It means that a unit cell of a crystal lattice is the smallest block or geometrical figure, from which the entire crystal can be built up by repeating it in three dimensions. It shows the structural properties of a given crystal. The complete information about the crystalline structure is present within a unit cell, which repeats itself in three dimensions to form a crystal.

If we know the exact arrangement of atoms in a unit cell, we know their arrangement in the whole crystal.

Representation of a Unit Cell:

The quantitative aspects of a crystal lattice are deduced from the size and shape of the unit cell. There are three unit cell lengths a, b, c and three unit cell angles α, β and γ. These six parameters are shown in Figure.

The angle ‘α’ is between the lengths b and c, the angle ‘β’ is between the sides a and b. The unit cell lengths a, b, c, may be assigned to any axis but angles α, β and γ have to be decided accordingly. These six parameters of the unit cell are called **unit cell dimension or crystallographic elements**.



Six crystallographic elements specify the size and shape of unit cell

Keeping in view the structure of the unit cell we can understand the crystal system.

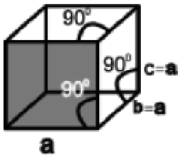
CRYSTAL SYSTEM AND THEIR CLASSIFICATION

A crystal system can be identified by the dimensions of its unit cell along its three axes, a, b, c and three angles α, β and γ. These seven crystal system, are describe below.

1. Cubic System:

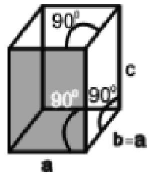
In this system all the length and their corresponding angles are equal.

$a = b = c$ and $\alpha = \beta = \gamma = 90^o$.



Cubic

2. Tetragonal System:

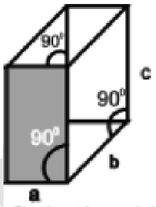


Tetragonal

Length a and b are equal but c is different. All the angles are equal.

$a = b \neq c \qquad \alpha = \beta = \gamma = 90°$

3. Orthorhombic System:

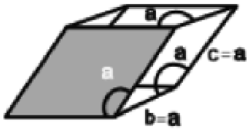


Orthothombic

All the lengths are unequal and all the angles are equal to 90^o.

$a \neq b \neq c \qquad \alpha = \beta = \gamma = 90°$

4. Trigonal or Rhombohedral System:

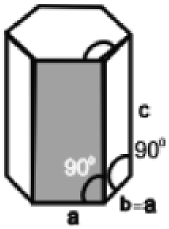


Rhombohedral

All the lengths are equal. None of the angle is of 90^o, thus.

$a = b = c \qquad \alpha = \beta = \gamma \neq 90°$

5. Hexagonal System:



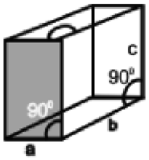
Haxagonal

Length a and b are equal but c is different and the angles α and β are of 90^o and γ is 120^o.

$a = b \neq c$ and $\alpha = \beta = 90^o$

$\gamma = 120^o$.

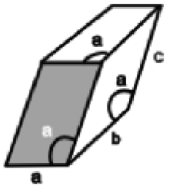
6. Monoclinic System:



Monoclinic

All the lengths are different $a \neq b \neq c$. The angle α and γ are of 90^o but $\beta \neq 90^o$.

7. Triclinic System:



Triclinic

All the lengths and angles are different. None of angles is 90^o.

Thus $a \neq b \neq c$ and

$\alpha \neq \beta \neq \gamma \neq 90^o$.

TABLE

Seven Crystal Systems

Sr. No.	Crystal system	Axes	Angles	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	Diamond, NaCl, NaBr, Fe, Cu, Ag
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	Sn, SnO_2, MnO_2, NH_4 Br
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	$BaSO_4$, I_2, Rhombic sulphur, K_2SO_4, $FeSO_4$, $7H_2O$, $ZnSO_4$, $7H_2O$
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o, \beta \neq 90^o$	Sugar, Sulphur, Borax ($Na_2B_4O_7.10H_2O$) $Na_2SO_4 . 10H_2O$, $Na_2CO_3 . 10H_2O$
5.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o, \gamma = 120^o$	Graphite, ice, ZnO CdS
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	Bi, Al_2O_3, $NaNO_3$, KNO_3, $CaCO_3$
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	H_3BO_3, $K_2Cr_2O_7$, $CuSO_4 . 5H_2O$

LATTICE ENERGY

"The amount of energy required to break one mole of an ionic solid into its ions is called **lattice energy**. It is represented by positive sign."

$$NaCl_{(s)} \longrightarrow \overset{+}{Na}_{(g)} + \overset{-}{Cl}_{(g)} \; \Delta H^0 = +787 \text{ kJ mole}^{-1}$$

A crystal may be made up of atoms, ions or molecules, held together through chemical bonds. To remove these atoms, ions or molecules from their fixed position, a definite amount of energy is required called **lattice energy**. It is also defined as "the amount of energy released when gaseous ions of opposite charges combine to give one mole of a crystalline ionic compound." Sign of energy in this case will be negative.

$$\overset{+}{Na}_{(g)} + \overset{-}{Cl}_{(g)} \longrightarrow NaCl_{(s)} \; \Delta H^0 = -787 \text{ kJ mole}^{-1}$$

It is clear from the table that lattice energy decreases with the increase in the size of the cation keeping the anion same. It also decreases with increase in the size of anion. The reason in both cases is the same. With the increase in the size of either cation or anion, the packing of oppositely charged ions becomes less and less tight.

TABLE

Lattice Energies of Some Ionic Compounds.			
Ionic Compound	**Lattice Energy ($kJ\ mole^{-1}$)**	**Ionic Compound**	**Lattice Energy ($kJ\ mole^{-1}$)**
LiCl	– 834	NaF	– 895
NaCl	– 787	NaCl	– 787
KCl	– 690	NaBr	– 728
LiBr	– 787	NaI	– 690
NaBr	– 728	KBr	– 665

CLASSIFICATION OF SOLIDS

On the basis of types of forces between atoms, ions or molecules, the crystalline solids are divided into four types.

1. Ionic solids
2. Covalent solids
3. Molecular solids
4. Metallic solids

1. Ionic Solids:

"Solids in which ionic bond is present are called **ionic solids**."

Oppositely charged ions are held together by strong electrostatic forces in them. For example, NaCl, KBr, CsCl, etc are ionic solids.

Properties of Ionic Solids:

1. Physical State:

The cations and anions are arranged in a well defined geometrical pattern, so they are crystalline solids at room temperature. Under ordinary conditions of temperature and pressure, they never exist in the form of liquids or gases.

2. High Melting and Boiling Points:

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

3. Non Directional and Close Packing:

Ionic solids do not exist as individual neutral independent molecules. Their cations and anions attract each other and these forces are non–directional. The close packing of the ions enables to occupy minimum space. A crystal lattice is developed when the ions arranged themselves systematically in an alternate manner.

4. Structure:

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.

5. Formula Mass:

In the case of ionic crystals, we always talk about the formula mass of these substances and not the molecular mass, because they do not exist in the form of molecules.

6. Conductivity:

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.

7. 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 hence begin to repel. The application of a little external force develops repulsion between two layers causing brittleness.

8. Density:

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

9. Reactions and Solubility:

Ionic compounds are mostly soluble in polar solvents. The reactions of ionic compounds are very fast.

10. Polymorphism and Isomorphism:

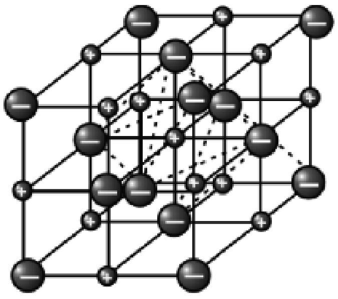
The properties like isomorphism and polymorphism are also associated with ionic crystals.

STRUCTURE OF SODIUM CHLORIDE

1. Location of Ions:

The structure of ionic crystals depends upon the structure and size of their ions. Each positive ion is surrounded by a certain number of negative ions. In case of NaCl, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. It is called co-ordination number arrangement of these ions is shown in the cubic lattice. The size of Cl^- ion is bigger than Na^+ because Cl^- has 18 electrons while Na^+ has 10 around it.

The distance between two nearest ion i.e. Cl^- ions is 5.63^oA ($1^oA = 10^{-10}$ m) so the distance between two adjacent ions of different kind is $\frac{5.63}{2} = 2.815^oA$.



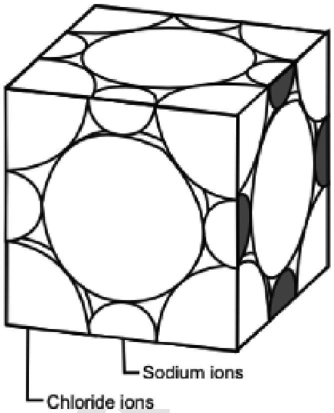
(b)

Sodium chloride lattice

Coordination Number:

“The number of negative ions, which contact with positive ion is called **coordination number**.”

Each Na^+ ion contact with six Cl^- ions at the corners of regular octahedron. So the coordination number of Na^+ ion is six. In this way coordination number of Cl^- is also six. The distance between all Na^+ ions and Cl^- is same. An independent pair of NaCl does not exist in solid form however, it has been observed that independent molecule of NaCl do exist, in the vapour phase.



Number of NaCl in each Unit Cell:

In NaCl, there are eight Cl^- ions at the each corner of cube. Each Cl^- ion shared among the eight unit cells. Each face share with two unit cells. So the number of Cl^- ions in each unit cell can be calculated.

$$\frac{8}{8}+\frac{6}{2} = 4\ Cl^-\text{ ions.}$$

or $\quad 8\text{ corners} \times \frac{1}{8}\ Cl^-\text{ per corner} = 1\ Cl^-$

$$6\text{ faces} \times \frac{1}{2}\ Cl^-\text{ per face} = \frac{3\ Cl^-}{\text{Total } 4\ Cl^-}$$

In this way number of Na^+ ions can also be calculated, Na^+ ions are present at the edges. In a cube 12 edges are present and one Na^+ is present in the center of cube. Each edge of the cube contribute one quarter to the unit cell.

So, $\quad 12\text{ edges} \times \frac{1}{4}\ Na^+\text{ per edge} = 3\ Na^+$

$1\ Na^+$ ion in center $= 1\ Na^+$

Total $= 4\ Cl^-$

Each unit of cell of NaCl consist of $4\ Na^+$ ions and $4\ Cl^-$ ions or 4 NaCl.

2. COVALENT SOLIDS OR ATOMIC SOLIDS

“The solid in which atoms are held together through a network of covalent bond are called **covalent solids**.”

For example, diamond, graphite, silicon carbides, silicon oxide (SiO_2) aluminum nitride (AlN).

Covalent Solids are of Two Types:

1. When the covalent bonds give giant molecules like diamond, silicon carbide or aluminum nitride.
2. When atoms join to form the covalent bond and separate layers are produced like that of graphite, cadmium iodide (CdI_2) and boron nitride (BN).

PROPERTIES OF COVALENT CRYSTALS

1. Network Covalent Bond:

Covalent crystals are extended in three dimensions. They contain a network of atoms. The valences of atoms are directed in definite directions, so the packing of atoms in these crystals is looser than those of ionic and metallic crystals. Thus covalent crystals have open structure.

2. Hardness:

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.

3. Conductivity:

Due to the absence of free electrons and ions they are bad conductor of electricity. However, graphite has a layered structure and the electrons are available in between the layers. These electrons become mobile and the conductivity becomes possible.

4. Solubility:

Mostly covalent crystalline solids are insoluble in polar solvents like water but they are readily soluble in non–polar solvents like benzene and carbon tetrachloride. Covalent crystals having joint 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.

5. Chemical Reactivity:

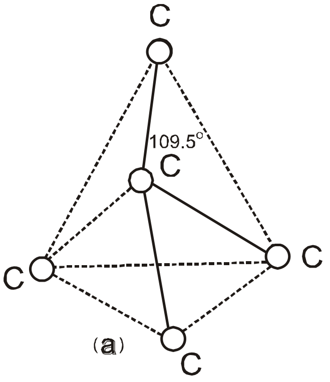
The chemical reactions of such crystalline solids are very slow.

STRUCTURE OF DIAMOND

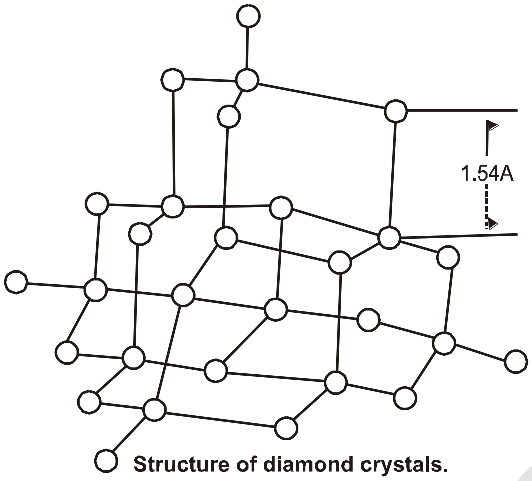
Diamond is one of the allotropic modifications of carbon. It is best understood by taking into consideration the number of electrons in the outermost shell of carbon, which are four. The four atomic orbital (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbital which are directed in space along the four corners of a tetrahedron.

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. All the bond angles are $109.5^{o}C$ and the bond lengths are 154 pm. The whole lattice is therefore 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.

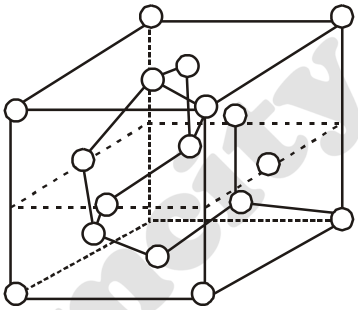


Tetrahedral unit in carbon atoms in diamond crystals



Structure of diamond crystals.

This is also called a **macromolecule**. The overall structure of diamond looks for centered cubic.



Face-centered cubic structure of diamond

Each unit cell of diamond consists of 18 carbon atoms. Eight carbons are present at corner of cube, six carbon atoms at face and four carbon atoms in tetrahedral sites.

3. MOLECULAR SOLIDS

"The crystal in which intermolecular forces are present between the individual particles are called **molecular crystals**."

Molecular solids may be polar or non–polar. For example, in solidified nobles gases, there are non–polar atoms. Sugar and glucose are polar molecular solids. Two types of intermolecular forces hold them together.

1. Dipole – Dipole Interactions.
2. Vander Waal's Forces.

These intermolecular forces are much weaker than the forces of attraction between the cations and the anions in ionic crystals, and between the atoms in the covalent crystals.

Ice and sugar are the best examples of crystals having polar molecules whereas **iodine, sulphur, phosphorous and carbon dioxide** form the molecular crystals containing **non–polar** molecules. Polar molecular solids have usually higher melting and boiling points are compared to non–polar molecular solids.

Properties of the Molecular Solids:

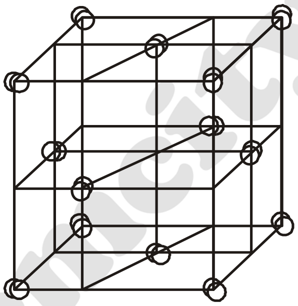
The forces, which hold the molecules together in molecular crystals, are very weak so they are soft and easily compressible.

They are mostly volatile and have low melting and boiling points. They are bad conductor of electricity, have low densities and sometimes transparent to light. Polar molecular crystals are soluble in polar solvents, while non–polar molecular crystals are usually soluble in non–polar solvents.

STRUCTURE OF IODINE (I_2) CRYSTALS

Iodine crystals has face centered cubic structure. The lattice positions are occupied by diatomic iodine molecules I_2. The lattice is held together by weak Vander Waal forces, each unit cell of I_2 consists of the fourteen I_2 molecules. Eight I_2 molecules are at the corner and six I_2 molecules are present at six faces. These unit cells combine to form further layer lattice. In solid form $I-I$ bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine which is 266.6 pm.

(1 Pico meter or pm $= 10^{-12}$ m).



The iodine crystal: iodine has a face-centered cubic structure

4. METALLIC SOLIDS

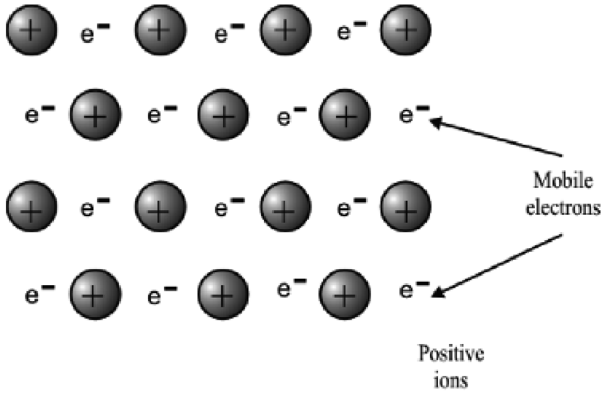
"Those solids which have metallic bond in them are called **metallic solids**."

For example, Cu, Fe, Sn, Al, Au, etc are metallic crystals.

In order to explain the properties of metallic solids, various theories about bonding have been proposed. A few of them are mentioned here.

(a) 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. These positively charged ions occupy definite positions at measurable distances from each other in the crystal lattice. Valence electrons are not attached to any individual ion or a pair of ions rather belong to the crystals as a whole. These electrons are **free to move** about from one part of the crystal to the other. The force which binds a metal cations to a number of electrons within its sphere of influence is known as metallic bond.



Positive ions surrounded mobile electrons

(b) Valence Bond Theory:

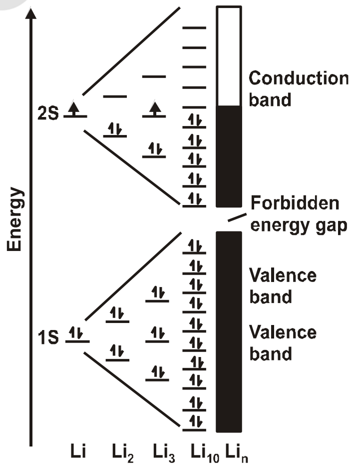
L. Pauling has tried to explain the metallic bond, according to valence bond theory. According to this theory, the metallic bond is treated essentially as covalent in character. However, it is assumed that the covalent bond is not localized but are highly delocalized in metal structure.

Delocalized electrons or mobile electrons which are responsible for the conductance in metals.

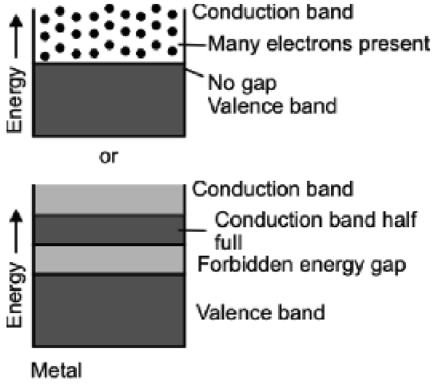
(c) Band Theory of Metals:

According to molecular orbital theory of metallic bond, orbital after overlapping form energy bands. The core electrons (inner electrons) form the valence band and valence electrons (which are present in outer shell) from conduction band. Gap between valence band and conduction band is called **forbidden energy gap**. The energy gap between two bands determines the properties of metallic solids. If conduction bands are not full, the electrons have enough energy that they can jump into higher level and are conductor of electricity.

Band structure of all alkali metals resembles to the lithium. Metallic band of lithium is shown in the Figure.



Formation of electron bands with lithium

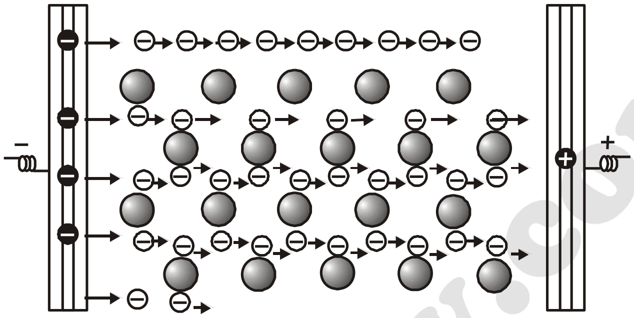


Energy bands of Metals

PROPERTIES OF METALLIC SOLIDS

1. Electrical Conductivity:

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. Sometimes, the **electrical conductivity** of metals **decrease** with the **increase in temperature**. The reason is that with the increase in temperature, the positive metal ions also **begin to oscillate** and this motion hinders the free movement of mobile electrons between the positive ions. This hindrance decreases the electrical conductivity.



Explanation of electrical conductivity of a metal

2. Thermal Conductivity:

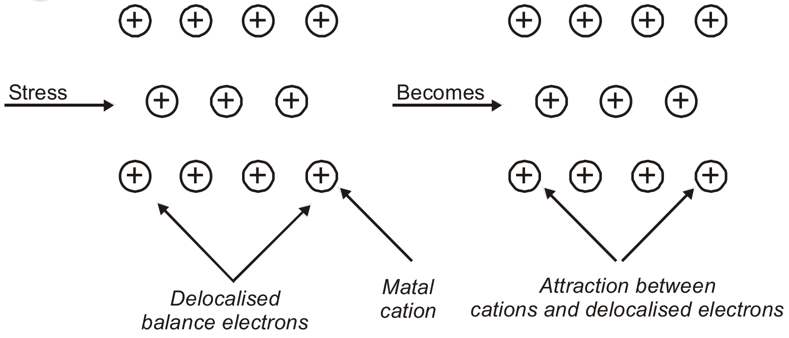
When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy and move very rapidly through the metallic lattice towards the cooler end. During the process they collide with adjacent electrons and transfer their heat energy to them.

3. Luster or Reflectivity:

Whenever the metals are freshly cut, most of them possess metallic luster, which means that they have a shining surface. When light falls on the metallic surface, the incident light collides with the mobile **electrons** and they are **excited**. These excited electrons **come back** to the original position and give off some energy in the form of light. This light appears to be reflected from the surface of the metal, which gives a shining look.

4. Ductility and Malleability:

Metal are ductile and malleable, metals can be drawn into sheets and wires. When stress is applied at metal ions, layer moves, but no internal change take place. The sea of electrons adjusts position rapidly and crystal lattice is restored. The structure of the metal changes without fracturing.



Deformation of metal structures

Structure of Metals:

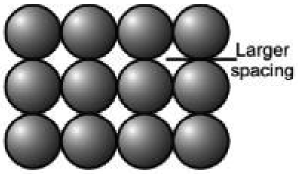
A pure metal is a crystalline solid in which metal atoms are closely packed in a repeating, three–dimensional arrangement. Many metals have high density, due to this close packing.

To understand the closed packing of atoms in metal structures, let us suppose that the metals atoms are like hard spherical balls. These balls are packed in a box. When the box is shaken, the balls will rearrange as shown in Figure.

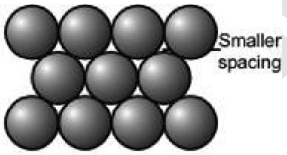
The arrangement of these balls is stable and more closely packed.

In order to understand how various unit cells of the crystal lattice are developed, consider three balls which join together in one plane. The fourth ball is inserted in the space created by the other three as a second layer. In this way tetrahedral structure is obtained.

The ball of the second layer is placed in the depression created by the first three balls. These depressions are also called **interstices or crevices**.

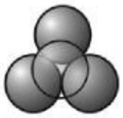


Packing of twelve sphere in a box (two dimensional view

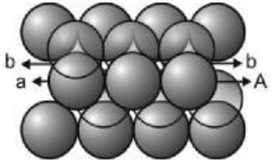


Packing of eleven spheres in a box (two dimensional view

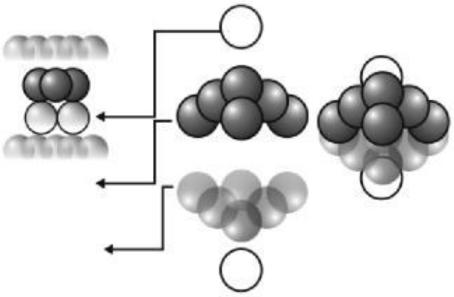
Consider the figure in which eleven balls are present in the first layer (circles with shade) can fit into the depressions or interstices created by the first layer. When the balls of the second layer are arranged then all the depressions of the first layer are not occupied. The depressions marked t are not occupied by the second layer and one can see the ground from looking at the top through depressions t. The new depressions marked a are created by the second layer. Through the depression a, we cannot see ground but balls of the first layer.



The formation of a tetrahedral site. Due to four balls



Close packing of spheres, showing 11 balls in first layer and 6 balls in second layer.



Cubic close packing

When the balls of third layer are placed above the second layer, then there are two possibilities. Third layer balls may be accommodated in a–type or t–type interstices or depressions.

(i) Cubic Close Packing:

When the atoms of the third layer (circle with broken line) fit into the interstices marked B, then the atoms of the third layer will not lie directly above those of the atoms of first layer. This pattern of arrangement is called ABCABC ------ or 123123 ------, it is named as face centered cubic arrangement Figure.

(ii) Hexagonal Close Packing:

When the atoms of the third layer are arranged in such a way that they occupy the depressions created by the second layer atoms marked A, then these atoms will directly lie above the atoms of first layer. This pattern of arrangement is usually written as ABAB ------ or 1212 ------. This pattern has been named as hexagonal close packing Figure.

Type of Crystalline Solids

Types of Solid	Structural Particles	Force of attraction	Typical Properties	Examples
Metallic	Cations and delocalized electrons	Metallic bond	Lustrous, malleable, ductile, conductor of heat and electricity high melting points and usually hard	Al, Cu, Fe, Ag, Au, Na, Mg, Zn, W
Ionic	Cations and anions	Electrostatic attraction	Hard, high melting points, non conductor of electricity in solid state but good conductor in aqueous form and in molten state, Brittle	NaCl, $NaNO_3$, MgO
Molecular	Molecules	Intermolecular forces	Soft, low melting point and sublime easily, non conductor of heat and electricity	S_8, I_2, ice, dry ice, sugar, glucose
Network covalent	Atoms	Covalent bond	Very hard, high melting points, non conductor of electricity	Diamond graphite, SiO_2, SiC

Determination of Avogadro's Number (N_A):

Avogadro's number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids.

The volume of one–gram atom of a solid can be calculated from its density while the spacing between its atoms can be measured by x–rays.

The method of determining Avogadro's number is explained with a help of following example, which gives at reasonably good value of this number.

Example:

The density of LiF is 2.65 g cm^{-3}. It is made up of cubic array of alternate Li^+ and Br^- ions and the distance between these ions is 2.01°A (2.01 x 10^{-8} cm). Calculate the Avogadro's number.

Solution:

$$\text{The formula unit mass of LiF} = 6.939 + 18.9984$$

$$= 25.9374 \text{ g mole}^{-1}$$

$$\text{Density of LiF} = 2.65 \text{ g cm}^{-3}$$

$$d = \frac{m}{v} \text{ or } v = \frac{m}{d}$$

$$\text{The volume occupied by one gram–atom of LiF} = \frac{25.9374 \text{ g mole}^{-1}}{2.65 \text{ g cm}^{-3}}$$

$$= 9.788 \text{ cm}^3 \text{ mole}^{-1}$$

From this volume, we can calculate the edge length of the cube.

$l \times l \times l = v$ or $l_3 = v$

$$\text{Edge length of the cube} = \sqrt[3]{9.788 \text{ cm}^3} = 2.139 \text{ cm}$$

$$\text{The number of ions} = \frac{\text{length of edge}}{\text{distance between ion}^{-1}}$$

$$\text{Along one edge length} = \frac{2.139 \text{ cm}}{2.01 \times 10^{-8} \text{ cm ion}^{-1}}$$

$$= 1.064 \times 10^8 \text{ ions}$$

$$\text{Total number of ions in the cube} = (1.064 \times 10^8)^3$$

$$= 1.204 \times 10^{24}$$

Since the cube of LiF crystal contain one Avogadro number of Li^{+1} and one Avogadro number of F^-, so the Avogadro number will then be

$$\frac{1.204 \times 10^{24}}{2} = 6.02 \times 10^{23}$$

EXERCISE

Q.1 Choose the best answers:

(i) London dispersion forces are the only forces present among the:

- (a) Molecules of water in liquid state
- (b) Atoms of helium in gaseous state at high temperature
- (c) Molecules of solid iodine.
- (d) Molecules of hydrogen chloride gas.

(ii) Acetone and chloroform are soluble in each other due to:

- (a) Intermolecular hydrogen bonding
- (b) Dipole-dipole interaction
- (c) Instantaneous dipoles
- (d) All of the above

(iii) NH_3 shows a maximum boiling point among the hydrides of vth group elements due to:

- (a) Very small size of nitrogen
- (b) Lone pair of electrons present on nitrogen.
- (c) Enhanced electronegative character of nitrogen
- (d) Pyramidal structure of NH_3

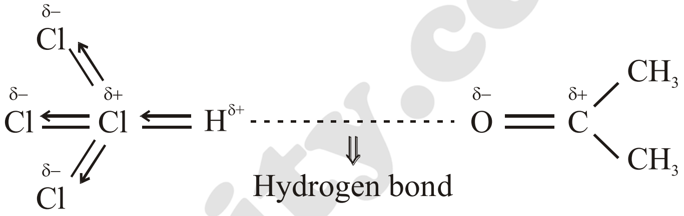
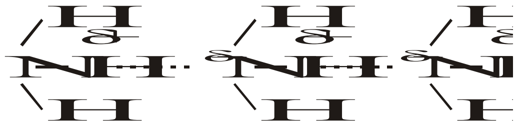
(iv) When water freezes at 0^oC, its density decreases due to:

- (a) cubic structure of ice
- (b) empty spaces present in the structure of ice
- (c) change of bond angles
- (d) Change of bond lengths

(v) In order to mention the boiling point of water at 110°C the external pressure should:

- (a) between 760 torr and 1200 torr
- (b) between 200 torr and 760 torr
- (c) 765 torr
- (d) any value of pressure.

ANSWERS

Answers	Reasons
(i) (c)	London dispersion forces between non-polar iodine molecules are appreciably operative in solid. At high temperature, London dispersion forces are not present between the atoms of helium atoms are weaker and can only operate at low temperature. The molecules of water in liquid state experience hydrogen bonding. The molecules of hydrogen chloride gas experience dipole-dipole forces.
(ii) (a)	In chloroform molecule three Cl-atom being more electronegative attract electrons from carbon atom. This carbon atom being highly electron deficient strongly withdraws (attracts) electrons from hydrogen atom. As a result hydrogen atom develops enough positive charge to make hydrogen bond with partial negative oxygen atom of acetone. Hence acetone and chloroform are soluble into each other.  (Chloroform) (Acetone)
(iii) (c)	In case of NH_3 due to enhanced electronegative character of nitrogen, it attracts electrons so strongly from hydrogen atoms that it becomes highly partial positive and nitrogen develops greater partial negative charge. As a result partial positive hydrogen of one molecule makes a strong hydrogen bond with partial negative nitrogen atom of its neighbour molecule. Due to this strong intermolecular hydrogen bonding, the boiling point of NH_3 is maximum amongst the hydrides of V-A group elements. 
(iv) (b)	When water is cooled below 4°C, intermolecular hydrogen bonding between its molecule becomes stronger, that starts holding the water molecules at specific angles. At 0°C, water freezes and molecules become fixed at specific angles and empty spaces are created between molecules and 9% space is increased. As a result, density decreases to 9%.
(v) (a)	The boiling point of a liquid is directly related to external pressure. Greater the external pressure, greater will be boiling point (because boiling point is the temperature at which vapour pressure of a liquid becomes equal to external pressure). To boil water at 110°C, the external pressure should be between 760 torr and 1200 torr because water boils at 100°C when external pressure is 760 torr.

Q.2 Fill in the blanks with suitable words:

(i) The polarizability of noble gases —————— down the group and results in the increase in their boiling points.

(ii) —————— is developed in acetone and chloroform when they are mixed together.

(iii) Exceptionally weak —————— of HF is due to strong hydrogen bonding present in it.

(iv) The concept of dynamic equilibrium is the ultimate —————— of all reversible systems.

(v) ΔH_v of C_6H_{14} should be —————— than that of C_2H_6.

(vi) During the formation of ice from liquid water there is a —————— % increase in volume.

(vii) The rate of increase of vapour pressure of water —————— at high temperature.

(viii) A layer of ice on the surface of water —————— the water underneath for further heat loss.

(ix) Evaporation is a —————— process.

(x) Liquid crystals are used in the display of —————— devices.

ANSWERS

Answers	Explanation
(i) Increases	Polarizability is the measure of the extent to which electronic cloud can be polarized or distorted. It increases with the increasing size of non-polar atoms or molecules. Down the group, the sizes of atoms of noble gases increases which results in the stronger forces between atoms and higher boiling points. Size $\propto$ Polarizability $\propto$ London forces $\propto$ Boiling point
(ii) Hydrogen bonding	For explanation see answer of MCQ (iii) in Q.1.
(iii) Acidic strength	Due to strong intermolecular hydrogen bonding, hydrogen atom is entrapped between two flourine atoms. As result of this release of hydrogen atom as ion is difficult and HF becomes weak acid.
(iv) Goal	At 0°C, when many of the water molecules freeze, some of them also melt because 0°C is the melting point of water as well. Gradually, rate of freezing goes on decreasing and that of melting goes on increasing. Finally a stage comes when both the opposing processes equalize the rate of each other and state of dynamic equilibrium establishes. Similarly, every reversible reaction attains dynamic equilibrium.
(v) Greater	C_6H_{14} is a large molecule containing greater no. of atoms. Due to this reason it is more polarizable than C_2H_6 (small molecule less no. of atoms, and less polarizable). As a result of this C_6H_{14} experience strong intermolecular force and have high value of ΔH_V than C_2H_6.

(vi)	9%	For explanation, see answer to MCQ (iv) of Q.1.
(vii)	Increase	At high temperature intermolecular forces are weaker between the molecules than at lower temperature and there is a greater increase of vapour pressure with the rise of temperature further.
(viii)	Insulates	The layer of ice on the surface of water insulates the water below it for further heat loss. That is the reason why water below the layer of ice remains as liquid.
(ix)	Cooling	When evaporation takes place high energy molecules are escaped from the surface of liquids and low energy molecules are left behind, temperature decreases and cooling takes place.
(x)	Electrical	

Q.3 Indicate true of false as the case may be:

(i) Dipole-Dipole forces are weaker than dipole-induced dipole forces.

(ii) The ion dipole interactions are responsible for the dissolution of an ionic substance in water.

(iii) The high polarizability of iodine is responsible for its existence in solid form, different from other halogens.

(iv) The strong hydrogen bonding in H_2S makes it different from water.

(v) Hydorcarbons are soluble in water because they are polar compounds.

(vi) The viscosities of liquids partially depend upon the extent of hydrogen bonding.

(vii) The state of equilibrium between liquid state and vapours is dynamic in nature.

(viii) Heat of vaporization of liquids depend upon the intermolecular forces of attractions present between their molecules.

(ix) Ice does not show any vapour pressure on its surface at −10°C.

(x) Boiling point of a liquid is independent of external pressure.

ANSWERS

Answers		Correct Statements
(i)	False	Dipole-dipole forces are stronger than dipole-induced dipole forces.
(ii)	True	
(iii)	True	
(iv)	False	The strong hydrogen bonding in H_2O makes it different from H_2S.
(v)	False	Hydrocarbons are insoluble in water because they are non-polar compounds.
(vi)	True	
(vii)	True	
(viii)	True	
(ix)	False	At 0°C the vapour pressure of water is 4.57 torr. It can't be zero at −10°C.
(x)	False	Boiling point of a liquid is dependent on external pressure. (Boiling point increases with the increase of external pressure).

Q.4 (a) What type of intermolecular forces will dominate in the following liquids?

(i)	Ammonia,	NH_3
(ii)	Octane,	C_8H_{18}
(iii)	Argon,	Ar
(iv)	Propanone,	$CH_3\ COCH_3$
(v)	Methanol,	$CH_3\ OH$

(b) Propanone (CH_3COCH_3) propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

Ans. (a)

(i) **Ammonia (NH_3)**

= Hydrogen bonding

(ii) **Octane (C_8H_{18})**

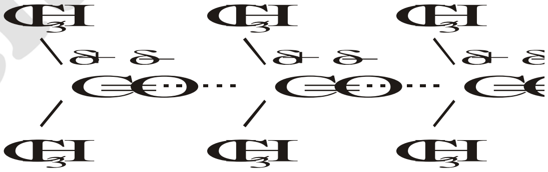
= London forces or instantaneous dipole induced dipole forces

(iii) **Argon (Ar)**

= London forces or instantaneous dipole induced dipole forces

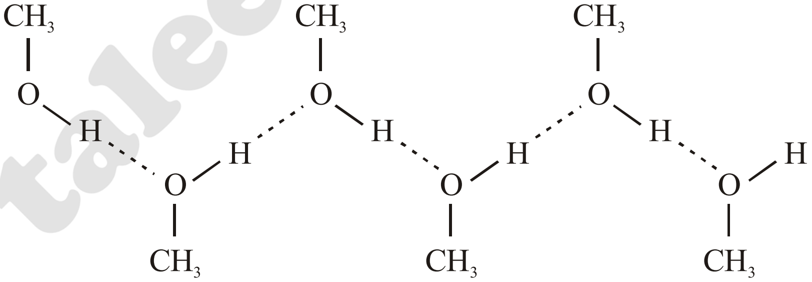
(iv) **Propanone (CH_3COCH_3)**

= Dipole-dipole forces



(v) **Methanol (CH_3OH)**

= Hydrogen bonding



(b) Butane being non-polar experience weak instantaneous dipole-induced dipole force (London force) between its molecules and have lowest boiling point. Propanone being polar molecule experience stronger intermolecular dipole-dipole force between its molecules and have high boiling point whereas propanol experience stronger intermolecular hydrogen bonding and hence have highest boiling point.

Increasing order of boiling point is as follows:

$CH_3 - CH_2 - CH_2 - CH_3 < CH_3COCH_3 < CH_3 - CH_2 - CH_2 - OH$

London force < Dipole-diople force < Hydrogen bonding

Q.5 Explain the following with reasons.

(i) In the hydrogen bonded structure of HF, which is the stronger bond: the shorter covalent bond or the longer hydrogen bond between different molecules?

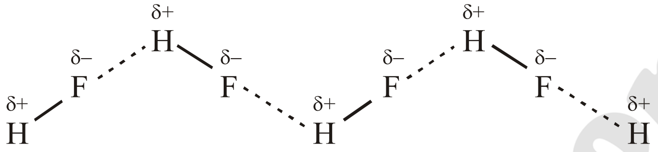
(ii) In a very cold winter fish in garden ponds owe their lives to hydrogen bonding? (Hint: density of ice)

(iii) Water and ethanol can mix easily and in all proportions.

(iv) The origin of the intermolecular forces in water.

Ans.

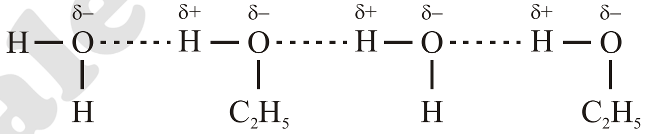
(i) The hydrogen bonded structures of HF is zig-zag (protonic bridges) as shown.



The shorter covalent bond (H − F) is stronger because it is formed by overlapping of atomic orbitals and mutual sharing of electrons. Whereas longer hydrogen bond (H …… F) is weaker because it is formed by the weak electrostatic force between partial charges on 'H' and 'F' atoms.

(ii) When temperature of surrounding falls upto 0°C, the water on the surface freezes. During freezing, water molecules arrange in hexagonal fashion due to hydrogen bonding and spaces are created. As a result, volume increases and density decreases. The frozen ice being less denser stays at the top in the form of compact layer. This layer of ice insulates water under it, for further heat loss, which stays at 4°C, as liquid. Hence fish can easily survive at this temperature. All this is due to hydrogen bonding.

(iii) Both water and ethanol have intermolecular hydrogen bonding in pure states when they are mixed together. Due to this intermolecular hydrogen bonding, they can mix easily in all proportions.



$$H-\underset{\underset{H}{|}}{\overset{\delta-}{O}}\cdots\cdots\overset{\delta+}{H}-\underset{\underset{C_2H_5}{|}}{\overset{\delta-}{O}}\cdots\cdots\overset{\delta+}{H}-\underset{\underset{H}{|}}{\overset{\delta-}{O}}\cdots\cdots\overset{\delta+}{H}-\underset{\underset{C_2H_5}{|}}{\overset{\delta-}{O}}$$

(iv) In water electronegativity difference between the bonded 'H' (E.N = 2.1) and 'O' (E.N = 3.5) atoms is 1.4. This greater electronegativity difference causes strong polarity in (O − H) bond responsible for opposite charges on the bonded atoms ($O^{\delta-}$ — $H^{\delta+}$). Due to this polarity, water molecules attract each other with oppositely charged ends. This strong force is named as hydrogen bonding.

Q.6 (a) Briefly consider some of the effects on our lives if water has only a very weak hydrogen bonding present among its molecules.

(b) All gases have a characteristic critical temperature. Above the critical temperature it is impossible to liquefy a gas. The critical temperatures of carbondioxide and methane are 31.14°C and −81.9°C, respectively. Which gas has the stronger intermolecular forces? Briefly explain your choice?

Ans.

(a) The effects of weak hydrogen bonding on our lives could be as follows:

1. If the boiling point and melting point of water become lower than 100°C and 0°C respectively then due to low boiling point of water, cooking time of food stuffs prolonges and some of the food materials may not be cooked easily.
2. The density of ice may not be less than that of water. As a result of that living pattern of fish and plants in frozen water bodies may be very much different.
3. Dissolving power of water will become less. And it may not be called universal solvent.

In other words, in case of weak hydrogen bonding in water, the pattern of whole life would have been altogether different.

(b) From the information of critical temperature of CO_2 and CH_4 it is clear that intermolecular forces for CO_2 are stronger than CH_4 because CO_2 has high value of critical temperature (T_C). The gas with strong intermolecular forces has more tendency to be liquefied even at high temperature (high T_C).

Both the gases are non-polar and experience London forces between their molecules CO_2 has stronger intermolecular London forces due to its large size and greater polarizability.

Q.7 Three liquids have the properties, mentioned against their names:

No.	Properties	Water	Propanone	Pentane
(i)	Molecular formula	H_2O	C_3H_6O	C_5H_{12}
(ii)	Relative molecular mass	18	58	72
(iii)	Enthalpy change of Vapourization (kJ mol^{-1})	41.1	31.9	27.7
(iv)	Boiling point ^0C	100	56	36

(a) What type of intermolecular force predominates in each liquid?

(i) in water (ii) in propanone (iii) in pentane

(b) What do you deduce about the relative strength of these forces in the liquids? Justify your conclusions.

(c) If the liquids are shaken together in pairs,

(i) Which pair would be unlikely to mix?

(ii) Explain this immiscibility in terms of the forces between the molecules.

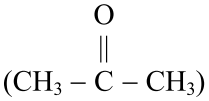
(iii) Choose one of the pairs that mix and say whether the enthalpy change on mixing would be positive or negative.

Ans. (a)

(i) **Water**

⇒ Hydrogen bonding (H_2O)

(ii) **Propanone**

⇒ Dipole-dipole forces 

$(CH_3 - \overset{\overset{\Large O}{\|}}{C} - CH_3)$

(iii) **Pentane**

⇒ London dispersion forces ($CH_3 - CH_2 - CH_2 - CH_2 - CH_3$)

(b) The hydrogen bonding in the case of water is stronger than dipole-dipole attraction between propanone molecules. That is the reason why heat of vaporization and boiling point of water is higher than propanone.

Pentane molecules being non-polar experience London forces (of least strength) between them. That's why it has least values of its thermodynamic properties.

(c) (i) The pairs most unlikely to mix are:

(a) water – pentane

(b) propanone – pentane

(ii) Water and propanone both are polar molecules, don't mix with pentane which is non-polar molecule.

Polar and non-polar molecules are unlikely to mix.

(iii) Water and propanone mix with each other because both are polar in nature enthalpy change is negative because attractive forces are developed between their molecules when they are mixed.

Q.8 Describe the various forces responsible for keeping the particles together in the following elements and compounds and their effects on physical properties making use of the data below:

No.	Substance	Formula	Molar Mass (a.m.u.)	M.P°C
1.	Neon	Ne	20	– 248
2.	Argon	Ar	40	– 189
3.	Water	H_2O	18	0
4.	Sodium fluoride	NaF	42	993
5.	Diamond	C	12	3350

Ans. Neon and Argon are noble gases experiencing weak London forces between their atoms and have low melting points. But the melting point of Argon is higher than Neon due to its large size and greater polarizability.

In case of water, there are strong intermolecular hydrogen bonding and its melting point is higher than Neon and Argon.

For NaF, oppositely charged ions are held together through electrostatic force (ionic bond) and are arranged in three dimensional manner. This arrangement through strong ionic bonds make it hard and its melting point is high.

Diamond is a three dimensional network of covalent bonds formed by $sp^3 - sp^3$ overlapping. Overall binding in diamond is very strong. That's why it is very hard and have very high melting point.

Q.9 The boiling points and molar masses of hydrides of some first row elements are tabulated below:

No.	Substance	Boiling Point (K)	Molar Mass (g mol^{-1})
1.	CH_4	109	16
2.	NH_3	240	17
3.	H_2O	373	18

Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Ans. CH_4 is a non-polar molecule and have weak London forces between its molecules. That's why its boiling point is low.

Ammonia and water both are polar molecules and their molecules attract each other through hydrogen bonding. Due to the greater electronegativity difference between the atoms in water, it experience strong hydrogen bonding and its boiling point is higher than Ammonia.

Q.10 Explain the term saturated vapour pressure. Arrange in order of increasing vapour pressure: 1dm^3 water, 1 dm^3 ethanol, 50cm^3 water, 50 cm^3 ethanol and 50 cm^3 of ether.

Ans. **Saturated Vapour Pressure:** Vapour pressure of a liquid when its vapours are in equilibrium with liquid at a given temperature is called saturated vapour pressure.

- Vapour pressure doesn't depend upon the amount of liquid.
- Vapour pressure depends upon the intermolecular forces and is inversely proportional to intermolecular forces.

Between ether molecules, there are weak dipole-dipole forces and its vapour pressure is high.

Intermolecular forces in case of ethanol are hydrogen bonding, which is stronger than dipole-dipole forces of ether. That's why its vapour pressure is lesser than ether.

Intermolecular forces in water is hydrogen bonding which are more stronger than ethanol. Hence, its vapour pressure is the least.

The increasing order of vapour pressure for these liquids is as follows:

50 cm^3 ether > 50 cm^3 ethanol = 1 dm^3 ethanol > 50 cm^3 – Water = 1 dm^3 water

Q.11 While a volatile liquid standing in a breaker evaporates, the temperature of the liquid remains the same as that of its surrounding. If the same liquid is allowed to vaporize into atmosphere which is insulated, its temperature falls below that of its surrounding. Explain the difference in behaviour.

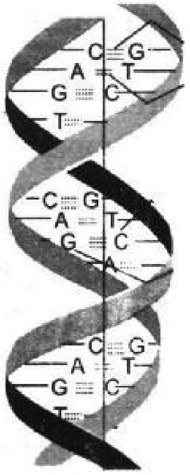
Ans. When evaporation takes place in a beaker, high energy molecules escape and low energy molecules left behind and temperature of the liquid falls. Liquid absorbs energy from the surrounding until both have same temperature.

When evaporation takes place in an insulated beaker, temperature of liquid falls due to the escape of high energy molecules. In this case, liquid can't absorb heat from surrounding due to insulated walls of beaker. Hence, temperature of the system remains lower than surrounding.

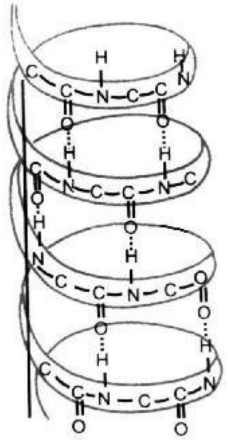
Q.12 How does hydrogen bonding explain the following indicated properties of the substances?

(i) Structure of DNA.
(ii) Hydrogen bonding in proteins.
(iii) Formation of ice and its lesser density than liquid water.
(iv) Solubilities of compounds.

Ans. (i) **Structure of DNA:** DNA has double helical structure of two oppositely running strands of DNA molecules. These two strands are held together through hydrogen bonds between their components (A = T and G ≡ C). The double helical structure of DNA is maintained due to hydrogen bonding.



(ii) **Hydrogen Bonding in Proteins:** The α-helix is a secondary structure of protein. It is formed when polypeptide chain twists in right handed fashion. The (–CO–) group of one turn form hydrogen bond with (–NH–) group of second turn. Due to these hydrogen bonds coiled structure is maintained.



(iii) Formation of ice and its lesser density than liquid water: When water is cooled at 0°C, ice is formed. During the formation of ice, water molecules arrange themselves at specific angles to form hydrogen bond. Water molecules become fixed at their positions and spaces are created between them. As a result volume increases and density decreases.

(iv) **Solubility of Compounds:** Many compounds like alcohols, phenol and carbohydrates are soluble in water due to its strong bonding. e.g., when ethanol is dissolved in water, there develops hydrogen bonding between water and ethanol molecules and ethanol becomes soluble.

Q.13 **What are liquid crystals? Give their uses in daily life.**

Ans. Consult the chapter.

Q.14 Explain the following with reasons.

i. Evaporation causes cooling.
ii. Evaporation takes place at all temperatures.
iii. Boiling needs a constant supply of heat.
iv. Earthenware vessels keep water cool.
v. One feels sense of cooling under the fan after bath.
vi. Dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.
vii. The boiling point of water is different at Murree hills and at Mount Everest.
viii. Vacuum distillation can be used to avoid decomposition of a sensitive liquid.
ix. Heat of sublimation of substance is greater than that of heat of vapourization.
x. Heat of sublimation of iodine is very high.

Ans.

(i) Evaporation Causes Cooling:

Temperature is measure of average kinetic energy of the molecules. As the liquid evaporates, the high energy molecules escape from the liquid and there is lowering of the average kinetic energy of the remaining molecules of the liquid and the temperature of the liquid falls. Thus evaporation causes cooling. As the evaporation proceeds, it absorbs more heat from the surroundings and the temperature of the surroundings also falls.

(ii) Evaporation Takes Place at Every Temperature:

Evaporation is a surface phenomenon. It takes place at every temperature. When high energy molecules come at the surface of a liquid, they escape out of surface. However, by increasing temperature, the average K.E. of the molecules increases. Hence by increasing temperature evaporation is accelerated.

(iii) Boiling Needs a Constant Supply of Heat:

The heat energy supplied to a liquid, is mostly consumed in increasing the average kinetic energy of the molecules. This also increases the rate of evaporation, The temperature and the rate of evaporation goes on increasing till liquid starts boiling. Any more heat supplied is now used to overcome the intermolecular attractive forces and excessive energy is carried away by the molecules into their vapour state. Thus the average kinetic energy of the molecules of the liquid or the temperature of the liquid remains constant at its at its boiling point.

(iv) Earthenware vessels keeps water cool.

Earthenware vessels have very small pores in them. Evaporation of water takes place through these pores. When a molecule goes into the atmosphere, it requires some amount of energy to overcome the intermolecular forces. These molecules accept energy from the neighbours and as a result the average kinetic energy of molecules decreases. The process of evaporation reduces in old earthenware because number of pores decreases due to dust and they become less effective for cooling.

(v) One feel sense of cooling under the fan after bath.

It is also due to the evaporation process. When some one takes a bath, some water molecules are present at the body. These molecules absorb energy from the body and evaporate. As a result the body temperature decreases by evaporation of water vapours.

(vi) Dynamic equilibrium is established during evaporation of a liquid in a closed Vessel at constant temperature.

If we put some liquid in a close vessel, evaporation starts. The vapours of liquid are accumulated over the surface as they cannot escape from the container. Because the molecules in the vapour state are also in motion, some of them strike back at the surface of the liquid and are recaptured there. The condensation also starts when some vapours are collected over liquid. Initially, rate **of** evaporation is high but rate of condensation is very slow. After some times, rate of evaporation becomes equal to the rate of condensation and dynamic equilibrium is established.

(vii) The boiling point of water is different at Murree and at Mount Everest.

The temperature at which vapour pressure of liquid becomes equal to the atmospheric pressure is called boiling point. At sea level atmospheric pressure is 760 torr and boiling point of water is 100°C. By reducing external pressure, the boiling point also reduces. As we go at higher altitude atmospheric pressure decreases. Atmospheric pressure at Mount Everest is less than at Murree hills. At Murree hills, atmospheric pressure is 700 torr and boiling point of water is 98°C but at mount Everest water boils at 69°C (atmospheric pressure = 323 mm Hg).

(viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid.

Boiling point of liquid depends upon the external pressure of a liquid. If external pressure is decreased, the boiling point also decreases. By applying vacuum distillation process, we can boil liquid at low temperature . Some compounds decompose at, their boiling point, such compounds can be distilled under vacuum. For example, normal boiling point of glycerin is 290°C but it is decomposes at this temperature. Glycerine is purified at low temperature (210°C) by applying external pressure of only 50 torr. In th's way, we can obtain pure glycerine at low temperature, without decomposition.

(ix) Heat of sublimation of a substance is **greater than heat of vapourization**.

The conversion of one mole of solid into vapours at constant pressure is called molar heat of sublimation. It is always greater than heat of vaporization. In heat of vapourization, only one.phase change (from liquid to vapours) takes place. In case of sublimation, two steps are involved, i.e., from solid to liquid and liquid to vapours.

$$\Delta H_{sub} = \Delta H(_{fus})\ \Delta H_{vap.}$$

(x) **Heat of sublimation of iodine is very high.**

Among halogens, the heat of sublimation of iodine is higher than F_2, Cl_2 and Br_2. In groups of periodic table, size of atom increases. Due to increase in the size of atom, its polarizability increases. Due to greater polarizability of I_2 than other halogens, it has greater induced dipole-induced dipole or London dispersion forces. So, its heat of sublimation is high.

(SOLIDS)

Q.1 Choose the best answers (Multiple Choice Questions):

(i) Ionic solids are characterized by:
- (a) Low melting points
- (b) Good conductivity in solid state
- (c) High vapour pressures
- (d) Solubility in polar solvents

(ii) Amorphous solids:
- (a) Have sharp melting points
- (b) Undergo clean cleavage when cut with knife
- (c) Have perfect arrangement of atoms
- (d) Can possesses small regions of orderly arrangement of atoms

(iii) The molecules of CO_2 in dry ice form the:
- (a) Ionic crystals
- (b) Covalent crystals
- (c) Molecular crystals
- (d) Any type of crystals

(iv) Which of the following is a pseudo solid:
- (a) CaF_2
- (b) Glass
- (c) $NaC1$
- (d) All

(v) Diamond is a bad conductor because:
- (a) It has a tight structure.
- (b) It has a high density.
- (c) There is no free electron present in the crystal of diamond to conduct electricity.
- (d) Is transparent to light.

ANSWERS

Answers	Reasons
(i) (d)	Positive and negative ions in ionic compounds are only attracted by oppositely charged ends of polar solvent molecules. Hence they are only soluble in polar solvents. Ionic bonds between the ions are very strong. Due to which ionic compounds have high melting point and low vapour pressure. They are not conductor in solid state because ions are fixed at their positions through ionic bonds. i.e., they have no free movement of ions required for conduction.
(ii) (d)	Amorphous solids don't have orderly arranged particles. However they can posses small regions of orderly arrangement called crystallites.
(iii) (c)	The molecular species like CO_2 in solid state form molecular crystals, in which molecules are held together through Vander Waal's forces. In ionic crystals ions are held together through ionic bond and in covalent crystals, atoms are held together through covalent bonds.
(iv) (b)	Glass is a pseudo solid having no orderly arrangement of particles, because it is formed by super cooling of liquids. CaF_2 and NaCl being ionic compounds are crystalline in nature.
(v) (c)	The diamond crystal is formed by the $sp^3 - sp^3$ overlapping of hybrid orbitals of carbon atoms. This overlapping results in covalent bond formation in which electrons are tightly bound between atoms and are unable to move freely in the crystal. Hence, free electrons are not available for conduction.

Q.2 Fill in the blanks words:

(i) In a crystal lattice, the number of nearest neighbours to each atom is called the ——————.

(ii) There are —————— Bravis Lattices.

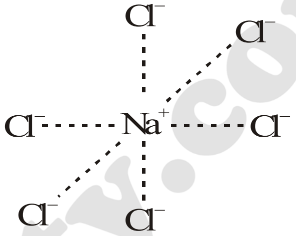
(iii) A pseudo solid is regarded as —————— liquid.

(iv) Glass may begin to crystallize by a process called ——————.

(v) Crystalline solids which exhibit the same —————— in all reactions are called ——————.

(vi) The branch of science which deals with the —————— crystals is called crystallography.

ANSWERS

Answers	**Explanation**
(i) Co-ordination number	 In ionic crystals, ions are alternatively arranged and around one ion, there are no. of oppositely charged ions called its co-ordination no. e.g., co-ordination no. of Na^+ is '6' in NaCl crystal.
(ii) 14	
(iii) Super cooled	When solids are melted, and their molten form is cooled rapidly then particles find no. time to arrange themselves and pseudo solid is formed. It is also called as super cooled liquid because it is formed by super cooling of molten state (liquid). The terms used for solids having no regular arrangement of particles are: (i) Amorphous solids (ii) Pseudo solids (iii) Vitreous solids (iv) Super cool liquids
(iv) Annealing	Glass is usually considered as Amorphous solid because it is formed by super cooling of liquid. When this liquid is cooled with moderate rate, the particles find time to arrange themselves and glass will crystallize. The process of slow and gradual cooling at moderate rate is called annealing.
(v) Properties, isotropic	
(vi) Structure of	

Q.3 Indicate true or false as the case my be:

(i) There are five parameters in unit cell dimensions of a crystal.

(ii) Ionic crystals are very hard have low volatility and very low melting and boiling points.

(iii) The value of lattice energy of the ionic substances, depends upon the size of ions.

(iv) Molecular orbital theory of metallic solids is also called band theory.

(v) Ionic solid is good conductor of electricity in the molten state.

ANSWERS

Answers		Correct Statement
(i)	False	There are six parameters in unit cell dimensions of a crystal (three are three unit cell-lengths 'a', 'b', 'c' and three unit cell angles α, β, γ)
(ii)	False	Ionic crystals are very hard, low valatility and very high melting and boiling points (in ionic crystals ions are held together by strong ionic bonds that's why they have high melting and boiling points).
(iii)	True	Smaller the size of cation and anion greater will be the lattice energy and vice versa.
(iv)	True	
(v)	True	In molten state ions are free to move and conduct electricity ionic compounds are conductor in molten state or solution form (having free ions) where as non-conductor in solid state (having no free ions).

Q.4 What are solids? Give general properties of solids. How do you differentiate between crystalline solids and amorphous solids?

Ans. There are substances which are rigid hard have definite volume are called solids e.g., glass, plastic, sugar, crystals, ice etc.

General Properties of Solids: These are as follows:

(i) Atoms, ions or molecules are closely packed.

(ii) Particles are held together by strong cohesive force. That's why they have:

  (a) high melting points

  (b) high boiling points

  (c) low volatility

  (d) low vapour pressure

(iii) Constituent atoms, ions or molecules in a solid can't move randomly.

(iv) There may exist well ordered arrangement of particles such solids are called crystalline solids while others having no ordered arrangement of particles are called amorphous solids.

Difference between Crystalline and Amorphous Solids:

Crystalline solids	Amorphous solids
1. They have regular arrangement of particles.	1. They have irregular arrangement of particles.
2. They have regularity in their shapes.	2. They have irregular shapes.
3. They have sharp melting points.	3. They don't have sharp melting points.
4. They have cleavage planes.	4. They don't have cleavage planes.
5. They are true solids.	5. They are pseudo-solid.
6. Examples: NaCl, Sugar, CO_2 and I_2.	6. Examples: Glass, plastic, rubber etc.

Q.5 (a) Explain the following properties of crystalline solids. Give three examples in each case.

(i) Anisotropy
(ii) Cleavage
(iii) Habit of a crystal
(iv) Isomorphism
(v) Polymorphism
(vi) Transition temperature
(vii) Symmetry
(viii) Growing of crystal

(b) How polymorphism and allotropy are related to each other? Give examples.

Ans.

(a) For answer consult text book.

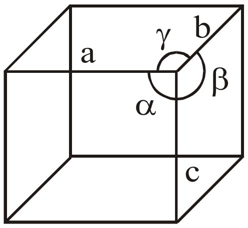
(b) Both the polymorphism and allotropy are related to existence of one substance in more than one crystalline form. Allotropy is related to elements e.g., sulphur (rhombic and monoclinic).

Polymorphism is related to compounds e.g., $AgNO_3$ (Rhombohedral, orthorhombic).

Q.6 (a) Define unit cell. What are unit cell dimensions? How the idea of crystal lattice developed from the concept of unit cell?

(b) Explain seven crystal systems and draw the shapes of their unit cells.

Ans.



(a) **Unit Cell:** The smallest part of the crystal lattice that has all the characteristic features of the entire crystal is called unit cell.

Unit Cell Dimensions: Three unit cell length (a, b, c) and three unit cell angles (α, β & γ) that give characteristic shape of unit cell are called unit cell dimensions or crstyallographic elements.

Idea of Crystal Lattice from Unit Cells: A unit cell is a geometric shape or box, with the repetition in three dimensional manner, crystal lattice is formed. Unit cell in other words is the building block of crystal lattice.

(b) Descriptive question, for answer consult text book.

Q.7 (a) What are ionic solids? Give their properties. Explain the structure of NaC1.

(b) What are covalent solids? Give their properties. Explain the structure of diamond.

(c) What are molecular crystals? Give their properties. Justify that molecular crystals are softer than ionic crystals.

Ans.

(a) For answer consult text book.

(b) For answer consult text book.

(c) Molecular crystals are softer than ionic crystals. In case of molecular crystals, molecules are held together through weak Vander Waal's forces. Due to this weak bonding, molecular crystals are soft and have lower melting point e.g., ice (0°C).

Whereas in case of ionic crystals, ions are held together through very strong bonding, ionic crystals are hard and have higher melting points. e.g., NaCl (801°C).

Q.8 (a) Give different theories of a metallic bond. How does electron sea theory justify the electrical conductivity, thermal conductivity and shining surfaces of metals?

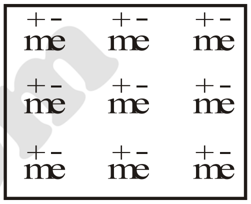
(b) Explain with the help of a diagram:

(i) Cubic close packing in the structure of metals.

(ii) Hexagonal close packing in the structure of metals.

Ans.

(a) Different theories of metallic bond. (Descriptive question, consult text book).



Electron Gas Theory: According to this theory, all the metal atoms loose their valence electrons and cations are formed. The free electrons move freely in the entire crystal. The force, which binds metal cations to no. of electrons around it is called metallic bond.

Thermal Conductivity: When a piece of metal is heated, mobile electrons at this end absorbs heat and move to the other end. During this process they collide with other electrons and transfer heat to them. Also, new cold electrons come to take their place, absorbs heat and move to other parts. In this way heat is conducted in the entire crystal.

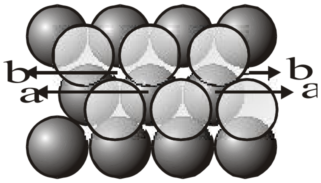
Electrical Conductivity: When electrical field is applied between two ends of metals free electrons in the crystal move towards positive pole and new electrons from negative pole enters the crystal. In this electricity is conducted.

Shining Surface of Metals OR Metallic Luster: Freshly cut metal have shining surface, when metal is cut, incident light collides with the mobile electrons and they are excited. When they come back, they give off energy in the form of light that appears to be reflected from the metal surface.

(b) Atoms of metals arrange themselves in the form of layers. When two layers are arranged, then two types of spaces can be seen:

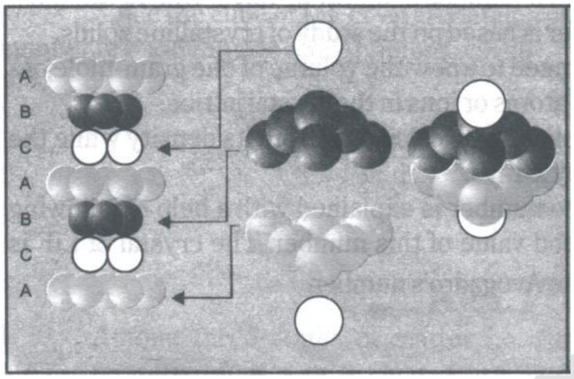
(i) a-type through which balls of first layer are seen

(ii) b-type through which ground can be seen as shown in the diagram below:



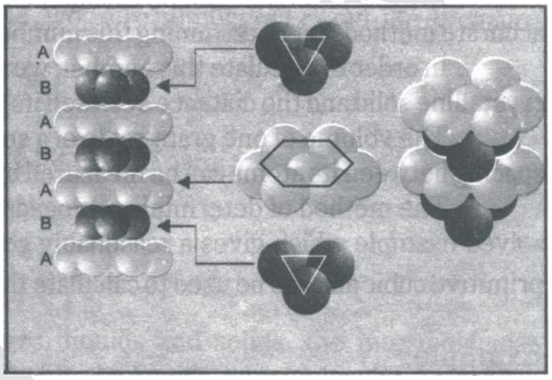
Close packing of spheres, showing 11
balls in first layer and 6 balls in second layer.

(i) **Cubic Close Packing:** When the atoms of third layer fit into b-type spaces then the atoms of third layer will not lie directly above those of first layer. This arrangement is called ABC ABC or 123 123 and is named as cubic close packing. It is shown in figure below.



Cubic close packing or face centred cubic arrangement (ABCABC …)

(ii) **Hexagonal Close Packing:** When atoms of third layer fits into a-type spaces, then atoms of third layer exactly lie above the atoms of first layer. This arrangement is called AB AB or 12 12 and is named as hexagonal close packing. It is shown in figure below.

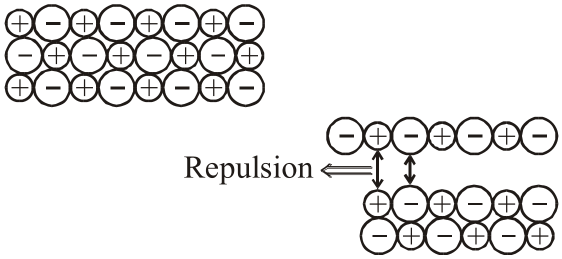


Hexagonal close packing (ABAB …)

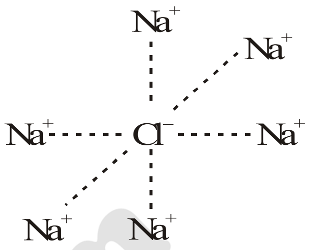
Q.9 Crystals of salts fracture easily, but metals are deformed under stress without fracturing. Explain the difference.

Ans. In case of salts, ions are arranged in alternate manner in the form of layers. As a result oppositely charged ion come to lie and face each other.

When stress is applied the layers slip over each other and similarly charged ions come face to face. Due to this, there exist severe repulsion between the layers and layers are separated causing the fracturing of salt crystal. In case of metals atoms are also, arranged in the form of layers above each other when stress is applied, layers are slipped over each other and the layer is deformed instead of fracturing because there is no repulsion between the layer after being slipped.



Q.10 What is the coordination number of an ion? What is the coordination number of the cation in (a) NaC1 structure and (b) CsC1 structure? Explain the reason for this difference?



Ans. **Co-ordination number:** The number of ions surrounding the oppositely charged ion in a crystal is called its co-ordination no. e.g., co-ordination no. of Cl^- ion is 6.

The co-ordination number of Na^+ ion in NaCl structure is 6 and that of Cs^+ ion in CsCl structure is 8.

Co-ordination no. of cation depends upon its size Na^+ ion being smaller in size can only be surrounded by 6-Cl^- ions. Whereas Cs^+ ion being larger in size can be surrounded by greater number of ions i.e., 8 Cl^- ion.

Hence co-ordination no. of Na^+ is 6 and that of Cs^+ is 8.

Q.11 Give examples of ionic solids, molecular solids and covalent macromolecular solids. What are the factors which determine whether each of these types of solids will dissolve in water or not?

Ans. The examples of these solids are:

(i) **Ionic solids:**

⇒ e.g., NaCl, CsCl, $AgNO_3$, CaF_2.

(ii) **Molecular solids:**

⇒ e.g., $CO_{2(s)}$, $H_2O_{(s)}$, $I_{2(s)}$.

(iii) **Covalent macromolecular solids:**

⇒ e.g., Diamond, graphite.

The strength and type of forces binding the particles in the crystals determine whether a compound is soluble in water or not.

Diamond, graphite both are insoluble in water due to strong binding force (covalent bonds) between the atoms in the crystal and also due to their non-polar nature. Solid I_2 being non-polar is insoluble in water whereas polar molecules are soluble in water.

In case of ionic compounds, lattice energy plays a role. Greater the lattice energy for ionic compound lesser is the solubility. Ionic compounds are usually soluble in water.

Q.12 Explain the following with reasons.

(i) Sodium is softer than copper but both are very good electrical conductors.

(ii) Diamond is hard and an electrical insulator.

(iii) Sodium chloride and cesium chloride have different structures.

(iv) Iodine dissolves readily in tetrachloro methane.

(v) The vapour pressures of solids are far less than those of liquids.

(vi) Amporphous solid like glass is also called super cooled liquid.

(vii) Cleavage of the crystals is itself an isotropic behavior.

(viii) The crystals showing isomorphism mostly have the same atomic ratio.

(ix) The transition temperature is given by elements having allotropic forms and by compounds showing polymorphism.

(x) One of the unit cell angle of hexagonal crystals is 120º.

(xi) The electrical conductivity of the metals decreases by increasing temperature.

(xii) In the closest packing of atoms of metals, only 74% space is occupied.

(xiii) Ionic crystals don't conduct electricity in the solid state.

(xiv) Ionic crystals are highly brittle.

(xv) The number of positive ions surrounding the negative ion in the ions crystal lattice depends upon the sizes of the two ions.

Ans. **(i) Sodium is softer than copper but both are very good conductor of electricity:**

Sodium metal has relatively weaker metallic bond than copper. The bonds are formed by the delocalised valence electrons. Copper has greater number of valence electrons as compared to sodium. These delocalised electrons form a glue to hold these positive ions together. The strength of bond also depends upon the metallic radius of atom.

$$\text{Strength of metallic bond} = \frac{\text{Number of delocalised electron per atom}}{\text{metallic radius}}$$

Copper is harder than sodium due to greater number of valence electrons and smaller metallic radius. Both metals are good conductor of electricity due to movement of free electrons.

(ii) Diamond is hard and electrically insulator:

Diamond has network covalent bond in it and hardest substance. Each carbon atom of diamond is covalently bounded with four carbon atoms. Electrons of carbon atoms cannot move freely from one atom to another so it is insulator and heat and electricity cannot pass through it.

(iii) Sodium chloride and Cesium Chloride have different Structures:

The crystal structure of ionic compounds depends upon the coordination number of cations. Na^+ ion has smaller size and its coordination is six because in its neighbour, six Cl^- ion has bigger size and its coordination number is eight. In the neighbour of Cs^+ eight Cl^- ions are present. NaCl has face centered cubic structure while CsCl has body-centered cubic structure.

(iv) Iodine dissolves readily in tetra chloromethane:

Iodine is more soluble in CCl_4 because both are non polar in nature. Non-polar solutes are more soluble in non-polar solvent. I_2 is 85 times soluble in CCl_4 as compared to water.

(v) The vapour pressures of solids are for less than those of liquids:

Vapour pressure of solid or liquids depends upon the intermolecular forces in them. Solids have greater intermolecular forces than liquids. So a solid has less vapour pressure than liquids.

(vi) Amorphous solid like glass is also called super cooled liquid:

The temperature of many liquids may be lowered, below the freezing points before crystallization begins. A liquid existing at a temperature below its freezing point is said to be undercooled or super cooled. It has a metastable condition. It is not in equilibrium with its solid. Liquid material such as fused glass cannot move readily into the position of a regular crystal lattice. As the temperature is lowered, the mobility of particles decreases and it becomes hard without a regular arrangement. Such materials are called amorphous solids.

(vii) Cleavage of a crystal is itself anistoropic behaviour:

Anisotropic Crystals having different intensity of property in different directions is called cleavage. Cleavage is an anistoropic property because many crystal have a specific cleavage plane and can be cut only in that plane. For example, mica sheets can be cleaved only parallel to length of sheet and not easily in any other direction.

(viii) The crystals showing isomorphism mostly have same atomic ratio:

Isomorphous substances have same ratio of atoms in them e.g;

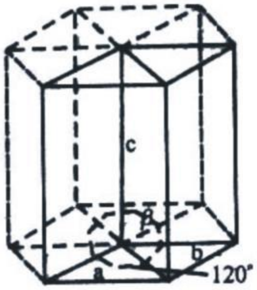
Isomorphs	**Atomic ratio**	**Crystals Shape**
NaF and MgO	1 : 1	Cubic
$NaNO_3$ and $CaCO_3$	1 : 1 : 3	Rhombohedral

The above examples show that isomorphs have same atomic ratio. The spatial arrangement of different atoms is similar in isomorphous substances.

(ix) The transition temperature is given by elements having allotropic forms and by compound showing polymorphism:

The temperature at which two crystalline forms of a substance (element or compound) can co-exist at equilibrium is called transition temperature. If a substance has only one form, no concept of transition temperature used.

(x) One of the unit cell angles of hexagonal crystal is 120º:



In a unit cell, two lengths a and b are equal but c is different. Two angels α and β are of 90º but γ is of 120º. At the top view of each hexagonal has angle of 120º at corner.

The magnitude of γ angle is hexagonal system can be calculated by this formula.

Magnitude of angle in hexagon = 180º – 360º/6 = 120º

(xi) The electrical conductivity of metals decreases by increasing temperature:

Electrical conductivity of metal decreases by increasing temperature. When we increase the temperature of metal, the positive metal ions also begin to vibrate. By the increase of the vibration of positive ions, the movement of free electrons is hindered. This hindrance in the mobility of free electrons, decrease the electrical conductivity.

(xii) In the closet packing of atoms of metals, only 74% space is occupied:

When sphere are packed according to cubic or hexagonal closest packing, there is always space left unoccupied between them. This empty space is known as hole. The magnitude and shape of these holes depends upon the way of close packing.

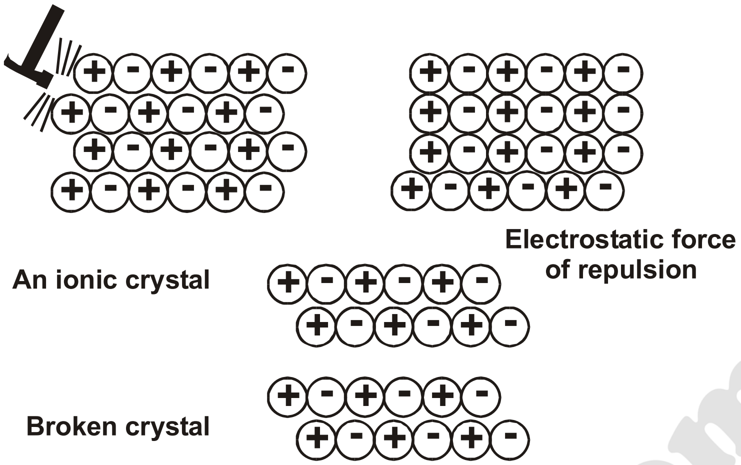
If we want to pack together spheres of identical diameter, there are two different ways to do so. These are called hexagonal closest packing and cubic closest packing. In both these ways 74% of the total volume is filled by the spheres, 26% space remains unoccupied as hole.

(xiii) Ionic crystals do not conduct electricity is solid state:

Ionic crystals do not conduct electricity in solid state because they have no free or moveable electrons in them. Ionic crystals are only conductor in fused form or in aqueous from. In ionic solid, ions cannot move from one place to another place, but in aqueous form, ions can move. Solid NaCl is not conductor of electricity in solid state.

(xiv) Ionic crystals are highly brittle:

Ionic crystals are brittle in nature. When some stress is applied to the ionic crystals, the layer of ions move and similar ions come in front of each other. These same charge repel each other and solid break into pieces. So by the application of external pressure, repulsion is created between two layers of ionic solid, which cause brittleness.



(xv) The number of Positive ions surrounding the negative ions in the ionic crystal lattice depends upon the sizes of two ions:

The number of positive ions, which surround the negative ion, is called its coordination number. Number of negative ions, which are present around the positive ion, depends upon the size of positive ions or the radius ratio of two ions. Greater will be the radius ratio, greater, will be coordination number. In NaCl, the coordination number of Na^+ in six. In CsCl, the coordination number of Cs^+ ion is eight.

DID YOU KNOW?

1. HF cannot be stored in glass vessels because it dissolve glass.
2. HF is the weakest of all halogen acids.
3. The distortion of electronic cloud of an atom or molecule is called polarizability.
4. DNA is double helix of nucleotides.
5. When water freezes, it occupies 9% more space and its density decreases.
6. Acetone and chloroform are miscible due to hydrogen bonding.
7. Boiling point of HF is less than H_2O.
8. Condensation is exothermic process.
9. The distillation process which is carried out under reduced pressure or in vacuum is called vacuum distillation.
10. Intramolecular forces are stronger than intermolecular forces.
11. Glass is vitreous or Pseudo solid or amorphous solid.
12. The smallest part of the crystal lattice that has all the characteristic features of the entire crystal is called unit cell.
13. Electrical conductivity of metals decreases with the rise of temperature.
14. The amount of energy required to break one mole of ionic solid into its ions is called lattice energy.
15. Heat of sublimation of a substance is greater than heat of vaporization.
16. NaCl has face centred cubic structure but CsCl has body centred cubic structure.
17. Glass is also called super cooled liquid.
18. Co-ordination number of Na^+ is six in NaCl.
19. Co-ordination number of Cs^+ is eight in CsCl.
20. In the closest packing of atoms of metals 74% space is occupied.
21. Liquid crystals are also classified as Thermotropic (organic), Lyotropic (organic), Metallotropic (organic + inorganic).
22. The force of attraction between the atoms within a molecule is called intramolecular force.

Chapter 5

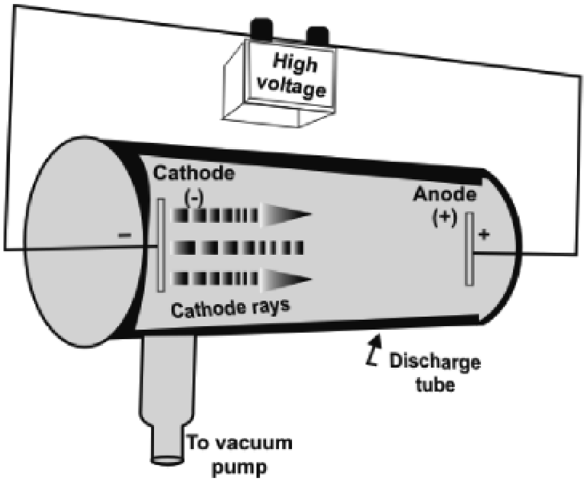
ATOMIC STRUCTURE

DISCOVERY OF ELECTRON (DISCHARGE TUBE EXPERIMENT)

William Crooks in 1876 performed series of experiments.

Discovery of electron was done by the **cathode ray tube (CRT)** or discharge tube. It is a glass tube having two electrodes in it. It may contain air, any gas or vapours of any substance at very low pressure. The electrode are connected to a source of high voltage. The exact **voltage** required depends upon the **length** of tube and the pressure inside the tube. By increasing the length voltage also increases. The tube is attached to the vacuum pump by means of small tube so that the conduction of electricity may be studied at any value of low pressure.

It was observed that current did not flow through the gas at ordinary pressure, even at high voltage of 5000 volts. When the pressure inside the tube was reduced and a high voltage of **5000 – 10000** volts was applied, then an electric discharge took place through the gas producing a uniform glow inside the tube. When the pressure was reduced further to about **0.01 torr**, the original glow disappeared. Some rays were produced which created fluorescence on the glass wall opposite to the cathode. These rays were called **cathode rays**. The colour of the glow or the fluorescence produced on the walls of the glass tube, depends upon the composition of glass.

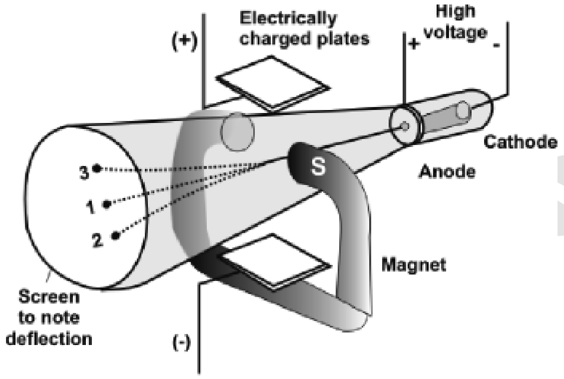


Production of the cathode rays in a discharge tube

PROPERTIES OF CATHODE RAYS

1. Cathode Rays are Negatively Charged Particles:

Cathode rays are negatively charged. In 1895, J. Perrin showed that cathode rays are deflected in a magnetic field perpendicular to the line joining the two poles. In 1897, J.J. Thomson established that when these rays were passed though the electric field, they deflect toward positive plate, it means these rays are negatively charged.



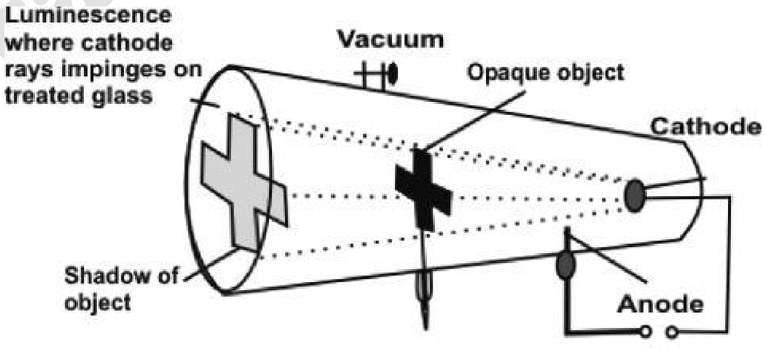
Deflection of cathode rays in electric and magnetic fields

2. Cathode Rays Produce 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, alumna glows red and tin stone yellow.

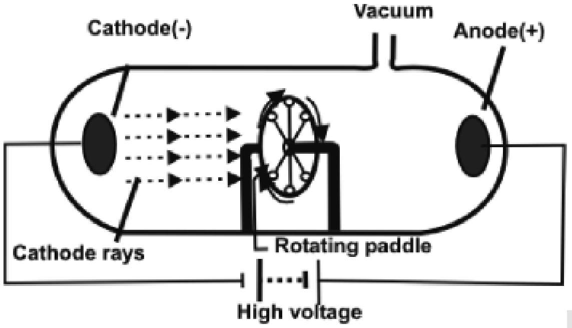
3. Cathode Rays Cast Shadow:

Hittorf in 1869 studied that cathode rays cast shadow. If an opaque (not transparent) object is place in their path, its shadow is formed at the discharge tube wall. This experiment proves that cathode rays travel in a straight line perpendicular to the surface of cathode.



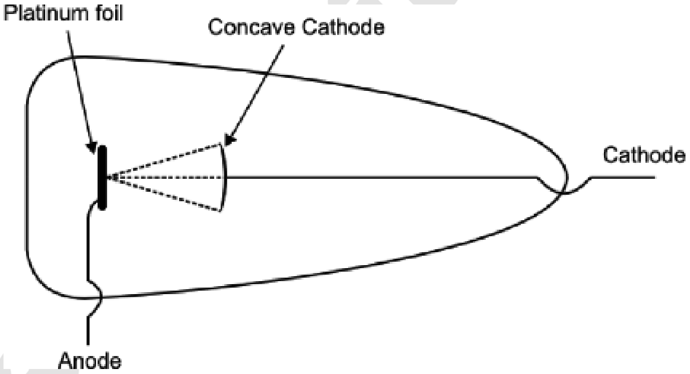
Cathode rays cast a shadow of an opaque object

4. **Cathode Rays are Material Particles (William Crooks performed this experiment):** These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. From this observation, it is inferred that cathode rays are not rays but material particles having a definite mass and velocity.



Cathode rays derive
a small paddle wheel

5. Cathode rays can produce x–rays when they strike an anode particularly with large atomic masses.
6. Cathode rays can produce heat when they fall on a metal foil. When concave cathode is used, it focuses the rays at a point. If those rays falls on a thin metal foil it become red hot and begins to glow.



7. Cathode rays can ionize gases.
8. They can cause a chemical change, because they have a reducing effect.
9. Cathode rays can pass through a thin metal foil like aluminum or gold.
10. Mass of one electron is 9.1×10^{-31} kg or 5.4858×10^{-4} a.m.u.

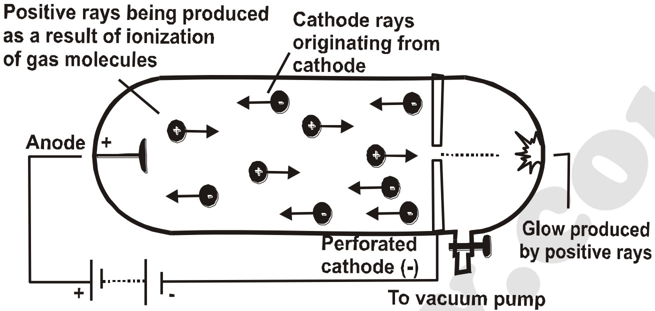
Conclusion: J.J. Thomson concluded from his experiments that cathode rays consist of stream of negatively charged particles. G.J. Stoney named these particles as electrons. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube. He concluded that all atoms contained electrons.

Daily Life Uses:

1. Now a days cathode rays are used as advertisement neon signs.
2. Television picture tube and monitor of computer is also cathode ray tube (CRT).

DISCOVERY OF PROTON

In 1886, German physicist, **E. Goldstein** took a discharge tube provided with a cathode having extremely fine holes in it. When a large potential difference was applied between electrodes, it was observed that while cathode rays were traveling away from cathode, there were other rays produced at the same time. These rays after passing through the perforated cathode produced a glow on the wall opposite to the anode. Since these rays passed through the canals or the holes of cathode, they were called **canal rays**. Later on, these rays were named as positive rays because they carry positive charge.

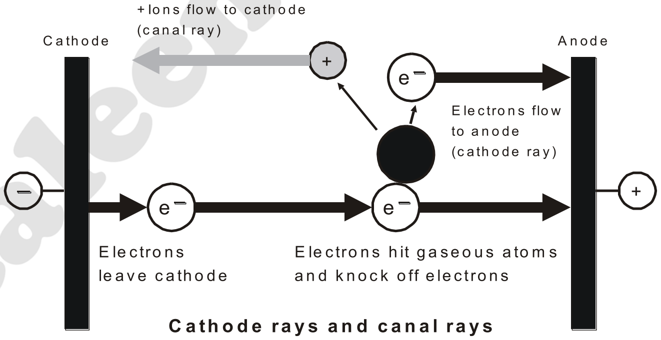


Production of positive rays

Reason for the Production of Positive Rays:

These positive rays were produced, when high speed cathode rays (electrons) strike the molecules of a gas enclosed in the discharge tube. They knocked out electron from the gas molecules and positive ions were produced which started moving towards the cathode.

$$M + e^- \longrightarrow M^+ + e^-$$



Cathode rays and canal rays

PROPERTIES OF POSITIVE RAYS

1. They are deflected by an electric as well as a magnetic field showing, these are positively charged.
2. They rays travel in a straight line in a direction opposite to the cathode.
3. They produce flashes on ZnS plate.
4. The **e/m** value for the positive rays is always **smaller** than that of electron and depends upon the nature of gas used in side the tube. Heavier gas has smaller e/m ratio.

5. When hydrogen gas is used in the discharge tube, the e/m value is found to be the maximum in comparison to any other gas because the value of m is the lowest for the positive particle obtained from the hydrogen gas. Hence the positive particle obtained from hydrogen gas is the lightest among all the positive particles. This particle is called **proton**, a name suggested by Rutherford.

6. The mass of a proton is 1836 times more than that of a an electron.

7. Mass of one proton is 1.0073 a.m.u. or 1.6726×10^{-27} kg.

DISCOVERY OF NEUTRON

Discovery of neutron was led by the artificial radioactivity.

Artificial Radioactivity:

"The phenomenon in which isotopes of certain lighter element are made radioactivity by bombarding them with energy particles (α–particles) is called **artificial radioactivity**."

Neutron was discovered by the James Chadwick in 1932 with the help of artificial radioactivity. He was awarded Noble Prize in 1935.

Experiment:

A stream of α–particles produced from a polonium source was directed at beryllium ($^{9}_{4}Be$) target. It was noticed that some penetrating radiations were produced. These radiation were called **neutrons** because the charge detector showed them to be neutral. The nuclear reaction is as follows:

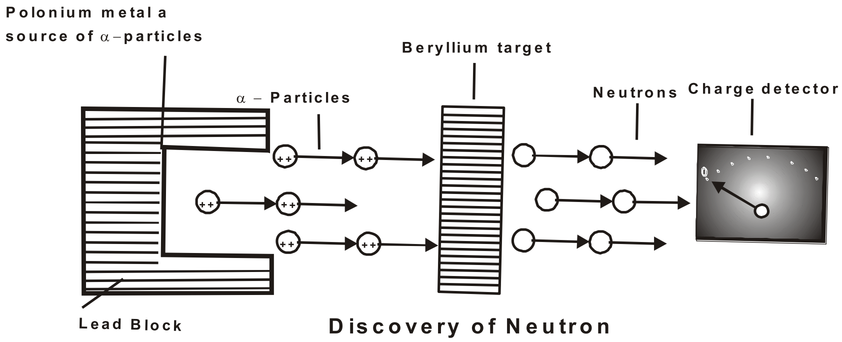
Formation of α–Particles:

$$^{216}_{84}Po \longrightarrow {}^{212}_{82}Pb + {}^{4}_{2}He$$

Formation of Neutron:

$$^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

This reaction is (α–n) reaction because incoming particle is α and out going is neutron. In this reactions α–particles and nuclei of Be are rearranged and extra neutron is emitted.



Discovery of Neutron

PROPERTIES OF NEUTRON

1. Free neutron decays into a proton with the emission of an electron and a neutrino.

   $${}_{0}^{1}n \longrightarrow {}_{+1}^{1}P + {}_{-1}^{0}e + {}_{0}^{0}n$$

2. Neutrons cannot ionize gases.
3. Neutrons are highly penetrating particles.
4. They can expel high speed protons from paraffin, water, paper and cellulose.
5. When neutrons travel with an energy 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. When neutrons are used are projectile, they can carry out the nuclear reactions.

   A fast neutron ejects α–particles from the nucleus of nitrogen atom and Boron is produced.

   $${}_{7}^{14}N + {}_{0}^{1}n \longrightarrow {}_{5}^{11}B + {}_{2}^{4}He$$

7. When slow moving neutrons hit the copper metal, then gamma radiations (γ) are emitted and the radioactive copper ${}_{29}^{66}Cu$ changes to zinc.

   $${}_{29}^{65}Cu + {}_{0}^{1}n \longrightarrow {}_{29}^{66}Cu + h\upsilon \text{ (gamma rays)}$$

   $${}_{29}^{66}Cu \longrightarrow {}_{30}^{66}Zn + {}_{-1}^{0}e$$

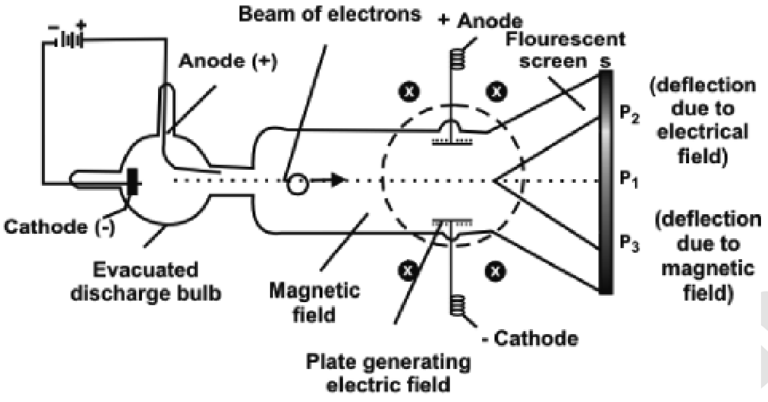
Uses:

Because of their intense biological effects, they are being used in treatment of cancer. Neutron is also used to produce radioactive elements by nuclear reactions, which are used in a diagnosis of some diseases. It is also used in nuclear fission, in which heavy nucleus changes to smaller nuclei.

MEASUREMENT OF CHARGE/MASS RATIO (e/m) OF ELECTRON

In 1897, J.J. Thomson devised an instrument to measure the e/m value of electrons. The apparatus consists of a discharge tube shown in Figure. the cathode rays are allowed to pass through electric and magnetic fields. When both the fields are **off** then a beam of cathode rays, consisted of electrons, produces bright luminous spot at P_1 on the fluorescence screen. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point P_2. When only electric field is applied, the cathode rays produce a spot at P_3. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point P_1. The charge to mass ratio which was determined by J.J. Thomson was 1.7588×10^{11} C kg^{-1}.

This means 1 kg of electrons have 1.7588×10^{11} Coulombs charge.

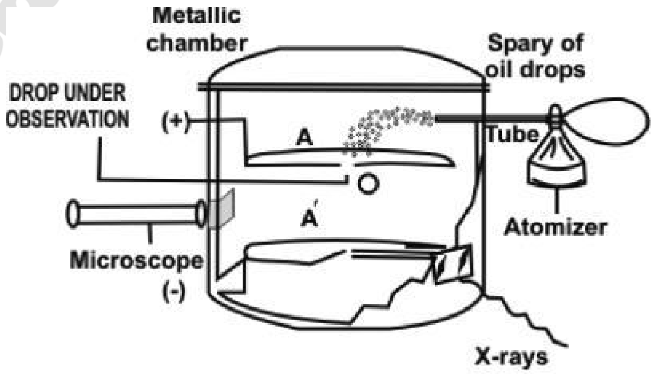


Measurement of e/m value of an electron

MEASUREMENT OF CHARGE ON ELECTRON (MILLIKAN'S OIL DROP EXPERIMENT)

In 1909 R.A. Millikan determined the charge on electron by the following arrangement. The apparatus consists of a metallic chamber. It has two parts. The chamber is filled with air, whose pressure can be adjusted by a vacuum pump. There are two electrodes A and A′. These electrodes are used to generate an electrical field in the space between the electrodes. The upper electrode has a hole in it as show in Figure.

A **fine spray** of oil droplets is created by an **atomizer**. A few droplets enter the hole. Then the hole is closed. An arc lamp is used to illuminate the space between the electrodes. The droplet is observed through telescope. This droplet when illuminated perpendicularly to the direction of view, appears in the telescope as a bright speck against a dark background. The droplet falls under the force of gravity, without applying the electric field. the velocity of the droplet is determined. The velocity of the droplet (v_1) depends upon its weight.



Millikan's oil drop method

$v_1 \propto mg$ (1)

where 'm' is the mass of the droplet and 'g' is the acceleration due to gravity. After that the air between the electrodes is ionized by x–rays, the droplet under observations takes up an electron and gets charged. Now connect A and 'A' to a battery which generates an electric field having a strength E. The droplet moves upwards against the force of gravity with a velocity (v_2).

$v_2 \propto Ee - mg$ (2)

where 'e' is the charge on the electron and Ee is upward driving force on the droplet, due to applied electric field of strength E.

Dividing Equation (2) by Equation (1).

$$\frac{v_1}{v_2} = \frac{mg}{Ee - mg}$$

v_1, v_2, g and E are known then, 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.

By changing the strength of electrical field, Millikan found that the charge on each droplet was different. The smallest charge which he found was 1.59×10^{-19} coulombs, which is very close to the recent value of 1.622×10^{-19} coulombs. The charge present on an electron is the smallest charge of electricity that has been measured so far.

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 $$\frac{1.6022 \times 10^{-19} \text{ coulombs}}{\text{mass of electron}} = 1.7588 \times 10^{11} \text{ coulombs kg}^{-1}$$

$$\text{Mass of electron} = \frac{1.6022 \times 10^{-19} \text{ coulombs}}{1.7588 \times 10^{11} \text{ coulombs k}^{-1}}$$

$$= 9.1095 \times 10^{-31} \text{ kg}$$

Comparison of Properties of Proton, Electrons and Neutrons

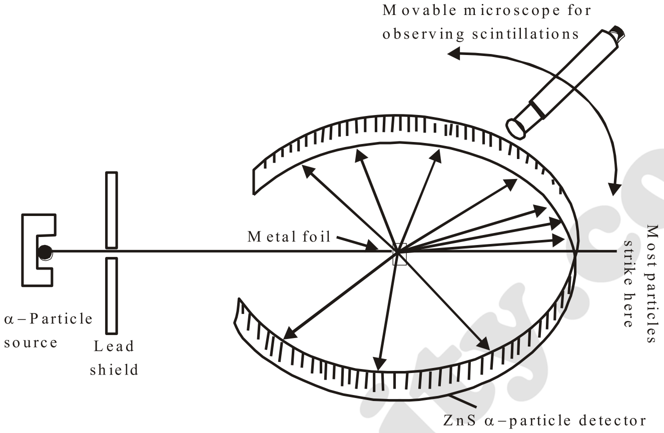
Properties	Electron	Proton	Neutron
1. Year of Discovery	1885	1886	1932
2. Discoverer	J.J. Thomson	Eugene Goldstein	James Chadwick
3. Way of Discovery	Discharge Tube	Discharge Tube	Artificial Radioactivity
4. Relative Charge	– 1	+ 1	0
5. Mass (a.m.u.)	5.4858×10^{-4}	1.0073	1.0087
6. Mass (kg)	9.1×10^{-31}	1.6726×10^{-27}	1.6750×10^{-27}
7. Charge (coulomb)	-1.6022×10^{-19}	$+1.6022 \times 10^{-19}$	0
8. Heavier than electron	--	1836	1842

DISCOVERY OF NUCLEUS (RUTHERFORD'S ATOMIC MODEL)

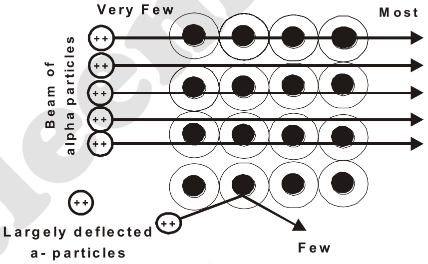
In 1911, Lord Rutherford performed classic experiment. In his experiment, the position of the nucleus and electrons is determined.

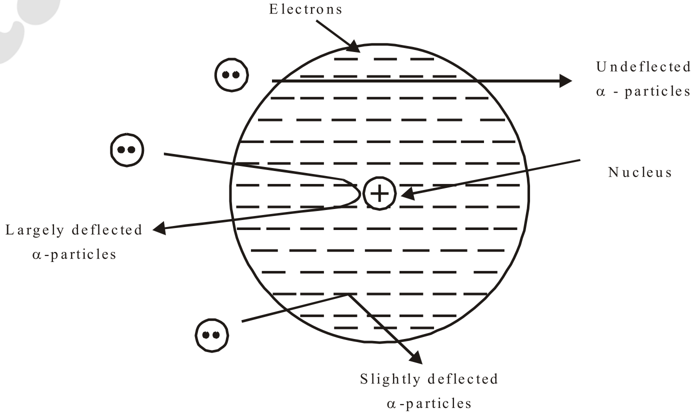
α–Particles Scattering Experiment:

Rutherford bombarded a thin gold foil (0.00004 cm) with fast moving α–particles, from a radioactive material (Polonium or radium). He observed that out of approximately 20,000 α–particles, only one was deflected at an angle of more than 90^o and almost all of them go straight through the foil.



(Rutherford's experiment. Positively charged α–particle from a radioactive source are scattered by a thin metal foil. Scattering occurs in all directions as detected by fluorescence on ZnS detector)





MODEL OF ATOM (PROPOSED)

Rutherford on the basis of his experiment proposed a model of an atom which was similar to solar system. According to this model.

(i) An atom consists of a nucleus containing positive charge.

(ii) The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.

(iii) The electrons are in constant motion around the nucleus like planets around the sun. The centripetal force required to keep the electrons moving in a circle round the nucleus is provided by the electrostatic force of attraction between the electrons and positive nucleus.

(iv) A small volume of atom is occupied by the nucleus and most volume of atom is occupied by extra nuclear electrons.

(v) Whole mass of atom is present in the nucleus.

(vi) All the fundamental particles except electrons lie in the nucleus and are called **nucleon**.

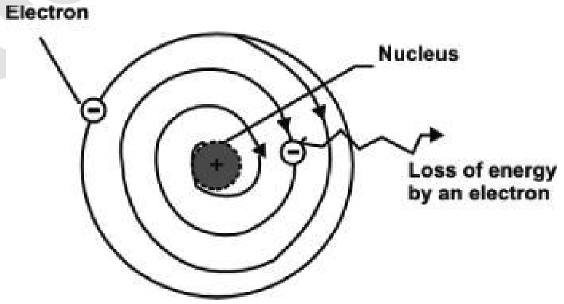
DEFECTS IN RUTHERFORD’S ATOMIC MODEL

Rutherford’s atomic model was based on the laws of gravitation and motion which could easily be applied to the neutral bodies like planets, but not to the charged bodies such as protons and electrons.

The behaviour of electron could not be understood by the model. Following defects were observed in this model.

(1) In this model outer electrons could not be stationary, if they were, they would gradually be attracted by the nucleus till they ultimately fall into it. This atomic structure proposed by the Rutherford would collapse.

(2) Since an electrons is revolving around the nucleus continuously, so a continuous spectrum should be formed but actually, a **line spectrum** is obtained.



PLANCK’S QUANTUM THEORY

Max Planck proposed the Quantum theory in 1900, emission of radiation takes place from hot bodies at different temperatures by vibration of atoms. This effect can be seen in the change of colour from “orange” to “red hot” and red hot to “white” when the metal is heated.

According to this theory, energy, travels in a discontinuous manner and it is composed of large number of tiny discrete units called **quanta**. The main points of his theory are:

1. Energy is not emitted or absorbed continuously. Rather it is emitted or absorbed in a discontinuous manner and in the form of wave packets.

   Each wave packet or quantum of energy is often called **photon**.

2. The amount of energy associated with a quantum of radiation is proportional to the frequency (v) of the radiation. Frequency is the number of waves passing through a point per second.

   $E \propto \upsilon$

   $E = h\upsilon \quad (1)$

   $$\boxed{h = \frac{E}{\nu} = \frac{\text{Joules}}{\text{sec}^{-1}} = \text{Joules sec.}}$$

   Where 'h' is a constant known as Planck's constant and its value is 6.625×10^{-34} Js

3. A body can emit or absorb energy only in terms of integral multiples of a quantum.

   $E = n\,h\upsilon$ where $n = 1, 2, 3, \ldots\ldots\ldots$

   The frequency 'υ' is related of the wavelength of the photon as

   $$\upsilon = \frac{c}{\lambda} \qquad (2)$$

Where c is the speed of light which is $3 \times 10^{8}\ \text{ms}^{-1}$ and λ is the wavelength of any light radiation.

By putting the value of 'υ' in Equation (i) we get

$$E = h \times \frac{c}{\lambda} = \frac{hc}{\lambda} \qquad (3)$$

Wavelength:

"The distance between two adjacent crests or two adjacent troughs is called **wavelength**."

Frequency:

"The number of waves passing through a point in one second is called **frequency**."

Its units are cycles/second or hertz.

$$\upsilon = \bar{\upsilon}c \quad , \quad \bar{\upsilon} = \frac{\upsilon}{c} \qquad (4)$$

where $\bar{\nu}$ is **wave number** and is defined as the number of waves present in one centimeter distance. Its unit is per centimeter cm^{-1}. The SI unit of wave numbers is per meter (m^{-1}).

$\bar{\nu} = \frac{1}{\lambda}$ putting this value in Equation (3).

$$E = hc\bar{\nu} = \frac{hc}{\lambda} \qquad (5)$$

Energy of photon is related to frequency wavelength and wave number.

SPECTRUM

"The series of images formed when a beam of radiation is passed through a slit and then dispersed so that component waves are separated and arranged in order of their wavelength is called **spectrum**."

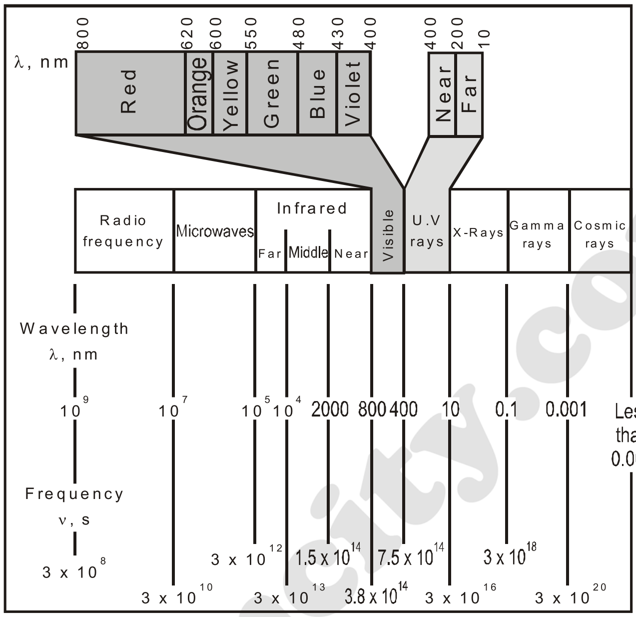


Fig. The visible and other regions of spectrum

When a radiation of light is passed through a prism, the radiations undergoes refraction or bending. The extent of bending depends upon the wavelength. A radiation of **longer wavelength bends less** than the radiation of smaller wavelength. Hence the dispersion of components of light takes place which is called a **spectrum**. There are total eight regions of spectrum on the basis of magnitude of wavelength, i.e., Cosmic rays, Gamma rays, x–rays, ultra violet rays, visible, infrared, microwaves and Radio waves.

On the basis of arrangement of waves spectrums are of two types:

(i) Continuous spectrum (ii) Line spectrum

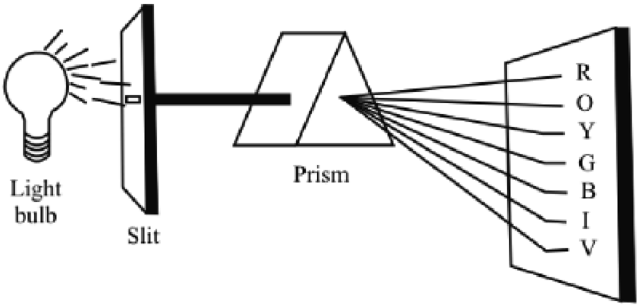
(i) Continuous Spectrum:

"The type of visible spectrum in which coloured lines are diffused into one another and no definite boundary can be marked between them is called **continuous spectrum**."

When sun light or incandescent (electric bulb) light is passed through the prism, it resolve into seven, component colours. The separation of white light into seven colours is known as dispersion and band of seven colours obtained is called **spectrum**. As these colours are diffused into one another, it is therefore a continuous spectrum.

"The composition of spectrum is given as violet, indigo, blue, Green, Yellow, orange, and red abbreviated as "Vibgyor" Rainbow is the best example of continuous spectrum."

The combination of all these colours is white.



(Continuous spectrum, Light consisting of all wavelengths when passed through a prism is separated into various colour bonds.)

On passing through the prism each radiation is deviated to a different extent, because, light of different colours have its particular wavelength as shown in the following Table.

TABLE

Range of Wavelengths of the Visible Spectrum		
Colour	**Range of Wavelengths in Nanometer (nm)**	**Wavelength in A°**
Red	630 to 750	6300 – 7500
Orange	600 to 630	6000 – 6300
Yellow	580 to 600	5800 – 6000
Green	510 to 580	5100 – 5800
Blue	460 to 510	4600 – 5100
Indigo	420 to 460	4200 – 4600
Violet	400 to 420	4000 – 4200

(ii) Line Spectrum:

The type of spectrum in which coloured lines are not diffused into one another and are separated by dark region in such a way one colour can be distinguish from the other is called **line spectrum**. There are two types of line spectrum or atomic spectrum.

(i) Atomic or line emission spectrum.

(ii) Atomic or line absorption spectrum.

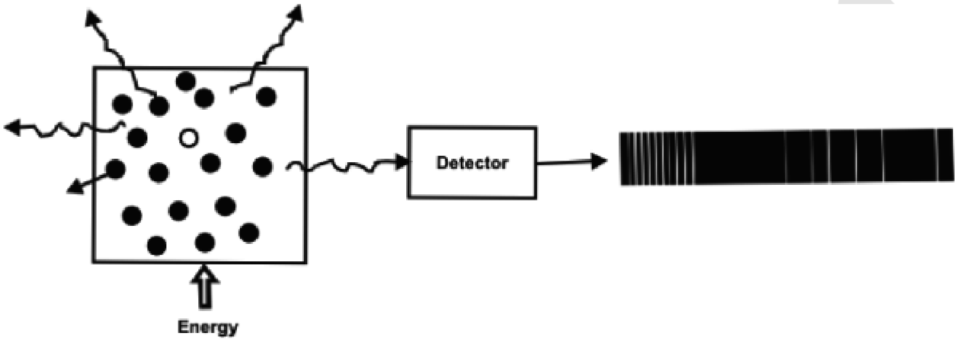
(i) Atomic Emission Spectrum:

When solids are volatilized or elements in their gaseous states are heated to high temperature or subjected to an electrical discharge, radiation of certain wavelengths are emitted. The spectrum of this radiation contained bright lines against a dark background. This is called **atomic emission spectrum**.

Origin of Atomic Emission Spectrum:

When an element or its compound is heated on flame some radiation are emitted which is seen through the spectrometer. This emission of radiation is due to excitation of electron from lower energy level to the higher energy level. When an **electron at higher energy** level come back to the ground state, it **emits some radiation** in the form of lines. When sodium or its compound is heated two yellow lines are seen (589 nm and 596 nm). When hydrogen is heated in the discharge tube, four different lines are seen in the spectrometer.

It has also be seen the distance between lines decreases by decreasing the wavelength and spectrum become continuous spectrum.

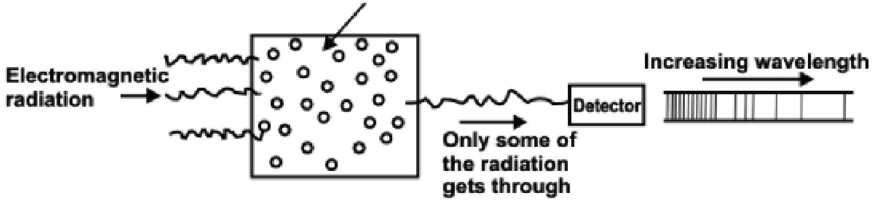


Atomic emission spectrum

(ii) Atomic Absorption Spectrum:

"When a beam of white light is passed through a gaseous sample of an element, the element absorbs certain wavelengths while the rest of wavelengths pass through it. The spectrum of this radiation is called an **atomic absorption spectrum**."

The wavelengths of the radiation that have been absorbed by the element appear as dark lines and the background is bright.



Atomic absorption spectrum

It is interesting to note that the positions or the wavelengths of lines appearing in both emission and absorption spectra are exactly the same. In emission spectrum these lines appear bright because the corresponding wavelength are being emitted by the element, whereas they appear dark in absorption spectrum because the wavelengths are being absorbed by the element.

Difference between Continuous Spectrum and Line Spectrum:

Continuous Spectrum		Line Spectrum	
(i)	In this spectrum line or waves are diffused into one another.	(i)	In this spectrum line are separated from each other by some dark spaces.
(ii)	There is no sharp boundary between the colours.	(ii)	There is a gap between the lines.
(iii)	It can be formed dispersing some typical lights like sun slight, incandescent bulbs light, etc.	(iii)	It is produced by heating the element or its compound on flame or some other source of heat.
(iv)	It is a polychromatic light.	(iv)	It is monochromatic light.
(v)	It has only one type.	(v)	It has two types (a) Line emission spectrum (b) Line absorption spectrum
(vi)	Example: rainbow, sun light, electric bulb light.	(vi)	Heating of sodium or potassium or their salts on flame.

BOHR'S MODEL OF HYDROGEN ATOM

In order to remove the objections against Rutherford's atomic model and to explain the line spectrum of hydrogen atom, Neil Bohr put forward an atomic Model in 1913. Bohr's atomic model based upon the following assumptions.

(i) Electron revolves in one of the circular orbits outside the nucleus. Each orbit has a **fixed energy** and a quantum number is assigned to it.

(ii) Electron present in a particular orbit does not radiate energy. The energy is emitted or absorbed only when an electron jumps from one orbit to another.

(iii) When an electron jumps, the energy change ΔE is given by the Planck's equation

$$\Delta E = E_2 - E_1 = h\nu \qquad (1)$$

Where ΔE is the energy difference of any two orbits with energies E_1 and E_2. Energy is absorbed by the electron when it jumps from an inner orbit to an outer orbit and vice versa.

(iv) Electron can revolve only in those orbits having fixed angular momentum (mvr). The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor.

$$\frac{h}{2\pi} \quad \text{i.e.} \quad mvr = \frac{nh}{2\pi} \qquad (2)$$

Where $n = 1, 2, 3, \ldots\ldots\ldots$

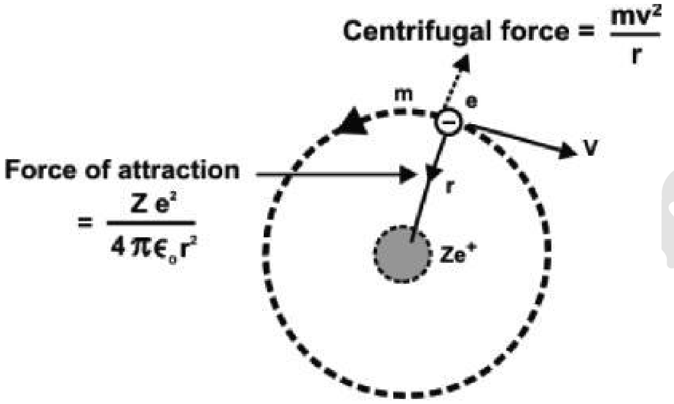
The permitted values of angular momentum are, therefore,

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi} \ldots\ldots\ldots$$

The electron is bound to remain in one these orbits and not in between them. So, angular momentum is quantized.

DERIVATION OF RADIUS OF REVOLVING ELECTRON IN nth ORBIT

By applying these ideas, Bohr derived the expression for the radius of nth orbit in hydrogen or ions like He^+, Li^{2+} etc.



Electron revolving in hydrogen atom

For a general atom, consider an electron of charge 'e' revolving around the nucleus having charge Ze. Z being the proton number and e is the charge on the proton. Let m be the mass, r the radius of the orbit and v the velocity of the revolving electron. The electrostatic force of attraction between the electron and the nucleus will be given by the following formula;

$$F = \frac{Ze^2}{4\pi \in_0 r^2} \qquad (3)$$

where $\in_0$ is the vacuum permitted and its value is $8.84 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$. This force of attraction is balanced by the centrifugal force, $\frac{mv^2}{r}$.

$$F = \frac{mv^2}{r} \qquad (4)$$

Equate Equation (3) and Equation (4).

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi \in_0 r^2}$$

$$v^2 = \frac{Ze^2}{4\pi \in_0 r^2} \times \frac{r}{m} \qquad (5)$$

$$v^2 = \frac{Ze^2}{4\pi \in_0 rm} \qquad (6)$$

$$r = \frac{Ze^2}{4\pi \in_0 mv^2} \qquad (7)$$

According to Equation (7) the radius of moving electron is inversely proportional to the square of its velocity. **The electron which is nearer to the nucleus is faster than that electron which is away from the nucleus**. In order to eliminate the velocity factor from equation (6) we use angular momentum equation.

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

$$v = \frac{nh}{2\pi\, mr}$$

By applying square on both sides.

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \qquad (8)$$

From Equation (6) and Equation (8).

$$\frac{Ze^2}{4\pi \in_0 rm} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

Cross multiplying we get

$$Ze^2 \times 4\pi^2 m^2 r^2 = n^2 h^2 \times 4\pi \in_0 rm$$

$$r = \frac{n^2 h^2 \in_0}{Ze^2 \pi m}$$

$$r = \frac{n^2}{Z} \times \frac{\in_0 h^2}{\pi me^2} \qquad (9)$$

(1) According to the Equation (9) the radius of an atom is directly proportional to the square of number of orbit (n). So higher orbits have more radii and vice versa. The collection of parameters $\frac{\in_0 h^2}{\pi me^2}$ in Equation (9) is a constant factor.

(2) Radius of an orbit is inversely proportional to the atomic number or proton number of atom. Atomic number of hydrogen is less so radius of an atom will be high.

$$\frac{\in_0 h^2}{\pi me^2} = 0.529\ A^o \quad \text{or} \quad 0.529 \times 10^{-10}\ m$$

$(1A^o = 10^{-10}\ m)$

Hence $r = 0.529\ A^o \times n^2$

By putting the value of n as 1, 2, 3, …… in Equation (9) we get

$r_1 = 0.529 \times A^o \times (1)^2 = 0.529\ A^o$

$r_2 = 0.529 \times A^o \times (2)^2 = 2.11\ A^o$

$r_3 = 0.529 \times A^o \times (3)^2 = 4.75\ A^o$

$r_4 = 0.529 \times A^o \times (4)^2 = 8.4\ A^o$

$r_5 = 0.529 \times A^o \times (5)^2 = 13.22\ A^o$

The comparison of radii shows that the distance between orbits of H–atom goes on increasing as we move from first orbit to higher orbits.

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \ldots\ldots\ldots$$

The 2nd orbit is four times away from nucleus as compared to first orbit. Third orbit is nine time away and similarly fourth orbit is 16 times away.

ENERGY OF REVOLVING ELECTRON

The total energy of an electron in an orbit is composed of two parts; the kinetic energy which is equal to $\frac{1}{2}mv^2$ and the potential energy which can be calculated as follows:

The electrostatic force of attraction between the nucleus and the electron is given by $\frac{Ze^2}{4\pi \in_0 r^2}$. If the electron moves through a small distance dr, then the work done for moving electron is given by

$$\frac{Ze^2}{4\pi \in_0 r^2}\, dr \qquad \text{(force x distance)}$$

In order to calculate 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 infinity and r.

$$\int_{\infty}^{r} \frac{Ze^2 \times dr}{4\pi \in_0 r^2} \quad \Rightarrow \quad \frac{Ze^2}{4\pi \in_0} \int_{\infty}^{r} \frac{dr}{r^2}$$

$$\Rightarrow \quad \frac{Ze^2}{4\pi \in_0} \int_{\alpha}^{r} r^{-2}\, dr \quad \Rightarrow \quad \frac{Ze^2}{4\pi \in_0} \left[\frac{r^{-2+1}}{-2+1} \right]_{\alpha}^{r}$$

$$\frac{Ze^2}{4\pi \in_0} \left[\frac{-1}{r} \right]_{\alpha}^{r} \quad \Rightarrow \quad \frac{-Ze^2}{4\pi \in_0 r} \tag{10}$$

The work done is the potential energy of electron, so

$$E_{\text{potential}} = \frac{-Ze^2}{4\pi \in_0 r} \tag{11}$$

The minus sign indicates that the potential energy of electron decrease when it is brought from infinity to a point at a distance r from the nucleus. At infinity the electron is not being attracted by the nucleus whereas at a point nearer to the nucleus it will be attracted by the nucleus.

The total energy of the electron is

$$E = E_{\text{kinetic}} + E_{\text{potential}}$$

$$E = \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi \in_0 r} \qquad (12)$$

From equation (5) substituting the value of mv^2 in Equation (12).

$$E = \frac{Ze^2}{8\pi \in_0 r} - \frac{Ze^2}{4\pi \in_0 r} = \frac{Ze^2}{4\pi \in_0 r}\left(\frac{1}{2} - 1\right) = \frac{Ze^2}{4\pi \in_0 r}\left(-\frac{1}{2}\right)$$

$$E = \frac{-Ze^2}{8\pi \in_0 r} \qquad (13)$$

Now substitute the value of r from Equation (9) into Equation (13) we get

$$E_n = -\frac{m Z^2 e^4}{8 \in_0^2 n^2 h^2} \qquad (14)$$

Where E_n is the energy of nth orbit.

For hydrogen atom $Z = 1$.

$$E_n = -\frac{m e^4}{8 \in_0^2 h^2}\left[\frac{1}{n^2}\right] \text{ Joules / atom} \qquad (15)$$

The factor outside the brackets in Equation (15) are all constants. When the values of these constants are substituted along with their units, then it comes out to be 2.18×10^{-18} J.

$$E_n = -2.18 \times 10^{-18}\left[\frac{1}{n^2}\right] \qquad (16)$$

This equation gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value show 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 E_n will become

$$E_n = \frac{-2.18 \times 10^{-18} \times 6.02 \times 10^{23}}{1000 \times n^2} = \frac{-1313.315}{n^2} \text{ kJ/mole}$$

$$E_n = -\frac{1313.315}{n^2} \text{ kJ/mole} \qquad (17)$$

Substituting the values of n as 1, 2, 3, 4, 5 etc, in Equation (17) we get the energy associated with an electron revolving in 1st, 2nd, 3rd, 4th and 5th orbital of H–atom.

$$E_1 = -\frac{1313.31}{1^2} = -1313.31 \text{ kJ/mole}$$

$$E_2 = -\frac{1313.31}{2^2} = -328.32 \text{ kJ/mole}$$

$$E_3 = -\frac{1313.31}{3^2} = -145.93 \text{ kJ/mole}$$

$$E_4 = -\frac{1313.31}{4^2} = -82.08 \text{ kJ/mole}$$

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ kJ/mole}$$

$$E_\infty = -\frac{1313.31}{\alpha^2} = -0 \text{ kJ/mole (Electron is free from the nucleus)}$$

Differences of energy between adjacent orbits:

The values of energy differences between adjacent orbits can be calculated as follows:

$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99$ kJ/mole

$E_3 - E_2 = (-145.92) - (-328.32) = 182.40$ kJ/mole

$E_4 - E_3 = (-82.08) - (-145.92) = 63.84$ kJ/mole

The differences in the values of energy go on decreasing from lower to higher orbits.

$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \ldots\ldots\ldots$

The energy difference between fist and infinite levels of energy is calculated as:

$E_\infty - E_1 = 0 - (-(1313.31) = 1313.31$ kJ/mole

IONIZATION ENERGY

"The amount of energy required to remove an electron from an atom in gaseous state is called **ionization energy**."

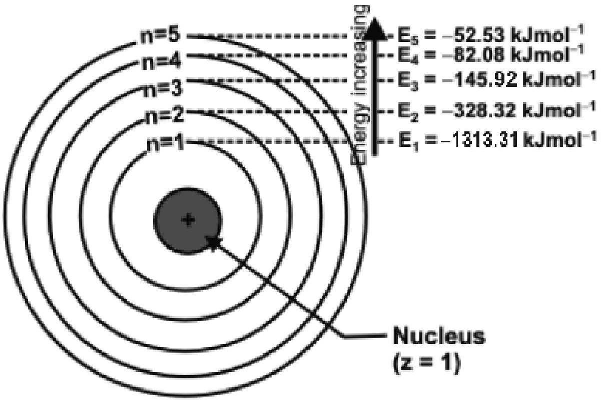
$$\frac{1}{2}H_2 \xrightarrow{\qquad} H^+ + 1e^- \ \Delta H = -1313.31 \text{ kJ/mole}$$

It is difference of energies between the infinite distance and of first level.

$E_\infty - E_1 = 0 - (-(1313.31) = 1313.31$ kJ/mole

This I.P value of hydrogen is same, experimentally and theoretically.

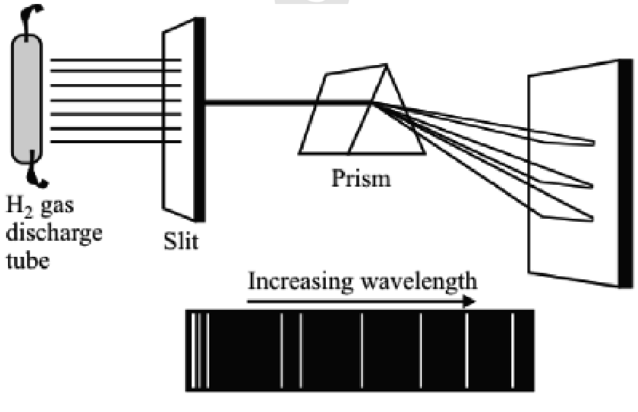
These values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply. Keep in mind that distance between adjacent orbits increases. The following figure makes the ideas clear.



Energy values associated with an electron in various orbits in hydrogen atom.

HYDROGEN SPECTRUM

It is an example of atomic emission spectrum. When hydrogen gas is filled in discharge tube at very low pressure and high voltage is applied, a bluish light is emitted from the discharge tube. If this light is dispersed through spectrometer, many lines are isolated from each other, which is called line or **atomic emission spectrum**. The wavelength of these lines lie in the visible, ultra–violet and infra–red regions. These spectral lines can be classified into five groups called **spectral series**. These series are named after their discoverers as shown below:



(Atomic emission spectrum, Light emitted by a sample of excited hydrogen atoms when passed through a prism is separated into discrete wavelength)

1. Lyman series (U.V. region)
2. Balmer series (Visible region)
3. Paschen series (I.R. region)
4. Brackett series (I.R. region)
5. Pfund series (I.R. region)

The first four series were discovered before Bohr's atomic model (1913). The wave–numbers (m^{-1}) of the series of lines in hydrogen spectrum are given in Table.

TABLE

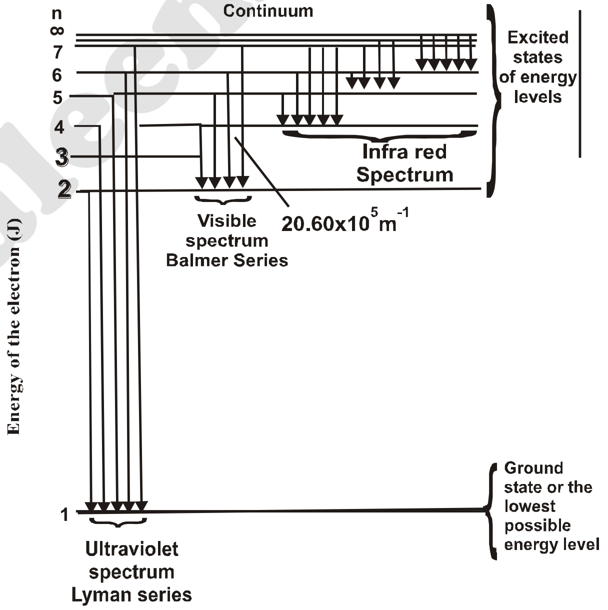
Wave numbers (m^{-1}) of Various Series of Hydrogen Spectrum				
Lyman series (U.V. region)	**Balmer series (Visible region)**	**Paschen series (I.R. region)**	**Brackett series (I.R. region)**	**Pfund series (I.R. region)**
82.20×10^5	15.21×10^5 (H_α line)	5.30×10^5	2.46×10^5	1.34×10^5
97.60×10^5	20.60×10^5 (H_β line)	7.80×10^5	3.80×10^5	2.14×10^5
102.70×10^5	23.5×10^5 (H_γ line)	9.12×10^5	4.61×10^5	
105.20×10^5	24.35×10^5 (H_δ line)	9.95×10^5		
106.20×10^5	25.18×10^5			
107.10×10^5				

It is seen from the table that as we proceed from Lyman series to Pfund series, the wave numbers (m^{-1}) of spectral lines decrease.

ORIGIN OF HYDROGEN SPECTRUM ON THE BASIS OF BOHR'S MODEL

According to Bohr, electron in hydrogen atom may revolve in any orbit depending upon its energy. When hydrogen gas is heated or subjected to an electric discharge, its electron moves from one of the lower orbits to higher orbit absorbing particular wavelength of energy.

Subsequently when it comes back, the same energy is released. This energy is observed as radiation of particular wavelengths in the form of bright lines seen in the visible region of the emission spectrum of hydrogen gas.



Electronic transitions in hydrogen atom

The spectral lines of Lyman series are produced when the electron jumps from $n = 2, 3, 4, 5, \ldots\ldots$ to $n = 1$ (Lyman did not know this reason). Similarly spectral lines of Balmer series discovered in 1887 originated when an electron jumps from $n = 3, 4, 5, 6, \ldots\ldots$ to $n = 2$ orbit.

In the same way Paschen, Brackett and Pfund series of lines are produced as the result of electronic transitions from higher orbits to 3rd, 4th and 5th orbits respectively Figure.

CALCULATION OF WAVE NUMBERS OF PHOTONS OF VARIOUS SPECTRAL SERIES BY THE BOHR'S THEORY

(1) Wave number:

"The number of wave present in one meter distance is called **wave number**."

The SI unit of wave number is m^{-1}, other unit is cm^{-1}.

The wave number, wavelength or frequency of radiation depends upon the light emitted by the electron.

Frequency of Radiation emitted when Electron Jumps from n_2 to n_1:

The number of waves passing through a point in one second is called frequency from Equation (14).

$$E_n = \frac{-Z^2 m e^4}{8 \epsilon_0^2 n^2 h^2}$$

$$E_1 = \frac{-Z^2 m e^4}{8 \epsilon_0^2 n_1^2 h^2}$$

$$E_2 = \frac{-Z^2 m e^4}{8 \epsilon_0^2 n_2^2 h^2}$$

E_1 and E_2 are the energies of electrons in n_1 and n_2 respectively. The energy difference between the two can be calculated as follows:

$$\Delta E = E_2 - E_1 = -\frac{Z^2 m e^4}{8 \epsilon_0^2 n_2^2 h^2} - \left(-\frac{Z^2 m e^4}{8 \epsilon_0^2 n_1^2 h^2} \right)$$

$$= -\frac{Z^2 m e^4}{8 \epsilon_0^2 n^2 h^2} + \frac{Z^2 me^4}{8 \epsilon_0^2 n_1^2 h^2}$$

$$= \frac{Z^2 m e^4}{8 \epsilon_0^2 n_1^2 h^2} - \frac{Z^2 m e^4}{8 \epsilon_0^2 n_2^2 h^2} \qquad (18)$$

$$\Delta E = \frac{Z^2 m e^4}{8 \epsilon_0^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{Joules}$$

For H–atom; $Z = 1$.

$$\text{Since } \frac{m e^4}{8 \epsilon_0^2 h^2} = 2.18 \times 10^{-18} \text{ J}$$

(By putting the values of constants).

$$\Delta E = 2.18 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{J} \qquad (19)$$

With the help of Equation (19) the energy difference between any two orbits of H–atom can be calculated where n_1 is the lower level and n_2 higher level.

Since $\Delta E = h\nu$

Therefore $h\nu = \frac{m e^4}{8 \epsilon_0^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$\nu = \frac{m e^4}{8 \epsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{Hz} \qquad (20)$$

Unit of frequency is s^{-1} or cycle per second or hertz (Hz).

Equation (20) shows the frequency of photon emitted when an electron jumps from higher energy level to lower energy level. Frequency values go on decreasing between adjacent levels.

$E_2 - E_1 > E_3 - E_2 > E_4 - E_3$ and so on.

Calculation of wave number ($\bar{\nu}$):

We know from Planck's concept that

$\nu = \bar{\nu} c$

Putting the value of Equation (20) we get

$$\bar{\nu} c = \frac{Z^2 m e^4}{8 \epsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{\nu} = \frac{Z^2 m e^4}{8 \epsilon_0^2 h^3 c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] m^{-1} \qquad (21)$$

$$\bar{\nu} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The value of the factor $\frac{m e^4}{8 \epsilon_0^2 h^3 c}$ in Equation (21) has been calculated to be $1.09678 \times 10^7 \ m^{-1}$. R is called **Rydberg's constant**.

$$\bar{\nu} = 1.09678 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] m^{-1} \qquad (22)$$

$$Z = 1 \text{ and } \frac{Z^2 m e^4}{8 \epsilon_0^2 h^3 c} = 1.09678 \times 10^7 \ m^{-1}$$

Lyman Series:

It is the series when an electron jumps from higher orbit to n_1.

First line $n_1 = 1$ (lower orbit) $n_2 = 2$ (higher orbit)

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = 82.26 \times 10^5 \text{ m}^{-1}$$

Second line $n_1 = 1$ $n_2 = 3$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{3^2} \right] = 97.49 \times 10^5 \text{ m}^{-1}$$

Limiting line $n_1 = 1$ $n_2 = \infty$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = 109.678 \times 10^5 \text{ m}^{-1}$$

The values of all these wave–numbers lie in the U.V. region of the spectrum. It means that when electron of H–atom falls from all the possible higher levels to $n = 1$, then the photons of radiation emitted lie in the range of U.V. region.

Balmer Series:

The series of lines when an electron jumps from higher orbit to n_2.

First line $n_1 = 2$ $n_2 = 3$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = 15.233 \times 10^5 \text{ m}^{-1}$$

Second line $n_1 = 2$ $n_2 = 4$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{4^2} \right] = 20.564 \times 10^5 \text{ m}^{-1}$$

Third line $n_1 = 2$ $n_2 = 5$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{5^2} \right] = 23.03 \times 10^5 \text{ m}^{-1}$$

Limiting line $n_1 = 2$ $n_2 = \infty$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right] = 27.419 \times 10^5 \text{ m}^{-1}$$

The limiting line of Balmer series lies in **U.V. region** while other lines fall in **visible region**. Similarly, we can calculate the wave numbers for all the lines of Paschen, Brackett and Pfund series. These three series of lines lie in the infra–red region.

Defects of Bohr's Atomic Model:

1. 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.

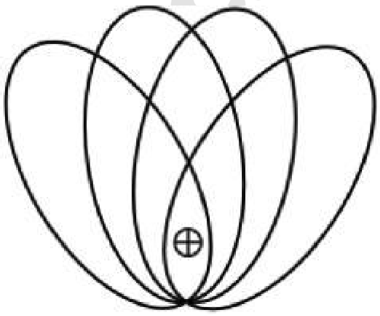
2. When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very **fine lines**, i.e. original lines are seen divided into other lines. The H_α– line in the Balmer series is found to consist of five–component lines. This is called **fine structure or multiple structure**. Actually 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. 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. Actually the atomic model is **not flat**.

4. 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**. So if the source which is producing the Na–spectrum is placed in a weak magnetic field, it causes the splitting of two lines of Na into component lines (589 nm and 596 nm). Similarly 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.

Sommerfeld's Modification of Bohr's Atomic Model:

In 1915 Sommerfeld suggested that moving electron around the nucleus have elliptical path in addition to the circular path. The nucleus is situated at one of the foci of the ellipse.



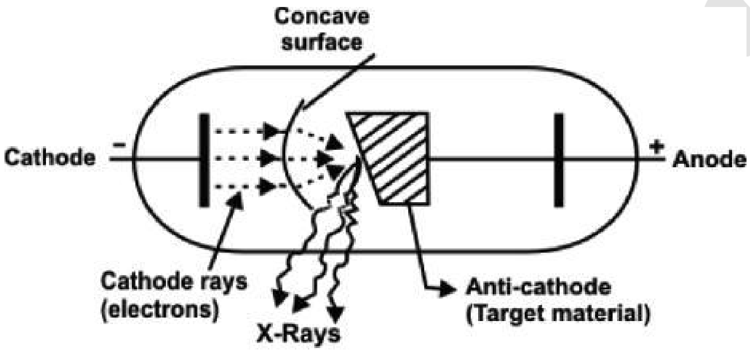
Elliptical orbits of Hydrogen atom

X–RAYS AND ATOMIC NUMBER

X–rays were discovered by Roentgen in 1895. Moseley (1913) a student of Rutherford used this technique of X–ray spectroscopy to determine the atomic number. X–rays are produced in cathode ray tube, when the electron beam (cathode rays), fall on the metal target. When an electron of cathode rays hits the metal atom in the target, it **knock out** an electron from the inner k–shell of an atom. A metal ion is produced with an electron missing from an inner orbital. Its electronic configuration becomes unstable. An electron from an orbital of **higher energy drops** into the half–filled orbital and a photon of light is emitted. This photon is electromagnetic radiation in the X–ray region.

The energies of inner orbital of an atom and energy changes between them depend upon the nuclear charge. Therefore the frequency υ of X–rays depends upon the atomic number Z of metal atom in the target. Every metal has its own characteristic X–rays.

X–rays are passed through a slit in platinum plate and then emerged through aluminum window. This is thrown on a crystal of Potassium Ferro cyanide $K_4\left[Fe\,(CN)_6\right]$ which analyses the X–ray beam. The rays are diffracted from the crystals and are obtained in the line spectrum of X–rays. This is allowed to fall on photographic plate. This line spectrum is the characteristic of target material used (anode). This characteristic X–rays spectrum has discrete spectral lines. These are grouped into K–series, L–series and M–series. Each series has various lines as K_α, K_β, L_α, L_β, M_α, M_β, etc.



Production of X-rays

Moseley researches covered or range of wavelength from 0.04 – 8^{o}A. He employed **thirty eight element**, from aluminum to gold as target in X–ray tube. Moseley concluded that;

(1) Spectral lines obtained from X–ray spectroscopy could be classified into the distinct groups. One of the shorter wavelength are identified by K–series and other comparatively longer wavelengths are identified as L–series.

(2) If target element has higher atomic number, the wavelength of X–rays become shorter.

(3) A very simple relationship was found between the frequency (v) of a particular line in X–rays and the atomic number Z of the element emitting it.

$$\sqrt{v} = a\,(Z - b)$$

b = screening constant

a = proportionality constant

This linear equation is known as **Moseley's Law**.

This law states that the frequency of a spectral line in X–ray spectrum varies as the square of atomic number of an element emitting it. This law convinces us that atomic number is the fundamental property of an element on which physical and chemical properties are based. These properties are not based upon their atomic masses.

Importance of Moseley's Law:

1. Moseley arranged K and Ar, Ni and Co, Te and I in a proper way in a Mendeleev's Periodic tale.
2. This law has led to the discovery of many new element like Tc (43), Pr (59), Rh (45).
3. The atomic number of rare earth elements have been determined by this law.

WAVE–PARTICLE NATURE OF ELECTRON

Planck's quantum theory of radiation tells us that light shows a dual character it behaves both as a material particle and as a wave. This idea was extended, to matter particles in 1924 by Louis de Broglie.

1. de-BROGLIE CONCEPT

According to de-Broglie all material particles in motion have a dual character. It means that electrons, protons, neutrons, atom and molecules posses the characteristics of both the material particle and a wave. This is called wave-particle duality in matter. de-Broglie derived a mathematical equation which relates the wavelength (λ) of the electron to the momentum of electron.

$$\lambda = \frac{h}{mv} \qquad (1)$$

Here λ = de Broglie's wave–length,
m = mass of the particle
v = velocity of electron

According to this equation the wavelength associated with an electron is inversely proportion its momentum (mv).

This equation is derived as follows.

According to Planck's equation.

$$E = h\upsilon \qquad (2)$$

According to Einstein's mass energy relationship.

$$E = mc^2 \qquad (3)$$

Where 'm' is the mass of the photon and 'c' is the velocity of photon. Equating Equation (2) and Equation (3) we get.

$$mc^2 = h\upsilon$$

$$mc = \frac{hv}{c} \qquad (4)$$

From Planck's equation we know that

$$\upsilon = \frac{c}{\lambda}$$

$$\frac{v}{c} = \frac{1}{\lambda}$$

Put this value in Equation (4) we get

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

If this concept is applied to moving electron with velocity v.

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

or $\lambda = \frac{h}{mv}$ (This is called de-Broglie's equation)

Let us consider an electron is moving with a velocity of $2.188 \times 10^{6}\ ms^{-1}$ then wavelength associating with it, can be calculated as follows.

$$h = 6.626 \times 10^{-34}\ Js$$

$$m = 9.1 \times 10^{-31}\ Kg$$

$$\lambda = \frac{6.625 \times 10^{-34}\ Js}{9.1 \times 10^{-31}\ kg \times 2.188 \times 10^{6}\ ms^{-1}} \qquad (\text{since } J = kg\ m^{2}\ s^{-2})$$

$$= 0.33 \times 10^{-9}\ m$$

$$= 0.33\ nm$$

This value of wavelength (λ) of electron while moving in the first orbit of H–atom is comparable to the wavelength of X–rays, and can be measured. If we imagine a **proton** moving in a straight line with the same velocity as mentioned for electron, it's wavelength will be **1836 times** smaller than that of electron. Similarly an **α–particle** moving with the same velocity should have a wavelength **7344 times** smaller compared to that of electron. Now, consider a stone of mass one gram moving with a velocity of $10\ ms^{-1}$ then its wavelength will be:

$$\lambda = \frac{6.625 \times 10^{-34}\ Js}{10^{-3}\ kg \times 10\ ms^{-1}} = 6.625 \times 10^{-30}\ m$$

This wavelength is so small that it cannot the measured by any conceivable method. it means that heavy material particles have waves associated with them, but they cannot be captured and we say that the macroscopic bodies don't have the waves.

2. DAVISSION AND GERMER EXPERIMENTAL VERIFICATION

In 1927, two American scientists Davission and Germer did an experiment to verify the wave–nature of moving electron. Electrons were produced from heated tungsten filament and accelerated through charged plates. Davission and Germer proved that the **accelerated electrons undergo diffraction**, like waves, when they fall on a nickel crystal. In this way, the wave nature of electron got verified.

(Diffraction is property of waves in which the waves spread out when they encounter on obstruction or small hole about the size of wavelength).

HEISENBERG'S UNCERTAINTY PRINCIPLE

Heidelberg's principle of uncertainty refers to the simultaneous determination of the position and momentum of an electron. According to this principle.

"It is impossible to specify, simultaneously and precisely, both the position and the momentum of an electron."

According to Bohr's theory, an electron is a material particle and its positions as well as momentum can be determined with great accuracy. But with the advent of the concept of wave nature of electron, it has not been possible for us to measure simultaneously the exact position and velocity of electron. This was suggested by Heisenberg in 1927. suppose that Δx is the uncertainty in the measurement of the position and Δp is the uncertainty in the measurement of momentum of an electron, then

$$\Delta x \, \Delta p \geq \frac{h}{4\pi}$$

This relationship is called **uncertainty principle**. This equation shows that if Δx is small then Δp will be large and vice versa. So, if one quantity is measured accurately then the other becomes less accurate. Hence, certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

The uncertainty principle is applicable only for **microscopic particles** like electrons, neutrons etc, and has no significance for large particle, i.e. macroscopic particles.

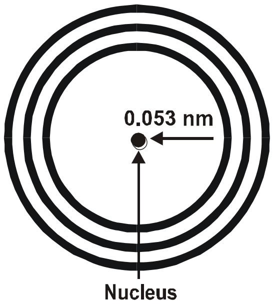
Compton's effect can help us understand the uncertainty principle. Suppose we wish to determine the position of electron. Visible light cannot help us because the wavelength of visible light is millions time large as compared to the diameter of electron. For this purpose, we have to use X–rays, which have very short wavelength as compared to that of visible light. When this photon of X–rays strikes an electron, the momentum of electron will change. In other words, uncertainty of momentum will appear due to change of velocity of electron. **Smaller the wavelength** of X–rays, greater will be the **energy** of the photon. Hence the collision of X–rays with electron will bring about the greater uncertainty in momentum. So an effort to determine the exact position of electron has rendered its momentum uncertain. When we use the photons of longer wavelength to avoid the change of momentum, the determination of the position of electron becomes impossible.

ORBIT

This term was used in Bohr's theory. "The path of an electron around the nucleus is called orbit."

ORBITAL

"The space or region around the nucleus where probability of finding the electron is maximum (more than 95%) is called orbital."



Probable electron density diagram for hydrogen atom.

In Bohr's atom the electrons are moving with specific velocities in orbits of specified radii, and according to uncertainty principle both these quantities cannot be measured experimentally. A theory involving quantities which cannot be measured does not follow the tradition of scientific work. In order to solve this difficulty, Schrodinger, Heisenberg and Dirac worked out wave theories of the atom. The best known treatment is that of Schrodinger.

He set up a wave equation for hydrogen atom. According to Schrodinger, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at anytime can be found. The solution of the wave equation gives probability of finding an electron present in a given small region of space. When the probability of finding the electron at a distance r from the nucleus is calculated for the hydrogen atom in the ground state given figure is obtained.

The **maximum probability** of finding the electron is at a distance of **0.053 nm**. It is the same radius as calculated for the Bohr's first orbit. There is possibility that the electron is either closer to the nucleus or outside the radius of 0.053 nm, where probability of finding electron decreases sharply.

"The volume of space in which there is 95% chance of finding an electron is called atomic orbital."

The term orbital should not be confused with the term orbit as used in the Bohr's theory. The orbital can be regarded as a spread of charge surrounding the nucleus. This is often called the "electron cloud".

QUANTUM NUMBERS

"A set of integral numbers which describes the behaviour (energy, shape, orientation) of electron in an orbital is called quantum number."

These quantum numbers specify position of electron in an atom. These quantum numbers are the solution of Schrodinger wave equation.

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

Principal Quantum Number (n):

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger. Its values are non–zero, positive integers upto infinity.

n = 1, 2, 3, 4, 5, ...

The value of n represents the shell or energy level in which the electron revolves around the nucleus. 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. The values of n also determine the **location of electron** in an atom, i.e. the distance of electron from the nucleus, greater the value of 'n' greater will be the distance of electron from the nucleus. It is quantitative measure of the size of an electronic shell. 'n' also provides us the energy of electron in a shell.

Azimuthal Quantum Number (l):

It is also called **sub–shell quantum number**. It has already been mentioned in the defects of Bohr's model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into **several very fine lines**. This thing can be explained by saying that each shell is divided into **sub–shells**. Therefore only principal quantum number (n) is not sufficient to explain the line spectrum. There is another subsidiary quantum number called **azimuthal quantum number** and is used to represent the sub–shells. The values of azimuthal quantum number (l) are

$l = 0, 1, 2, 3, \ldots\ldots\ldots\ldots (n-1)$.

Its value depends upon n. These values represent different sub–shells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffuse and fundamental. These are the spectral terms used to describe the series of lines observed in the atomic spectrum. The values of azimuthal quantum number always start from zero.

A sub–shell may have different shape depending upon the value of 'l'. It may be spherical, dumb–bell, or some other complicated shape. The value of 'l' is related to the shape of the sub–shell as follows:

$l = 0$	s–sub–shell	(Spherical)
$l = 1$	p–sub–shell	(Dumb–bell)
$l = 2$	d–sub–shell	(Sausage)
$l = 3$	f-sub-shell	(Complicated)

The relationship between principal and azimuthal quantum numbers is given in the Table.

TABLE

Shell	n	l	Sub–shell	Number of electron 2 ($2l + 1$)
K	1	0	1s	2
L	2	0	2s	2
		1	2p	6
M	3	0	3s	2
		1	3p	6
		2	3d	10
N	4	0	4s	2
		1	3p	6
		2	4d	10
		3	4f	14

Magnetic Quantum Number (m):

It is also called **orbital quantum number**. In the defects of Bohr's model, it has been mentioned that **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.

Its values are

$m = 0 \pm 1, \pm 2, \pm 3, \ldots\ldots\ldots$

The value of 'm' depends upon values of 'l'.

When	$l = 0$	s–sub–shell	$m = 0$
	$l = 1$	p–sub–shell	$m = 0, \pm 1$ (p–sub–shell has three degenerate orbital)
	$l = 2$	d–sub–shell	$m = 0, \pm 1, \pm 2$ (d–sub–shell has five degenerate orbits)
	$l = 3$	f–sub–shell	$m = 0, \pm 1, \pm 2, \pm 3$ (f–sub–shell has seven degenerate orbits)

This above description shows that for a given value of 'l' the total values of 'm' are $(2l + 1)$.

Actually the value of m gives us the information of **degeneracy of orbits** in space. It tells us the number of different ways in which a given s, p, d or f–sub–shell can be arranged along x, y and z–axes in the presence of a magnetic field. Thus different values of 'm' for a given value of 'l', represent the total number of different space orientations for a sub–shell.

In case of **'s' sub–shell l** $= 0$, so, $m = 0$. It implies that s–sub–shell 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. So s–sub–shell 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' sub–shell l** $= 1$ and $m = 0, \pm 1$. These values of 'm' imply that p–sub–shell of any energy level has three space orientations and can be arranged in space along x, y and z–axes. These three orbital are perpendicular to each other and named as p_x, p_y and p_z. They have egg shaped lobes which touch each other at the origin. They are disposed symmetrically along one of the three axes called **orbital axis**.

In the absence of the magnetic field all the three p–orbital have the same energy and are called **degenerate orbital**. Since they are three in number, so these orbital are said to be 3–fold degenerate or triply degenerate.

For **'d' sub–shell l** $= 2$ $m = 0, \pm 1, \pm 2$. It implies that it has five space orientations and are designated as d_{xy} $(m = -2)$, d_{yz} $(m = -1)$, d_{xz} $(m = +1)$ $d_{x^2-y^2}$ $(m = +2)$ and d_{z^2} $(m = 0)$.

All these five d–orbital are not identical in shape. In the absence of a magnetic field all five d–orbital have the same energy and they are said to be five fold degenerate orbital.

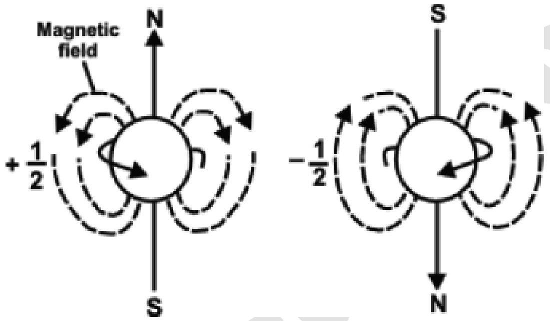
For **f–sub–shell l** $= 3$ and $m = 0, \pm 1, \pm 2, \pm 3$. They have complicated shapes.

The whole discussion shows magnetic quantum number determines the orientation of orbital, so it is also called **orbital orientation quantum number**.

Spin Quantum Number (s):

Alkali metals have one electron in their outermost shell. We can record their emission spectra when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high resolving power spectrometer, each line in the spectrum is found to consist of pair of lines, this is called **doublet line structure**. We should keep it in mind that doublet line structure is different from the fine spectrum of hydrogen (as we have discussed in azimuthal quantum number). It should be made clear that line of doublet line structure are widely separated from each other, while those of fine structure are closely spaced together.

In **1925, Goudsmit and Uhlenbech** suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti–clockwise direction. This is also called **self rotation**. This spinning electron is associated with a magnetic field hence a magnetic moment. Hence



Hence opposite magnetic fields are generated by the clockwise and anti–clockwise spins of electrons. This spin motion is responsible for doublet line structure in the spectrum.

The four quantum numbers of all the electron in the first four shells are summarized in Table. Notice that each electron has its own set of quantum numbers and this set is different for each electron.

TABLE

Principal Q–number 'n'	Azimuthal Q–number '*l*'	Magnetic Q–number 'm'	Spin Q–number 's'	Number of electrons accommodated
1 K	0 s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2 L	0 s 1 p	0 + 1, 0, – 1	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6 } 8
3 M	0 s 1 p 2 d	0 + 1, 0, – 1 + 2, + 1, 0, – 1, – 2	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6 10 } 18

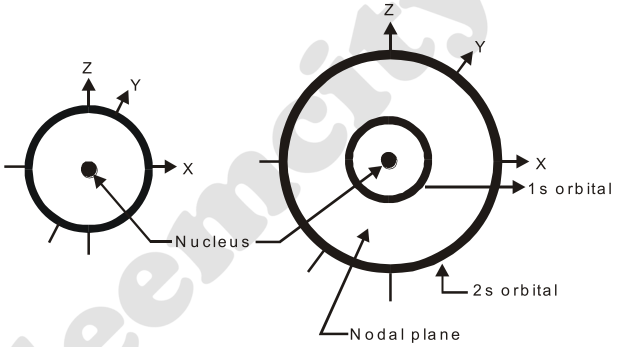
4 N	0 s 1 p 2 d 3 f	0 + 1, 0, – 1 + 2, + 1, 0, – 1, – 2 +3, +2 +1, 0, –1, –2, –3	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6 10 14 } 32

Shapes of Orbital:

The shapes of s, p and d orbital are discussed here. The shape of f orbital is more complicated.

Shape of s–orbital:

s–orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere. With the increase of value of principal quantum number (n), the size of s–orbital increases. 2s–orbital is larger in size than 1s–orbital. 2s–orbital is also further away form the nucleus. The probability for finding the electron is zero between two orbital. This place is called **nodal plane or nodal surface**.

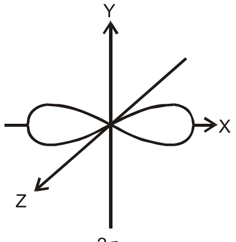


Spherical 1s orbital **1s orbital lying completely within the 2s orbital**

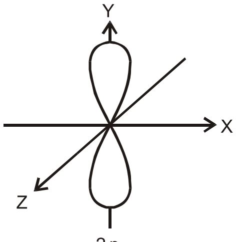
2s Orbital is bigger in size than 1s orbital, since the value of principal quantum number (n) for 2s orbital (n = 2) is higher than that for 1s orbital. (n = 1)

Shapes of p–orbital:

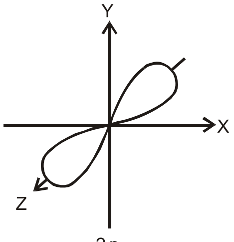
There are three values of magnetic quantum number for p–sub–shell. So p–sub–shell has three orientations in space i.e. along x, y and z–axes. All the three p–orbital namely p_x, p_y and p_z have dumb–bell shapes.



$2p_x$



$2p_y$

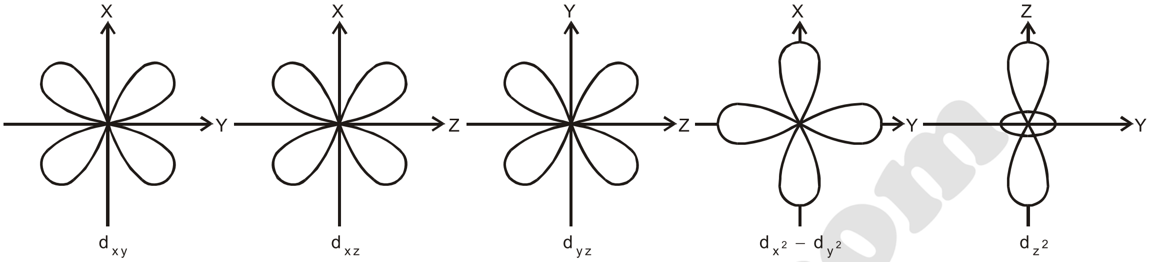


$2p_z$

So p–orbital have directional character which determines the geometry of molecules. All the p–orbital of all the energy levels have similar shapes but with the increase of principal quantum number of the shell their sizes are increased.

Shape of d–orbital:

The d–sub–shell we have five orbital in it. d–orbital has $l = 2$ and m is + 2, + 1, 0, – 1, – 2, each for one d –orbital, d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2} are shown in the Figure.



The orbital **dz^2 has dumbbell** shape along z–axis, with a collar in the x–y plane surrounding this dumbbell. It contains two lopes.

Other four "d" orbital have "Cloverleaf" shape each differing from one another only in the orientation of the orbital in space. Thus, the "Cloverleaf" orbital $d_{x^2-y^2}$ has its four lobes along the x and y axis.

Orbital d_{xy}, d_{yz} and d_{xz} have their four lobes directed between two set of axes designated in the orbital labeled. For example, orbital d_{xy} has its lobes lying between the x and y axes.

Electronic Distribution:

In order to understand the distribution of electrons in an atom we should know the following facts.

1. An orbital like s, p_x, p_y, p_z and p_{xy}, etc. can have at the most two electrons.
2. The maximum number of electrons that can be accommodated in a shell is given by $2n^2$ formula where n is principal quantum number and it can not have zero value.

   Moreover, following rules have been adopted to distribute the electrons in sub–shell or orbital.

1. Auf–bau principle
2. Paul's exclusion principle
3. Hund's rule

1. Auf–bau Principle:

"The electrons are added to energy sub–shells by the order of increasing energy level."

Filling of electrons of low energy sub–shells takes places first of all. The order of increasing energy level of a various sub–shell is given below:

$1s < 2s < 2p < 3s < 3p,$

$4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$

2. Paul's Exclusion Principle:

"The electrons in an orbital have opposite spin ($\uparrow\downarrow$)".

or "No two electrons in the same orbital have same set of four quantum numbers."

For example, take the case of helium which have two electron. These two electrons will be present in lowest energy level 1s. These orbital have opposite spin like,

$\boxed{\uparrow\downarrow}$ allowed

An orbital occupied by two electrons with parallel spin is not permitted

$\boxed{\uparrow\uparrow}$ or $\boxed{\downarrow\downarrow}$ not allowed.

The value of four quantum numbers for both electrons of He are given below:

	n	l	m	s
First electron	1	0	0	$+\frac{1}{2}$
Second electron	1	0	0	$-\frac{1}{2}$

Therefore the orbital containing two electrons always have opposite spin.

Hund's Rule:

"If degenerate orbital (same energy orbital) are available and more than one electrons are to be placed in them, they should be placed in separate orbital with same spin rather to put them in same orbital with opposite spin."

C = 6 $1s^{\downarrow\uparrow}$, $2s^{\downarrow\uparrow}$, $2px^{\uparrow}$, $2py^{\uparrow}$, 2pz

N = 7 $1s^{\downarrow\uparrow}$, $2s^{\downarrow\uparrow}$, $2px^{\uparrow}$, $2py^{\uparrow}$, $2pz^{\uparrow}$

O = 8 $1s^{\downarrow\uparrow}$, $2s^{\downarrow\uparrow}$, $2px^{\downarrow\uparrow}$, $2py^{\uparrow}$, $2pz^{\uparrow}$

Electronic Configuration of Elements:

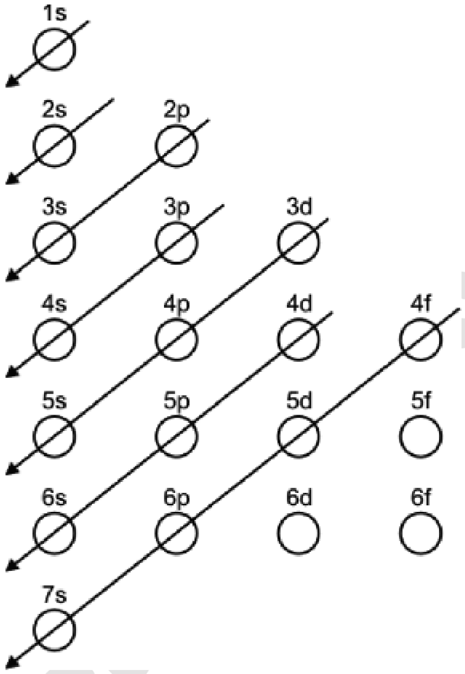
"The electron will first enter into that orbital which have lower value of $(n + l)$. If $n + l$ value is same for two orbital, electron will enter into that orbital which have lower value of n(Principal quantum number)."

Where n is principal quantum number and l is azimuthal quantum number. Value of l is 0, 1, 2, 3 for s, p, d and f respectively.

According to rule find $n + l$ values for two sub–shell, if $n + l$ value is different, then electron will go to the sub–shell with lower $n + l$ value.

Given diagram is helpful to known the value of $n + l$ according to their increasing energy level.

1s,	2s,	2p,3s,	3p,	4s
1 + 0	2 + 0	2 + 1 3 + 0	3 + 1	4 + 0
3d,	4p,	5s,	4d,	5p
3 + 2	4 + 1	5 + 0	4 + 2	5 + 1
6s,	4f,	5d,	6p,	7s
6 + 0	4 + 3	5 + 2	6 + 1	7 + 0



The value of $n + l$ is increasing gradually and energy is also increasing. The order of increasing energy level is given below.

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p
5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s
and so on.

However, this rule for electronic distribution is not applicable to the degenerate orbital.

Examples:

${}_{2}He^{4}$ = $1s^2$
${}_{7}N^{14}$ = $1s^2, 2s^2, 2p^3$
${}_{8}O^{16}$ = $1s^2, 2s^2, 2p^4$
${}_{11}Na^{23}$ = $1s^2, 2s^2, 2p^6, 3s^1$
${}_{17}Cl^{35}$ = $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
${}_{19}K^{39}$ = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}_{51}sb^{122}$ = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^3$

Electronic configuration first thirty elements is given below.

TABLE

Element	Symbol	Atomic Number	Electronic Configuration Notation
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2\ 2s^1$
Beryllium	Be	4	$1s^2\ 2s^2$
Boron	B	5	$1s^2\ 2s^2\ 2p_x^1\ 2p_y\ 2p_z$
Carbon	C	6	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z$
Nitrogen	N	7	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
Oxygen	O	8	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
Fluorine	F	9	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$
Neon	Ne	10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$
Sodium	Na	11	$[Ne]\ 3s^1$
Magnesium	Mg	12	$[Ne]\ 3s^2$
Aluminum	Al	13	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y\ 3p_z$
Silicon	Si	14	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z$
Phosphorus	P	15	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
Sulfur	S	16	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Chlorine	Cl	17	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
Argon	Ar	18	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$
Potassium	K	19	$[Ar]\ 4s^1$
Calcium	Ca	20	$[Ar]\ 4s^2$
Scandium	Sc	21	$[Ar]\ 4s^2\ 3d_{xy}^1\ 3d_{yz}\ 3d_{xz}\ 3d_{x^2\,.\,y^2}\ 3d_{z^2}$

Titanium	Ti	22	$[Ar]\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d_{xz}\ 3d_{x^2 . y^2}\ 3d_{z^2}$
Vanadium	V	23	$[Ar]\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d_{x^2 . y^2}\ 3d_{z^2}$
Chromium	Cr	24	$[Ar]\ 4s^1\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2 . y^2}\ 3d_{z^2}$
Manganese	Mn	25	$[Ar]\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2 . y^2}\ 3d^1_{z^2}$
Iron	Fe	26	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2 . y^2}\ 3d^1_{z^2}$
Cobalt	Co	27	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^1_{xz}\ 3d^1_{x^2 . y^2}\ 3d^1_{z^2}$
Nickel	Ni	28	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^1_{x^2 . y^2}\ 3d^1_{z^2}$
Copper	Cu	29	$[Ar]\ 4s^1\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2 . y^2}\ 3d^1_{z^2}$
Zinc	Zn	30	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2 . y^2}\ 3d^2_{z^2}$
Gallium	Ga	31	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x\ 4p_y\ 4p_z$
Germanium	Ge	32	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x\ 4p^1_y\ 4p_z$
Arsenic	As	33	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x\ 4p^1_y\ 4p^1_z$
Selenium	Se	34	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x\ 4p^1_y\ 4p^1_z$
Bromine	Br	35	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x\ 4p^2_y\ 4p^1_z$
Krypton	Kr	36	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x\ 4p^2_y\ 4p^2_z$

Note:

(1) [Ne] means electronic configuration of 10 electrons $1s^2, 2s^2, 2p^6$ [Ne].

(2) [Ar] means electronic configuration of 18 electrons $1s^2, 2s^2, 2p^6, 3p^6 =$ [Ar].

(3) Sub–shells (full filled or half filled) they are more stable. p–orbital is more stable when it has 6 electrons or 3 electrons. d–orbital is more stable when it has 10 electrons or 5 electrons. In case of Cr and Cu one electron jumps from s–orbital to d–orbital to give stability.

Similarly one electron jumps from nearest s-orbital to d-orbital in case of Mo (42), Ag (47), W (74) and Au (79) because half-filled and completely filled d-orbitals are more stable.

ACKNOWLEDGEMENT

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EXERCISE

Q.1 Select the most suitable answer for the given questions:

(i) The nature of the positive rays depend on:

(a) The nature of the electrode (b) The nature of the discharge tube

(c) The nature of the residual gas (d) All of the above

(ii) The velocity of the photon is:

(a) Independent of its wavelength (b) Depend on its wavelength

(c) Equal to square of its amplitude (d) Depends on its source

(iii) The wave number of the light emitted by a source is 2×10^6 m^{-1}. The wavelength of this light will be:

(a) 500 nm (b) 500 m

(c) 200 nm (d) 5×10^7 m

(iv) Rutherford's model of atom failed because:

(a) The atom did not have a nucleus and electrons

(b) It did not account for the attraction between protons and neutrons

(c) It did not account for the stability of the atom

(d) There is actually no space between the nucleus and the electrons

(v) Bohr model of atom in contradicted by:

(a) Planck's quantum theory (b) Dual nature of matter

(c) Heisenberg's uncertainty principle (d) All of the above

(vi) Splitting of spectral lines when atoms are subjected to strong electric field is called:

(a) Zeeman effect (b) Stark effect

(c) Photoelectric effect (d) Compton effect

(vii) In the ground state of an atom, the electron is present:

(a) In the nucleus (b) In the second shell

(c) Nearest to the nucleus (d) Farthest from the nucleus

(viii) Quantum number values for 2p orbitals are:

(a) n = 2, l = 1 (b) n = 1, l = 2

(c) n = 1, l = 0 (c) n = 2, l = 0

(ix) Orbitals having same energy are called:

(a) Hybrid oribtals (b) Valence orbitals

(c) Degenerate orbitals (d) d-orbitals

(x) When 6d orbital is complete, the entering electron goes into:

(a) 7f (b) 7s

(c) 7p (d) 7d

ANSWERS

Answers	Reasons
(i) (c)	Positive rays produced in the discharge tube are the cations of gas used in the tube. Different gases have different masses and e/m value. That is the reason why when gas in the tube is changed, nature of positive rays also changes. • Nature of cathode do not disturb the nature of positive as well as cathode rays. • Nature of the discharge tube may affect the colour of fluorescence produced.
(ii) (a)	Velocity of photon (light) has a constant value of $3 \times 10^8\ ms^{-1}$. It does not depend upon its wavelength or source of light.
(iii) (a)	$\bar{v} = 2 \times 10^6\ m^{-1}$, $\lambda = ?$ $\lambda = \frac{1}{\bar{v}}$ or $\lambda = \frac{1}{2 \times 10^6\ m^{-1}} = 0.5 \times 10^{-6}\ m$ $= 500 \times 10^{-3} \times 10^{-6}\ m$ $= 500 \times 10^{-9}\ m$. $1\ nm = 10^{-9}\ m$ $\boxed{\lambda = 500\ nm}$
(iv) (c)	Rutherford gave unstable picture of atom, because moving electron must be accelerated towards the nucleus and atom may collapse.
(v) (c)	Bohr calculated the both the momentum $\left(mvr = \frac{nh}{2\pi}\right)$ as well as position (radius of orbit) of electron at the same time. But according to Heisenberg, it is impossible to determine both the above values simultaneously and

		accurately. It was contradiction of Heisenberg with Bohr. • Plank's theory was the basis of Bohr model. • Dual nature of matter is extended form of Plank's theory.
(vi)	(b)	Splitting of spectral line in magnetic field is called Zeeman effect and that in electric field is called Stark effect.
(vii)	(c)	When electrons are present nearest to the neucleus, this state is called as ground state.
(viii)	(a)	For 2p subshell the values of n and l are 2 and 1 respectively.
(ix)	(c)	Orbitals with same energy are called degenerate orbitals. e.g., All the p-orbitals P_x, P_y, P_z are degenerate orbitals.
(x)	(c)	(n + l) For 6d n = 6 , l = 2 8 7f n = 7 , l = 3 10 7s n = 7 , l = 0 7 7p n = 7 , l = 1 8 7d n = 7 , l = 2 9 The order of these orbital for filling of electrons. 7s > 6d > 7p > 7d > 7f

Q.2 Fill in the blanks:

(i) β-particles are nothing but ———— moving with a very high speed.

(ii) The charge on one mole of electrons is ———— coulombs.

(iii) The mass of hydrogen atom is ———— grams.

(iv) The mass of one mole of electrons is ————.

(v) Energy is ———— when electron jumps from higher to a lower orbit.

(vi) The ionization energy of hydrogen atom can be calculated from ———— model of atom.

(vii) For d-subshell, the azimuthal quantum number has value of ————.

(viii) The number of electrons in a given subshell is given by formula ————.

(ix) The electronic configuration of H^- is ————.

ANSWERS

Answers	**Explanation**
(i) Electrons	Radioactive substances emit three types of radiations, (i) α-rays are the fast moving Helium nuclei called α-particles, (ii) β-rays are the fast moving electrons called β-particles, and (ii) γ-rays are the electromagnetic radiations.
(ii) 96500 coulombs = 1 Faraday	Charge on one electron = 1.602×10^{-19} coulombs Charge on one mole (6.02×10^{23} electrons) of = $1.602 \times 10^{-19} \times 6.02 \times 10^{23}$ = 9.65×10^{4} = 96500 coulombs (app.)
(iii) 1.66×10^{-24}	In atomic mass units, the mass of one hydrogen atom is 1 a.m.u = 1.66×10^{-27} kg or 1.66×10^{-24} g. 1g is the mass of mole of hydrogen atoms (6.02×10^{23} hydrogen atoms).
(iv) 54.8×10^{-8} kg	Mass of one electron = 9.1095×10^{-31} kg Mass of one mole of electrons (6.02×10^{23} electrons) = $9.1095 \times 10^{-31} \times 6.02 \times 10^{23}$ kg = $\boxed{54.8 \times 10^{-8}\text{ kg}}$ or $\boxed{54.8 \times 10^{-6}\text{ g}}$ = 55×10^{-2} mg = $\boxed{0.55\text{ mg}}$
(v) Released	

(vi)	Bohr's	The energy of each orbit is calculated from Bohr's equation for energy of electron. Energy difference of infinite orbit (E_∞) and that of first orbit (E_1) is called ionization. And it is calculated from Bohr's equation.
(vii)	2	For d-subshell l = 2.
(viii)	2(2l + 1)	The no. of electrons in a subshell is given by formula 2(2l + 1) as follows: For s → l = 0 2(2(0) + 1) = 2(0 + 1) = 2(1) = 2e^-s For p → l = 1 2(2(1) + 1) = 2(2 + 1) = 2(3) = 6e^-s For d → l = 2 2(2(2) + 1) = 2(4 + 1) = 2(5) = 10e^-s For f → l = 3 2(2(3) + 1) = 2(6 + 1) = 2(7) = 14e^-s
(ix)	$1s^2$	The atomic no. of hydrogen is 1 and its electronic configuration is $1s^2$. When it is H^-, it has one extra electron and its electronic configuration will be $1s^2$.

Q.3 Indicate True or False as the case may be:

(i) A neutron is slightly lighter particle than a proton.

(ii) A photon is the massless bundle of energy but has momentum.

(iii) The unit of Rydberg constant is the reciprocal of unit of length.

(iv) The actual isotopic mass is a whole number.

(v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.

(vi) The nodal plane in an orbital is the plane of zero electron density.

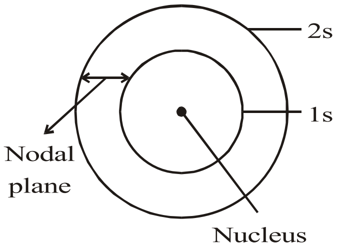
(vii) The number of orbitals present in a sublevel is given by the formula (2l + 1).

(viii) The magnetic quantum number was introduced to explain Zeeman and Stark effects.

(ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

ANSWERS

Answers		Correct Statement
(i)	False	A neutron is slightly heavier particle than proton (free neutrons decays into electrons, proton and neutrino decays into electrons, proton and neutrino it

		means that it is heavier than proton).
(ii)	True	
(iii)	True	In Bohr's equation for wave no. $\bar{v} = \frac{Z^2me^4}{8\in_o^2h^3c}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] m^{-1}$ The values $\frac{Z^2me^4}{8\in_o^2h^3c}$ = Rydberg constant (R) and its units will be the same as that for wave no. (m^{-1}) because n_1 and n_2 in the equation are the integers having no. units. Find m^{-1} is the reciprocal of the unit of length (m). $R = \frac{Z^2me^4}{8\in_o^2h^oC} m^{-1}$
(iv)	True	
(v)	False	It is applicable to microscopic bodies.
(vi)	True	The plane between two orbitals where the probability of finding the electrons is zero is called nodal plane. This is the plane with zero electron density. 
(vii)	True	The no. of orbitals in a sublevel is calculated by using (2l + 1) as follows: For s → 1 = 0 2(0) + 1= 1-orbitals For p → 1 = 1 2(1) + 1= 3-orbitals For d → 1 = 2 2(2) + 1= 5-orbitals For f → 1 = 3 2(3) + 1= 7-orbitals
(viii)	True	
(ix)	False	Spin quantum no. tells us the direction of spin of electron around its own axis (not around neucleus).

Q.4 Keeping in mind the discharge tube experiment, answer the following questions.

(a) Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays?

(b) Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why?

(c) Why e/m value of the cathode rays is just equal to that of electrons?

(d) How the bending of cathode rays in the electric and magnetic fields shows that they are negatively charged?

(e) Why the positive rays are also called canal rays?

(f) The e/m value of positive rays for different gases are different but those for cathode rays, the e/m values are the same. Justify it.

(g) The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. Justify it.

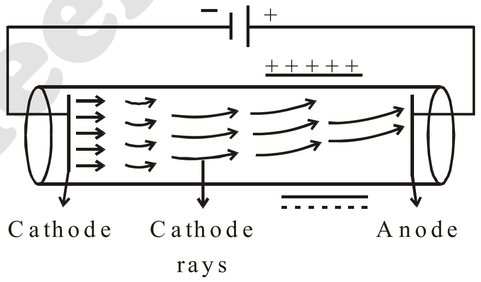
Ans.

(a) At high pressure, there is over crowding of gas molecules in the discharge tube. Under this condition, cathode rays fail to pass through due to hinderance. When pressure is reduced the molecules are less crowded and there is less hinderance for the free movement of cathode rays.

(b) Cathode rays are produced from cathode at high voltage and low pressure. Cathode rays are actually fast moving electrons. While passing through the gas cathode rays knock out electrons from atoms / molecules. These electrons move along with cathode rays. Cathode rays are electrons ejected from cathode or gas and are of identical nature, since electron is the fundamental particle of matter. Hence, its nature remains the same which ever gas is used.

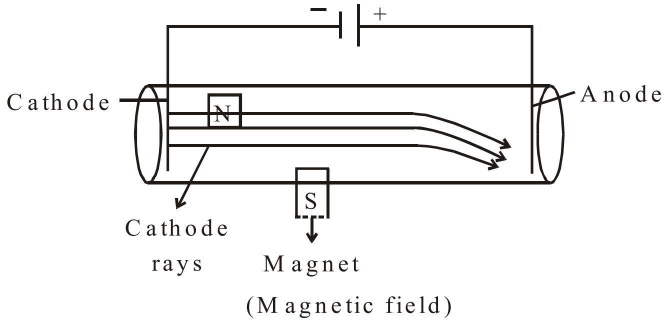
(c) Since, cathode rays are actually fast moving electrons and the e/m value is also just equal to that of electrons. Its value is 1.7588×10^{11} c/kg.

(d) When cathode rays are passed through electric field, they bend towards the positive plate showing that they are negatively charged.

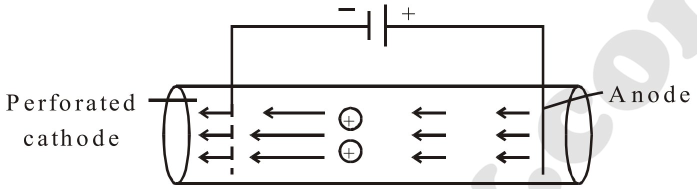


(Electric field)

When cathode rays are passed through magnetic field they bend perpendicular to the joining line of two poles showing that they are negatively charged because positive particles bend in opposite direction.



(e) The perforations (holes) in the cathode are called as canals. Since cathode rays pass through these perforations i.e., canals so they are called as canal rays.



(f) The positive rays are cations of gas used in the discharge tube. Since, masses of different gases are different (H_2 = 2g and O_2 = 32g). Hence, their e/m value is different. Lightest positive particle and highest e/m value is obtained for hydrogen.

Cathode rays are electrons which are ejected from (i) cathode as rays and from (ii) gas atoms or molecules when cathode rays are passed through them. Electron is the fundamental particle of matter. Hence e/m value for cathode rays remain same for different electrode and different gases.

(g) When hydrogen gas is used in the discharge tube, the positive ion produced is H^+ ion and it contain only one proton. (H_1^1 has one proton in the nucleus and one electron revolving around it. When this electron is knocked out by the cathode rays, only proton is left is H^+ ion). This H^+ ion is called proton whose mass is 1836 times greater than electron (cathode rays), hence, e/m value will 1836 times lesser.

Q.5 (a) Explain Millikan's oil drop experiment to determine the charge of an electron.

(b) What is J.J. Thomson's experiment for determining e/m value of electron?

(c) Evaluate mass of electron from the above two experiments.

Ans. For descriptive question, consult text book.

Q.6 (a) Discuss Chadwick's experiment for the discovery of neutrons. Compare the properties of electron, proton and neutron.

(b) Rutherford's atomic model is based on the scattering of α-particles from a thin gold foil. Discuss it and explain the conclusions.

Ans. For descriptive question, consult text book.

Q.7 (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

(b) Derive the equation for the radius of nth orbit of hydrogen atom using Bohr's model.

(c) How does the above equation tell you that:

(i) Radius is directly proportional to the square of the number of orbit.

(ii) Radius is inversely proportional to the number of protons in the nucleus.

(d) How do you come to know that the velocities of electrons in higher orbits are less than those in lower orbits of hydrogen atom?

(e) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits.

Ans.

(a) For postulates see text book. First postulate of Bohr's theory tells us orbits are stationary and energy is quantized.

(b) For derivation of equation see text book.

(c) (i) Bohr's equation for radius:

$$r = 0.529\left(\frac{n^2}{Z}\right) A^o$$

For one element Z = Constant

$$r = \frac{0.529}{Z}(n^2)$$

$$r = \text{Constant}\ (n^2)$$

$$\boxed{r \propto n^2}$$

This shows that radius is directly proportional to square of no. of shell.

For example, radius of 2nd orbit of hydrogen is four times of first orbit. It is clear from calculations.

$$r = 0.529\left(\frac{n^2}{Z}\right)$$

$$\text{For first orbit } r_1 = 0.529\left(\frac{(1)^2}{1}\right) = \boxed{0.529\ A^\circ}$$

$$\text{For second orbit } r_2 = 0.529\left(\frac{(2)^2}{1}\right) = 0.529 \times 4 = \boxed{2.11\ A^\circ}$$

(ii) Bohr's equation for radius:

$$r = 0.529\left(\frac{n^2}{Z}\right) A^\circ$$

For any fixed orbits of different element having different proton no. n^2 is constant. And

$$r = 0.529 \times n^2 \left(\frac{1}{Z}\right)$$

$$r = \text{Constant} \left(\frac{1}{Z}\right)$$

$$\boxed{r \propto \frac{1}{Z}}$$

This shows that radius is inversely proportional to atomic number.

For example, the radius of first orbit of H-atom is half of the radius of first orbit of He-atom. It is clear from calculation.

$$r = 0.529 \left(\frac{n^2}{Z}\right) \text{A°}$$

For first orbit of H-atom⇒ $r = 0.529 \left(\frac{(1)^2}{1}\right) = \boxed{0.529 \text{ A°}}$

For first orbit of He-atom ⇒ $r = 0.529 \left(\frac{(1)^2}{2}\right) = \frac{0.529}{2} = \boxed{0.2649 \text{ A°}}$

(d) According to Bohr's theory, in a fixed orbit, the centrifugal force on electron is balanced by electrostatic force of nucleus on electron and is shown as:

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_o r^2}$$

$$r = \frac{Ze^2}{4\pi\epsilon_o mv^2}$$

For any element, $\frac{Ze^2}{4\pi\epsilon_o m}$ is constant.

Hence, $r = \text{Constant} \times \frac{1}{v^2}$

$$\boxed{r \propto \frac{1}{v^2}}$$

It is clear from above relation that radius and square of velocity is inversely proportional to each other. Larger the radius, lesser will be the velocity.

(e) For hydrogen atom we can calculate radius of different orbits and their difference is as follows:

$$r = 0.529\left(\frac{n^2}{Z}\right)A^\circ$$

For 'H' Z = 1 and

$$r = 0.529 \times n^2 A^\circ$$

$$r_1 = 0.529\ A^\circ$$

$$r_2 = 0.529 \times 4 = 2.11\ A^\circ$$

$$r_3 = 0.529 \times 9 = 4.76\ A^\circ$$

$$r_4 = 0.529 \times 16 = 8.46\ A^\circ$$

And the differences are:

$$r_2 - r_1 = 2.11 - 0.529 = 1.58\ A^\circ$$

$$r_3 - r_2 = 4.76 - 2.11 = 2.65\ A^\circ$$

$$r_4 - r_3 = 8.46 - 4.76 = 3.7\ A^\circ$$

These values shows that gaps between adjacent orbits increases from lower to higher orbits.

Q.8 Derive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the following:

(a) The potential energy of the bounded electron is negative.

(b) Total energy of the bounded electron is also negative.

(c) Energy of an electron is inversely proportional to n^2, but energy of higher orbits are always greater than those of the lower orbits.

(d) The energy difference between adjacent levels goes on decreasing sharply.

Ans. For derivation of equation see text book. Final equation for calculating energy of electron in nth orbit is:

$$E_n = -\frac{me^4}{8\in_o^2 h^2}\left(\frac{1}{n^2}\right)$$

(a) The potential energy of electron at infinity point is zero. When it comes closer to the nucleus, nucleus attracts it and energy is released. The potential energy of electron nearest to nucleus will be least since it has released energy due to increasing attraction. This value closer to the nucleus is lower than zero at point infinity. Any value lesser than zero is negative. That's the reason why potential energy of bond electron is negative.

$$P.E = -\frac{Ze^2}{4\pi\in_o r}$$

(b) Since, total energy is the sum of kinetic energy and potential energy. Hence, its value will also be negative because one of the adding value is a negative value.

$$E_T = K.E + (-P.E) = -ve$$

$$E_T = -\frac{me_4}{8\in_o^2h^2}\left(\frac{1}{n^2}\right)$$

(c) Formula for energy of revolving electron in any orbit is:

$$E_n = \frac{-1313.315}{n^2}\text{ KJ/mole}$$

This equation shows that value of energy is the negative inverse of ‘n’ i.e., greater “n” value in the above equation will give smaller negative value of energy. Decrease in negative value of energy shows the increasing trend of value of n. Hence, we can say that energy of electron increases with increasing value of “n”.

(d) Energy of the orbits can be calculated as:

$$E = \frac{-1313.315}{n^2}\text{ KJ/mole}$$

$$E_1 = \frac{-1313.315}{(1)^2} = -1313.315$$

KJ/mole

$$E_2 = \frac{-1313.315}{(2)^2} = -328.32$$

KJ/mole

$$E_3 = \frac{-1313.315}{(3)^2} = -145.92$$

KJ/mole

$$E_4 = \frac{-1313.315}{(4)^2} = -82.08\text{ KJ/mole}$$

Energy differences are given as:

$E_2 - E_1 = (-328.32) - (-1313.315) = 984.99$ KJ/mole

$E_3 - E_2 = (-145.92) - (-328.32) = 182.40$ KJ/mole

$E_4 - E_3 = (-82.08) - (-145.92) = 63.84$ KJ/mole

Above values of differences of energies between the successive orbits shows the decreasing trend.

Q.9 (a) Derive the following equations for hydrogen atom, which are related to:

- (i) Energy difference between two levels, n_1 and n_2.
- (ii) Frequency of photon emitted when an electron jumps from n to n_2.
- (iii) Wave number of the photon when the electron jumps from n_2 to n_1.

(b) Justify that Bohr’s equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Ans. Q.9 is a descriptive question, for answer see text book.

Q.10 (a) What is spectrum? Differentiate between continuous spectrum and line spectrum.

(b) Compare line emission and line absorption spectra.

(c) What is the origin of line spectrum?

Ans.

(a) Spectrum: "Dispersion of components of white light in order of their wavelengths after passing through prism is called spectrum". e.g., rainbow.

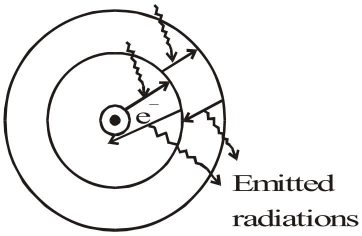
Difference between Continuous and Line Spectrum:

Continuous Spectrum	Line Spectrum
1. In this spectrum, colours are diffused into each other.	1. In this spectrum, colours are not diffused into each other.
2. There is no sharp boundary between the colours.	2. There are sharp boundaries between the colours.
3. It is the characteristic of matter in bulk.	3. It is the characteristic of pure element or compound.
4. It is polychromatic.	4. It is monochromatic.
5. Examples: Rainbow, spectrum of bulb light or sunlight.	5. Examples: Spectrum of Na, K, Ca, Ba.

(b)

Emission Spectrum	Absorption Spectrum
1. Spectrum of emitted radiation of a heated element.	1. Spectrum of a radiation after being absorbed by an element in ground state.
2. It is the characteristic of an element in excited state.	2. It is the characteristic of an element in ground state.
3. It appears as bright lines against dark background.	3. It appears as dark lines against bright background.
4. Examples: Spectrum of excited hydrogen.	4. Examples: Spectrum of O_2 in the ground state.

(c) **Origin of Line Spectrum:** When a substance is heated at high temperature or subjected to electric discharge, their valence electrons jump (excite) from lower to higher orbit absorbing particular amount of energy. When this substance is cooled, excited electrons come back releasing same amount of energy. This energy is released as light radiations of particular wavelength. As a result we obtain line spectrum (emission).



Q.11 (a) Hydrogen atom and He^+ are monoelectronic system, but the size of He^+ is much smaller than H^+. Why?

(b) Do you think that the size of Li^{+2} even smaller than He^+? Justify with calculations.

Ans.

(a) The reason for smaller size He^+ ion than H-atom is its greater nuclear charge (proton no). Lets calculate and compare the radius of first orbit for H and He^+.

Radius of first orbit for hydrogen $= r_H = 0.529 \times \frac{n^2}{Z}$

$$= 0.529 \times \frac{(1)^2}{1}$$

$$= \boxed{0.529\ A^\circ}$$

n = 1 and for H Z = 1.

Radius of first orbit for He^{+1} $= r_{He} = 0.529 \times \frac{n^2}{Z}$

$$= 0.529 \times \frac{(1)^2}{2}$$

$$= \boxed{0.2645\ A^\circ}$$

The comparison of radius of first orbits of two species shows that the size of He^+ is nearly half the size of hydrogen.

(b) Both the species are monoelectronic i.e., have one electron in first orbit each. Lets calculate radius of first orbit for Li^{+2} and He^{+1}.

Radius of first orbit for He^{+1}.

n = 1 and for He^{+1} Z = 2.

$$r = 0.529 \times \frac{n^2}{Z} = 0.529 \times \frac{(1)^2}{2}$$

$$= \frac{0.529}{2} = \boxed{0.2645\ A^\circ}$$

Radius of first orbit for He^{+1}.

n = 1 and for Li^{+2} Z = 3.

$$r = 0.529 \times \frac{n^2}{Z} = 0.529 \times \frac{(1)^2}{3}$$

$$= \frac{0.529}{3} = \boxed{0.176\ A^\circ}$$

The comparison of radius of first orbits of both the species shows that the size of Li^{+2} is smaller than He^{+1}.

Q.12 (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

(b) How does the Bohr's model justify the Moseley's equation?

Ans.

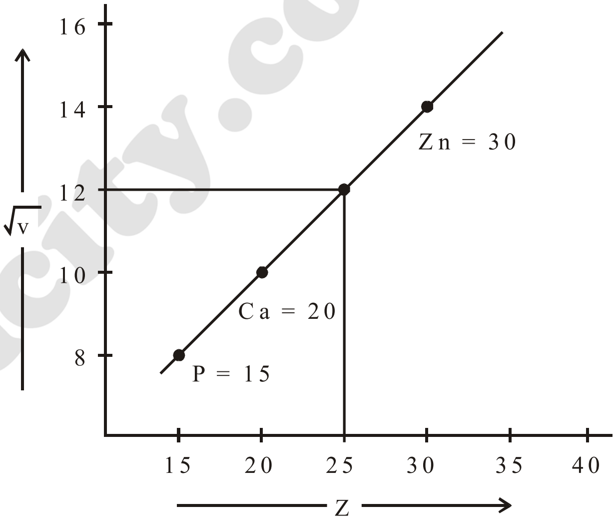
(a) X-rays are the electro-magnetic radiations with high frequency and wavelength shorter than visible light.

Origin of X-rays: When cathode rays are converged on a metal target (taken as anode), then highly penetrating radiations are produced called X-rays. Their frequency is greater and wavelength is shorter than visible light.

X-rays and Atomic Number (Z): The frequency of X-rays depends upon the proton no. (Z) of an element and is the characteristic of the element. It is given by Moseley's laws as

$$\sqrt{v} \propto Z$$

when graph is plotted between $\sqrt{v}$ on y-axis and Z on x-axis, a straight line is obtained for different elements. If $\sqrt{v} = 12$ for an unkown element is determined by this experiment and it cuts straight line, then we can determine its (Z) by observing. The point (Z = 25) on x-axis corresponding to $\sqrt{v}$.



(b) Bohr's equation for frequency is:

$$v = \frac{Z^2me^4}{8\varepsilon_0^2h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

If we consider it for similar transition ($n_2 = 2$ to $n_1 = 1$) of electron for different elements.

Then we have a relation.

$$v \propto Z^2$$

$$\sqrt{v} \propto Z$$

or $$\sqrt{v} \propto Z - b$$

$$\sqrt{v} = a(Z - b) \quad \text{Moseley's equation}$$

$\frac{me^4}{8\in_o^2h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$ is constant for similar transition of different elements. Since frequency is reduced by screening constant (b).

Q.13 Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainity principle?

Ans. For defects of Bohr's model, see text book:

(i) Bohr considered electron as a material particle of small mass moving round the nucleus in fixed circular orbits. But de-Broglie suggested that an electron has a dual nature i.e., wave as well as particle (material). Means orbits of electrons are the waves of electrons around the nucleus.

(ii) Bohr in his fourth postulate determined the angular momentum $\left(mvr=\frac{nh}{2\pi}\right)$ of electron and calculated radius of orbit (position of electron) at the same time accurately. It is not possible according to Heisenburg. He proved that at a time you can determine either the position of electron or its momentum accurately.

Q.14 (a) Briefly discuss the wave mechanical model of atom. How has it given the idea of orbital? Compare orbit or orbital.

(b) What are quantum numbers? Discuss their significance.

(c) When Azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number. Give reasons.

Ans.

(a) **Wave Mechanical Model of Atom:** This model was presented by Schrodinger. According to this model, an atom is a positively charged nucleus surrounded by a standing or stationary electron wave. This model describes electron as three dimensional wave in the electric field of positively charged nucleus.

Idea of Orbital from this Model: According to Schrodinger, the position of an electron cannot be found exactly, the probability of finding the electron at a certain position at any time can be found. The solution of Schrodinger's wave equations gives the probability of finding an electron present in a small region of space. It is defined as:

"The volume of a space around the nucleus in which there is 95% chance of finding the electron is called atomic orbital.

Comparison of Orbit and Orbital:

Orbit	Orbital
1. According to Bohr, electron revolve around the nucleus in circular path called orbit. e.g., K, L, M, N etc.	1. According to Schrodinger, the volume of space in which there is 95% chance of finding the electron is called orbital. e.g., s, p, d, f.

2. The orbit can accommodate maximum of electrons given by formula $2n^2$.	2. An orbital can have maximum of two electrons.
3. Orbit is flat.	3. An orbital is three dimensional.

(b) **Quantum Numbers:** Sets of numerical values that give the acceptable solution to the Schrodinger wave equation for hydrogen atom. There are four quantum numbers. Principal, Azimuthal, Magnetic and Spin quantum number.

Significance of Quantum Numbers: The significance of four quantum numbers is as follows:

1. **Principal quantum number (n)** tells us the size and energy of a shell. Greater the value of ‘n’ greater will be the energy and size of shell. It also tells us no. of electrons in a shell by $2n^2$ formula.
2. **Azimuthal quantum number (*l*)** tells us the shape of orbital and energy of sub-shell. It also tells us maximum no. of electrons in a subshell by $2(2l + 1)$ formula. It explains the splitting of spectral line in spectrometer.
3. **Magnetic quantum number (m)** tells us the no. of orientations (orbitals) in subshell. An orbital can have maximum of two electrons. It explains the splitting of spectral line in magnetic field (Zeeman effect).
4. Spin quantum number (s) tells us spin of electron about its own axis and direction of magnetic field produced due to spin.

(c) The values of magnetic quantum number depends upon the value of Azimuthal quantum number. The values of ‘m’ $= -l \rightarrow 0 \rightarrow +l$. When $l = 3$ then $m = -3 \rightarrow 0 \rightarrow +3. = -3, -2, -1, 0, +1, +2, +3$.

Hence ‘m’ has seven values when l = 3. When l = 3, it means f-subshell has seven orbitals.

Q.15 (a) Discuss rules for the distribution of electrons in energy sub-levels and in orbitals.

(b) What is (n + l) rule? Arrange the orbitals according to this rule. Do you think that this rule is applicable to degeneratic orbitals?

(c) Distribute electrons in orbitals of La_{57}, Cu_{29}, Au_{79}, Cr_{24}, I_{53}, Rn_{86}.

Ans.

(a) The rules for the distribution of electrons in energy subshells and orbitals are as follows:

1. (n + l) rule
2. Auf-bau principle
3. Hund’s rule
4. Pauli’s exclusion principle

(b) For (n + l) rule and arrangement of orbitals according to this rule, see text book. No, (n + l) rule is not applicable to degenerate orbitals. For example 2px, 2py and 2pz. All are degenerate having same 'n' value (2) and as well as same (n + l) value (3). No priority for filling of electrons can be set on the basis of (n + l) rule.

For de-generate orbitals Hund's rule is applicable.

(c) The distribution of electrons in various orbitals of following atoms are as follows:

$La_{57} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^0, 5d^1$

$Cu_{29} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$Au_{79} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1, 4f^{14}, 5d^{10}$

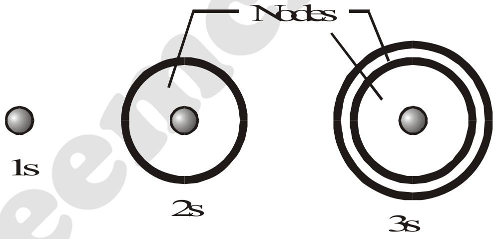
$Cr_{24} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$

$I_{53} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$

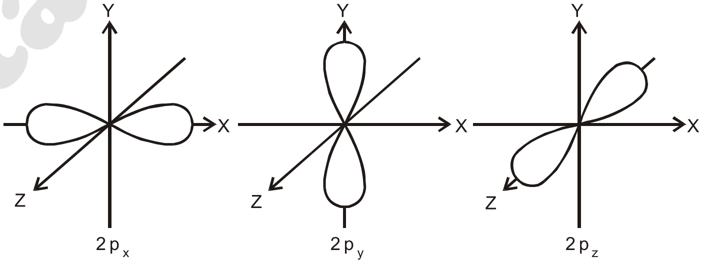
$Rn_{86} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6$

Q.16 Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

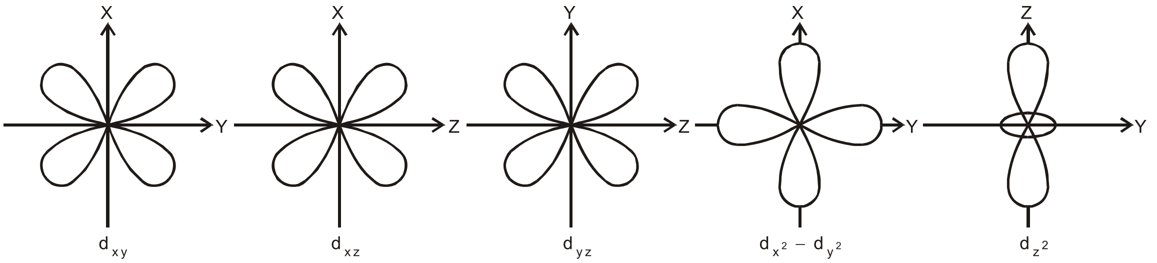
Ans.



Shapes of s-orbitals with increasing principal quantum number



Shapes of p-orbitals



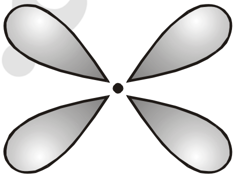
Shapes of d-orbitals

Azimuthal quantum no. tells us the shapes of orbitals. According to it.

s-orbital is spherical like.

p-orbital is dumb-bell like.

d-orbital is susage like.



Magnetic quantum number tells us the orientation of orbitals. e.g., p-orbitals have three orientations P_x, P_y and P_z as shown in the figures.

Q.17 A photon of light with energy 10^{-19} J is emitted by a source of light.

(a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and m^{-1}, respectively.

(b) Convert this energy of the photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm^{-1}.

Ans. Energy of photon = 10^{-19} J

Wavelength λ = ?

Frequency v = ?

Wave number $\bar{v}$ = ?

(i) First of all we calculate v:

Frequency (v):

$$E = hv$$

and $$v = \frac{E}{h}$$

$$h = 6.625 \times 10^{-34}\ \text{Js}$$

$$v = \frac{10^{-19}}{6.625 \times 10^{-34}}$$

$$v = 0.151 \times 10^{15}\ \text{Hz}$$

$$\boxed{v = 1.51 \times 10^{14}\ \text{Hz}}$$

(ii) Wavelength (λ):

$$v \propto \frac{1}{\lambda}$$

$$v = \frac{C}{\lambda}$$

$$\lambda = \frac{C}{v}$$

$$C = 3 \times 10^{8}\ \text{ms}^{-1}$$

$$v = 1.51 \times 10^{14}\ \text{Hz}$$

$$\lambda = \frac{C}{v}$$

$$= \frac{3 \times 10^{8}}{1.51 \times 10^{14}}$$

$$\boxed{\lambda = 1.98 \times 10^{-6}\ \text{m}}$$

(iii) Wave number ($\bar{v}$):

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

$$\bar{v} = \frac{1}{1.98 \times 10^{-6}\ \text{m}}$$

$$= 0.50 \times 10^{6}\ \text{m}^{-1}$$

$$\boxed{\bar{v} = 5 \times 10^{5}\ \text{m}^{-1}}$$

(b) For converting the energy of photon from joules into ergs we use:

$$1\ \text{J} = 10^{7}\ \text{erg}$$

$$E = 10^{-19} \times 10^{7}\ \text{erg} = 10^{-12}\ \text{ergs}$$

$$h = 6.625 \times 10^{-27}\ \text{ergs}$$

(i) Frequency (v):

$$v = \frac{E}{h}$$

$$= \frac{10^{-12}}{6.625 \times 10^{-27}}$$

$$= 0.151 \times 10^{15}\ \text{Hz}$$

$$\boxed{v = 1.51 \times 10^{14}\ \text{Hz}}$$

(ii) Wavelength (λ):

$$\lambda = \frac{C}{v}$$

$$C = 3 \times 10^{10}\ \text{cms}^{-1}$$

$$\lambda = \frac{3 \times 10^{10}}{1.51 \times 10^{+14}}$$

$$\boxed{\lambda = 1.98 \times 10^{-4}\ \text{cm}}$$

(iii) Wave Number ($\bar{v}$):

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

$$\bar{v} = \frac{1}{1.98 \times 10^{-4}}$$

$$\boxed{\bar{v} = 5 \times 10^{3}\ \text{cm}^{-1}}$$

Q.18 The formula for calculating the energy of an electron in hydrogen atom given by Bohr's model

$$E_n = \frac{-me^4}{8\epsilon_o^2 h^2 n^2}$$

Calculate the energy of the electron in first orbit of hydrogen atom.

Ans. To calculate the energy of electron in first orbit of H-atom, put the values of various parameters as follows:

$$m = 9.108 \times 10^{-31}\ \text{kg}$$

$$e = 1.602 \times 10^{-19}\ C$$

$$h = 6.625 \times 10^{-34}\ Js$$

$$\in_o = 8.854 \times 10^{-12}\ C^2J^{-1}m^{-1}$$

Formula:

$$E_n = \frac{-me^4}{8\in_o^2 n^2h^2}$$

Putting the values:

$$E_1 = \frac{9.108 \times 10^{-31} \times (1.602 \times 10^{-19})^4}{8 \times (8.854 \times 10^{-12})^2\ (1)^2\ (6.625 \times 10^{-34})^2}$$

$$\boxed{E_1 = -2.18 \times 10^{-18}\ J}$$

Q.19 Bohr's equation for the radius of nth orbit of electron in hydrogen atom is:

$$r_n = \frac{\in_o h^2n^2}{\pi e^2m}$$

(a) When the electron moves from n = 1 to n = 2, how much does the radius of the orbit increases?

(b) What is the distance travelled by the electron when it goes from n = 2 to n = 3 and n = 9 to n = 10?

While doing calculations take care of units of energy parameters.

$[J = kg\ m^2s^{-2}, C = kg^{1/2}\ m^{3/2}\ s^{-1}]$

$[\in_o = 8.85 \times 10^{-12}\ c^2J^{-1}m^{-1}, h = 6.624 \times 10^{-34}\ Js, \pi = 3.14,$

$m = 9.108 \times 10^{-31}\ kg, e = 1.602 \times 10^{-19}]$

Ans.

(a)

$$r_n = \frac{\in_o h^2}{\pi e^2m}(n^2)$$

Since $\frac{\in_o h^2}{\pi e^2m} = 0.529\ A°$

So,

$$r_n = 0.529\ A°\ (n^2)$$

$$r_1 = 0.529\ A°$$

$$r_2 = 0.529 \times 4$$

$$= 2.116\ A^\circ$$

So, the increase of radius $= (2.116 - 0.529)\ A^\circ = \boxed{1.587\ A^\circ}$

(b) $r_2 = 0.529\ A^\circ\ (2)^2 = 0.529 \times 4 = 2.116\ A^\circ$

$r_3 = 0.529\ A^\circ\ (3)^2 = 0.529 \times 9 = 4.761\ A^\circ$

$$\boxed{r_3 - r_2 = 2.645\ A^\circ}$$

$r_9 = 0.529\ A^\circ\ (9)^2 = 0.529 \times 81 = 42.85\ A^\circ$

$r_{10} = 0.529\ A^\circ\ (10)^2 = 0.529 \times 100 = 52.9\ A^\circ$

$$\boxed{r_{10} - r_1 = 10.05\ A^\circ}$$

Q.20 Answer the following questions, by performing the calculations:

(a) Calculate the energy of first five orbits of hydrogen atom and determine the energy differences between them.

(b) Justify that energy difference between second and third orbits is approximately five times smaller than that between first and second orbits.

(c) Calculate the energy of electron in He^+ in first five orbits and justify that the energy differences are different from those of hydrogen atom.

(d) Do you think that groups of the spectral lines of He^+ are at different places than those for hydrogen atom? Give reasons.

Ans.

(a) The formula of energy of an electron of H-atom is:

$$E_n = -2.18 \times 10^{-18} \left(\frac{1}{n^2}\right) J$$

Where 'n' is the no. of orbit, putting values of n, as n = 1

$$E_1 = -2.18 \times 10^{-18}\ J$$

$n = 2 \quad E_2 = -2.18 \times \frac{10^{-18}}{4} = -0.545 \times 10^{-18}\ J$

$n = 3 \quad E_3 = -2.18 \times \frac{10^{-18}}{9} = -0.242 \times 10^{-18}\ J$

$n = 4 \qquad E_4 = -2.18 \times \frac{10^{-18}}{16} = -0.14 \times 10^{-18}$ J

$n = 5 \qquad E_5 = -2.18 \times \frac{10^{-18}}{25} = -0.08 \times 10^{-18}$ J

(b) $E_2 - E_1 = \boxed{1.63 \times 10^{-18}\ \text{J}}$

$E_3 - E_2 = \boxed{0.303 \times 10^{-18}\ \text{J}}$

Hence the energy difference between second and third orbit is approximately five times less than that of first and second.

$$E_2 - E_1 \simeq (E_3 - E_2)5$$

$$1.63\times10^{-18}\ \text{J} \simeq (0.303 \times 10^{-18}\ \text{J})5 \simeq 1.515 \times 10^{-18}\ \text{J}$$

In first shell electron is very tightly bound by the nucleus and greater amount of energy is required to move from first to second shell. Hence, $E_2 - E_1$ is very high.

When electron is in second shell, being away from the nucleus is less tightly bound and less amount of energy is required to move it from 2nd to 3rd shell. Hence $E_3 - E_2$ is low. As a result $E_2 - E_1$ is five times of $E_3 - E_2$ approximately.

(c) For $He^{\oplus}$ Z = 2.

$$E_n = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right) \text{J} = -2.18 \times 10^{-18}\left(\frac{4}{n^2}\right) \text{J}$$

Where ‘n’ is the no. of orbit. Putting the values of n, as

$n = 1, \qquad E_1 = -2.18 \times 10^{-18}\left(\frac{4}{(1)^2}\right) = -8.72 \times 10^{-18}$ J

$n = 2, \qquad E_2 = -2.18 \times 10^{-18}\left(\frac{4}{(2)^2}\right) = -2.18 \times 10^{-18}$ J

$n = 3, \qquad E_3 = -2.18 \times 10^{-18}\left(\frac{4}{9}\right) = -0.968 \times 10^{-18}$ J

$n = 4, \qquad E_4 = -2.18 \times 10^{-18}\left(\frac{4}{16}\right) = -0.54 \times 10^{-18}$ J

n = 5, $E_5 = -2.18 \times 10^{-18}\left(\frac{4}{25}\right) = -0.35 \times 10^{18}$ J

The energy differences are greater than those of H-atoms. So, photons of greater energies are involved in electron jumping. The energy differences in case of $He^{\oplus}$ ion is greater than those for H-atom due to its greater proton no. (stronger nuclear force).

(d) Since energy differences are different from those of H-atom, so the positions of spectral lines will be at different places.

However the energy of each spectral line for $He^{\oplus}$ ion will be greater than those for H-atom, if we consider similar transitions ($n_2 = 2$ to $n = 1$) or ($n_2 = 3$ to $n_1 = 2$).

Q.21 Calculate the value of principle quantum number if an electron in hydrogen atom revolves in an orbit of energy -0.242×10^{-18} J.

Ans. Energy of orbit $= -0.242 \times 10^{-18}$ J

Principal quantum no. n = ?

$$E_n = -2.18 \times 10^{-18}\,J\left(\frac{1}{n^2}\right)$$

$$E_n = -0.242 \times 10^{-18}\,J$$

So, $-0.242 \times 10^{-18}\,J = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right)$

$$n^2 = \frac{-2.18 \times 10^{-18}}{-0.242 \times 10^{-18}} = \frac{2.18}{0.242} = 9.00$$

Therefore $n = \sqrt{9}$

$n = 3$

Hence, the electron is in 3rd orbit of H-atom.

Q.22 Bohr's formula for the energy levels of hydrogen atom for any system say H, He^+, Li^{+2}, etc. is

$$E_n = \frac{-Z^2e^4m}{8\in_o^2 h^2n^2} \quad \text{or} \quad E_n = -K\left[\frac{Z^2}{n^2}\right]$$

For hydrogen: Z = 1 and for He^+, Z = 2.

(a) Draw an energy level diagram for hydrogen atom and He^+.

(b) Thinking that $K = 2.18 \times 10^{-18}$ J, calculate the energy needed to remove the electron from hydrogen atom and from He^+.

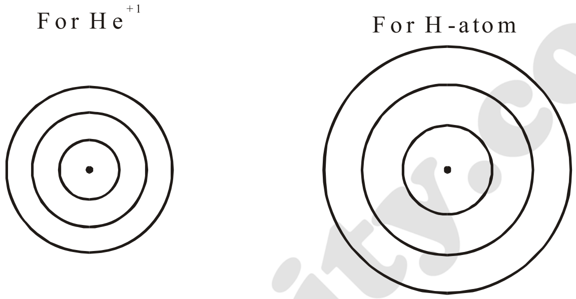
(c) How do you justify that the energies calculated in (b) are the ionization energies of H and He^+.

(d) Use Avogadro's number to convert ionization energy values in kJ mol^{-1} for H and He^+.

(e) The experimental values of ionization energy of H and He^+ are 1331 kJ mol^{-1} and 5250 kg mol^{-1} respectively. How do you compare your values with experimental values?

Ans.

(a) The energy level diagrams of H and $He^{\oplus}$ are similar in sense that, the difference go on decreasing from lower to highest levels, but gaps of energies in $He^{\oplus}$ are more than those of H. Energy level diagram for H-atom and $He^{\oplus}$ ion.



(b) For H-atom:

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

$$K = 2.18 \times 10^{-18}\ J$$

$$Z = 1(\text{H-atom})$$

Putting the values:

$$E_1 = -2.18 \times 10^{-18} \times \frac{(1)^2}{(1)^2}\ J$$

$$= -2.18 \times 10^{-18}\ J$$

$$E_\infty = -2.18 \times 10^{-18}\left(\frac{(1)^2}{\infty^2}\right)$$

$$= 0.00$$ (electron is removed from the atom)

$$E_\infty - E_1 = 0.00 - (-2.18 \times 10^{-18})$$

$$= 2.18 \times 10^{-18}\ J$$ (ionization energy of H-atom)

For $He^{\oplus}$ ion.

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

$$K = 2.18 \times 10^{-18}\ \text{J}$$

$$Z = 2(\text{for He}^{\oplus})$$

Putting the values:

$$E_1 = -2.18 \times 10^{-18}\left(\frac{4}{(1)^2}\right) = -8.72 \times 10^{-18}\ \text{J}$$

$$E_{\infty} = -2.18 \times 10^{-18}\left(\frac{4}{\infty}\right) = 0.00$$

$$E_{\infty} - E_1 = 0.00 - (-8.72 \times 10^{-18})$$

$$= 8.72 \times 10^{-18}\ \text{J (ionization energy for He}^{\oplus})$$

(c) Above mentioned energies are the energies required to remove electron from H-atom and He^+ and are called ionization energies.

(d) When ionization energies of respective species are multiplied with 6.02×10^{23} and divided by 1000 it gives us values in KJ mol^{-1}.

$$E_{I.P.}(\text{H}) = \frac{2.18 \times 10^{-18} \times 6.02 \times 10^{23}}{1000}$$

$$= 1313.3\ \text{KJ/mol}$$

$$E_{I.P.}(\text{He}^{\oplus}) = \frac{8.72 \times 10^{-18}\ \text{J} \times 6.02 \times 10^{23}}{1000}$$

$$= 5249.4\ \text{KJ/mol}$$

(e) The experimental values are very close to theoretical values. This shows that Bohr's model is precisely appreciable to mono-electronic system.

Q.23 Calculate the wave number of the photon when the electron jumps from:

(i) n = 5 to n = 2

(ii) n = 5 to n = 1

In which series of spectral lines these photons will appear.

Ans.

(i)

$$n_1 = 2$$

$$n_2 = 5$$

$$\bar{v} = ?$$

$$\bar{v} = 1.09678 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 1.09678 \times 10^7 \left(\frac{1}{4} - \frac{1}{25}\right)$$

$$= 0.23 \times 10^7\ m^{-1}$$

$$\bar{v} = 2.3 \times 10^6\ m^{-1}$$

The photon will appear in Balmar series, since transition is from $n_2 = 5$ to $n = 2$.

(ii)

$n_1 = 1$

$n_2 = 5$

$\bar{v} = ?$

$$\bar{v} = 1.09678 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 1.09678 \times 10^7 \left(\frac{1}{(1)^2} - \frac{1}{(5)^2}\right)$$

$$= 1.09678 \times 10^7 \left(1 - \frac{1}{25}\right)$$

$$= 1.09678 \times 10^7 \left(\frac{24}{25}\right)$$

$$\bar{v} = 1.05 \times 10^7\ m^{-1}$$

The photon will appear in Lyman series. Since transition is from $n_2 = 5$ to $n_1 = 1$.

Q.24 A photon of a wave number $102.70 \times 10^5\ m^{-1}$ is emitted when electron jumps higher to $n = 1$.

(a) Determine the number of that orbit from where the electron falls.

(b) Indicate the name of series to which this series belongs.

(c) If the electron will fall from higher orbit to $n = 2$, then calculate the wave number of the photon emitted. Why this energy difference is so small as compared to above calculations?

Ans.

(a) Determine the number of that orbit from where the electron falls.

$n_1 = 1$

$n_2 = ?$

$$\bar{v} = 1.09678 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 102.70 \times 10^5 = 1.02 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

$$= \frac{1.027 \times 10^7}{1.09678 \times 10^7} = 1 - \frac{1}{n_2^2}$$

$$0.936 = 1 - \frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = 1 - 0.936 = 0.064$$

$$n_2^2 = \frac{1}{0.064} = 15.6$$

Taking square root on both sides.

$$n_2 = \sqrt{15.6} = 3.9$$

$$n_2 = 3.9 = 4$$

$$\boxed{n_2 = 2}$$

So, the electron falls from n = 2 to n = 1.

(b) This photon belongs to Lyman Series, transition is from a higher shell $n_2 = 2$ to $n_1 = 1$.

(c) When electron falls from $n_2 = 4$ to $n_1 = 2$. The energy difference is very small.

$$\bar{v} = 1.09678 \times 10^7 \left(\frac{1}{4} - \frac{1}{16}\right) = 1.09678 \times 10^7 \left(\frac{4-1}{16}\right) \text{m}^{-1}$$

$$\bar{v} = 0.205 \times 10^7 \text{ m}^{-1}$$

$$\bar{v} = 2.05 \times 10^6 \text{ m}^{-1}$$

Wave number is directly proportional to energy difference. If value of wave number is so small, then energy difference will also be small for jump $n_2 = 4$ to $n_1 = 2$.

Note: When electron falls from higher shell to a shell closer to nucleus ($n_2 = 4$ to $n_1 = 1$) greater amount of energy is released because it experiences greater force closer to nucleus.

When electron falls from higher shell to a shell away from nucleus ($n_2 = 4$ to $n_1 = 2$) lesser amount of energy is released because it experiences weaker force away from nucleus. Hence, energy difference for jump $n_2 = 4$ to $n_1 = 1$ is greater than that for $n_2 = 4$ to $n_1 = 2$.

Q.25 (a) What is de-Broglie's wavelength of an electron travelling at half a speed of light?

m= 9.109×10^{-31} kg, C = $3 \times 10^{8}\ \text{ms}^{-1}$

(b) Convert the mass of electron into grams and velocity of light into cms^{-1}. Calculate the wavelength of an electron in cm.

(c) Convert the wavelength of electron from meters to:

(i) nm (ii) A° (iii) pm

Ans.

(a) When m = 9.109×10^{-31} kg,

C= $3 \times 10^{8}\ \text{ms}^{-1}$

Velocity of light C = $3 \times 10^{8}\ \text{ms}^{-1}$

Mass of electron m = 9.108×10^{-31} kg

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

Velocity of electron v = $1.5 \times 10^{8}\ \text{ms}^{-1}$

Plank's constant h = 6.625×10^{-34} Js

Putting the values:

$$\lambda = \frac{6.625 \times 10^{-34}\ \text{Js}}{9.1 \times 10^{-31}\ \text{kg} \times 1.5 \times 10^{8}\ \text{ms}^{-1}}$$

$$\lambda = \frac{6.625 \times 10^{-34}}{9.10 \times 10^{-31} \times 10^{8} \times 1.5}\,\frac{\text{Js}}{\text{kg ms}^{-1}}$$

$$\lambda = \frac{6.625}{9.108 \times 1.5} \times 10^{-11}\,\frac{\text{kg m}^2\text{s}^{-2}\ \text{s}^{+1}}{\text{kg ms}^{-1}}$$

$$\lambda = \frac{6.625}{9.108 \times 1.5} \times 10^{-11}\ \text{m}$$

$$\lambda = 0.48 \times 10^{-11}\ \text{m}$$

$$\lambda = 0.048 \times 10^{-10}\ \text{m}$$

$$\lambda = 0.048\ \text{A}^\circ\ \ (1\ \text{A}^\circ = 10^{-10}\ \text{m})$$

(b) Mass of electron m = $9.108 \times 10^{-31} \times 1000$

$= 9.108 \times 10^{-28}$ g

Velocity of light C $= 3 \times 10^{8}\ \text{ms}^{-1}$

$= 3 \times 10^{10}\ \text{cms}^{-1}$

Velocity of electron $= 1.5 \times 10^{10}\ \text{cms}^{-1}$

Wavelength λ = ?

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

$h = 6.625 \times 10^{-27}$ ergs (1 J = 10^{7} ergs)

$$\lambda = \frac{6.625 \times 10^{-27}\ \text{ergs}}{9.108 \times 10^{-28}\ \text{g} \times 1.5 \times 10^{10}\ \text{cms}^{-1}}$$

$$\lambda = \frac{6.625}{9.108 \times 1.5} \times 10^{-9}\ \text{cm}$$

$\lambda = 0.48 \times 10^{-9}$ cm

$\lambda = 0.048 \times 10^{-8}$ cm (1 A° = 10^{-8} cm)

(c) 1 m = 10^{2} cm

or 1 cm = 10^{-2} m

$\lambda = 0.048 \times 10^{-8}\ \text{cm} = 0.048 \times 10^{-8} \times 10^{-2}$ m

$\lambda = 0.048 \times 10^{-10}$ m

(i) $\lambda = 0.048 \times 10^{-10}$ m

$\lambda = 0.048$ A°

$$\begin{pmatrix} 1\ \text{m} = 10^{10}\ \text{A°} \\ 1\ \text{A°} = 10^{-10}\ \text{m} \end{pmatrix}$$

(ii) $\lambda = 0.048 \times 10^{-10}\ \text{m} = 0.048 \times 10^{-1} \times 10^{-9}$ m

$\lambda = 0.048 \times 10^{-1}$ nm (1 nm = 10^{-9} m)

(iii) $\lambda = 0.048 \times 10^{-10}$ m (1 nm = 10^{-10} cm)

or $\lambda = 4.8 \times 10^{-12}$ m

$$\lambda = 4.8 \text{ pm}$$

$$\begin{pmatrix} 1\text{ m} = 10^{12}\text{ pm} \\ 1\text{ pm} = 10^{-12}\text{ m} \end{pmatrix}$$

$$(1\text{ pm} = 10^{-10}\text{ cm})$$

DO YOU KNOW?

1. Cathode rays were named as electron by G.J. Stoney.
2. Television picture tube and monitor of Computer is also CRT (cathode ray tube).
3. Mass of electron is 9.1×10^{-31} kg.
4. Mass of proton is 1836 times more than that of electron.
5. Mass of proton is 1.6726×10^{-27} kg.
6. Neutron was discovered by James Chadwick in 1932. He was awarded Nobel Prize in 1935.
7. Slow neutrons are more effective than the fast neutrons.
8. Neutrons which travel with an energy of 1.2 Mev are called fast electrons.
9. J.J. Thomson in 1897 determined e/m ratio of electrons.
10. One kg of electrons has charge 1.7588×10^{11} coulombs.
11. R.A. Millikan in 1909 determined the charge on the electron.
12. Mass of Neutron is 1.675×10^{-27} kg.
13. Rutherford's atomic model is also called α-particles scattering experiment.
14. Bohr's model atom does not explain Zeeman's effect and Stark's effect.
15. X-rays were discovered by Roentgen in 1895.
16. Moseley employed 38 elements from Aluminium to gold as target in the X-ray tube.
17. In 1927, Davision and Germer did an experiment to verify the wave nature of moving electron.
18. Plank's quantum theory of radiations tells that light shows a dual nature (both as wave and material particle).
19. According to De-Broglie all material particles in motion have a dual character (wave and particle nature).
20. Smaller the wavelength of X-ray, greater will be the energy of the photon.
21. The volume in space in which there is 95% chance of finding an electron is called atomic orbital.
22. In the Schrodinger wave equation a set of integral numbers which describes the behaviour of electron (energy, size, shape, orientation, direction of spin) in an orbital is called quantum numbers.
23. The maximum probability of finding the electron is at a distance of 0.053 nm.
24. In 1925, Goldsmit and Uhlenbech suggested that an electron moving in an orbital around the nucleus also rotates or spins about its own axis in a clockwise or anti-clockwise direction. This is also called self-rotation.
25. Orbitals having same energy are called degenerate orbitals.

Chapter
6

CHEMICAL BONDING

CHEMICAL BOND

"The force which holds two or more atoms or ions together to form a variety of compounds is called **chemical bond**."

Cause of the Chemical Combination:

The chemical reactivity of elements depends upon the electronic configuration of the element. Noble gases are least reactive elements of the periodic Table. Only few compounds of noble gases are seen like XeF_2, KrF_2, $XeOF_2$ and XeO_3 etc. Noble gases (He, Ne, Ar, Kr, Xe) are the most stable element of the periodic Table.

Stability of Noble Gases:

Noble gases are stable due to the electronic configuration. They have two in He and 8–electrons in Ne, Ar, Kr, Xe and Rn. Element having two (duplet) or 8–electron (octet) are more stable than other element.

TABLE

Element	Period Number	Outer Electronic Configuration	Lewis Symbol
He	1	$1s^2$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{He}}:$
Ne	2	$2s^2, 2p^6$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Ne}}:$
Ar	3	$3s^2, 3p^6$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Ar}}:$
Kr	4	$4s^2, 4p^6$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Kr}}:$
Xe	5	$5s^2, 5p^6$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Xe}}:$

Cause of Reactivity of other Elements:

All other elements try to stabilize, or try to attain the noble gas configuration. They do this, by losing or gaining electrons, or by sharing electrons.

The tendency of an atom to attain a maximum of eight electrons in the valence shell is called “**octet rule**”.

The tendency of an atom to attain a maximum of two electrons in the valence shell is called “**duplet rule**”.

Some examples of change in electronic configuration during reactivity are given below in the Table.

TABLE

Electronic Configuration				
Element	**Tendency**	**Before electron loss or gain**	**After electron loss or gain**	**Nearest noble gas**
Li (3)	Electron loss	$1s^2, 2s^1$	$1s^2$	He (2)
Mg (12)	Electron loss	$1s^2, 2s^2, 2p^6, 3s^2$	$1s^2, 2s^2, 2p^6$	Ne (10)
F (9)	Electron gain	$1s^2, 2s^2, 2p^5$	$1s^2, 2s^2, 2p^6$	Ne (10)
S (16)	Electron gain	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$	Ar (18)

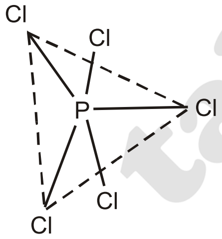
Reactivity of Elements with Conditions:

Tendency of an atom to share, lose or gain electrons, depends upon the condition. For example, in the chemical combination between sodium and hydrogen to form NaH, hydrogen atom gains an electron while in the formation of HF, the hydrogen atom mutually shares its electron with the fluorine atom. Hydrogen when reacts with Na it forms ionic bond but with F, it forms covalent bond.

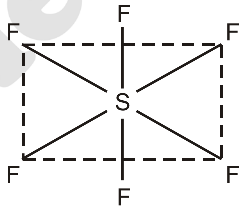
Deviation from Octet Rule:

There are many compounds in which atoms do not have eight electrons (octet) in the valence shell after the chemical combination. For example, BF_3, BCl_3, $AlCl_3$, SF_6 and PF_5 etc.

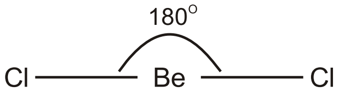
Some compounds have less electrons than octet. For example,



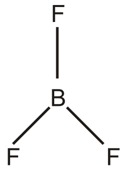
(Trigonal bipyramidal)



(Octahedral)



(Linear)



(Trigonal planar)

The molecules in which octet is not complete, are called **electron deficient molecules**, e.g. $BeCl_2$, BF_3, BCl_3 and $AlCl_3$. In some cases, the molecules have more electron than octet. PCl_5 has 10–electrons and SF_6 has 12–electrons in their valence shells.

Valence:

The combining capacity of an element with other elements is called **valence**. It is of two types.

(i) Electrovalence:

The number of electrons which an atom loses or gains during bond formation is called **electrovalence**.

For example electrovalence of Na is + 1 and Cl is – 1.

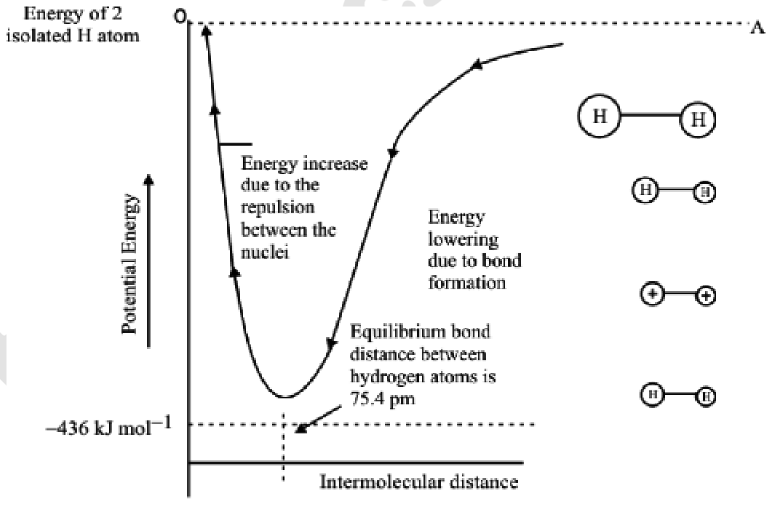
(ii) Covalence:

The number of electrons which an atom shares with other elements to form a covalent bond.

For example, covalence of oxygen, nitrogen and carbon in H_2O, NH_3 and CH_4 are 2, 3 and 4 respectively.

ENERGETIC OF BOND FORMATION

According to the modern theory of chemical bonding, atoms form bonds as it leads to a decrease in energy. For example, when **two hydrogen atoms** approach each other; forces of attraction and repulsion operate simultaneously. The attractive forces tend to bring the two atoms close to each other and the potential energy of the system is decreased. On the other hand, the repulsive forces tend to push the atoms apart and potential energy of the system is increased. It has been found that the magnitude of potential energy for attractive forces is more than for repulsive forces. Therefore, potential energy decreases as the two hydrogen atoms approach each other.



Potential energy curve for the formation of H_2 molecules.

When distance of 75.4 pm is reached, the attractive forces dominate the repulsive forces. This distance is called **equilibrium bond distance or bond length**. Here the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable molecule. When the atoms approach the distance of minimum energy, then the system of two hydrogen atom is stabilized maximum. The amount of energy evolved is 436 kJ mol^{-1} and it is called **bond formation energy**. Same amount of energy is required to break this bond.

When **two helium atoms** approach each other, they do not form any bond. In this case the force of repulsion dominates over the force of attraction and bond is not formed.

ATOMIC SIZE

The size of an atom is very important because many physical and chemical properties are related to it. If an atom is assumed to be spherical then the atomic size means "the average distance between the nucleus of the atom and its outermost shell." This distance is called **atomic radius**.

The size of an atom cannot be determined precisely due to the following reasons.

(i) There is no sharp boundary of an atom because 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 hence the size of an atom may change from one compound to another.

Due to these reasons, the sizes of atoms are expressed in terms of atomic radii, ionic radii and covalent radii, depending upon the type of compound used for its measurement.

Atomic radii can be determined with the help of x–rays analysis or by spectroscopy.

Atomic Radii:

"The one half distance between the nuclei of two similar bonded atoms is called **atomic radii**."

Table: First ionization energies, electron affinities and electronegativities values of elements.

Symbol	H
Atomic Number	1
First Ionization Energy (kJ mol^{-1})	1313
Electron Affinity (kJ mol^{-1})	-73
Electronegativity	2.1

I-A	II-A	III-B	IV-B	V-B	VI-B	VII-B	VIII-B			I-B	II-B	III-A	IV-A	V-A	VI-A	VII-A	VIII(o)
H 1 1313 -73 2.2																	He 2 2372 21 -
Li 3 520 -1.6 1.0	Be 4 900 240 1.6											B 5 801 -83 2.0	C 6 1086 -123 2.5	N 7 1402 - 3.0	O 8 1314 -141 3.5	F 9 1661 -322 4.0	Ne 10 2081 29 -
Na 11 496 -53 0.9	Mg 12 738 230 1.3											Al 13 578 -50 1.5	Si 14 787 -120 1.8	P 15 1012 -74 2.1	S 16 1000 -200 2.5	Cl 17 1251 -349 3.2	Ar 18 1521 35 -
K 19 419 -4.8 0.8	Ca 20 590 156 1.0	Sc 21 631 - 1.4	Ti 22 658 -38 1.5	V 23 650 -90 1.6	Cr 24 653 -64 1.7	Mn 25 717 - 1.5	Fe 26 759 -56 1.9	Co 27 758 -90 1.9	Ni 28 737 -123 1.8	Cu 29 746 -123 1.9	Zn 30 906 - 1.7	Ga 31 579 -36 1.8	Ge 32 762 -116 1.8	As 33 947 -77 2.0	Se 34 941 -195 2.4	Br 35 1140 -325 3.0	Kr 36 1351 39 -
Rb 37 403 -4.7 0.8	Sr 38 550 168 1.0	Y 39 616 - 1.2	Zr 40 660 - 1.4	Nb 41 664 - 1.6	Mo 42 685 -96 1.8	Tc 43 702 - 1.9	Ru 44 711 - 2.2	Rh 45 720 - 2.2	Pd 46 805 - 2.2	Ag 47 731 -126 1.9	Cd 48 868 - 1.7	In 49 558 -34 1.7	Sn 50 709 -121 1.8	Sb 51 834 -101 1.9	Te 52 869 -183 2.1	I 53 1008 -295 2.5	Xe 54 1170 41 -
Cs 55 376 -4.6 0.7	Ba 56 503 52 0.9	La 57 538 - 1.1	Hf 72 642 - 1.3	Ta 73 761 -80 1.5	W 74 770 -50 2.4	Re 75 760 -14 1.9	Os 76 840 - 2.2	Ir 77 880 - 2.2	Pt 78 870 -205 2.3	Au 79 890 -223 2.5	Hg 80 1007 - 2.0	Tl 81 589 -48 2.0	Pb 82 716 -101 1.8	Bi 83 703 -101 1.9	Po 84 812 -170 2.0	At 85 - -270 2.2	Rn 86 1038 41 -
Fr 87 - -4.4 0.7	Ra 88 509 - 0.9	Ac 89 490 - -	Unq104 - - -	Unp105 - - -	Unh106 - - -	Uns107 - - -	Uno108 - - -	Uno109 - - -									

Atomic Radii in Periods:

"Atomic radii decrease from left to right in a period."

The decreasing trend in a period is due to the increase in the nuclear charge. As the **nuclear charge increases**, the pull on the electron is increased and **size of an atom decreases**. The decrease in atomic radii is very prominent in second period but less in higher periods. The decrease in atomic radii of transition elements (from Sc – 21 to Zn – 30 and Y – 39 to Cd – 48) is very small due to intervening electrons. this regular decrease in atomic radii of transition elements is called **lanthanide contraction**.

Atomic Radii in Groups:

"Atomic radii increase from top to bottom is a group."

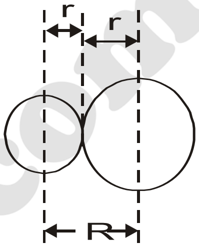
The increase in atomic radius in a group is due to **increase** in the number of shells and the screening effect of the intervening electrons. The screening effect is also called **shielding effect** and this is responsible for the decrease in force of attraction of the nucleus for the electrons present in the valence shell.

Ionic Radii:

"The measure of the size of the spherical region around the nucleus within which the electrons of an ion are most likely to be found is called **ionic radius**."

If we consider the ions a sphere of a definite size, we can obtain their radii from known distances in a crystal. Let us consider a positive and negative ion, which are held together by electrostatic force of attraction in a crystal lattice. The inter–ionic radii are shown in the Figure.

Where r^+ and r^- are the radii of two ions in contact with each other.



Interionic distance R and ionic radii (r^+ and r^-)

Ionic Radius of Cation:

The ionic radius of a cation is always smaller in size from its original atom. For example, radius of Na^+ is smaller than Na. The radius of Na^+ is 95 pm while atomic radius of Na is 186 pm. By losing electron the effective nuclear charge increases and shell shrinks to smaller size.

Decrease in the radius is larger for divalent (Mg^{2+}) and still larger for trivalent ion. By losing electrons the effective nuclear charge increases.

Ionic Radius of Anion:

The radius of anion is larger from its original atom. For example, size of Cl^- is greater than Cl. Size of Cl is 99 pm while size of Cl^- is 181 pm. The increase in the size of anion is due to the increase in the electron–electron repulsion because of the increase in the valence shell electrons. We can say that effective nuclear charge decreases by the increase of one electron, in the valence shell. This causes expansions of the shells. Variation of ionic radii in groups and periods have the same trend as for atomic radii.

Inter–Ionic Distance (R):

Let us consider, the positive and negative ions which are held together by electrostatic forces of attraction in a crystal lattice.

"The sum of cationic radius r^+ and anionic radius r^- in a crystal is called **inter–ionic distance**."

$$R = r^+ + r^-$$

r^+ is ionic radius of cation and r^- is anionic radius of anion.

Pauling was able to determine the distance between K^+ and Cl^- ions in potassium chloride crystal and found that it was equal to the sum of the radii of the two ions:

$$R = 133 \text{ pm} + 181 \text{ pm} = 314 \text{ pm}$$

Thus, 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:

$$r^+ = R - r^-$$

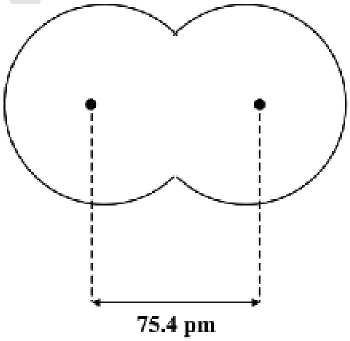
Similarly, the ionic radii of different cations were determined.

COVALENT RADIUS

"The covalent radius of an element is defined as half of the single bond length between two atoms covalently bonded in a molecule."

The covalent radius of hydrogen, for example, is 37.7 pm as it is half of the single bond (75.4 pm) between the two H atoms, in H–H molecule as shown in Figure.

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. The covalent radius of carbon can be calculated by subtracting the value of Cl from C–Cl.



Covalent radius of H atom, (75.4/2 = 37.7 pm)

Radius of C atom = 176.7 – 99.4 = 77.3 pm.

IONIZATION ENERGY

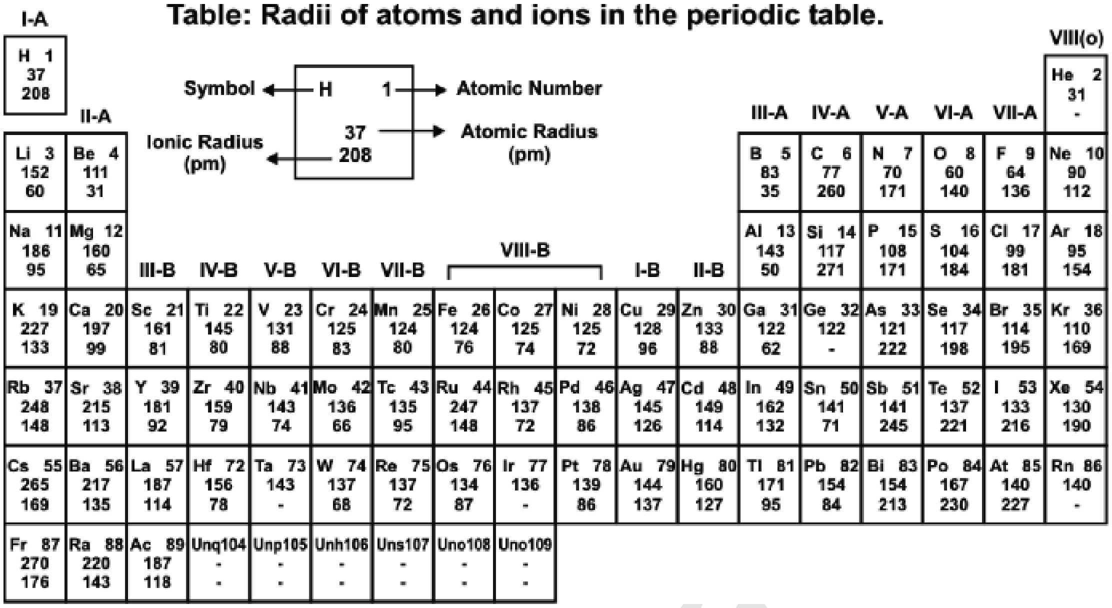
"The minimum amount of energy which is required to remove an electron from the valence shell of an atom in gaseous state is called **ionization energy**."

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \qquad \Delta H = 496 \text{ kJ mol}^{-1}$$

$$Mg_{(g)} \longrightarrow Mg^+_{(g)} + 1e^- \qquad \Delta H = 738 \text{ kJ mol}^{-1}$$

In the gaseous phase, the atoms and ions are isolated from all external influences. Thus, the ionization energy is the qualitative measurement of the stability of an isolated atom.

Table: Radii of atoms and ions in the periodic table.



I-A	II-A	III-B	IV-B	V-B	VI-B	VII-B	VIII-B			I-B	II-B	III-A	IV-A	V-A	VI-A	VII-A	VIII(o)
H 1 37 208																	He 2 31 -
Li 3 152 60	Be 4 111 31											B 5 83 35	C 6 77 260	N 7 70 171	O 8 60 140	F 9 64 136	Ne 10 90 112
Na 11 186 95	Mg 12 160 65											Al 13 143 50	Si 14 117 271	P 15 108 171	S 16 104 184	Cl 17 99 181	Ar 18 95 154
K 19 227 133	Ca 20 197 99	Sc 21 161 81	Ti 22 145 80	V 23 131 88	Cr 24 125 83	Mn 25 124 80	Fe 26 124 76	Co 27 125 74	Ni 28 125 72	Cu 29 128 96	Zn 30 133 88	Ga 31 122 62	Ge 32 122 -	As 33 121 222	Se 34 117 198	Br 35 114 195	Kr 36 110 169
Rb 37 248 148	Sr 38 215 113	Y 39 181 92	Zr 40 159 79	Nb 41 143 74	Mo 42 136 66	Tc 43 135 95	Ru 44 247 148	Rh 45 137 72	Pd 46 138 86	Ag 47 145 126	Cd 48 149 114	In 49 162 132	Sn 50 141 71	Sb 51 141 245	Te 52 137 221	I 53 133 216	Xe 54 130 190
Cs 55 265 169	Ba 56 217 135	La 57 187 114	Hf 72 156 78	Ta 73 143 -	W 74 137 68	Re 75 137 72	Os 76 134 87	Ir 77 136 -	Pt 78 139 86	Au 79 144 137	Hg 80 160 127	Tl 81 171 95	Pb 82 154 84	Bi 83 154 213	Po 84 167 230	At 85 140 227	Rn 86 140 -
Fr 87 270 176	Ra 88 220 143	Ac 89 187 118	Unq104 - -	Unp105 - -	Unh106 - -	Uns107 - -	Uno108 - -	Uno109 - -									

First Ionization Energy:

"The energy required to remove first electron from a neutral atom to form positive ion is called **first ionization energy** "e.g.

$$Na \xrightarrow{\hspace{2cm}} Na^{+} + 1e^{-} \qquad \Delta H = +496\ kJ/mole$$

$$Mg \xrightarrow{\hspace{2cm}} Mg^{+} + 1e^{-} \qquad \Delta H = +738\ kJ/mole$$

Second Ionization Energy:

"The energy required to remove second electron from positively charged ion to form di-positive ion is called **second ionization energy**."

For example, second (IE) of Mg is 1451 kJ/mole.

$$Mg^{+} \xrightarrow{\hspace{2cm}} Mg^{2+} + 1e^{-} \qquad \Delta H = +1451\ kJ/mole$$

Second I.P is always greater than first I.P.

Because when an electron is removed from an atom, the **nuclear charge increases**. The force of attraction between valence shell and nucleus increases. Third I.P is greater than the second I.P.

Third Ionization Energy:

"The energy required to remove third electron from di-positive ion is called **third ionization energy**."

Third ionization energy of Mg^{2+} is 7730 kJ per mole.

$$Mg^{2+} \xrightarrow{\hspace{2cm}} Mg^{3+} + 1e^{-} \qquad \Delta H = +7730\ kJ/mole$$

Due to increase in the nuclear charge, electrons are held more tightly and further removal of electrons become difficult. The gap between the first, second, third and higher ionization energies help to guess the valence of an element. If there is sufficient gap between first and second I.P, the valence of element will be one.

FACTORS AFFECTING THE IONIZATION ENERGY

Ionization energy depends upon following factors:

(i) Atomic radius
(ii) Nuclear charge or proton number
(iii) Shielding effect of electrons
(iv) Nature of orbital.

(i) Atomic Radius:

Ionization energy decreases with the increase of the atomic radii. For example, in alkali metals (group IA of periodic table) the atomic radius increases downward in a group and I.E decreases.

TABLE

Ionization Energy Values and Atomic Radii of Alkali Metals

Alkali Metal	Atomic Radii (pm)	Ionization Energy (kJ mol^{-1})
Li	152	520
Na	186	496
K	227	419
Rb	248	403
Cs	265	376

(ii) Nuclear Charge:

Greater is the nuclear charge, greater will be the ionization energy. Mono–positive ions have greater nuclear charge than its atoms, so second I.P is always greater than first ionization energy.

(iii) Shielding Effect:

Shielding effect depends upon the inner shell electrons. if the inner shell electrons are greater, shielding effect will be high and force of attraction between valence shell and nucleus will be low. In a group, number of shells increases from top to bottom and shielding effect also increases. The atoms with high shielding effect have low ionization energies.

Trend of Ionization Energy in the Periodic Table:

(i) In a Period:

In the periodic table, the ionization energy **increases** from left to right in a period with the increase in the proton number until a maximum value is reached at the end of the period. 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. The increase in the atomic number is associated with the **increase in nuclear charge** which 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.

For example, I.E of second period elements are given below. Values are in kJ/mole.

Li	Be	B	C	N	O	F	Ne
520	899	801	1086	1402	1314	1681	2081

The ionization energies of group III–A and VI–A show abnormal trend. This abnormal trend is due to electronic configuration of the elements.

(ii) In a Group:

In a groups the ionization energy **decreases** due to the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. 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. Moreover, the force of attraction also decreases due to shielding effect of the intervening electrons.

For example, first ionization values of alkali metals are given below.

	Li	Na	K	Rb	Cs
kJ/mol	520	496	419	403	376

Ionization Energy and Metallic Characters:

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.

ELECTRON AFFINITY

"The amount of energy evolved or absorbed when an electron is added to partially filled orbital of an isolated atom to form a negative ion is called **electron affinity**."

When a stable negative ion in formed, energy released is given a negative value. When an unstable ion is formed, the energy needed is given a positive value. Electron affinity is the measure of the attraction of the nucleus of an atom for extra electrons.

For example, the electron affinity of chlorine is

$$O_{(g)} + 1e^- \longrightarrow O^{-1} \quad (\Delta H = -141 \text{ kJ mol}^{-1})$$

$$Cl_{(1g)} + 1e^- \longrightarrow Cl^-_{(g)} \quad (\Delta H = -349 \text{ kJ/mole})$$

Second Electron Affinity:

If second electron is added to a uni-negative ion, the process will be endothermic because energy will be needed to overcome the repulsive forces between the electrons.

$$O^{-1} + e^- \longrightarrow O^{-2} \quad (\Delta H = +780 \text{ kJ mol}^{-1})$$

Factor Affecting the Electron Affinity:

Like ionization energy, electron affinity is also effected by the following factors.

1. The magnitude of the nuclear charge.
2. The distance of the outermost electron from the nucleus (atomic radius).
3. Shielding effect of the underlying shells of electrons.

Trend of Electron Affinity in Periodic Table:

The electron affinities, like ionization energies, are influenced by the factors such as atomic radius, the nuclear charge and the shielding effect of outer electrons. As the force of attraction between the valence electrons and the nucleus decreases with the increase in the atomic radius the electron affinities usually decrease. **In a period**, the atomic radius decreases due to increase in the nuclear charge. Thus, the electron affinities of elements **increase** from left to right in the Periodic Table. That is why the alkali metals have the lowest and the halogens have the highest electron affinities. **In groups**, on the other hand, the atomic radius increases with the increase in the proton number due to successive increase of electronic shell which also exert a shielding effect on the force of attraction between the nucleus and the valence electrons. Thus, the electron affinities usually **decrease** from top to bottom. There are, of course, **exceptions** to this generalization e.g. fluorine has electron affinity less than that of chlorine because it has a smaller atomic size than that of chlorine.

Electron affinity of group VII is very high. Electronic configuration of group VII is $ns^2 np^5$. They have one electron less than octet. They except one electron and form stable negative ions.

Elements of group II–A, VA and VIII show abnormally low values of electron affinity in every period of periodic table. It is due to electronic configuration pattern. Elements of these groups have relatively stable electronic configuration and less attraction for extra electrons.

ELECTRO–NEGATIVITY (E.N.)

"The measure of the ability of an atom in a molecule to attract the shared pair of electron toward itself is called its **electro–negativity**."

Luis Pauling calculated the electro–negativity value of elements from the difference between the expected bond energies of their normal covalent bond and the experimentally determined values. He devised an electro–negativity scale on which F is given an **arbitrary standard value 4.0**. It is the most electro–negative element. The electronegative values of other elements are compared with fluorine. Luis Pauling was awarded a Noble Prize in 1954 for work in chemical bonding.

Electro–negativity and Atomic Radius:

The electro–negativity mainly depends upon the size of atom. Smaller the size of atom, greater will be the force of attraction with bonded electrons and greater will be the electro–negativity.

For example, Alkali metals have greater size and less electro–negativity while halogens have smaller size and greater electro–negativity.

Trend of Electro–negativity in Periodic Table:

It is seen that the electro–negativities values ,in general, increase from left to right in the periodic table while it decrease from top to bottom in groups. Thus the most electronegative atoms are the non metals at the right of periodic table.

Electro–negativity and Nature of Chemical Bonds:

The difference in the electro–negativity values of the bonded atoms is an index to the polar nature of the covalent bond. 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. Elements of which show greater E.N. difference than 1.7 form ionic bonds. A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds.

The bond between Na (E.N = 0.9) and Cl (E.N = 3.0) in NaCl is ionic because E.N, difference is 2.1. The bond in HCl shows covalent character because electro–negativity difference is 0.9 (E.N of H = 2.1 and Cl = 3.0).

Types of Bonds:

Chemical bonds can be classified as:

(i) Ionic bond (ii) Covalent bond (iii) Coordinate covalent bond

We shall explain these bonds with the help of Lewis concept of chemical bonding.

(i) Ionic Bond (Electrovalent Bond):

"The electrostatic force of attraction between oppositely charged ions is called **ionic bond or electrovalent bond**."

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. In energy terms, the electropositive elements are at a higher energy state than the electronegative elements. The energy difference will be responsible for the transfer of electrons from a higher state to lower energy state.

Conditions Necessary for Ionic Bond Formation:

(1) Elements which form ionic bond, must form cations and anions by the transfer of electrons.

(2) Elements in group IA and IIA have low ionization energy and they form cation. Elements which are present in group VIA and VIIA have high electron affinity and they form negative ion by gaining electrons.

(3) Electro–negativity difference should be usually more than 1.7.

For example; E.N. of Cl = 3.0
E.N. of Na = 0.9
E.N. difference = 3.0 – 0.9 = 2.1
It is more than 1.7.
∴ NaCl is ionic compound.

E.N of O = 3.5
E.N of Mg = 1.2
E.N difference = 2.3
∴ MgO is ionic compound.

Examples:

(i) Formation of KCl:

Let us consider the example of the formation of potassium chloride. The electronic configuration of potassium is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ which may be represented as K (2, 8, 8, 1). It tends to lose the outermost electron and form K^+ ion. The energy needed to detach an electron from potassium atom is equal to its first ionization energy.

So $K\ (2, 8, 8, 1) \longrightarrow K^+\ (2, 8, 8) + 1e^- \quad \Delta H = 419\ kJ\ mol^{-1}$

After the loss of an electron, potassium attains the nearest inert gas configuration of Ar (2, 8, 8). Chlorine atom has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or Cl (2, 8, 7). It tends to gain electron lost from potassium atom to attain the nearest inert gas configuration of Ar (2, 8, 8) releasing 349 kJ mol^{-1} energy.

$$\cdot\underset{\cdot\cdot}{\ddot{Cl}}: + 1e^{-1} \longrightarrow :\underset{\cdot\cdot}{\ddot{Cl}}:^{-} \quad \Delta H = -349\ kJ\ mol^{-1}$$

2, 8, 7 2, 8, 8

The oppositely charged K^+ and Cl^- ions are held together by strong electrostatic force of attraction. K^+ and Cl^- ions arrange themselves to form a crystal lattice where proportionate number of cations and anions are packed together.

The coordination number of KCl crystal is six. Each K^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six K^+ ions.

The energy released during the crystal formation is 690 kJ/mole.

$$K^+ + Cl^- \longrightarrow KCl \quad \Delta H = -690 \text{ kJ mol}^{-1}$$

(ii) Formation of CaO:

$$Ca\ (2, 8, 8, 2) \longrightarrow Ca^{2+}\ (2, 8, 8) + 2e^-$$

$$O\ (2, 6) + 2e^- \longrightarrow O^{2-}\ (2, 8)$$

$$Ca^{2+} + O^{2-} \longrightarrow CaO$$

(iii) Formation of Al_2O_3:

$$Al\ (2, 8, 3) \longrightarrow Al^{3+}\ (2, 8) + 3e^-$$

$$O\ (2, 6) + 2e^- \longrightarrow O^{2-}\ (2, 8)$$

$$Al^{3+} + O^{2-} \longrightarrow Al_2O_3$$

The ratio of cation and anion is 2: 3 in Al_2O_3.

Criteria of electro–negativity also helps us to understand nature of bond and percentage ionic characters. If difference of E.N. is less than 1.7 bond will be covalent, if greater than 1.7, bond will be ionic and if 1.7, the 50% ionic and 50%. Covalent characters are present in that molecule. No bond in chemistry is 100% ionic in nature. NaCl has 72% ionic while 28% covalent characters in it. CsF contains 92% ionic and 8% covalent characters in it.

(ii) COVALENT BOND (ELECTRON PAIR BOND)

According to Lewis and Kossel.

"The bond formed by the mutual sharing of electrons between two atoms is called **covalent bond**."

While sharing each atom complete its valence shell and attains the inert gas configuration.

For example, Hydrogen atom has one electron in its valence shell. Two atoms share electrons together and attain the noble gas configuration.

$$H^\bullet + {}^\bullet H \longrightarrow H:H \quad \text{or} \quad H-H$$

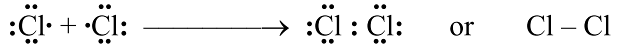
Types of Covalent Bond:

A covalent bond may be single, double or triple depending upon the number of shared pair of electrons. There are three types of covalent bonds.

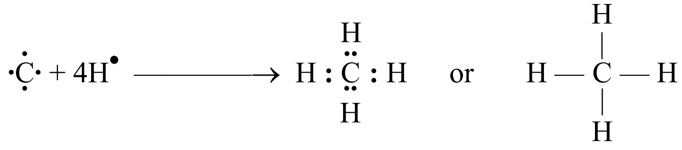
(a) Single Covalent Bond:

"A covalent bond between two atoms formed by mutual sharing of one electron pair is called **single covalent bond**."

For example:



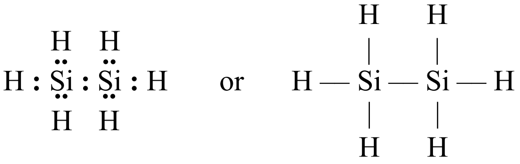
$$:\ddot{\underset{..}{Cl}}\cdot + \cdot\ddot{\underset{..}{Cl}}: \longrightarrow :\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}: \quad \text{or} \quad Cl-Cl$$



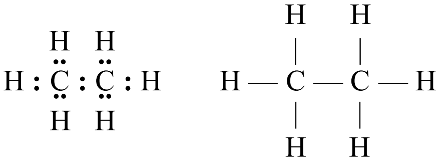
$$\cdot\dot{\underset{\cdot}{C}}\cdot + 4H^\bullet \longrightarrow H:\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}:H \quad \text{or} \quad H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$$

Single covalent bond is represented by single dash (–).

Some of the non–metallic atoms particularly C atoms (or Si atoms) mutually share their electrons with each other. This leads to the formation of extended chains which is the basis of the formation of large sized molecules called **macro–molecules**.



Silane



Ethane

(b) Double Covalent Bond:

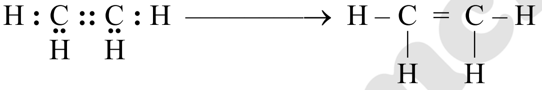
"A covalent bond between two atoms formed by mutual sharing of two electron pairs is called **double covalent bond**."

For example:

(i) $:\ddot{O}: + :\ddot{O}: \longrightarrow :\ddot{O}:\,:\ddot{O}:$ or O = O or O_2

(ii) Carbon dioxide (CO_2):

(iii) Ethene or Ethylene:



Double bond is represented by double line (=).

(c) Triple Covalent Bond:

"A covalent bond between two atoms formed by mutual sharing of three electron pairs is called **triple covalent bond**."

For example:

(1) Nitrogen Molecule (N_2)

:N **:::** N**:** or N ≡ N

(2) Acetylene or Ethyne

H **:** **:::** C **:** H or H – C ≡ C – H

Triple bond is represented by triple line (≡). Double bonds and triple bonds are also called **multiple bonds**.

Types of Covalent Bonds on Basis of Polarity:

(Polar or non–polar)

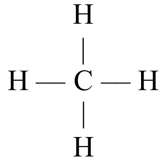
(a) Non–polar Covalent Bond:

"The covalent bond in which the bonding electrons shared equally on both the atoms is called **non polar covalent bond**."

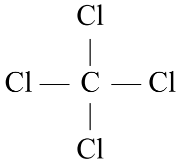
Bond which is formed between two identical atom is always non–polar e.g. N_2, O_2, F_2, Cl_2, Br_2 and I_2. Both atoms have same electro–negativity. Due to the equal distribution of electrons, the bonded atoms remains electrically neutral.

$H : H$ or $H – H$

Similarly CCl_4, and CH_4 are also non polar.



$$\begin{array}{c} H \\ | \\ H — C — H \\ | \\ H \end{array}$$

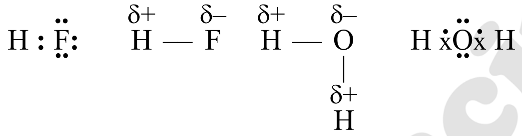


$$\begin{array}{c} Cl \\ | \\ Cl — C — Cl \\ | \\ Cl \end{array}$$

(b) Polar Covalent Bond:

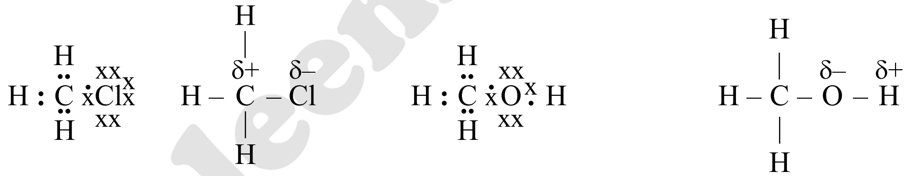
"The covalent bond in which the bonding electrons are not shared equally on both side of bonded atoms is called **polar covalent bond**."

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 atoms. The would make one end of the molecule partially positive and the other partially negative as shown by the following examples.



$$H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \qquad \overset{\delta+}{H} — \overset{\delta-}{F} \qquad \begin{array}{c} \overset{\delta+}{H} — \overset{\delta-}{O} \\ \quad\;\; | \\ \quad\;\; \overset{\delta+}{H} \end{array} \qquad H \times\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\times H$$

Hydrogen fluoride Water



$$\begin{array}{c} H \\ H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \times\overset{xx}{\underset{xx}{Cl}}\times \\ H \end{array} \qquad \begin{array}{c} H \\ | \\ H – \overset{\delta+}{C} – \overset{\delta-}{Cl} \\ | \\ H \end{array} \qquad \begin{array}{c} H \\ H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \times\overset{xx}{\underset{xx}{O}}\times H \\ H \end{array} \qquad \begin{array}{c} H \\ | \\ H – C – \overset{\delta-}{O} – \overset{\delta+}{H} \\ | \\ H \end{array}$$

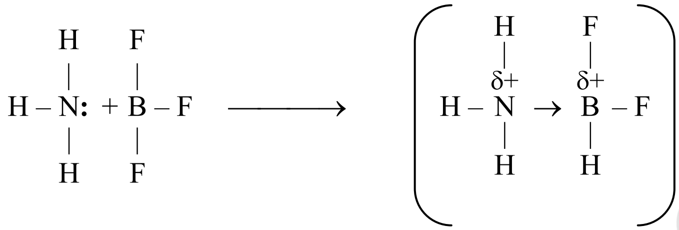
Methyl chloride Methyl alcohol

Polar Bond		Non-polar Bond	
(1)	Covalent bond between two different atoms.	(1)	Covalent bond between two similar atoms.
(2)	Unequal sharing of electrons between the bonded atoms.	(2)	Equal sharing of electrons between the bonded atoms.
(3)	Molecules having polar bond may or may not be polar.	(3)	Molecules having non-polar bond are always non-polar.
(4)	Bonded atoms have partial positive and negative charges. $\overset{+\delta}{H} – \overset{-\delta}{Cl}, \overset{+\delta}{CH_3} – \overset{-\delta}{Cl}$	(4)	Bond atoms have no partial positive or negative charges. $H – H, \overset{-\delta}{O} = \overset{+\delta}{C} = \overset{-\delta}{O}$

(iii) Coordinate Covalent Bond (Dative Bond) OR Semi-Polar Bond:

"A co–ordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms."

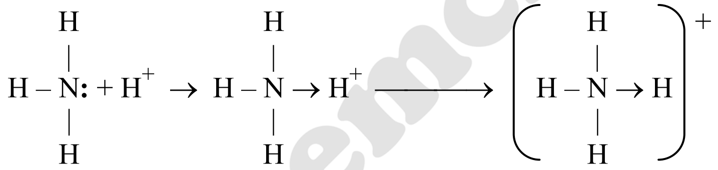
Let us consider the example of bond formation between NH_3 and BF_3. NH_3 has three covalent bonds and there is a lone pair of electrons on nitrogen atom. On the other hand, boron atom in BF_3 is deficient in electrons. Therefore, nitrogen can donate the pair of electrons to the acceptor BF_3 and this results in the formation of a coordinate bond:



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}: + \overset{\overset{F}{|}}{\underset{\underset{F}{|}}{B}}-F \longrightarrow \left(H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{\delta+}{N}}} \rightarrow \overset{\overset{F}{|}}{\underset{\underset{H}{|}}{\overset{\delta+}{B}}}-F \right)$$

Donor Acceptor Complex

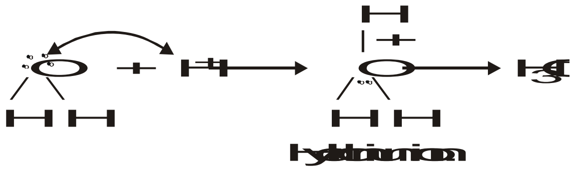
In some of the compounds, after the formation of a coordinate covalent bond, the distinction between covalent bond and coordinate bond vanishes. For example, in NH_4^+ ion, NH_3 donate a pair of electrons to H^+ and form a coordinate covalent bond.



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}: + H^+ \rightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\rightarrow H^+ \longrightarrow \left(H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\rightarrow H \right)^+$$

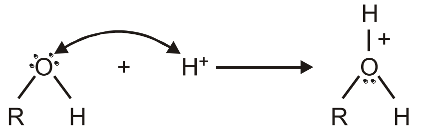
Formation of Hydronium Ion: (Protonated Water)

Water donates its electron pair to H^+ ion and H_3O^+ is formed. Spectroscopic evidences show that all the bond lengths of H and O are equal. Every bond is 33% coordinate covalent and 66% covalent in H_3O^+.

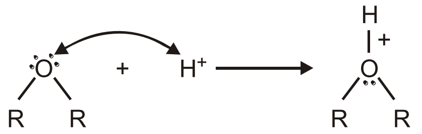


Formation of Oxonium Ion in Ether and Alcohol:

Lone pair of ether and alcohol oxygen are denoted to the H^+ just like water and oxonium ions are formed.

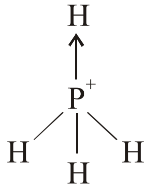


Oxonium ion of alcohol

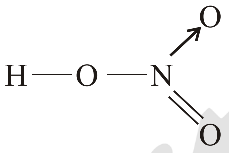


Oxonium ion of ether

All the primary, secondary and tertiary amines like ammonia make coordinate covalent bond with H^+. PH_3 form phosphonium ion PH_4^+ with H^+. Coordinate covalent bond is also present in many oxy–acids like HNO_3, $HClO_2$, $HClO_3$ and $HClO_4$.



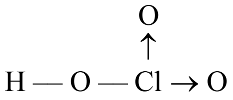
Phosphonium ion



Nitric Acid

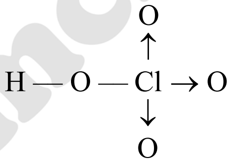
$H-O-Cl \longrightarrow O$

Chlorous Acid



$H-O-\overset{\overset{O}{\uparrow}}{Cl} \rightarrow O$

Chloric acid



$H-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{Cl}} \rightarrow O$

Per chloric acid

Basic Definitions:

Partially filled orbital or Half filled orbitals:

The orbital which has only one electron in it.

Atomic Orbital:

The region around the nucleus in which an electron with a specific energy is most probably located is called an **atomic orbital**.

or An orbital which extends over one nucleus only e.g.

s, p, d and f orbits are atomic orbitals.

Hybrid Atomic Orbital:

The orbital formed by mixing the atomic orbits of an atom are called **hybrid atomic orbitals** e.g. sp^3, sp^2, sp.

Molecular Orbital:

The orbital that extend over two or more atomic nuclei e.g.

Sigma orbital, sigma star, π, π^* orbital.

Bonding Molecular Orbital:

A low energy molecular orbital that gives a build–up of electron density between bonded nuclei and helps to stabilize the molecule e.g. σ–orbital, π–orbital.

Anti Bonding Molecular Orbital:

The orbital in which electron spend little time between nuclei. The energy of the orbital is above that of the orbital for the separated atoms.

Lone Pair or Unshared Pair of Electrons:

A pair of electrons in the valence shell of an atom that is not shared during covalent bond formation is called **lone pair or unshared pair of electrons**.

Bond Pair of Bond Electrons:

A pair of electrons results after the sharing and formation of a covalent bond is called **bond pair of electrons**.

Bond Axis:

A common region along the imaginary line between two bonded nuclei is called **bond axis**.

Central Atom:

That element which have less numbers in a compound e.g. C in CH_4, N in NH_3, O in H_2O, C in C_2H_4. If a compound consist of only two atoms, the more electronegative atom is central atom e.g. F in HF.

Half filled Orbital:

An orbital with single electron is called **half filled orbital or unpaired electron**.

Molecular Geometry:

The arrangement of atoms around a central atom is called **molecular geometry**.

Localized Electrons:

The shared pair of electron restricted to the region between the two bonded nuclei of atoms are called **localized electrons**.

Delocalized Electrons:

The shared pair of electron extended over more than two bonded atom nuclei are called **delocalized electrons**.

Diamagnetic:

The substance which is not attracted by the magnet is called **diamagnetic**. In this substance, all paired electrons are present. For example N_2 is diamagnetic.

Paramagnetic:

The substance which is attracted by the magnet. This substance has unpaired electron in it. For example, O_2 is paramagnetic.

Bond Order:

The number of electrons pairs in a bond in Lewis electron–dot formula. In molecular orbital theory bond order is equal to $\frac{nb - na}{2}$. For example, Bond order of $H_2 = 1$, $O_2 = 2$, $N_2 = 3$.

Modern Theories of Covalent Bond:

Limitations of the Lewis Model:

Classical Lewis model explains only that how bonds are formed between different atoms. Lewis model have following limitations.

(i) It does not explain the shape or geometry of the molecules. Shapes of molecules are very important because many physical and chemical properties are based upon the geometry of molecules.

(ii) It does not explain the bond length or bond distance between the bonded atoms and bond angles.

(iii) It does not explain the energetic and stability of the molecules.

(iv) It does not explain the paramagnetic nature of the molecules.

(v) It does not give the idea of bond dissociation energy.

Following are the modern theories, which explain satisfactorily the above requirements for covalent bond formation, based on wave–mechanical structure of atoms:

1. Valence shell electron pair repulsion theory (VSEPR).
2. Valence bond theory (VBT).
3. Molecular orbital theory (MOT).

In addition to above, crystal field theory and legend field theory explain the formation of coordination complex compounds formed by transition metals.

1. VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Sidgwick and Powell (1940) pointed out that the shapes of molecules could be interpreted in terms of electron pairs in the outer orbital of the central atom. Recently, Nylholm and Gillespie developed VSEPR theory, which explains the shapes of molecules for non–transition elements.

Basic Assumptions:

The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at maximum distance apart to keep repulsions at minimum.

Postulates of VSEPR Theory:

(i) Both the lone pairs as well as the bond pairs participate in determining the geometry of the molecules.

(ii) The electron pairs are arranged around the central polyvalent atom so as to remain at a **maximum distance** apart to avoid repulsions.

(iii) The electron pairs of **lone pairs occupy more space** than the bond pairs.

A bonding electron pair is attracted by both nuclei of atoms while non–bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result the non–bonding electron pairs exert greater repulsive forces on bonding and thus tend to compress the bond pairs.

The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:

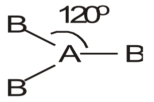
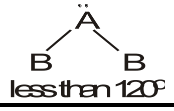
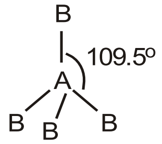
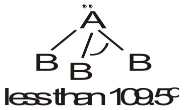
Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

These repulsions are called **Vander Waal's repulsions**.

(iv) The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density. Therefore, they occupy more space than one electron pair of a single bond, but considered as a single electron pair in determining the geometry of the molecule. This is because, they tend to occupy the same region between the two nuclei like a single bond.

In order to illustrate this theory, let us consider, that the central atom is 'A' and this atom is polyvalent. More than one 'B' type atoms are linked with 'A' to give AB_2, AB_3, AB_4, etc. type molecules. It depends upon the valence of A, that how many B are attached with it. Following table gives the shapes of different types of molecules.

TABLE

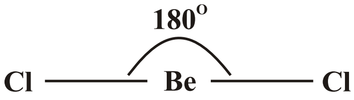
Type	Electron pairs			Arrangement of pairs	Molecular geometry	Shape	Examples
	Total	Bond	Lone				
AB_2	2	2	0	Linear	Linear	B – A – B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Trigonal planar	Trigonal planar		BH_3, BF_3, $AlCl_3$
		2	1		Bent (or angular)		$SnCl_2$, SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4, $SiCl_4$, CCl_4, BF_4, NH_4^+, SO_4^{-2}
		3	1		Trigonal pyramidal		NH_3, NF_3, PH_3
		2	2		Bent (or angular)		H_2O, H_2S

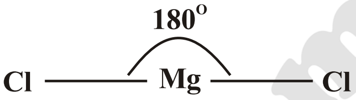
Geometries of Molecules:

1. Molecules containing two Electron Pairs (AB_2 – type)

In such, molecules two electrons pairs around the central atom are arranged at farther distance apart at an angle of 180°, in order to minimize repulsions between them. Thus, they form a **linear** geometry.

Beryllium chloride is a typical linear molecule, which contains two electrons pairs, $MgCl_2$, $CaCl_2$, $SrCl_2$, $CdCl_2$ and $HgCl_2$ are also linear molecules. The central atoms have two electrons in outer most orbits.



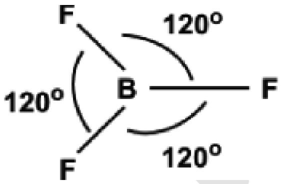


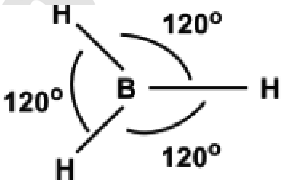
2. Molecules containing three Electron Pairs (AB_3 – type):

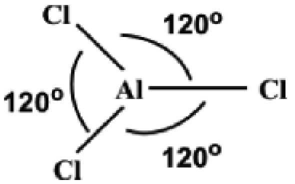
(a) AB_3 – type with no Lone Pairs:

In such molecules, central atom contains three bonding electron pairs, which are arranged at maximum distance apart at a angle of 120°, given a **triangular planar** geometry. The boron atom in BH_3 is surrounded by three charge clouds, which remains farthest apart in one plane, each pointing towards the corners of an equilateral triangle. Thus, BH_3 molecules have a trigonal planar geometry, with each H – B – H bond angles of 120°.

We expect similar geometries in hybrids of group IIII–A (AlH_3, GaH_3, InH_3 and TlH_3) and their halides (BF_3, $AlCl_3$ etc).



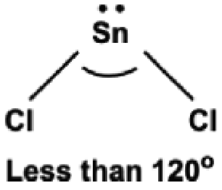


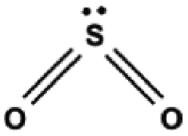


(b) AB_3 – type with One Lone Pair and Two Bond Pairs:

Sn and Pb are elements of group IV–A and have electronic configuration $ns^2\ np_x^1, np_y^1$ and np_z^0. Partially filled orbits of Sn or Pb overlap with partially filled orbital halogens atoms. Two s electrons do not take part in chemical bond formation.

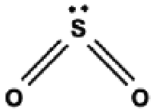
In $SnCl_2$ and $PbCl_2$ one of the corner of triangle is occupied by a lone pair giving rise to a angular or bent structure in vapour phase.

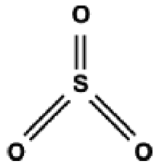




(c) AB_3 – type with Multiple Bond:

In SO_2, one corner of triangle is occupied lone pair and two corners each by S = O bond, while in SO_3 all three regions, each occupied by S = O bonds. This structure is perfectly triangular.





3. Molecules containing four Electron Pairs (AB_4 – types):

(a) AB_4 – type with no Lone Pairs:

The charge clouds due to four electron pairs avoid their electrostatic repulsions by drifting apart, so as to maintain a mutual bond angle of **109.5^o**, such geometry enables to a form a shape of regular **tetrahedron**.

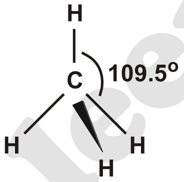
Examples:

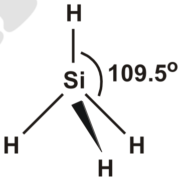
Each of the four valence electrons of carbon pair up with single electron of hydrogen in methane.

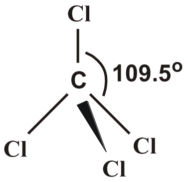
$C_6 = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ (ground state)

$_6C = 1s^2, 2s^1, 2px^1, 2py^1, 2py^1$ (excited state)

The four electron pairs are directed from the center towards the corners of a regular tetrahedron, with each apex representing a hydrogen nucleus. The arrangement permits a non–planar arrangement of electron pairs. Each H – C – H bond is perfectly 109.5^o. On the same grounds, SiH_4, CCl_4 form similar geometries. This structure has four corners, four faces, six edges and six bond angles.







(b) AB_4 – type with one Lone Pair and three Bonds Pairs:

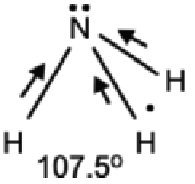
In such cases, the charge cloud of lone pair electrons (non–bonding electrons) spreads out more than that of bonding electrons. As a result, some what large lone pair charge cloud tend to compress the bond angles in rest of the molecules.

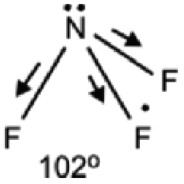
Ammonia, $\ddot{N}H_3$ is a typical example.

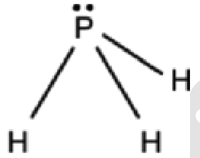
$_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

The non–bonding electron in 2s–orbital takes up more space and exerts a strong repulsive force on the bonding electron pairs. Consequently, to avoid a larger repulsion, the bonding electron pairs move closer that reduces the ideal bond angle from 109.5^o to 107.5^o. This effect compels ammonia to assume a **triangular pyramidal** geometry instead of tetrahedral, as in methane.

Similar, affects are evident in the geometries of molecules like $\ddot{\mathrm{P}}\mathrm{H}_3$, $\ddot{\mathrm{A}}\mathrm{sH}_3$, $\ddot{\mathrm{S}}\mathrm{bH}_3$ and $\ddot{\mathrm{B}}\mathrm{H}_3$. Substituting of hydrogen with electronegative atoms like F or Cl further reduces the bond angle. In NF_3, the strong polarity of N – F bond pulls the lone pair of N atom closer to its nucleus, which in turn exerts a stronger repulsion over bonding electrons. Thus, the angle further shrinks to 102°. Moreover, the bond pairs N – F bonds are more close to F atoms than N atoms. The increased distances in these bond pairs makes their repulsions less operative.





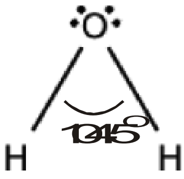


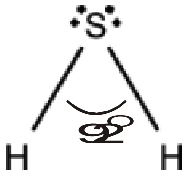
(c) AB_4 – type with Two Lone Pairs and Two Bonds Pairs:

Presence of two lone pairs, introduces three types of repulsion i.e. lone pair – lone pair, lone pair – bond pair and bond pair – bond pair repulsion. For example; water (H_2O), a tri–atomic molecule is expected to be an AB_2 type linear molecule like $BeCl_2$ and CO_2. But, experimental evidences confirm a bent or angular geometry. VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pairs, in addition to bond pairs in determining overall geometry of water molecule.

$_8O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

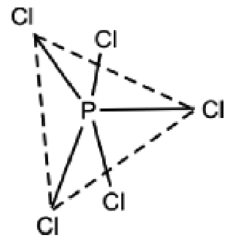
Two of the corners of a tetrahedron are occupied by each of the two lone pair remaining by bond pairs. But owing to arrangement of lone pairs and their repulsions among themselves and on bond pairs, the bond angle is further reduce to 104.5°. H_2S, H_2Se, H_2Te form similar geometries.





(d) AB_5 – type (Molecule containing five Electron Pairs):

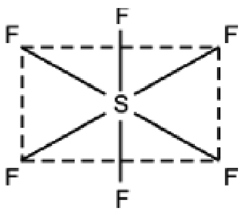
When the central atom has five unpaired electrons, they arrange in a triangular bipyramidal geometry. Three electron pairs are in one plane and other two are perpendicular to the plane.



For example; PCl_5

(e) AB_6 – type (Molecule containing six Electron Pairs):

When the central atom has six electron pairs, they arrange in a square bi pyramidal geometry. Four electron pairs are in one plane while the two are perpendicular to the plane.



For example; SF_6 is octahedral

2. Valence Bond Theory (VBT):

VSERP theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. VBT is concerned with both formation of bonds and the shapes of molecules.

This method of describing a covalent bond considers the molecule as a combination of atoms. According to the quantum mechanical approach, a covalent bond is formed when half – filled orbitals (partially filled) in the outer or valence shells of two atoms overlap, so that a pair of electrons, one electron from each atom, occupies the overlapped orbital. As a result of this overlap, electrons with opposite spin become paired to stabilized themselves. Larger the overlap, stronger the bond. Essential conditions for chemical bond formation are given below.

(1) Two orbitals overlap and overlapping region of both bonded atoms is same.

(2) Total number of electrons in both orbitals is not more than two.

According to VBT, covalent bond is defined as:

"The bond formed by the overlapping of partially filled atomic orbitals of two bonded atom is called **covalent bond**."

Covalent bonds are **directional bonds** and the direction of bond is determined by the direction of two overlapping orbitals. The strength of bond depends upon the overlapping. If **overlapping is greater** then strength of **bonds will also be greater**. Overlapping by s – s and s – p are shown in some examples.

SIGMA BOND (σ–BOND)

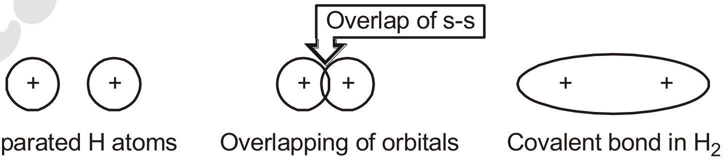
"When two partially filled atomic orbitals overlap in such a way, that probability of finding the electrons is maximum around the line joining the two nuclei, it is called **sigma bond**."

Overlapping of s – s and s – p always formed sigma bonds.

Formation of H_2 Molecule:

The electronic configuration of hydrogen is $1s^1$. Two partially filled $1s^1$ orbitals of hydrogen overlap to form covalent bond. The electron density is maximum between two nuclei or bond axis. A line joining of two bonded atoms is called **bond axis**.

$$H + H \xrightarrow{\qquad} H_2$$



Formation of HF Molecule:

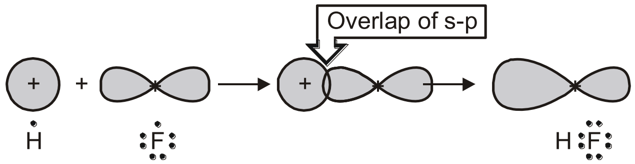
The H – F bond is formed by the pairing of electrons – one from hydrogen and one from fluorine. According to VB theory, we must have two half – filled orbitals – one from each atom that can be joined by overlap.

$_1H = 1s^{\uparrow}$

$_9F = 1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow}$

The overlap of orbitals provides a means for sharing electrons, thereby allowing each atom to complete its valence shell. The fluorine atom completes its 2p sub–shell by acquiring a share of an electron from hydrogen as shown below.

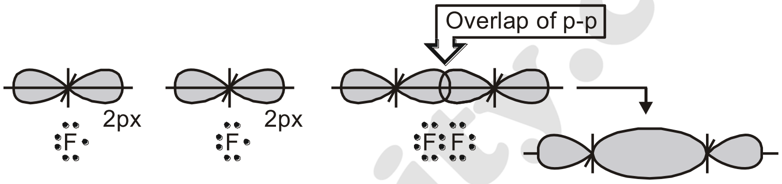
$_9F = 1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow}$



The requirements for bond formation are met by overlapping the half – filled 1s orbital of hydrogen with the half – filled 2p–orbital of fluorine. There are two orbitals plus two electrons whose spins can adjust so they are paired. The formation of the bond is illustrated in as shown in Figure.

Formation of F_2 Molecule:

The bond in the fluorine molecule, F_2 is formed by the overlap of half – filled $2p_z$ orbital on each fluorine atom Figure.



Formation of Fluorine molecule

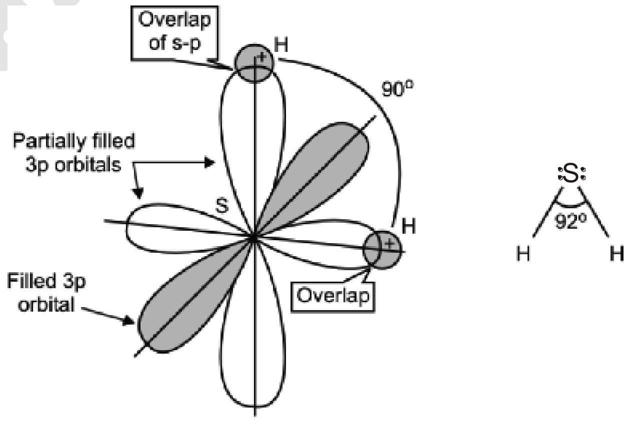
Formation of H_2S Molecule:

This is a non–linear molecule, and the bond angle between the two H – S bonds is about 92°.

$S_{16} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$

Each two 3p orbits of sulphur containing one electron can overlap with the 1s orbital of hydrogen atoms.

Thus, the VBT requires the idea of overlap to explain the geometry of the hydrogen sulphide molecule.



Bonding in H_2S showing overlap of orbitals

Pi – BOND (π–BOND)

"When two partially filled atomic orbitals overlap in such a way that probability of finding the electrons is above and below the bond axis is called **Pi bond**."

In π bond, electron density is maximum above and below the line joining of two nuclei or bond axis. A π bond is formed when two parallel orbitals are still available after strong sigma bond had formed.

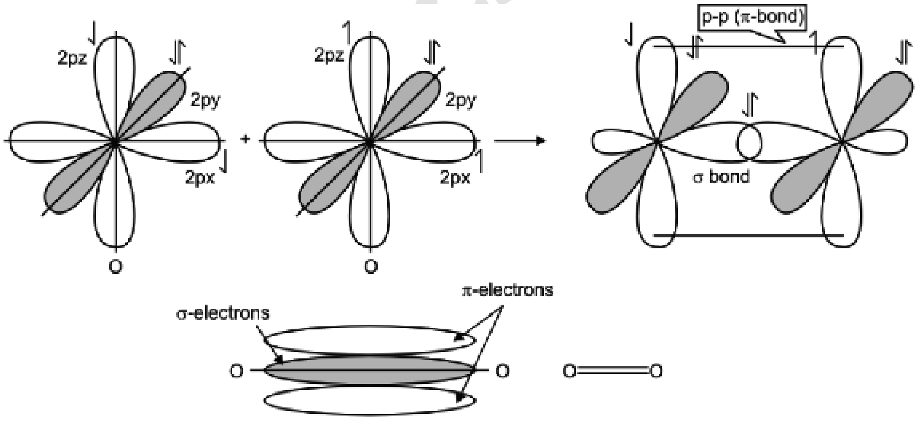
(i) Formation of O_2 Molecule:

O_2 molecule has sigma as well as π–bond is it. The electronic configuration of each oxygen atom is given below.

$O_8 = 1s^2, 2s^2, 2px^2, 2p_y^1, 2p_z^1$

There are two partially filled p–orbital on each oxygen atom. One bond between O – O is formed by linear overlap of p–orbital while other bond is formed by parallel overlap of 2p half filled orbital. The electron density in π molecular orbital is maximum in the overlapping region or above and below the bond axis.

$O + O \xrightarrow{\hspace{2cm}} O_2$



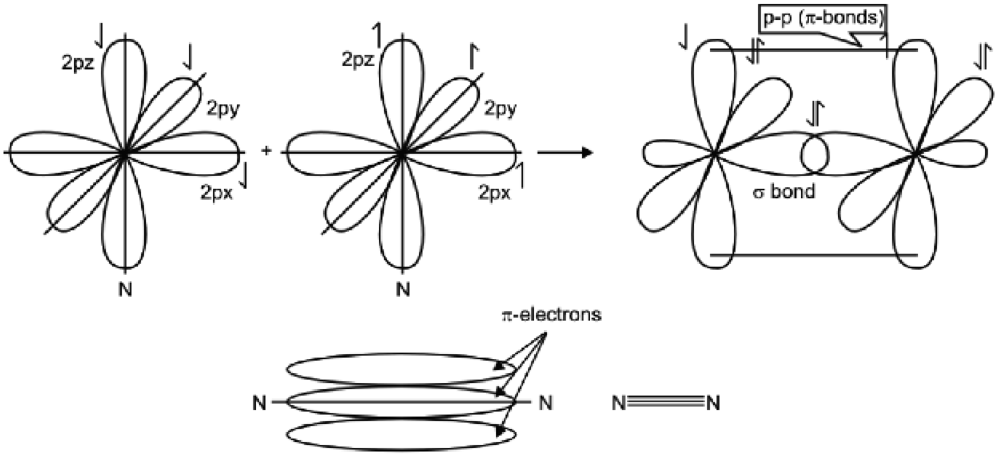
Formation of O_2 molecule

According to VBT, all electrons in oxygen molecules, are paired up, so it is diamagnetic.

(ii) Formation of N_2 Molecule:

In nitrogen there is one sigma and 2π bonds. The electronic configuration of nitrogen is,

$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$



Formation of N_2 molecule

Partially filled p_x orbital of one nitrogen form sigma bond with partially filled p_x orbital of other nitrogen by linear overlap. Partially filled p_y and p_z orbitals of one nitrogen form 2π bonds with other partially filled p_y and p_z orbitals by parallel overlap respectively.

Difference Between Sigma Bond and Pi Bond:

Sigma (σ) Bond	Pi (π) Bond
1. Sigma bond is formed by linear or head on overlapping of atomic or hybrid orbitals.	1. Pi bond is formed by parallel or sideways overlapping of atomic orbitals.
2. In sigma bond electron density is between two nuclei.	2. In Pi bond, electron density is above and below the bond axis.
3. Sigma bond has greater overlapping region and is stronger bond.	3. Pi bond has less overlapping region and is a weak bond.
4. It is less reactive than Pi bond.	4. It is more reactive than sigma bond.
5. Atoms are always bonded with sigma bond first.	5. π–bond is formed when atoms are already bonded with sigma bond.
6. It is formed by overlap of $s-s$, $s-p$, $p-p$, $s-sp^3$, $s-sp^2$, $s-sp$, $sp-sp$, sp^2-sp^2, sp^3-sp^3.	6. It is formed by overlapping of $p-p$ atomic orbitals only.
Example: $H-H$, $H-Cl$, $H-F$, CH_4 etc.	**Example:** $O=O$, $N\equiv N$, $CH_2=CH_2$ etc.

Simple valence bond theory does not explain the covalent bond formation of Be, B and C. The valence of these elements is not equal to the number of partially filled atomic orbitals in than.

Be (4) = $1s^2, 2s^2$
B (5) = $1s^2, 2s^2, 2p_x, 2p_y, 2p_z$
C (6) = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z$

Some modification in this theory was needed. This theory was modified and called **hybridization concept**.

ATOMIC ORBITAL HYBRIDIZATION

"The process of mixing atomic orbitals of different energy and shape to form set of new orbital of the same energy and same shape is called **Hybridization** and orbitals obtained are called **hybrid orbitals**."

Simple valence bond theory does not explain the tetra–valence of C. Tri–valence of B bivalence of Be. Same, bond angles were not well explain by simple VBT.

According to this, atomic orbitals differing slightly in energy intermix to form new orbital called **hybrid atomic orbitals** which differ from the parent atomic orbitals in shape and possess specific geometry. The atomic orbitals hybridization gives a satisfactory explanation for the valence of the elements. The electrons belonging to the ground state structure are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons. the electronic configuration of Be, B and C are shown in the Table.

TABLE

Change in valence after promotion of electrons from ground to excited state.

Element	**Electronic Configuration**		**Valence after excitation**
	Before excitation	**After excitation**	
Be (4)	1s 2s 2p $\boxed{\downarrow\uparrow}$ $\boxed{\downarrow\uparrow}$ $\boxed{}$	1s 2s 2p $\boxed{\downarrow\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	2
B (5)	1s 2s $2p_x$ $\boxed{\downarrow\uparrow}$ $\boxed{\downarrow\uparrow}$ $\boxed{\uparrow}$	1s 2s $2p_x$ $2p_y$ $\boxed{\downarrow\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	3
C (6)	1s 2s $2p_x$ $2p_y$ $\boxed{\downarrow\uparrow}$ $\boxed{\downarrow\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	1s 2s $2p_x$ $2p_y$ $2p_x$ $\boxed{\downarrow\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$	4

After acquiring the excited state, the atomic orbitals undergo hybridization. The energy required for the excitation is compensated by the energy released during the process of bond formation with other atoms. Since hybridization leads to entirely new shape and orientation of the valence orbital of an atom, it holds significant importance in determining the shape and geometry of molecules.

Depending upon the nature of orbital involved, there are many types of hybridizations.

(i) sp^3, (ii) sp^2, (iii) sp

sp^3 – HYBRIDIZATION

"The process in which one s and three p orbitals combine to form four orbitals of equivalent energy and shape is called **sp^3 – Hybridization**."

Some examples of sp^3 hybridization are given below.

(i) Formation of CH_4 Molecule:

Electronic configuration of C (6) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z$ ground state.

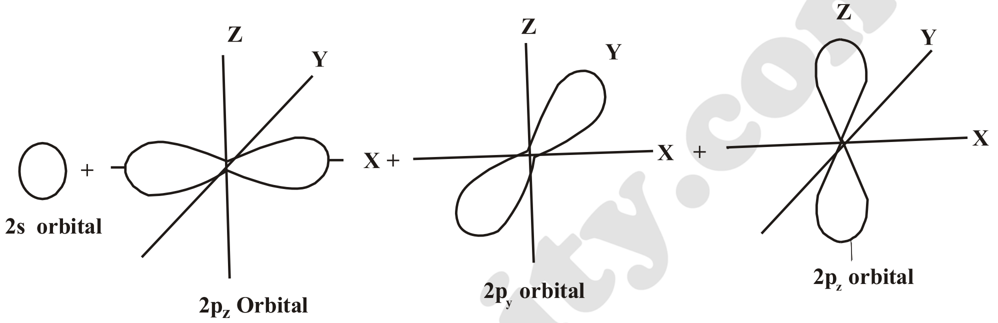
One electron is promoted from 2s to 2p.

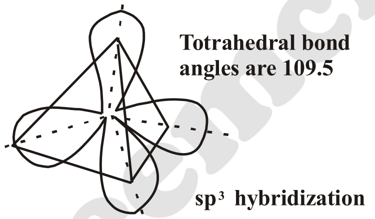
Excited state electronic configuration of C (6) = $1s^{\uparrow\downarrow}, 2s^{\uparrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$

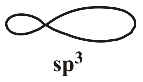
Four partially filled atomic orbitals combine to form same numbers (four) of hybrid orbitals. Each orbital has same energy and shape. Each hybrid orbital has one bigger and one smaller lobe and has **75% p and 25% s characters**.

"Each hybrid orbitals is directed towards the four corners of tetrahedron."

The hybrid orbitals are oriented in such a way that each angle of HCH is **109.5°**.

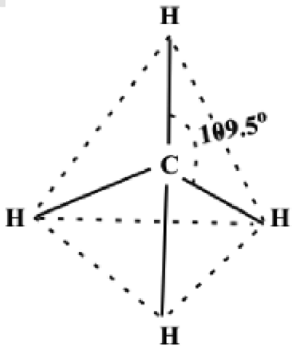


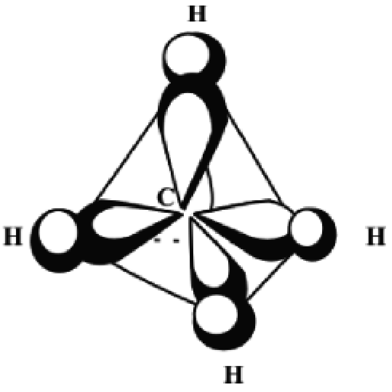




Methane molecule is formed by the overlap of partially filled sp^3 hybrid orbitals and $1s^1$ partially filled orbital of hydrogen. Four hydrogen atoms form four sigma bonds, separately with carbon.

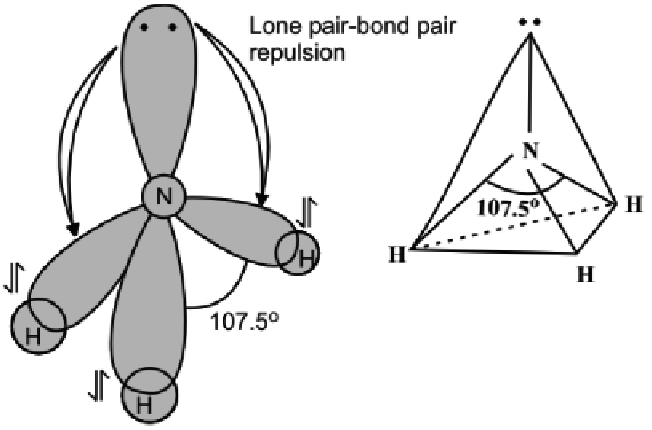
Experiments show that four bonds in C – H are identical. This show that four valence orbital of carbon involve equally and equal orbitals are obtained by hybridization process.





(ii) Formation of NH_3 Molecule:

Electronic configuration of N(7) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$



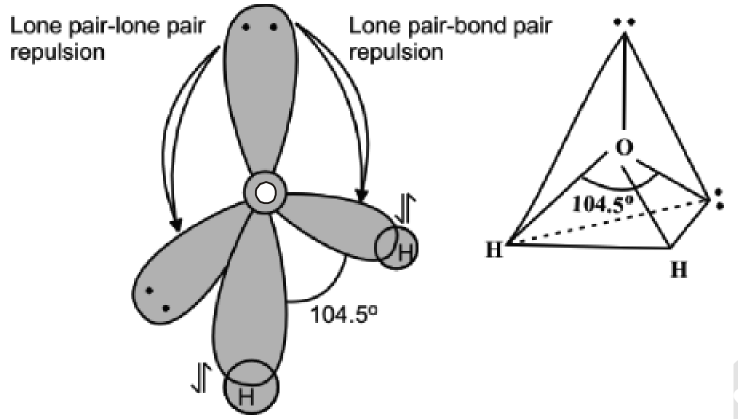
Three sp³-s overlaps in NH₃ molecule to form a pyramidal structure.

One 2s and three 2p–orbital of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals which are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled by an available lone pair of electrons and the remaining three orbitals are half filled. The nitrogen atom undergoes three $sp^3 - s$ overlaps with three s orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners whereas the lone pair of electrons is at the fourth corner of the tetrahedron. The result is a **pyramidal molecule** in which the three hydrogen atoms form the base and the lone pair of electrons the apex. The experimentally determined angle in ammonia is **107.5^{o}**. The deviation from the tetrahedral angle (109.5^{o}) is explained on the basis of repulsion between the lone pair and the bond pairs of electrons.

(iii) Formation of H_2O Molecule:

Electronic configuration of O (8) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$

In this case 2s and three 2p–orbital of oxygen hybridize to form 4 sp^3 hybrid orbitals which will have a tetrahedral arrangement. Two hybrid orbitals are completely filled by the two available lone pairs of electrons. The remaining two half filled hybrid orbitals undergo $sp^3 - s$ overlaps with H atoms to form two sigma bonds. The two H atoms occupy two corners of the tetrahedron and the remaining two are occupied by two lone pairs of electrons. The bond angle in water is **104.5^{o}**. The deviation from the tetrahedral angle (109.5^{o}) is explained on the basis of repulsion between the two lone pairs of electrons. Geometry of molecule depends upon the number bond pairs. H_2O has two bond pairs, so shape of molecule is **angular**.



Three sp^3-s overlaps in H_2O molecule to form a angular structure.

sp^2 – HYBRIDIZATION

"The process of mixing one 's' and two 'p' orbitals to form three equivalent sp^2 hybrid orbitals is called **sp^2 – Hybridization**."

Each sp^2 orbital consists of 's' and 'p' in the ratio of 1 : 2 respectively.

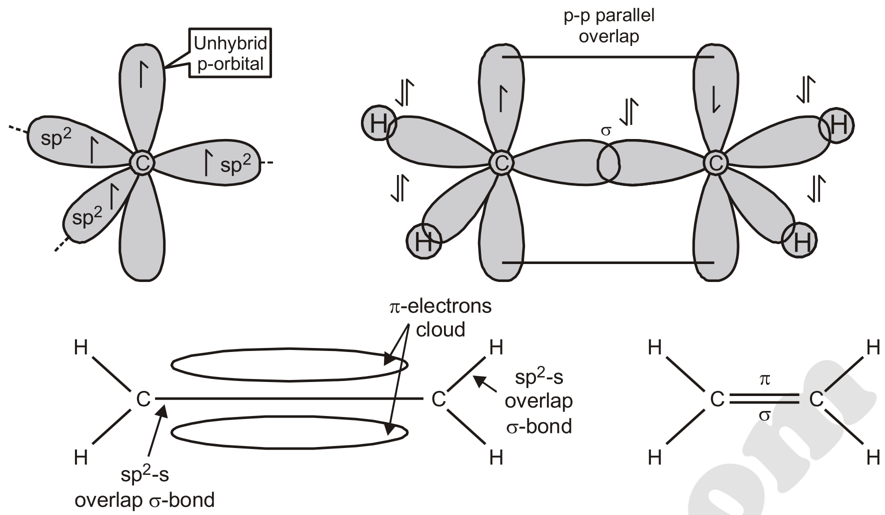
sp^2 – hybrid orbitals lie at the angle of 120^o in a plane. The geometry of the molecules is trigonal planar.

(i) Formation of Ethylene or Ethane (C_2H_4) Molecule:

Electron configuration of C (6) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z$

Excited state = $1s^{\uparrow\downarrow}, 2s^{\uparrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$

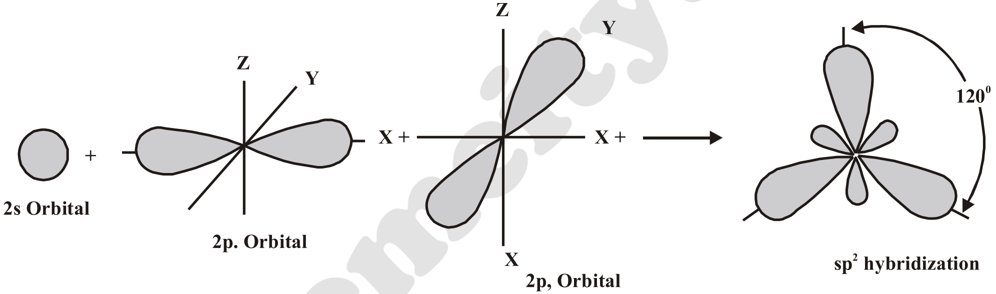
One s and two p orbitals intermix to form three hybrid (sp^2) orbitals. The geometry of molecules depends upon the number of hybrid orbitals. Hybrid orbitals are **trigonal planar** and are oriented at the angle of **120^o**. Each atom is left with one half filled p–orbital perpendicular to the planar sp^2 hybrid orbitals. Each carbon atom undergoes sp^2 – s, overlaps with two hydrogen atoms and sp^2 – sp^2 overlap between themselves to form sigma bonds. These overlaps lead to the following shapes. The partially filled p–orbital undergo **overlap sideways** to form a pi–bond. So, a pi–bond is formed by the sideways overlap of two half filled co–planar p–orbital in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei. It should be made clear that a π–bond is formed between two atoms only, when they are bonded with a sigma bond.



Formation of one sigma and one pi bond between two carbon atoms.

(ii) Formation of BF_3 Molecule:

Electronic configuration of F (9) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow}$



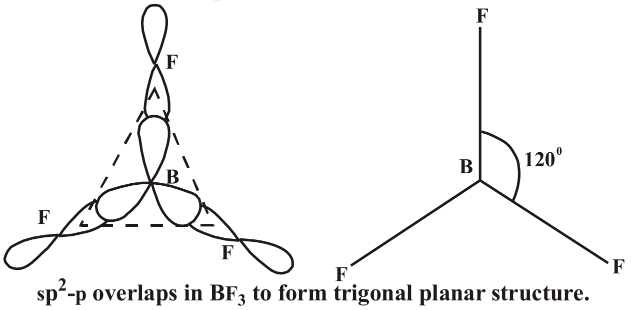
Electronic configuration of B (5) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y, 2p_z$

One electron is promoted from 2s to 2p.

Excited state = $1s^{\uparrow\downarrow}, 2s^{\uparrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z$

One s and 2p atomic orbitals intermixed to form three sp^2 hybrid orbitals.

One of the p–orbital of fluorine is half filled. BF_3 is formed by the overlap of three half filled sp^2 hybrid orbitals of boron with p–orbital of three fluorine atoms.



sp^2-p overlaps in BF_3 to form trigonal planar structure.
BF_3 molecule, thus formed, is trigonal planar.

Each angle between FBF is of **120^o** and the geometry is **trigonal planar**.

sp – HYBRIDIZATION

"The process in which one s and one p atomic orbitals intermix to form two hybrid orbitals is called **sp – Hybridization**."

Each sp hybrid orbitals consists of s and p in ratio of 1 : 1. Each sp hybrid orbitals contains 50% s and 50% p characters.

(i) Formation of Ethylene or Acetylene (C_2H_2) Molecule:

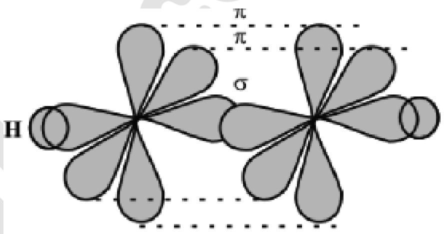
Electronic configuration of C (6) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z$

One electron is promoted from 2s to 2p.

Excited state configuration = $1s^{\uparrow\downarrow}, 2s^{\uparrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_x^{\uparrow}$

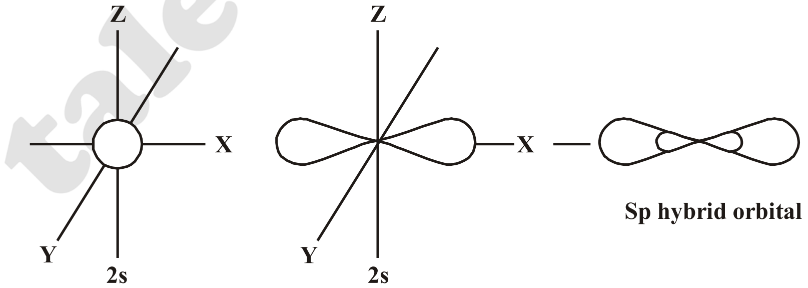
One s and one p atomic orbitals intermix to form two hybrid orbitals.

Each carbon atom undergoes sp – s overlap with one hydrogen atom and s overlap other carbon atom. Each carbon atom is left with two **un–hybridize orbitals** perpendicular to the planar sp hybrid orbitals. The two half filled p–orbital (on separate carbon atoms) are parallel to each other in one plane while the other p orbitals are parallel to each other in another plane. The **sideways π over** between the p–orbital in two planes results in the formation of two pi–boron shown in figure.

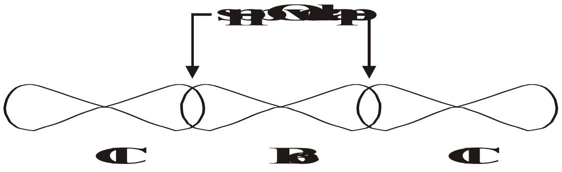


Formation of one sigma and two pi bonds in C_2H_2

In case of sigma bond electron density is maximum between two nuclei at line joining the two nuclei. In case of π bond, electron density is maximum all around the sigma bond.



Sp-hybridization to form a linear structure



(ii) Formation of $BeCl_2$ Molecule:

Electronic configuration of Be (4) = $1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}$

One electron is promoted from 2s to 2p.

Excited state configuration = $1s^{\uparrow\downarrow}, 2s^{\uparrow}, 2p_x^{\uparrow}$

Electronic configuration of Cl (17) = $1s^2, 2s^2, 2p^6, 3s^{\uparrow\downarrow}, 3p_x^{\uparrow\downarrow}, 3p_y^{\uparrow\downarrow}, 3p_z^{\uparrow}$

One s and one p atomic orbitals intermix to form two hybrid orbitals. These hybrid orbitals are oriented at the angle of **180^o** with **linear** geometry. Each sp hybrid orbital of Be overlap with half – filled p–orbital of Cl to form two sigma bonds.

3. MOLECULAR ORBITAL THEORY (MOT)

According to molecular orbital theory, the **atomic orbitals** of bonding atoms **overlap** to form same number of **molecular orbital**. The molecular orbital which have **low energy** than original atomic orbitals is called **bonding molecular orbital**. The molecular orbital which have **high energy** than original atomic orbitals is called **anti–bonding molecular orbital**.

Two molecular orbitals result from the overlap of two atomic orbitals in such a way that the electron waves either reinforce each other or cancel each other. The low energy of bonding molecular orbital is formed when electronic waves reinforce each other (constructive interference). High energy anti–bonding molecular orbital is formed when electronic waves cancel each other (destructive interference).

Bonding Molecular Orbital	Antibonding Molecular Orbital
(1) It has low energy than the isolated atomic orbitals.	(1) It has high energy than the isolated atomic orbitals.
(2) It has high electron density between the nuclei.	(2) It has no electron density between the two nuclei.
(3) It is formed by the addition of electron waves.	(3) It is formed due to the subtraction of electron waves.
(4) It is lower energy.	(4) It is of high energy.
(5) It is more stable.	(5) It is less stable.
(6) It is called B.M.O or sigma orbital (σ).	(6) It is called ABMO or sigma star orbital (σ^*).

Filling of Electrons in Molecular Orbital:

The filling of electrons in the molecular orbital takes place according to the Auf-bau principle, Paul's exclusion principle and Hund's rule which are also applied in the filling of the atomic orbitals. The two electrons (one from each hydrogen atom), thus fill the low energy σ–orbital and have paired spin (↑↓) while high energy σ^* orbital remains empty.

Types of Overlapping:

There are two types of overlapping in molecular orbital theory;

(i) Head on approach (Linear overlapping)

(ii) Sideways approach (Parallel overlapping)

(i) Head on approach (Linear Overlapping):

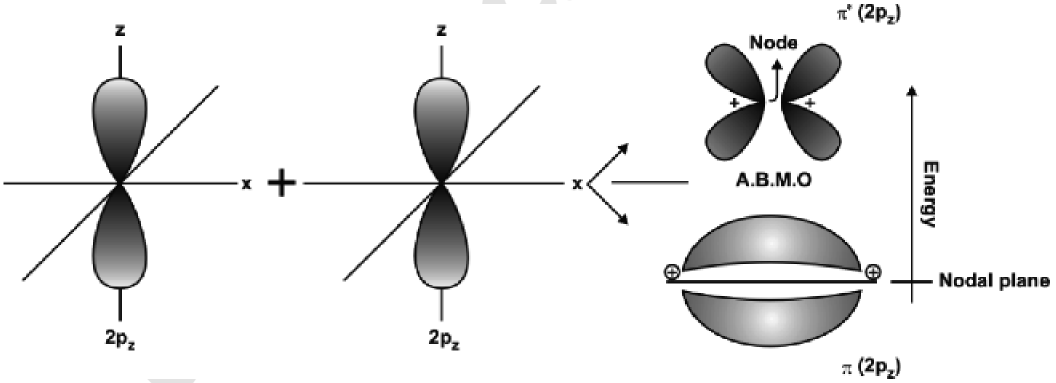
Head on approach can take place between S – S, S – P and p – p atomic orbitals. P – p linear overlap is discussed below.

When two s–atomic orbital overlap, they form two molecular orbitals. Molecular orbital of low energy than atomic orbital is called **σs**. Molecular orbital which has high energies than atomic orbital is called **σ^*s orbital**.

When two p–orbital overlap to each other, they form same number of molecular orbital. One molecular orbital has low energy than atomic orbital and are called **$\sigma\ p_x$** while molecular orbital of high energy is called **$\sigma^x\ p_x$**. In $\sigma\ p_x$ the electronic cloud is maximum between two nuclei.

(ii) Sideways approach or Parallel Overlap:

When the axes of two p–orbital (i.e. p_y or p_z orbital) are parallel to each other, they interact to form molecular orbital as shown in Figure.



The bonding molecular orbital $\pi\ (2p_y)$ or $\pi\ (2p_z)$ has zero electron density on the nuclear axis (called **the nodal plane**). The electron density is uniformly distributed above and below the nodal plane. On the other hand, $\pi^*\ (2p_y)$ or $\pi^*\ (2p_z)$ anti–bonding molecular orbital i.e. $\pi\ (2p_y)$ are also degenerate. So there are also the $\pi^*\ (2p_y)$ and $\pi^*\ (2p_z)$ molecular orbitals.

Overall six molecular orbitals (three bonding and three anti–bonding) are formed from two sets of 2p atomic orbitals. The bond formed as a result of linear overlap is σ bond while that formed as a result of sideways overlap is called a **π (pi) bond**. As there are three bonding molecular orbitals, the p–orbital overlaps can lead to the formation of at the most three bonds: one sigma and two pi–bonds.

Relative Energies of the Molecular Orbital:

The relative energy order for molecular orbital of homo–atomic molecule is given below. These energy levels of molecular orbital, are obtained from the spectroscopic studies.

Energy Order for Li_2, Be_2, C_2 and N_2:

$$\sigma(2s) < \sigma^*(2s) < \pi(2p_y) = \pi(2p_z) < \sigma(2p_x) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$$

Energy Order for O_2 and F_2:

$$\sigma(2s) < \sigma^*(2s) < \sigma(2p_x) < \pi(2p_y) = \pi(2p_z) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$$

Reason:

It has been observed that in case of B_2, C_2 and N_2 $\sigma\ 2p_x$ is higher in energy that $\pi\ 2p_y = \pi\ 2p_x$ molecular orbitals. This reversal is due to mixing of 2s and $2p_x$ atomic orbitals.

Actually the energy difference of 2s and 2p atomic orbitals is small. There is a possibility of mixing of these orbitals (i.e. hydrogen of A.O.) as a result of which σ_{2s} and σ^* 2s MOs do not retain pure s – character. Similarly, $\sigma\ 2p_x$ and $\sigma^*\ 2p_x$ MOs do not have pure p – character. All the four MOs acquire sp – character due to this mixing, their energy change in such a way that MOs σ 2s and σ^* 2s become more stable and are lowered in energy MOs as $\sigma\ 2p_x$ and $\sigma^*\ 2p_x$ become less stable and are raised in energy. Since, πp – orbital are not involved in mixing, so energy of $\pi\ 2p_y = \pi\ 2p_z$ remains unchanged. $\sigma\ 2p_x$ is raised to such an extend that it becomes higher in energy than π – bonding.

Anyhow, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 and 2078 kJ mol^{-1}, for O_2 and F_2, respectively. These values are 554 kJ mol^{-1} for boron, 846 kJ mol^{-1} for carbon and 1195 kJ mol^{-1} for nitrogen. These energy differences have been calculated by spectroscopic techniques.

BOND ORDER

"The number of bonds that exist between two atoms called **bond order**."

The bond order of diatomic molecules is define as one–half the difference between number of electrons in bonding orbital nb, and number of electrons in anti–bonding orbital na.

Mathematically,

$$\text{Bond order} = \frac{1}{2}(nb - na)$$

For H_2 which has two bonding electrons, we have

$$\text{Bond order} = \frac{1}{2}(2 - 0) = 1$$

Molecular Orbital Structure of Some Diatomic Molecules:

(i) Formation of H_2 Molecule:

The electronic configuration of hydrogen is $1s^1$. Two atomic orbitals of two hydrogen atoms overlap to form two molecular orbitals. The molecular orbital having low energy then $1s^1$ (atomic orbital) is called **σ** molecular orbital while that of high energy is called **σ^*** or **anti–bonding molecular orbital**.

Both the electrons are present in σ orbital (bonding molecular orbital) and σ^* orbital (anti–bonding molecular orbital) is empty.

Two hydrogen atoms combine to form H_2 and give stability of 436 kJ/mol^{-1}.

The bond order of H_2 is 1.

Bond order of $H_2^+ = 0.5$

$$\text{Bond order} = \frac{nb - na}{2} = \frac{2 - 0}{2} = 1$$

$$H\,(1s^1) + (H\,1s^1) \longrightarrow H_2\,[(\sigma\,1s)^2]$$

(ii) Helium, He:

The electronic configuration of He is $1s^2$. The 1s orbital of He–atoms combine to form one bonding molecular orbital σ (1s) and one anti–bonding molecular orbital σ^* (1s) orbital as shown in figure.

Each He–atom contributes two electrons. Two electrons enter bonding molecular orbital $\sigma\,(1s^2)$ and the remaining two go to anti–bonding σ^* (1s) molecular orbital. The bond order for He_2 is zero i.e. $\frac{(2-2)}{2} = 0$ and thus He_2, molecule is not formed.

(iii) Formation of N_2 Molecule:

Electronic configuration of N (7) $= 1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$

The valence shell electrons of two nitrogen atoms overlap to form N_2 molecule,

Out of outer ten electrons of both atoms, eight electrons are present in bonding molecular orbital while two electrons are present in anti–bonding molecular orbital.

Electronic configuration of N_2 molecule is

$[K\,K\,(\sigma\,2s)^2, (\sigma^*\,2s)^2, (\pi\,2p_y)^2, (\pi\,2p_z)^2, (\sigma\,2p_x)^2]$

$$\text{Bond order} = \frac{nb - na}{2} = \frac{6 - 0}{2} = 3.$$

There bonds are formed when two nitrogen atoms combine to form molecule, $(N \equiv N)$. The bond dissociation energy of N_2 is 941 kJ/mole which is very high.

(iv) Formation of O_2 Molecule:

Electronic configuration of O (8) $= 1s^{\uparrow\downarrow}, 2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z^{\uparrow}$

Two atoms of oxygen to form a molecule. Bond dissociation energy of a molecule is 496 kJ/mole. Each oxygen contribute six electrons from its valence shell to form O_2 molecules. Twelve electrons are present in molecular orbital. The arrangement of electrons is as follow.

Bond Order:

Eight electrons are present in bond and four electrons are present in anti–bonding.

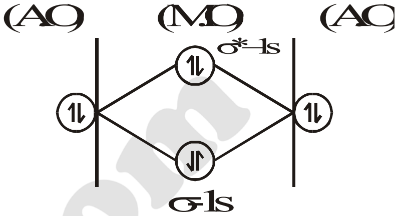
$$\text{Bond order} = \frac{nb - na}{2} = \frac{6 - 2}{2} = 2.$$

Electronic configuration of O_2 molecule is

$[K\,K\,(\sigma\,2s)^2, (\sigma^*\,2s)^2, (\sigma\,2p_x)^2, (\pi\,2p_y)^2, (\pi\,2p_z)^2, (\pi^*\,2p_z)^1, (\pi^*\,2p_y)^1]$

Due to the presence of two partially filled orbital ($\pi^* 2p_y$ and $\pi^* 2p_z$), O_2 molecule have paramagnetic behaviour. When two more electrons are given to O_2, it becomes O_2^{-2} and paramagnetism changes to diamagnetism. Similarly, when two electrons are removed from O_2, it changes to O_2^{+2} which is also diamagnetic in nature. Molecular orbital theory is superior in this respect than VBT or VSEPR. According to VBT O_2 molecule is diamagnetic, but actually liquid O_2 is paramagnetic in nature.

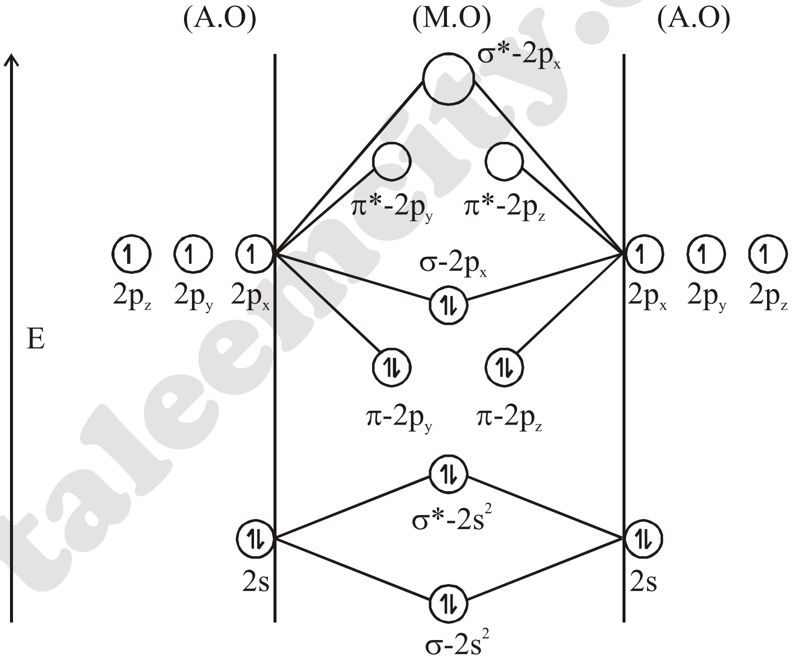
(1) $He_2 = 1s^2$



Bond order $= \dfrac{2-2}{2} = \dfrac{0}{2} = 0$

Since bond order for He_2-molecule is zero. Hence, it does not exist in nature.

(2) **Formation of N_2:** $N_7 = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$



Bond order $= \dfrac{8-2}{2} = \dfrac{6}{2} = 3$

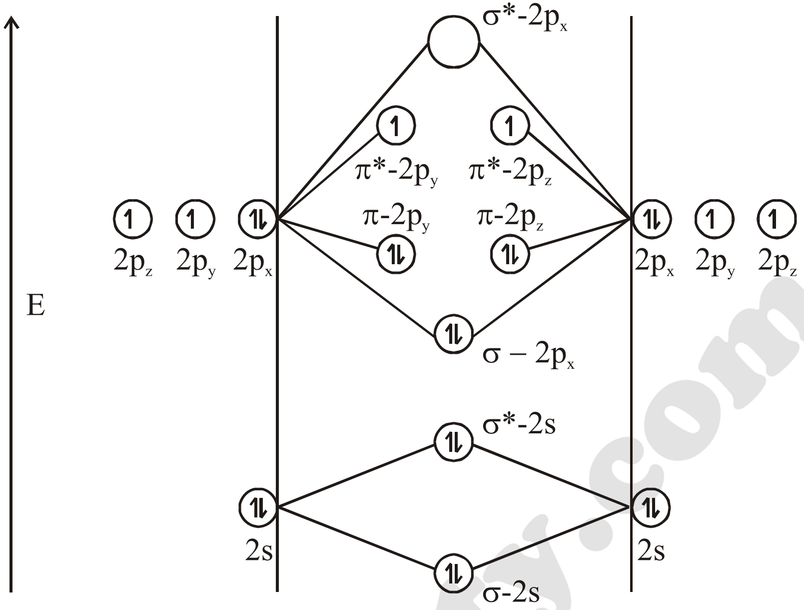
Bond order shows that there are three bonds between nitrogen atoms.

$\sigma - 2s < \sigma^*\text{-}2s < \pi\text{-}2p_y = \pi - 2p_z < \sigma - 2p_x < \pi^*\text{-}2p_y = \pi^* - 2p_z < \sigma^*\text{-}2p_x$

N_2-molecule is diamagnetic because it has no un-paired electrons in its antibonding molecular orbitals.

(3) **Formation of O_2:** O = $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z$

Molecular orbital diagram:



Bond order $= \frac{8-4}{2} = \frac{4}{2} = 2$

Two bonds between oxygen atoms.

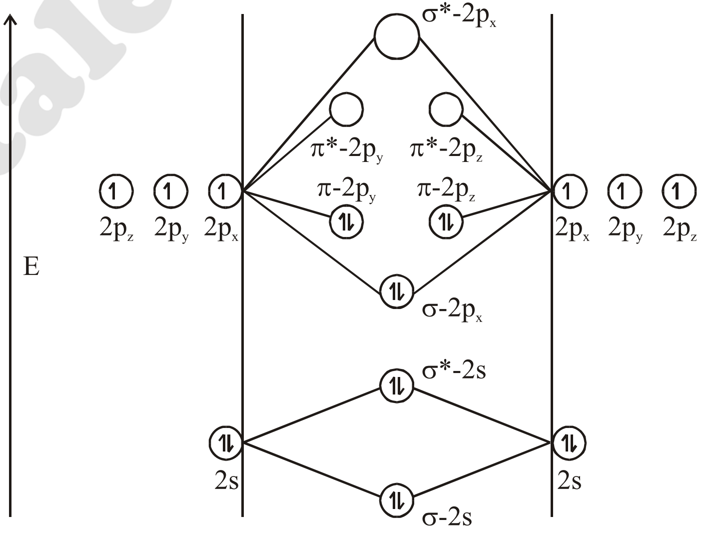
σ-2s < σ*-2s < σ-$2p_x$ < π-$2p_y$ = π-$2p_z$ < π*-$2p_y$ = π*$2p_z$ < σ*-$2p_x$

O_2-molecule is paramagnetic due to presence of unpaired electrons in antibonding molecular orbitals.

(4) O_2^{+2}

O_8^{+1} = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

Molecular orbital diagram:



$$\text{Bond order} = \frac{8-2}{2} = \frac{6}{2} = 3$$

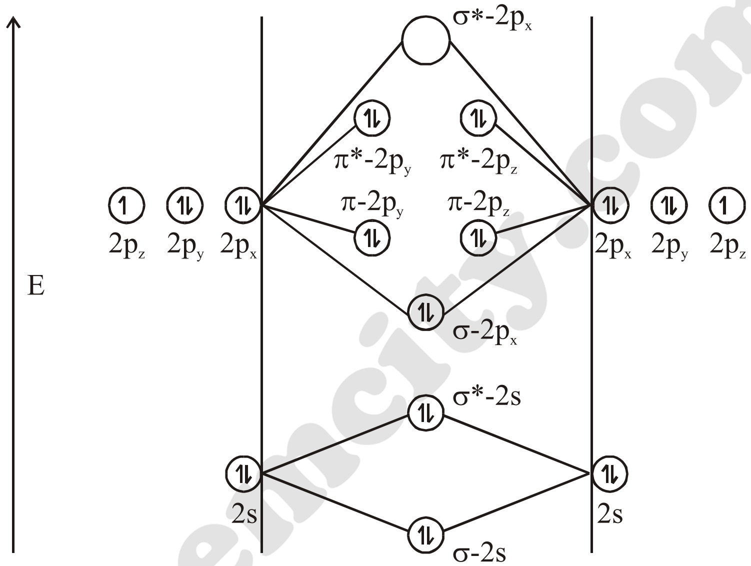
Three bonds between two O^{+1} ions in O_2^{+2}.

$\sigma 2s < \sigma^*\text{-}2s < \sigma\text{-}2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^*\text{-}2p_z < \sigma^*\text{-}2p_x$

Diamagnetic → No. unpaired electrons in antibonding molecular orbitals.

(5) O_2^{-2}

$O_8^{-1} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$



$$\text{Bond order} = \frac{8-6}{2}$$

$$= \frac{2}{2}$$

$$= 1$$

Only one bond between two O^{-1} ions in O_2^{-2}.

$\sigma\text{-}2s < \sigma^*\text{-}2s < \sigma\text{-}2p_x < \pi\text{-}2p_y = \pi\text{-}2p_z < \pi^*\text{-}2p_y = \pi^*\text{-}2p_z < \sigma^*\text{-}2p_x$

O_2^{-2}-molecule is diamagnetic. There are no unpaired electrons in antibonding molecular orbitals rather paired electrons are present.

O_2 is paramagnetic whereas O_2^{+2} and O_2^{-2} both are diamagnetic.

In case the molecular orbital diagram of O_2 there are two unpaired electrons in $\pi^*\text{-}2p_y$ and $\pi^*\text{-}2p_z$.

When O_2^{+2} is formed, then two unpaired electrons in π^*-$2p_y$ and π^*-$2p_z$ are removed. Hence, no unpaired electrons are left and specie is diamagnetic.

When O_2^{-2} is formed, then two more electrons are gained in π^*-$2p_y$ and π^*-$2p_z$. There orbitals are filled and now have paired electrons. Hence the specie is diamagnetic.

Difference between VBT and MOT:

Both valence bond theory (VBT) and molecular orbital theory (MOT) based upon the wave mechanics model.

According to valence bond theory, the atomic orbitals overlap to form a bond. The electron density is maximum between two nuclei or bond axis. The molecular orbital formed, do not lose their identity or shape. There is no concept of anti-bonding molecular orbital in VBT.

According to molecular orbital theory, atomic orbitals overlap to form bonding molecular and anti–bonding molecular orbital. The electron density is maximum in bonding region.

MOT explains the paramagnetic behaviour of O_2 while VBT do not. Difference between valence bond theory and molecular orbital theory can be explain well, by the diagram.

BOND ENERGY (BOND ENTHALPY)

"The amount of energy required to break all bonds of particular type in one mole of a substance is called **bond energy or bond enthalpy**."

When a bond is formed between two atoms, energy is released. The same amount of energy is required to break this bond. Bond breaking is an endothermic process. Bond energy is determined experimentally by measuring the heat involved in a chemical reaction. It is also called **bond enthalpy** as it is a measure of enthalpy change at 298 K. The enthalpy change in splitting a molecule into its component atoms is called **enthalpy of atomization**.

Units:

The bond energy is given in kJ mol^{-1} which is the energy required to break an Avogadro number (6.02×10^{23}) of bonds or the energy released when an Avogadro number of bonds are formed.

TABLE

(a) Average bond enthalpies of some important bonds (kJ mol^{-1}).

Bond	Bond energy (kJ mol^{-1})	Bond	Bond energy (kJ mol^{-1})	Bond	Bond energy (kJ mol^{-1})	Bond	Bond energy (kJ mol^{-1})
C – C	348	H – H	436	O – O	146	Si – H	323
C = C	614	H – F	567	O = O	495	Si – Si	226
C ≡ C	839	H – Cl	431	O – H	463	Si – C	301
C – H	413	H – Br	366	O – F	190	Si – O	368
C – N	293	H – I	299	O – Cl	203	F – H	155

C = N	615	N – N	163	O – I	234	Cl – F	253
C ≡ N	891	N = N	418	S = S	266	Cl – Cl	242
C – O	358	N ≡ N	941	S = O	418	Br – F	237
C = O	799	N – H	391	S – H	523	Br – Cl	218
C ≡ N	1072	N – O	201	S – F	339	Br – Br	193
C – F	485	N – F	272	S – Cl	327	I – Cl	208
C – Cl	328	N – Cl	200	S – Br	253	I – Br	175
C – Br	276	N – Br	243		218	I – I	151
C – I	240						
C – S	259						

(b) Bond energies of multiple bonds in kJ mol^{-1}.

$H_2C = CH_2$	614	C = N	615	C = O	707	HN = NH	456	O = O	494
HC ≡ CH	839	HC ≡ N	937	N ≡ N	945				

Bond Energy and Multiple Bonds:

Bond energies for double and triple bonds between two atoms are generally higher than those for the single bond, between same two atoms.

But double bond is not, in general, twice as strong as a simple bond. For example bond energy for carbon – carbon are shown below.

C – C	(single bond)	348 kJ mol^{-1}
C = C	(double bond)	614 kJ mol^{-1}
C ≡ C	(triple bond)	839 kJ mol^{-1}

Bond energy and polarity or strength of bond and ionic characters:

Polar bonds are stronger than non–polar bonds and greater amount of energy is required to break these bonds. Due to the ionic characters, the strength of bond increases. Increase in strength of H – Cl bond can be calculate from the given data.

(i) Bond energy of H_2 is 436 kJ mol^{-1}

$$H_2 \xrightarrow{\qquad} H + H \qquad \Delta H = 436 \text{ kJ mol}^{-1}$$

1 mole of $H_2 = 6.02 \times 10^{23}$ molecules of $H_2 = 436$ kJ.

$$\text{Bond energy for one molecule of } H_2 = \frac{436}{6.02 \times 10^{23}} = 7.2 \times 10^{-22} \text{ kJ}$$

$$\text{Bond energy for one H–atom} = \frac{7.2 \times 10^{-22}}{2} = 3.6 \times 10^{-22} \text{ kJ}$$

(ii) Bond energy of Cl_2 is 240 kJ per mole

$Cl_2 \xrightarrow{\hspace{2cm}} Cl + Cl \quad \Delta H = 240\ kJ\ mol^{-1}$

1 mole of Cl_2 = 6.02×10^{23} molecules of Cl_2 = 240 kJ.

Bond energy for one molecule of $Cl_2 = \dfrac{240}{6.02 \times 10^{23}} = 3.986 \times 10^{-22}$ kJ

Bond energy for one Cl–atom $= \dfrac{3.986 \times 10^{-22}}{2} = 1.993 \times 10^{-22}$ kJ

(iii) The bond energy of HCl from above data

$H + Cl \xrightarrow{\hspace{2cm}} HCl$

$3.6 \times 10^{-22} + 1.993 \times 10^{-22} = 5.93 \times 10^{-22}$ kJ

The amount of energy for one mole of HCl molecule.

Energy of one mole HCl $= 5.93 \times 10^{-22} \times 6.02 \times 10^{23} = 356\ kJ\ mol^{-1}$

It is the calculate amount of energy of HCl while H_2 and Cl_2 and both one non–polar in nature.

The experimentally found bond energy of HCl is 431 kJ mol^{-1}. The observed bond energy is significantly greater than the calculated value and that means a more stable H – Cl bond. This stability is due to the ionic character present in the molecule.

FACTORS AFFECTING THE BOND STRENGTH

Bond energy is a measure of the strength of a bond. The strength of a bond depends upon.

(i) Electro–negativity
(ii) Size of the atoms
(iii) Bond length

(i) Electro–negativity

Bond strength is high if the electro–negativity difference between bonded atom is greater. Let us consider H – X type of bond (x = F, C, Br or I). In such bonds, the electro–negativity of halogen is greater than hydrogen and shared electron pair is not equally attracted. Ionic characters one developed in all these bonds.

$H^{\delta+} - F^{\delta-}$, $H^{\delta+} - Cl^{\delta-}$, $H^{\delta+} - Br^{\delta-}$, $H^{\delta+} - I^{\delta-}$

Due to these ionic characters, there is difference between observed bond energies and calculated bond energies. Observed values are greater than the calculate values of bond energies. This difference is high in HF (271 kJ) and less in HI (8 kJ) as show in the Table.

We can say that HF has more ionic character than HI. The decreasing polarity trend from HF to HI shows a trend toward equal sharing of electrons which is consistent with decreasing electro–negativity from F to I. A knowledge of bond energies is useful for calculating heat of gaseous reaction involving covalent bonds.

TABLE

Bond Energies of H – X Molecules

Bond	**Bond**	**Energies**	**(kJ mol^{-1})**	
	X = F	X = Cl	X = Br	X = I
X – X	155	242	193	151
H – X (Calculated)	293	336	311	291
H – X (Observed)	567	431	366	299
Difference	274	95	55	8

(ii) Size of atom:

Bond energies decrease by increasing the size of atoms. For example, bond energy of Cl_2 is 240 kJ mol^{-1} while that of I_2 is 151 kJ mol^{-1}.

(iii) Bond length:

By decreasing bond length, the bond energy increases. For example, bond energies of C – C bonds increases by decreasing bond length.

Bond length (pm)		**Bond energy (kJ mol^{-1})**
C – C	154	348
C = C	133	614
C ≡ C	120	839

"The distance between the nuclei of two atoms forming a covalent bond is called **the bond length**."

The bond lengths are experimentally determined by physical techniques e.g. electron diffraction, X–ray diffraction or spectral studies.

The covalent bond length between two atoms is often not always independent of the nature of the molecules. For example, in most the aliphatic hydrocarbons, the C – C bond length is very close to 154 pm. The C – C bond length is also found to be the same in diamond.

The covalent radii for different elements are almost **additive** in nature. The single bond covalent radius of carbon is 77 pm which is half of the C – C bond length (154 pm). Similarly, the covalent radius of Cl is 99 pm i.e. one half of the Cl – Cl bond length (198 pm). Some selected bond lengths are given in Table.

TABLE

Compound	Bond	Bond Length (pm)
BF_3 Boron tri–fluoride	B – F	130
BCl_3 Boron tri–chloride	B – Cl	175
SiH_4 Silane	Si – H	148
SiF_4 Silicon tetra–fluoride	Si – F	155
C_2H_6 (Ethane)	C – C	154
C_2H_4 (Ethene)	C = C	133
C_2H_2 (Ethyne)	C ≡ C	120
$(CH_3)_2 - C = O$ (Acetone)	C = O	122

FACTORS AFFECTING THE BOND LENGTH

Bond length depends upon the following factor.

(i) Atomic size
(ii) Difference of electro–negativity
(iii) Hybridization involved

(i) Atomic Size (Trend in Periodic Table):

"By increasing size of the atom, bond length increases."

The **bond length increases** as we move from top to bottom in a **group** of the Periodic table. Thus Si – Si bond length is more than C – C bond length and P – P bond length is much more than N – N bond length. As the atomic radii increase in a group (N to P or C to Si), the effect of the effective nuclear charged decreases on electrons. As a result the bond length will increase.

In the **Periodic table**, **shortening of bond** lengths occur from left to right in a period. This can be attributed to the pull by nuclear charge with the same value of (principal quantum number). Therefore, C – C bond length is greater than N – N bond length.

(ii) Difference of Electro–negativity:

With an increase in electro–negativity difference between the bond atoms, the bond becomes shortened and departure from additively of bond lengths takes place. For example, Si – F bond length in SiF_4 is found to be 154 – 159 pm whereas the addition of their covalent radii (Si = 117 pm and F = 64 pm) give Si – F bond length to be equal to 181 pm. Calculated values of bond length is always higher due to electro–negativity difference. By increasing the ionic characters, shortening in bond lengths take place due to greater attraction.

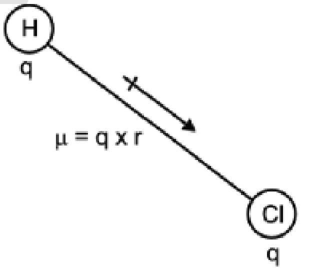
(iii) Type of Hybridization:

Hybridization involved also explains the shortening of bonds due to the predominant participation of s–orbital. Since the 2s–orbital of carbon has smaller mean radius than the 2p–orbital, it would be expected that greater the s–character in the hybrid orbital used, the shorter will be the bond distance. Thus the C – C bond lengths are 154, 133 and 120 pm for ethane, ethene and ethylene respectively where s–orbital contribution increases from sp^3 to sp. Further π–bonding also reduces the inter nuclear bond distance.

DIPOLE MOMENT

"The product of electric charge (q) on either end of a polar bond and the distance (r) between them, is called **dipole moment**."

In hetero nuclear molecules e.g. HCl where the bonded atoms are of different elements, the molecule becomes polar due to the electro–negativity difference. Partial positive and negative charges become separated on the bonded atoms. The separation of these charges on the molecule is called a **dipole** and the molecule is said to have a dipole moment.



Dipole moment and its vector representation

The dipole moment is a **vector quantity** which has a magnitude as well as a direction. The direction of dipole moment is from positive toward negative and represented by an arrow.

Mathematically,

Dipole moment = charge x distance

$$\mu = q \times r$$

If the molecule is poly atomic and contains two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments. For examples of CO_2 and H_2O are shown in Figure.

(a) Resultant moment (b)

Vector addition of bond moment in (a) linear CO_2 molecule and (b) angular molecule H_2O

Unit:

The unit of dipole moment is **Debye**. The SI unit of dipole moment is coulomb x meter or C_m.

$1D = 3.336 \times 10^{-30}$ C.m

$1D = 10^{-18}$ esu. C.m

For example, for an electron separated from a unit positive charge 1.6022×10^{-19} C and distance r = 100 pm, the dipole moment will be

$$\mu = q \times r$$

$$= (1.6022 \times 10^{-19})\ C \times 100 \times 10^{-12}\ m$$

$$= 1.6022 \times 10^{-29}\ C.m$$

Where 1 pm = 10^{-12} m

$$\text{So } \mu \text{ in Debye} = \frac{1.6022 \times 10^{-29}}{3.336 \times 10^{-30}\ C.m} = 4.8\ D$$

$\mu = 4.8$ D

TABLE

Dipole Moments of Some Substances

Compound	Dipole Moment (D)	Compound	Dipole Moment (D)
HF	1.90	CO	0.12
HCl	1.08	NO	0.16
HBr	0.78	H_2O_2	2.2
HI	0.38	CH_4	0.00
H_2O	1.85	CH_3F	1.81
H_2S	1.95	CH_3Cl	1.45
NH_3	1.49	CH_3Br	1.85
SO_2	1.61	CH_3I	1.35
CO_2	0.00	C_2H_5OH	1.69

Dipole Moments and Molecular Structure:

Dipole moment provides two types of information about the molecular structure:

(1) Percentage ionic character of a bond.

(2) Angles between the bonds or the geometry of molecules.

(1) Percentage Ionic Character:

From the experimentally determined dipole moments, the percentage ionic character in a bond can be calculated. The percentage ionic characters of H – F, H – Cl, H – Br and H – I bonds are 43, 17, 12 and 5 respectively. If value of dipole moment is zero, bond is 100% covalent and ionic character are absent.

$$\text{\% age ionic characters} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

Example:

The observed dipole moment of HF is 1.90 D. Find the percentage ionic character in H – F bond. The distance between the charges is 0.917×10^{-10} m.

(Unit positive charge = 1.6022×10^{-19} C).

Solution:

% ionic character:
HF = 43%
HCl = 17%
HBr = 12%
HI = 5%

Let the hypothetical ionic model of the acid be $\overset{+}{H}\overset{-}{F}$, then

$$\mu_{\text{ionic}} = q \times r$$
$$= (1.6022 \times 10^{-19}\ \text{C})\ (0.917 \times 10^{-10}\ \text{m})$$
$$= 1.469 \times 10^{-29}\ \text{C.m}$$

Since $1\text{D} = 3.336 \times 10^{-30}$ C.m

$$\mu_{\text{ionic}} = \frac{1.469 \times 10^{-29}\ \text{C.m}}{3.336 \times 10^{-30}\ \text{C.m}} = 4.4\ \text{D}$$

$$\mu_{\text{ionic}} = 4.4\ \text{D}$$

$$\text{\% ionic character} = \frac{\mu_{\text{observed}} \times 100}{\mu_{\text{ionic}}}$$
$$= \frac{1.90\ \text{D} \times 100}{4.4\ \text{D}} = 43.2\ \%$$

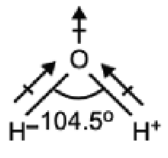
(2) Bond Angles or the Geometry of Molecules

Dipole moment is helpful to determine the shapes of the molecules.

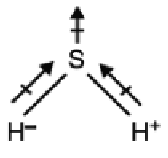
For example:

(i) Water Molecule:

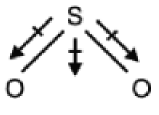
The dipole moment of water is 1.85 D which rules out the linear structure. The calculations show that there is an angular structure with a bond angle 104.5 between the two O – H bonds.



μ = 1.85 D



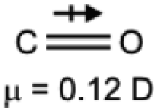
μ = 0.95 D

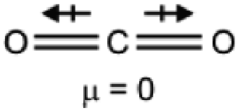


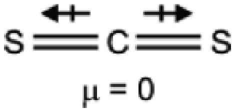
μ = 1.61 D

(ii) CO and CO_2:

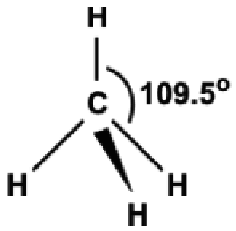
CO has a dipole moment while CO_2 does not have any dipole moment. The reason is that CO_2 has a linear structure where the dipoles being equal and opposite, cancel out each of other's effect.

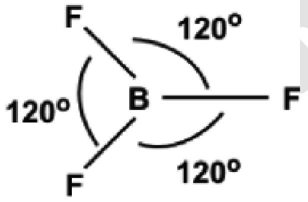






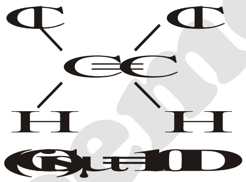
Symmetrically triangular planar molecules of BF_3, AlF_3 and $AlCl_3$ have zero dipole moment. Perfectly tetrahedral molecules like CH_4, SiH_4 and CCl_4 also have zero dipole moment.

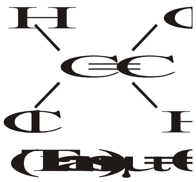




(iii) Identification of Cis and Trans Structures:

Dipole moment is helpful to determine the geometrical isomers (cis-trans). For example, cis-1,2 dichloroethene has dipole moment of 1 D while trans form has zero dipole moment.





EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

Physical and chemical properties of substances depend upon the types of bonding present in them. Properties of some ionic and covalent compounds are given below.

(1) Solubility:

(a) Solubility of Ionic Compounds:

Mostly ionic compounds are **soluble in water** but insoluble in non–aqueous solvents. When a crystal of an ionic substance is placed in water, the polar water molecules detach the cation and anion from the crystal lattice by their electrostatic attraction. Thus the ions are freed from the crystal lattice by hydration. This happens when the hydration energy is greater than the lattice energy. The energy given up in hydration is used to overcome the lattice energy and the ions are freed from their positions in the crystal. Many ionic compounds do not dissolve in water as the attraction of water molecules cannot overcome the attraction between the ions. For the same reasons, non–polar solvents like benzene and hexane do not dissolve ionic compounds.

(b) Solubility of Covalent Compounds:

In general, covalent compounds dissolve easily in non–polar organic solvents (benzene, ether etc). Here the attractive forces of solvent molecules are enough for overcoming the intermolecular forces of attraction. Mostly covalent compounds are **insoluble in water**. However, some of them like glucose, sucrose urea etc dissolve in water due to hydrogen bonding.

Hydration Energy:

"The amount of energy released when isolated ions are hydrated, is called **hydration energy**."

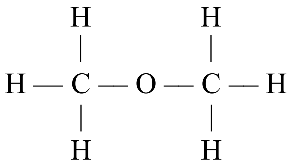
(2) Isomerism:

(a) Non–directional Nature of Ionic Bonds:

The ionic bond involves electrostatic lines of forces between oppositely charged ions. Therefore, such bonds are non–rigid and non–directional. Because of this, ionic compounds do not exhibit the phenomenon of isomerism.

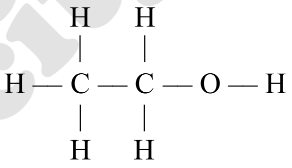
(b) Directional Nature of Covalent Bond:

Covalent bonds are rigid and directional. This leads to the possibility of a variety of isomerism. For example, structural isomerism is shown by the compound, C_2H_6O.



$$H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-H$$

Diethyl ether



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$

Ethanol

(3) Reaction Kinetics:

(a) Speed of Reaction of Ionic Compounds:

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occur rapidly. For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously. The reaction is rapid because on mixing the solutions, no bonds have to be broken, only a new bond is formed. The ions have already been broken while forming their aqueous solutions.

$$Ag^{+}_{(aq)} + NO^{-}_{3(aq)} + Na^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)} + Na^{+}_{(aq)} + NO^{-}_{3(aq)}$$

(b) Speed of Covalent Compounds:

Since there is no strong electrical force to speed up a chemical reaction (like in ionic reaction), the covalent bonds are generally much slower to react as they involve both breaking and making of bonds. The molecules undergo a chemical change as a whole. Covalent compounds react in a variety of ways and their reactivity depends upon the way a reaction proceeds and the kind of product we obtain at the end of a reaction.

EXERCISE

Q.1 Select the correct statements:

(i) An ionic compound A^+B^- is most likely to be formed when:

(a) The ionization energy of A is high and electron affinity of B is low

(b) The ionization energy of A is low and electron affinity of B is high

(c) Both the ionization energy of A and electron affinity of B are high

(d) Both the ionziation energy of A and electron affinity of B are low

(ii) The number of bonds in nitrogen molecule are:

(a) One σ and one π (b) One σ and two π

(c) Three sigma only (d) Two σ and one π

(iii) Which of the following statement is not correct regarding bonding molecular orbitals?

(a) Bonding molecular orbitals possess less energy than atomic orbitals from which they are formed

(b) Bonding molecular orbitals have low electron density between the two nuclei

(c) Every electron in the bonding molecular orbitals contributes to the attraction between atoms

(d) Bonding molecular orbitals are formed when the electron waves undergo constructive interference

(iv) Which of the following molecule has zero dipole moment?

(a) NH_3 (b) $CHCl_3$

(c) H_2O (d) BF_3

(v) Which of the hydrogen halides has the highest percentage of ionic character?

(a) HCl (b) HBr

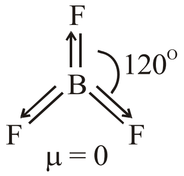
(c) HF (d) HI

(vi) Which of the following species has unpaired electrons in the antibonding molecular orbitals:

(a) O_2^{+2} (b) N_2^{-2}

(c) B_2 (d) F_2

ANSWERS

Answers		Reasons
(i)	(b)	For ionic bond formation, one atom 'A' should have low ionization energy that can easily lose electron and second atom 'B' should be with high electron affinity that can easily gain electron. This is Lewis concept.
(ii)	(b)	Bond order for N_2 molecule is three. It means three bonds between two nitrogen atoms. One bond between two atoms can be sigma, rest two bonds are always Pi. Hence, there is one σ and two π bonds in N_2 molecule. 
(iii)	(b)	According to MOT, atomic orbitals overlap to form molecular orbitals. One with low energy than atomic orbitals and high electron density. It is called bonding molecular orbital. It is responsible for the attraction between two atoms. The other one with high energy than atomic orbitals and low electron density. It is called antibonding molecular orbital. It is responsible for repulsion between atoms. It is also believed that bonding molecular orbital is formed due to constructive interference of electron wave whereas antibonding molecular orbital is formed due to destructive interference of electron wave.
(iv)	(d)	In case of BF_3, all the bond angles are of 120° and geometry is perfectly trigonal planner. Due to which all the dipole moments mutually cancel each other and resultant is zero.  In case of NH_3, the bond angle is 107.5° instead of 109.5°. Hence all the dipole moments are not cancelled and resultant is not zero ($\mu = 1.49D$). In case of $CHCl_3$, different atoms are attached to carbon atom. Dipole moments are not cancelled out and dipole moment is not zero ($\mu = 1.45$). In case of H_2O, geometry is angular due to which individual dipole moments add up and resultant is not zero ($\mu = 1.85D$).
(v)	(c)	Percentage ionic character depends upon (i) ΔEN and (ii) μ of the molecule. HF molecule has greatest value of $\Delta EN = 1.9$ and highest value of $\mu = 1.90$ D. Hence its percentage ionic character is highest amongst HF, HCl, HBr and HI. HFΔEN $= 4.0 - 2.1 = 1.9$ HCl ΔEN $= 3.0 - 2.1 = 0.9$ HBr ΔEN $= 2.8 - 2.1 = 0.7$ HI ΔEN $= 2.5 - 2.1 = 0.4$ Hence, order of percentage ionic character is: HF > HCl > HBr > HI

(vi) (b)	According to molecular orbital diagram of O_2, there are two unpaired electrons in antibonding molecular orbital. When O_2^{+2} is formed, two unpaired electrons from antibonding molecular orbitals are removed. No unpaired electron is left. The molecular orbital diagram of N_2 shows that it has no unpaired electrons in antibonding molecular orbitals. When N_2^{-2} is formed, it gains two unpaired electrons in its antibonding molecular orbitals. The molecular orbital diagram of B_2 is same as that for N_2. It also have two unpaired electrons but in bonding molecular orbital (π-$2p_y$ and π-$2p_z$). But F_2 has paired electrons in antibonding molecular orbitals.

Q.2 Fill in the blanks:

(i) The tendency of atoms to attain maximum of ———— electrons in the valence shell is called completion of octet.

(ii) The geometrical shape of $SiCl_4$ and PCl_3 can be explained on the basis of ———— and ———— hybridizations.

(iii) The VSEPR theory stands for ————.

(iv) For N_2 molecule, the energy of σ ($2P_x$) orbital is ———— than π ($2P_y$) orbital.

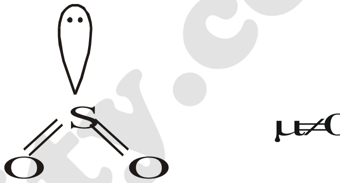
(v) The paramagnetic property of O_2 is well explained on the basis of MO theory in terms of the presence of ———— electrons is two antibonding molecular orbitals.

(vi) The values of dipole moment for CS_2 is ———— while for SO_2 is ————.

(vii) The bond order of N_2 is ———— while that of Ne_2 is ————.

ANSWERS

Answers	**Explanation**
(i) Eight	Elements form bond in order to attain the configuration of nearest noble gas. Since all the noble gases except He have eight electrons in the valence shell. Hence this tendency is called octet (octet rule).
(ii) $sp^3 - sp^3$	Excited state configuration of $Si_{14} = 1s^2, 2s^2, 2p^6, 3s^1, 3p_x^1, 3p_y^1, 3p_z^1$. Four valence electrons undergo sp^3-hybridization. These sp^3-orbitals will overlap with $3p_z$ orbitals of four Cl-atoms separately to form $SiCl_4$ with tetrahedral geometry. Electronic configuration of $P_{15} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$. Four valence orbitals undergo sp^3-hybridization with lone pair in one sp^3-orbital. The rest of three sp^3-orbitals

(iii)	Valence shell electron pair repulsion theory	It explains the geometry on the basis of repulsion between electron pairs in the valence shell of the central atom.
(iv)	Greater	In case of N_2 molecules, the energy difference between σ-$2p_x$ and $\pi 2p_y$ and $\pi 2p_z$ σ^*-2s is very small. As result of this σ-$2p_x$ is raised above the $\pi 2p_z$ to avoid repulsion.
(v)	Unpaired	There are two unpaired electrons in antibonding molecular orbitals π^*-$2p_y$ and π^*-$2p_z$ of M.O diagram of O_2-molecule. Due to which it is paramagnetic.
(vi)	Zero, 1.61 D	The two dipole moments in CS_2 molecule are cancelled out due to its linear geometry. And resultant is zero.  The geometry of SO_2 is angular, due to which individual dipole moments are not cancelled and resultant dipole moment is not zero. 
(vii)	Three, zero	The MO diagram of N_2-molecule shows that its bond order is three and that for Ne_2 molecule is zero. (Also, for all the noble gases is zero).

Q.3 Classify the statements as true or false. Explain the reason.

(i) The core of an atom is the atom minus its valence shells.

(ii) The molecules of nitrogen ($N \equiv N$) and acetylene ($HC \equiv CH$) are not isoelectronic.

(iii) There are four co-ordinate covalent bonds in NH_4^+ ions.

(iv) A σ-bond is stronger than a pi-bond or π-bond and the electrons of σ-bond are more diffused then π-bond.

(v) The bond energy of heteroatomic diatomic molecules increases with the decrease in the electronegativities of the bonded atoms.

(vi) With increase in bond order, bond length decreases and bond strength increases.

(vii) The first ionization energies of the elements rise steadily with the increasing atomic number from top to bottom is a group.

(viii) A double bond is stronger than a single bond and a triple bond is weaker than a double bond.

(ix) The bonds formed between the elements having electronegativity difference more than 1.7 are said to be covalent in nature.

(x) The repulsive force between the two bonding pairs is less than that between the two lone pairs.

(xi) The number of covalent bonds that an atom can form is related to the number of unpaired electrons it has.

(xii) The rules which govern the filling of electrons into the atomic orbitals also govern filling of electrons into the molecular orbitals.

ANSWERS

Answers	Correct Statement
(i) True	The nucleus and electronic shell of an atom excluding the valence shell is called core of atom.
(ii) False	The molecules of nitrogen (N_2) and acetylene ($HC \equiv CH$) are isoelectronic. For $_7N$ = 7 electrons N_2 molecule contains = 7×2 = 14 electrons For $CH \equiv CH$ $_6C$ = 6 electrons $2C$ = 6×2 = 12 electrons H = 1 electron $2H$ = 1×2 = 2 electrons $CH \equiv CH$ = 14 electrons Both the species N_2 and $CH \equiv CH$ has 14 electrons each and are called isoelectronic i.e., the species that have same number of electrons.
(iii) False	There are three covalent bonds and one co-ordinate covalent bond in NH_4^+. Nitrogen forms three covalent bonds with three hydrogen atoms separately still it has lone pair which it use to make coordinate covalent bond with fourth hydrogen (H^+) and it results in NH_4^+. After the coordinate covalent bond formation the three covalently bonded hydrogens coordinates 25% of their shared pair to nitrogen. As result of that, nature of all the four bonds becomes same i.e., 25% coordinate covalent and 75% covalent. Hence, the distinction between covalent and coordinate covalent bond vanishes.
(iv) False	A σ-bond is stronger than π-bond and electrons of π-bond are more diffused than σ-bond. σ-bond is formed by linear overlapping and π-bond is formed by parallel overlapping of atomic orbitals. Extent of linear overlapping is greater than parallel one. According to VBT, greater the overlapping, stronger is the bond form. Hence σ-bond is stronger than π-bond. π-bond is more diffused because its electronic cloud is above and below the inter-nuclear axis. Electronic cloud of σ-bond is around the inter-nuclear axis. Hence less diffused.
(v) False	The bond energy of heterodiatomic molecules decreases with the decrease in electronegativity difference of the bonded atoms. When electronegativity difference of the bonded atoms is less, it shows less polarity and weaker bond. Hence bond energy will be less (because bond strength increases with increasing polarity).
(vi) True	For example, we consider $C - C$, $C = C$, $C \equiv C$. The bond order is 1, 2 and 3 and bond length is 154 pm, 134 pm and 120 pm respectively. Also $C \equiv C$ is stronger than $C = C$ which is in turn stronger than $C - C$. Above given comparison of data shows that with the increasing bond order, bond length decreases and bond strength increases.

(vii)	False	The first ionization energies of the elements fall steadily with the increasing atomic number from top to bottom. As we move down the group, the value of ionization energy decreases due to increasing shielding effect and decreasing nuclear force.
(viii)	False	Double bond is stronger than single bond and tripple bond is stronger than double bond. Greater the number of bonds between the two atoms, greater will be the strength. Hence, order of strength of C – C, C = C, C ≡ C bond is $C \equiv C > C = C > C - C$
(ix)	False	A bond formed between the elements having electronegativity difference more than 1.7 are said to be ionic in nature. This is based on Pauling's formula e.g., NaCl. The electronegativity of Na is 0.9 and that for Cl is 3 and difference is 2.1. Hence, bond is ionic.
(x)	True	The lone pair-lone pair repulsion is greater. Lone pair being under the influence of one nucleus occupies more space and causes more repulsion. The bond pair being under the influence of two nuclei occupies less space and causes less repulsion.
(xi)	True	Valency of an atom (no. of bonds that it can form) is equal to number of unpaired electrons in the valence shell. e.g., $O_8 = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. It has two unpaired electrons in the valence shell. Hence, it can form two covalent bonds. e.g., H_2O.
(xii)	True	Electrons are distributed in molecular orbitals in increasing order of their energy. If degenerate orbitals are available and more than one electron is to be distributed then maximum number of electrons will remain unpaired with same spin. This is according to the rules of electronic distribution.

Q.4 What is a chemical bond? Discuss the formation of ionic and covalent bonds. How does the electronegativity differences differentiate between ionic and covalent bond?

Ans. **Chemical Bond:** The chemical force that holds the two or more than two atoms, ions or molecules together in a compound is called chemical bond.

It may be ionic, covalent or coordinate covalent.

Formation of Ionic Bond: It is formed by the transfer of electrons from one atom of low ionization energy to another atom of high electron affinity.

After the transfer of electron, both the atoms get oppositely charged and are held together by electrostatic force called ionic bond e.g.

1. Formation of NaCl:

$$Na \longrightarrow Na^{+}_{(g)} + 1e^{-} \qquad (496\ kJ/mol)$$

$$Cl + 1e^{-} \longrightarrow Cl^{-}_{(g)} \qquad (-349\ kJ/mol)$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow NaCl_{(s)} \qquad (-787\ kJ/mol)$$

2. Formation of CaO:

$$Ca \longrightarrow Ca^{+2} + 2e^-$$

$$O + 2e^- \longrightarrow O^{-2}$$

$$Ca^{+2} + O^{-2} \longrightarrow CaO$$

Formation of Covalent Bond: A covalent bond is formed by mutual sharing of unpaired electrons between two bonded atoms e.g., H × H or H – H. Both H-atoms have one unpaired electron each, which they share with each other to form covalent bond.

Covalent bond may be:

(i) Single = formed by mutual sharing of $1e^-$ pair e.g., H – H.

(ii) Double = formed by mutual sharing of $2e^-$ pairs e.g., O = O.

(iii) Triple formed by mutual sharing of $3e^-$ pairs e.g., N ≡ N.

Differentiation between Covalent and Ionic Bond by Electronegativity Difference: If the electronegativity difference between the bonded atoms is 1.7 or below, than bond will be covalent e.g., HCl, E.N (H) = 2.1, E.N (Cl) = 3 and ΔE.N = 0.9. This bond in HCl is covalent. In CH_4 ΔE.N = 0.4. Hence bonds are covalent.

If the electronegativity difference between the two bonded atoms is greater than 1.7, then bond will be ionic. e.g., NaF, E.N (Na) = 0.9 and E.N (F) = 4. The ΔE.N is 3.1 and bond is ionic. Other examples are LiF, LiCl, NaCl, KF, $CaCl_2$ etc.

Q.5 (a) Define ionization energy and electron affinity. How these quantities change in the periodic table. What factors are responsible for their variation?

(b) Explain what do you understand by the term electronegativity? Discuss its variations in the periodic table. How does it affect the bond strengths?

Ans.

(a) **Ionization Energy:** The amount of energy required to remove the most loosely bonded electron from valence shell of an isolated gaseous atom is called ionization energy.

$$Mg + Heat \longrightarrow Mg^{+1} + 1e^{-1} \qquad \Delta H = 738 \text{ kJ/mol}$$

Trend: Variation in periodic table.

1. **Period:** The value of ionization energy increases from left to right in the period due to increasing nuclear force. As we move from left to right in a period, nuclear charge increases with increasing proton number and size decreases. Due to which electrons become more tightly bound and difficult to remove. Hence, ionization energy increases.

2. **Group:** Ionization energy decreases from top to bottom in a group due to increasing atomic size and shielding effect. Due to addition of shells down the group, valence electrons become away from the nucleus and are loosely bound and easier to remove. Hence, ionization energy decreases down the group.

Factors (responsible for variation):

1. Atomic size (ionization energy increases with decreasing size and vice versa).
2. Nuclear charge (ionization energy increases with increasing nuclear charge and vice versa).
3. Shielding effect (ionization energy decreases with increasing shielding effect and vice versa).
4. Nature of orbital ionization energy is in the order of s > p > d > f.

Electron Affinity: The amount of energy released when an electron is added to the valence shell of an isolated gaseous atom is called electron affinity.

$$Cl_{(g)} + 1e^- \longrightarrow Cl^- + \text{Heat} \qquad (\Delta H = -349 \text{ kJ/mol})$$

Trends (variation in the period table):

1. Period: Electron affinity increases with the increasing nuclear charge in the period from left to right. In a period, nuclear charge increases and size decreases. Due to which attraction between nucleus and valence electron increases. Hence, value of electron affinity increases.
2. Group: Electron affinity decreases down the group due to increasing size and shielding effect. One to successive addition of shell down the group, attraction between nucleus and valence electron decreases. Hence, value of electron affinity also decreases.

Factors (responsible for the change):

1. Atomic size is inversely related to electron affinity.
2. Nuclear charge is directly related to electron affinity.
3. Shielding effect is inversely related to electron affinity.

(b) **Electronegativity:** The tendency of an atom to attract shared pair of electron towards itself is called electronegativity.

The comparison of electronegativity of the bonded atoms determines the properties of molecules (polar or non-polar) or compound is covalent or ionic.

If the ΔE.N of the bonded atoms is equal to or less than 1.7, the compound will be covalent otherwise ionic e.g., LiCl (ΔE.N = 2) is ionic compound and H_2O (ΔE.N = 1.4) is a covalent compound.

For covalent compounds, if ΔE.N is zero or less than 0.5 the compound will be non-polar covalent e.g., CH_4 (ΔE.N = 0.4), H_2 (ΔE.N = 0). And if the ΔE.N is greater than 0.5 and equal to or less than 1.7, then the compound will be polar covalent e.g., HCl (ΔE.N = 0.9).

Trend (variation in the periodic table):

1. Period: Electronegativity increases across the period due to increasing nuclear force and decreasing size.
2. Group: Electronegativity decreases down the group due to decreasing nuclear force and increasing size.

Electronegativity and Strength of Bond: Electronegativity difference between the bonded atoms directly affects the strength of bond. And the concept is operative for polar molecules only. When there is sufficient electronegativity difference between the bonded atoms, both the atoms develops partial opposite charges. As a result there exist an additional electrostatic force between them and bond gets additionally strong. For example, in case of $^{\delta+}HCl^{\delta-}$, the calculated bond energy is 338.9 kJ/mol and that of experimental is 436 kJ/mol. The experimental bond energy is high due to ΔE.N between H and Cl which is 0.9. Hence, greater electronegativity difference stronger is the bond and higher is the bond energy.

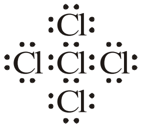
Q.6 Write the Lewis structure for the following compounds:

(i) HCN
(ii) CCl_4
(iii) CS_2
(iv) $H_3N \rightarrow AlF_3$
(v) NH_4OH
(vi) H_2SO_4
(vii) H_3PO_4
(viii) $K_2Cr_2O_7$
(ix) N_2O_5
(x) $Ag(NH_3)_2NO_3$

Ans.

(i)

(ii)



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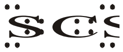

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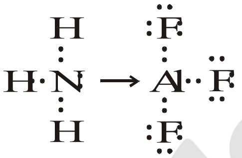

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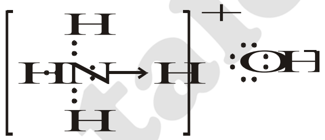

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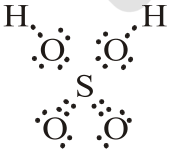

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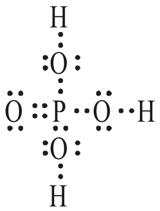

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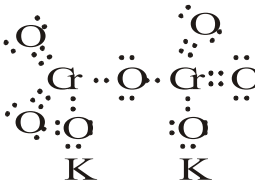

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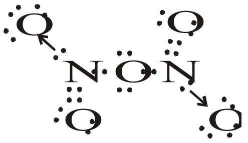
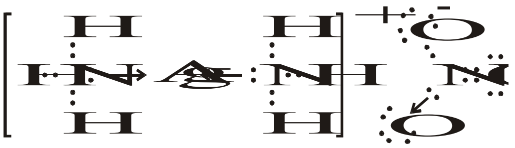


(x)



Q.7 (a) Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

(b) How the bonding in the following molecules can be explained with respect to valence bond theory? Cl_2, O_2, N_2, HF, H_2S.

Ans.

(a) For valence bond theory, consult text book.

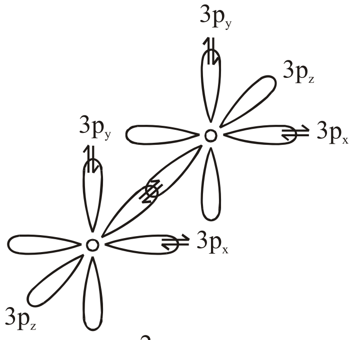
Difference between valence bond theory and molecular orbital theory

Valence Bond Theory	Molecular Orbital Theory
1. According to VBT, the atomic orbitals overlap and resulting shared pair reside in the overlapped atomic orbitals.	1. According to MOT, atomic orbitals overlap and molecular orbitals are formed. And resulting shared pair resides in molecular orbitals.
2. In resulting molecule, atomic orbitals retain their identity.	2. In resulting molecule, atomic orbitals loose their identity.
3. VBT does not explain paramagnetic character of molecules like O_2.	3. MOT successfully explains the paramagnetic behaviour of molecules like O_2.
4. VBT fails to explain the no molecular existence of noble gases.	4. MOT successfully explains no molecular existence of noble gases.

(b) (i) Cl_2-molecule:

$Cl_{17} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$

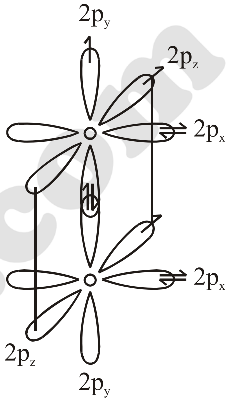
Two $3p_z$ orbitals of two Cl-atoms undergo linear overlapping to form one σ-bond.



(ii) O_2-molecule:

$O_8 = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

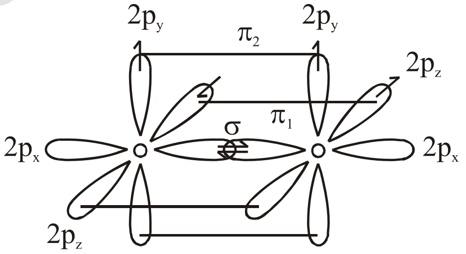
As set of $2p_y$ orbitals of two oxygen undergo linear overlapping to form σ-bond and a set of $2p_z$ orbitals undergo parallel overlapping to form π-bond.



(iii) N_2-molecule:

$N_7 = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

A set of $2p_x$ orbitals of two nitrogen atoms undergo linear overlapping to a σ-bond. A set of $2p_y$ and a set of $2p_z$ orbitals separately undergo parallel overlapping to form two π-bonds.

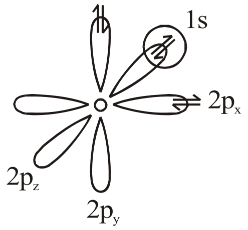


(iv) HF-molecule:

$F_9 = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

$H_1 = 1s^1$

$2p_z$ orbital of flourine atom and 1s orbital of hydrogen atom undergo linear overlapping to form σ-bond.

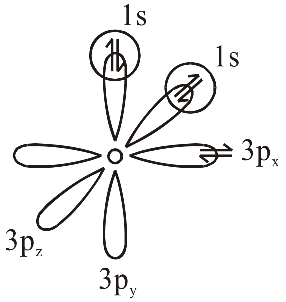


(v) H_2S-molecule:

$S_{16} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$

$H_1 = 1s^{11}$

$3p_y$ and $3p_z$ orbitals of sulphur separately undergo overlapping with 1s orbital of two hydrogen atoms to two σ-bonds.

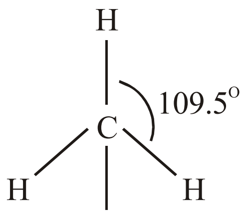


Q.8 **Explain VSEPR theory. Discuss the structures of CH_4, NH_3, H_2O, $BeCl_2$, BF_3, SO_2, SO_3 with reference to this theory.**

Ans.

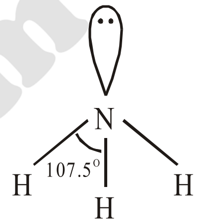
(i) **Structure of CH_4:** (AB_4-type four bond pairs)

In case of CH_4, carbon atom is sp^3-hybridized. Since, CH_4 molecule has four bond pairs around central carbon. Its geometry is tetrahedral and bond angle is 109.5°. This repulsion keeps the bond angle at equal distance and minimum repulsion.



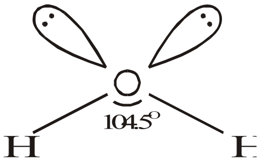
(ii) **Structure of NH_3:** (AB_4-type 3 bond pairs and 1 lone pair)

In case of NH_3, nitrogen atom is sp^3-hybridized. Since, NH_3 molecule has three bond pairs and one lone pair. Its geometry is pyramidal and bond angle is 107.5° instead of 109.5°. This reduction of bond angle is due to one lone pair that causes more repulsion.



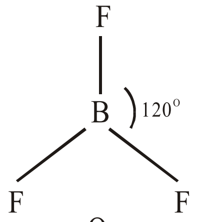
(iii) **Structure of H_2O:** (AB_4-type 2 bond pairs and 2 lone pairs)

In case of H_2O, oxygen atom is sp^3-hybridized. H_2O molecule has two bond pairs and two lone pairs and it has angular geometry with 104.5° bond angle. This reduction in bond angle is due to the presence of two lone pairs that causes more repulsion.

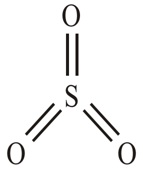


(iv) **Structure of BF_3:** (AB_3-type 3 bond pairs)

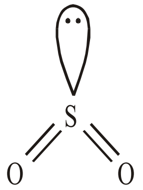
Boron atom is sp^2-hybridized in BF_3 molecule. It has all the three bond pairs. Due to which its geometry is perfectly trigonal planner and 120° bond angle.



(v) **Structure of SO_3:** (AB_3-type 3 bond pairs) with multiple bonds.
Three multiple bond pairs of SO_3 behave just like the three single bond pairs of BF_3. Hence, its geometry is also trigonal with 120° bond angle.



(vi) **Structure of SO_2:** (AB_3-type 2 bond pairs and 1 lone pair)
In case of SO_2, bond angle of two bond pairs is less than 120° due to lone pair and geometry is angular.



(vii) **Structure of $BeCl_2$:** (AB_2-type)
The most simple geometry is that of AB_2-type molecules. Two bond pairs finds maximum distance at 180° and geometry become linear.

Q.9 The molecules NF_3, BF_3 and ClF_3 all have molecular formula of the type XF_3. But they have different structural formals. Keeping in view VSEPR theory sketch the shape of each molecule and explain the origin of differing in shapes.

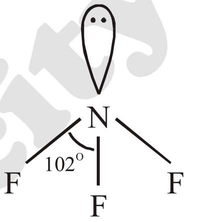
Ans. **Shape of BF_3: (AB_3-type 3 bond pairs)**

Boron atom is sp^2-hybridized and it forms three covalent bonds with three flourine atoms separately. These three bond pairs are adjusted at equal distance of 120°. The resultant geometry is trigonal planner. There is one lone pair in this molecule.

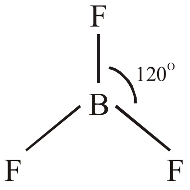
Shape of NF_3: (AB_4-type 3 bond pairs and 1 lone pair)

$N_7 \quad = \quad 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

Nitrogen has three unpaired electrons one lone pair of electron. It undergoes sp^3-hybridization and form three covalent bonds with three flourine atoms and have one lone pair. The geometry of three bond pairs is trigonal pyramidal and bond angle is 102° instead of 109.5°. The reason for reduction of bond angle is greater repulsion caused by lone pair.



Trigonal pyramid



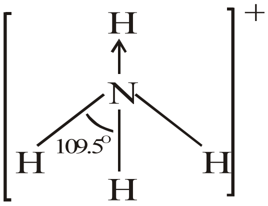
Trigonal planner

Origin of Different Shapes of BF_3 and NF_3: According to VSEPR theory, shape of molecule depends upon the number and type of electron pairs around central polyvalent atom. In case of BF_3, there are three bond pairs around Boron atom. Since, all the electron pairs are similar. Hence they will repel each other equally and will be at equal distance of 120°. As a result, geometry is perfectly trigonal planner.

In case of NF_3, there are three bond pairs and one lone pair. Lone pair causes more repulsion and bond angle reduces to 102° from 109.5°. And resultant geometry of three bond pairs is trigonal pyramid.

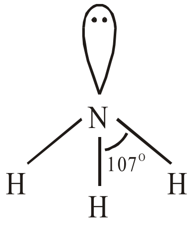
Q.10 The species $N\overline{H}_2$, NH_3, NH_4^+ have bond angles of 105°, 107.5° and 109.5 respectively. Justify these values by drawing their structures.

Ans.

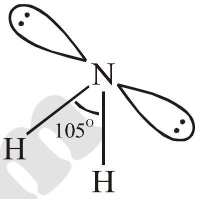


(i) In case of NH_4^+ ion, all the electron pairs are bond pairs that repel each other equally and have equal bond angle of 109.5°.

(ii) In case of NH_3, there are three bond pairs and one lone pair. This lone pair causes a more repulsion and responsible for reduction of bond angle between electron pairs (bonds) from 109.5° to 107.5°.



(iii) In case of $N\overline{H}_2$ ion, there are two bond pairs and two lone pairs. These two lone pairs cause even more repulsion and pushes the bond pairs further. As a result, bond angle is reduced further to 105°.



Q.11 (a) Explain atomic orbital hybridization with reference to sp^3, sp^2 and sp modes of hybridization for PH_3, C_2H_4 and C_2H_2. Discuss geometries of CCl_4, PCl_3 and H_2S by hybridization of central atoms.

(b) The linear geometry of $BeCl_2$ suggest that central Be atom is sp-hybridized. What type of hybridization a central atom undergoes, when the atoms bonded to it are located at the corners of (a) an equilateral triangle (b) a regular tetrahedron and (c) triangular bipyramid?

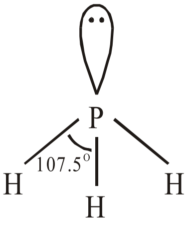
Ans.

(a) **Hybridization for PH_3:**

$P_{15} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$

$H_1 = 1s^1$

Phosphorous atom undergo sp^3-hydridization to form sp^3 orbitals. One of the sp^3-orbitals have lone pair while other three have unpaired electrons. These three sp^3-orbitals undergo overlap with 1s of three hydrogen atoms separately. One lone pair causes repulsion and bond angle is reduced to 107.5° and it results in trigonal pyramid geometry. PH_3 is similarly to NH_3.



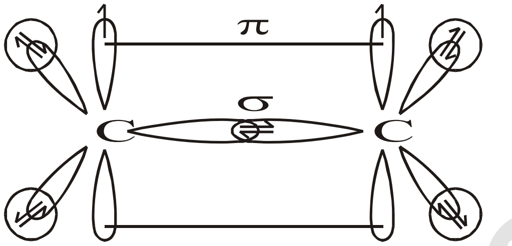
Hybridization of C_2H_4:

$C_6 = 1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ (excited state configuration)

$H_1 = 1s^1$

Carbon atom undergo sp^2-hybridization. The three sp^2-orbital are arranged trigonally. One sp^2-orbital from each carbon atom undergo overlap to form σ-bond between carbon atoms. Two sp^2-orbitals from each carbon atom undergo overlap with 1s orbitals of four hydrogen atoms separately to form σ-bonds between carbon and hydrogen.

Each of two carbon atoms have one unhybrid $2p_z$ orbital which undergo overlap in parallel fashion forming a π-bonds.



Hybridization for C_2H_2:

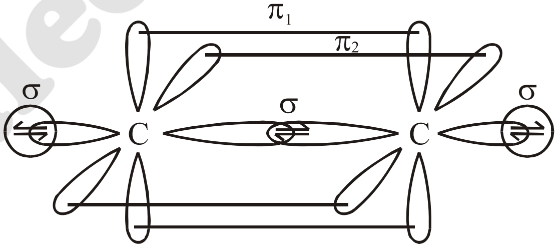
C_6 = $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ (excited state configuration)

H_1 = $1s^1$

Both the carbon atoms undergo sp-hybridization. The two sp-orbitals formed are arranged linearly. One sp-orbital from each carbon atom undergo mutual overlap to form σ-bond between carbon atoms. Rest of one sp-orbital from each carbon atom overlap with 1s-orbitals of two hydrogen atoms separately to form σ-bonds between carbon and hydrogen.

Unhybrid $2p_y$ orbital from each carbon atom overlap in parallel fashion to form π-bond.

The other pair of unhybrid $2p_z$ orbitals also undergo parallel overlaping to form 2 π-bonds.

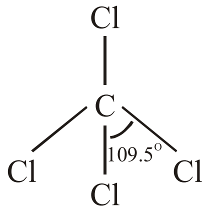


Hybridization of CCl_4:

C_6 = $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ (excited state configuration)

Cl_{17} = $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$

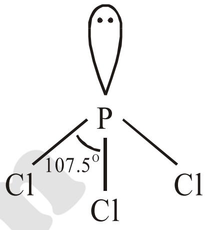
Carbon atom undergo sp^3-hybridization to form four sp^3-orbitals. These sp^3-orbitals overlap with four $3p_z$ orbitals of Cl-atoms to form four σ-bonds. The geometry with four bond pairs is perfectly tetrahedral and bond angle is 109.5°.



Hybridization for PCl_3:

P_{15} = $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$

Cl_{17} = $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$

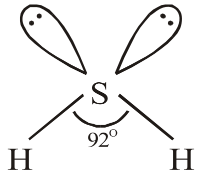


Phosphorus atom undergo sp^3-hybridization to form four sp^3-orbitals. Three sp^3-orbital contain unpaired electrons and undergo linear overlap with $3p_z$ orbitals from three Cl-atoms separately and form three σ-bonds. Three bond pairs results in trigonal pyramid geometry. Fourth sp^3-orbital contain lone pair that cause more repulsion and reduces angle to 107.5°. The structure of PCl_3 is similar to NH_3.

Hybridization for H_2S:

S_{16} = $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2, 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$

H_1 = $1s^1$



Sulphur atom undergo sp^3-hybridization to form four sp^3-orbitals. Two sp^3-orbitals have unpaired electrons and overlap with 1s-orbitals of two hydrogen atoms to form two σ-bonds. The other two sp^3-orbitals have lone pair that causes more repulsion and bond angle reduces to 104.5°. The geometry including two bond pairs is angular. The geometry of H_2S resembles with that of H_2O.

(b)

(a) When the geometry is equilateral triangular, the central atom undergoes sp^2-hybridization. e.g., BH_3, $AlCl_3$, BCl_3.

(b) In case of tetrahedral geometry, central atom undergoes sp^3-hybrdization. e.g., CH_4, CCl_4, $SiCl_4$, SiH_4.

(c) When geometry is triangular bipyramid then central atom undergoes dsp^3-hybridization. e.g., PCl_5.

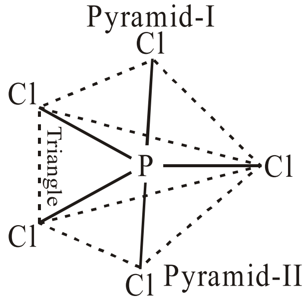
Explanation:

P_{15} = $1s^2, 2s^2, 2p^6, \overrightarrow{3s^2, 3p_x^1, 3p_y^1, 3p_z^1, 3d^0}$

(Ground state configuration)

= $1s^2, 2s^2, 2p^6, \boxed{3s^1, 3p_x^2, 3p_y^2, 3p_z^1, 3d^1}$ $5dsp^3$

(Excited state configuration)



Triangular bipyramid

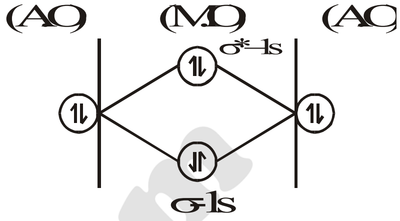
Phosphorus atom undergoes dsp^3 hybridization to form $5dsp^3$ hybrid orbitals. The orbitals arrange to give triangular bipyramid geometry as shown above.

Q.12 (a) Give the basis of the molecular orbital theory and discuss the molecular orbital configurations of the following molecules?

(i) He_2 (ii) N_2 (iii) O_2 (iv) O_2^{+2} (v) O_2^{-2}

(b) How does molecular orbital theory explain the paramagnetic character of O_2, O_2^{+2}, O_2^{-2} species.

Ans. (a)

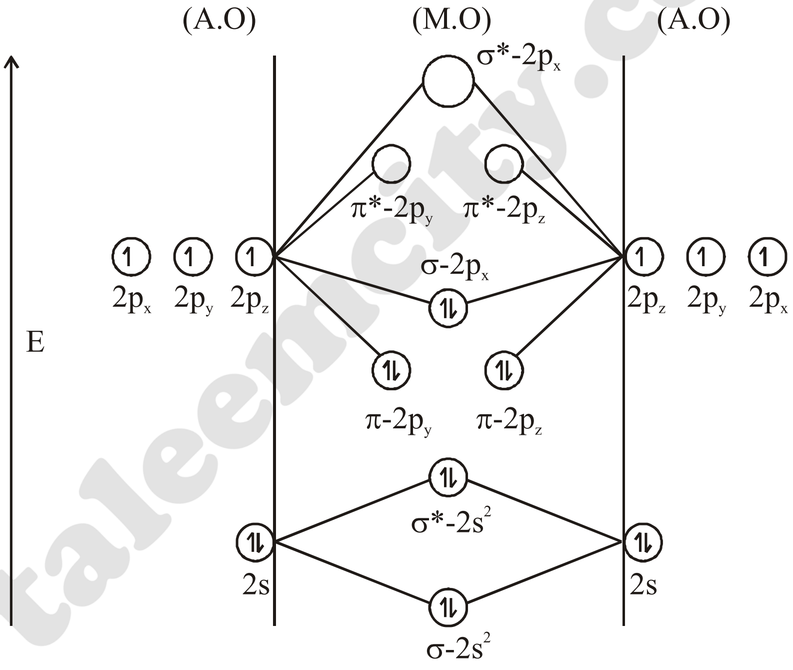


(i) $He_2 = 1s^2$

$$\text{Bond order} = \frac{2-2}{2} = \frac{0}{2} = 0$$

Since bond order for He_2-molecule is zero. Hence, it does not exist in nature.

(ii) $N_7 = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$



1. $$\text{Bond order} = \frac{8-2}{2} = \frac{6}{2} = 3$$

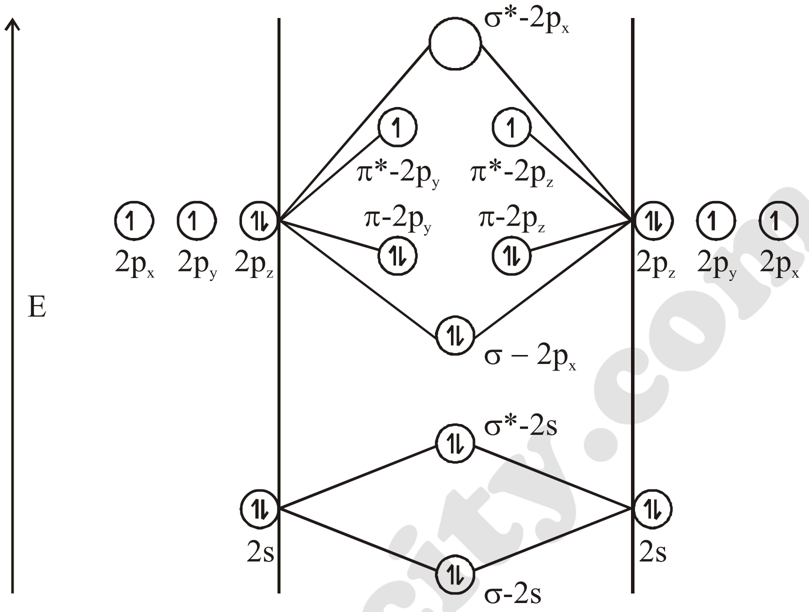
   Bond order shows that there are three bonds between nitrogen atoms.

2. $\sigma - 2s < \sigma^*\text{-}2s < \pi\text{-}2p_y = \pi - 2p_z < \sigma - 2p_x < \pi^*\text{-}2p_y = \pi^* - 2p_z < \sigma^*\text{-}2p_x$

3. N_2-molecule is diamagnetic because it has no un-paired electrons in its antibonding molecular orbitals.

(iii) $O_8 = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_x^1$

1. Molecular orbital diagram:



2. Bond order= $\frac{8-4}{2}$

$= \frac{4}{2}$

$= 2$

Two bonds between oxygen atoms.

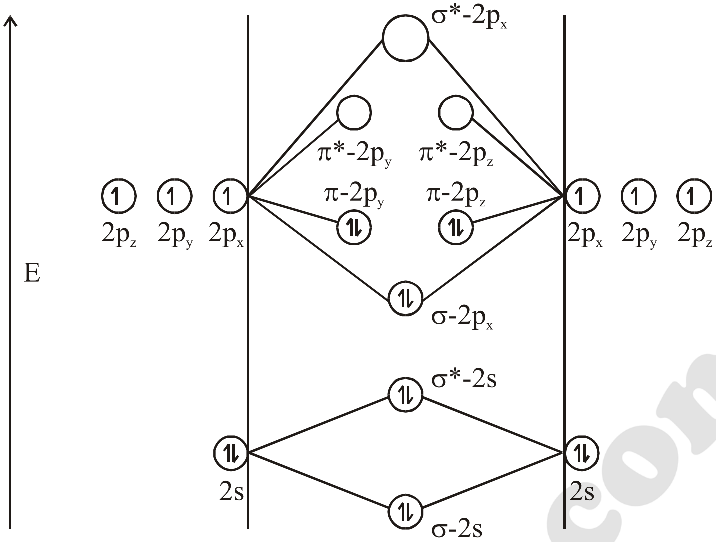
3. σ-2s < σ*-2s < σ-2p$_x$ < π-2p$_y$ = π-2p$_z$ < π*-2p$_y$ = π*2p$_z$ < σ*-2p$_x$

4. O_2-molecule is paramagnetic due to presence of unpaired electrons in antibonding molecular orbitals.

(iv) O_2^{+2}

$O_8^{+1} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

1. Molecular orbital diagram:



2. Bond order $= \frac{8-2}{2}$

$= \frac{6}{2}$

$= 3$

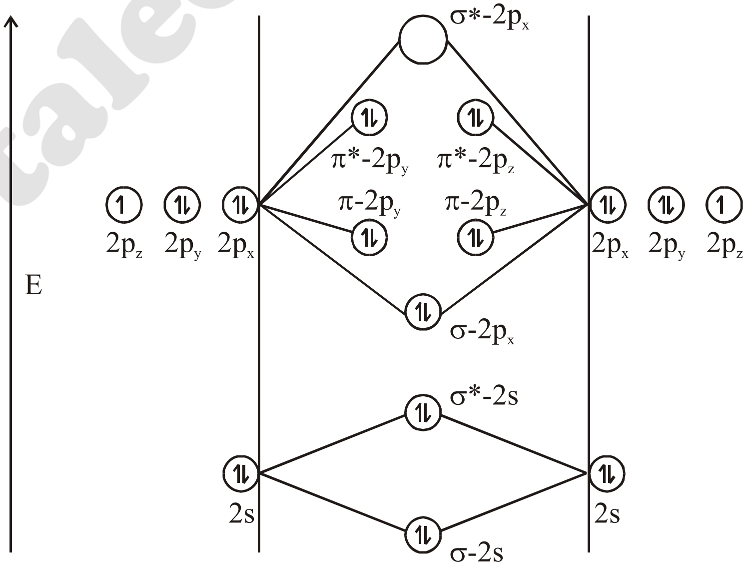
Three bonds between two O^{+1} ions in O_2^{+2}.

3. $\sigma 2s < \sigma^*\text{-}2s < \sigma\text{-}2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^*\text{-}2p_z < \sigma^*\text{-}2p_x$

4. Diamagnetic → No. unpaired electrons in antibonding molecular orbitals.

(v) O_2^{-2}

$O_8^{-1} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$



2. Bond order $= \frac{8-6}{2}$

$= \frac{2}{2}$

$= 1$

Only one bond between two O^{-1} ions in O_2^{-2}.

3. $\sigma\text{-}2s < \sigma^*\text{-}2s < \sigma\text{-}2p_x < \pi\text{-}2p_y = \pi\text{-}2p_z < \pi^*\text{-}2p_y = \pi^*\text{-}2p_z < \sigma^*\text{-}2p_x$

4. O_2^{-2}-molecule is diamagnetic. There are no unpaired electrons in antibonding molecular orbitals rather paired electrons are present.

(b) O_2 is paramagnetic whereas O_2^{+2} and O_2^{-2} both are diamagnetic.

In case the molecular orbital diagram of O_2 there are two unpaired electrons in $\pi^*\text{-}2p_y$ and $\pi^*\text{-}2p_z$.

When O_2^{+2} is formed, then two unpaired electrons in $\pi^*\text{-}2p_y$ and $\pi^*\text{-}2p_z$ are removed. Hence, no unpaired electrons are left and specie is diamagnetic.

When O_2^{-2} is formed, then two more electrons are gained in $\pi^*\text{-}2p_y$ and $\pi^*\text{-}2p_z$. There orbitals are filled and now have paired electrons. Hence the specie is diamagnetic.

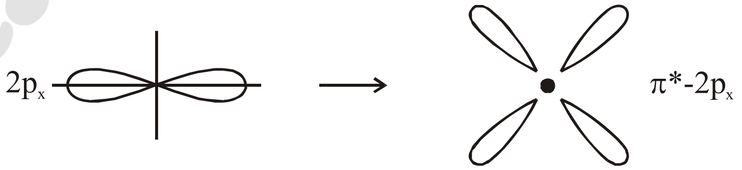
Q.13 (a) Sketch the molecular orbital pictures of:

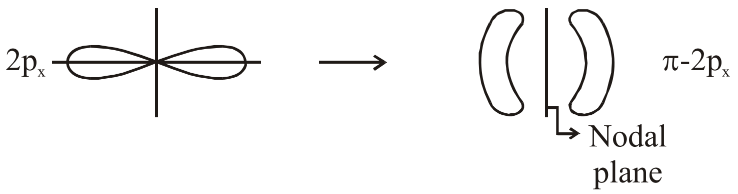
(i) $\pi(2p_x)$ and $\pi^*(2p_x)$ (ii) O_2, O_2^{+2}, O_2^{-2} (iii) He_2 and Ne_2

(b) Sketch hybrid orbitals of species PCl_3, SF_6, $SiCl_4$ and NH_4^+.

Ans. (a)

(i)



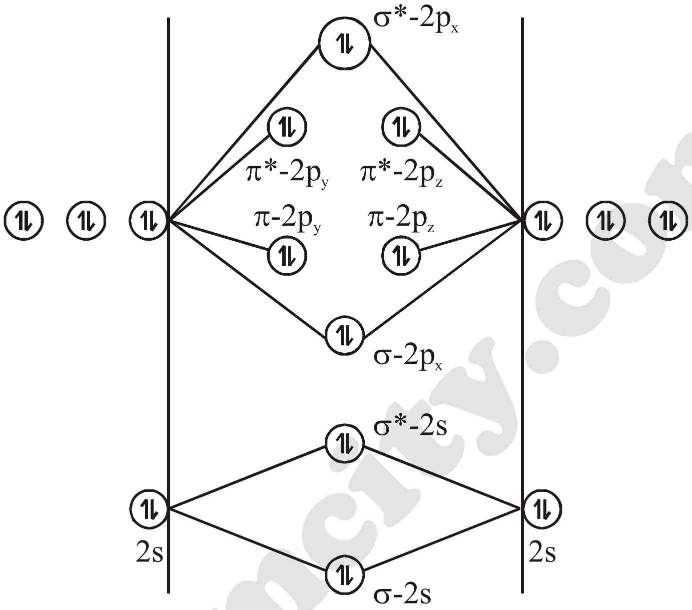


(ii) For molecular orbital diagrams of O_2, O_2^{+2}, O_2^{-2} see answer to Question No. 12 (a) (iii), (iv), (v).

(iii) For molecular orbital diagram of He_2 see answer to Question No. 12 (a) (i).

Molecular orbital diagram for Ne_2.

$Ne_{10} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$.



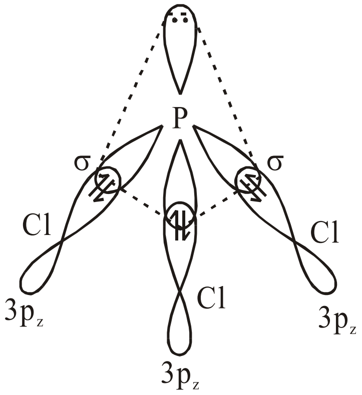
2. Bond order= $\frac{8-8}{2}$

$= \frac{0}{2}$

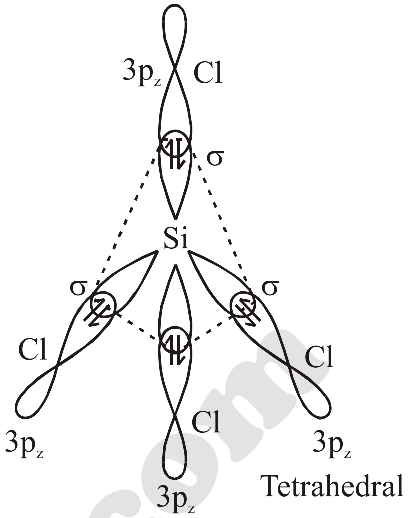
$= 0$

Ne_2-molecule does not exist in nature because bond order is zero.

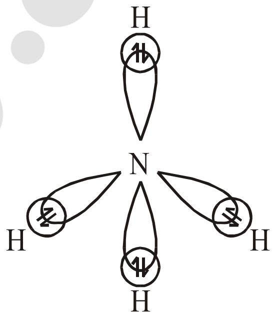
(b) (i) PCl_3: Phosphorus atom is sp^3 hybridized. All four sp^3-hybrid orbitals formed arranged tetrahedrally. Three half-filled sp^3-orbitals overlap with $3p_z$ orbitals of 3-Cl atoms.



(ii) $SiCl_4$: Silicon atom undergo sp^3-hybridization. Four sp^3-orbitals are arranged tetrahedrally and each of which overlap with $3p_z$ of 4-Cl atoms. As a result geometry is perfectly tetrahedral with bond angle 109.5°.



(iii) NH_4^+: Nitrogen atom undergo sp^3-hybridization. Four sp^3-orbitals formed are arranged tetrahedrally. Nitrogen form three covalent and one coordinate covalent bond. As a result of this four bond pairs give rise to perfect tetrahedral geometry.



Q.14 (a) Define bond energy. Explain the various parameters which determine its strength.

(b) How do you compare the bond strengths of:

(i) Polar and non-polar molecules.

(ii) σ-and π-bonds.

(c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 KJ mol^{-1} and that of Br-Br is 193 KJ mol^{-1}.

Ans.

(a) Descriptive question for answer consult text book.

(b)

(i) **Polar and non-polar molecules:** In case of polar molecules there are partial positive and partial negative charges on the bonded atoms. Due to these charges there exists an additional electrostatic force between bonded atoms. Hence, bond becomes more strong e.g., $H^{\delta+} — F^{\delta-}$.

In case of non-polar molecules, there are no charges on the bonded atoms. Hence, no additional force operates between them and bond for non-polar molecules is weaker than polar molecules.

(ii) σ-bond and π-bond: σ-bond is formed by:

(a) Linear overlapping in which extent of overlapping is greater.

(b) Electron pair revolve around the internuclear axis.

These two factors make σ-bond stronger.

π-bond is formed by:

(a) Parallel overlapping in which extent of overlapping is lesser.

(b) π-electron pair revolves above and below the internuclear axis.

These two factors make the π-bond weaker.

(c) Bond energy of H-H = 436 KJ/mol

Bond energy of Br-Br = 193 KJ/mol

Bond energy of H-Br = ?

To calculate the bond energy of H-Br, we have to calculate bond energy per H and per Br atoms.

(i) Bond energy for 1 Br-atom $= \dfrac{\text{Bond energy per mole}}{N_A \times 2}$

$$= \frac{193}{6.02 \times 10^{23} \times 2}$$

$$= 1.603 \times 10^{-22} \text{ KJ/atom}$$

(ii) Bond energy per H-atom $= \dfrac{\text{Bond energy per mole}}{N_A \times 2}$

$$= \frac{436}{6.02 \times 10^{23} \times 2}$$

$$= 3.62 \times 10^{-22} \text{ KJ/atom}$$

Now, we add the bond energy of 1H and 1 Br-atom to have it for:

Bond energy for H-Br $= 3.62 \times 10^{-22} + 1.603 \times 10^{-22}$

$$= 5.224 \times 10^{-22} \text{ KJ/molecule}$$

Bond energy of HBr per mole will be $= 5.224 \times 10^{-22} \times 6.02 \times 10^{23}$

$$= 314.48 \text{ KJ/mole}$$

Q.15 (a) Define dipole moment. Give its various units. Find relationship between Debye and mC. How does it help to find out the shapes of molecules?

(b) The bond length of H-Br is 1.4×10^{-10} m. Its observed dipole moment is 0.79D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022×10^{-19} C and 1 D = 3.336×10^{-30} mC.

Ans.

(a) **Dipole Moment:** The product of electric charge (q) on either end of polar bond and the distance (r) between them is called dipole moment.

$$\mu = q \times r$$

Units of Dipole Moment:

(i) meter columb (mC)

(ii) debye (D)

Relationship between Debye and mC:

$$1\text{D} = 3.336 \times 10^{-30}\ \text{mC}$$

Dipole Moment and Relationship of Molecules: Consider two molecules i.e., H_2O and CO_2. The dipole moment of H_2O is 1.85D. It is not linear. The resultant dipole moment of CO_2 is zero. It shows that CO_2 is a linear molecule. Due to which individual dipole moments are cancelled and net dipole moment is zero.

(b) Bond length of HBr (r) = 1.4×10^{-10} m

Observed dipole moment (μ_{obs}) = 0.79D

(i) Ionic dipole moment (μ_{ionic}) = ?

(ii) % age ionic character = ?

$$\mu_{ionic} = \text{Bond length (r)} \times \text{Unit charge (q)}$$

$$= 1.4 \times 10^{-10}\ \mu \times 1.602 \times 10^{-19}\ \text{C}$$

$$= 22.4 \times 10^{-30}\ \text{mC}$$

$$\mu_{ionic} = \frac{22.4 \times 10^{-30}}{3.336 \times 10^{-30}}$$

$$= 6.72\ \text{D}$$

$$\boxed{\mu_{ionic} = 6.72\ \text{D}}$$

$$\boxed{\mu_{obs} = 0.79\ \text{D}}$$

$$\%\ \text{ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

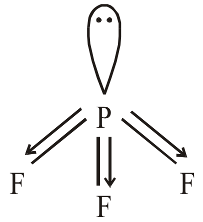
$$= \frac{0.79}{6.72} \times 100$$

$$= 11.75\%$$

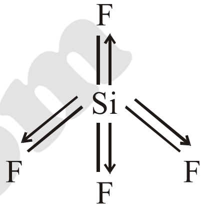
The % age of ionic character in HBr molecule is 11.75%.

Q.16 PF_3 is a polar molecule with dipole moment 1.02 D and thus the P-F bond is polar. Si, is in proximity of P in the periodic table. It is expected that Si-F bond would also be polar, but SiF_4 has no dipole moment. Explain it?

Ans. In case of PF_3, geometry is pyramidal. Due to which individual dipole moments cannot cancel each other. Hence, molecule has net dipole moment.



When we consider SiF_4, the individual bonds are polar. Due to regular tetrahedral geometry, all the four dipole moments cancel the effect of each other and hence resultant is zero.

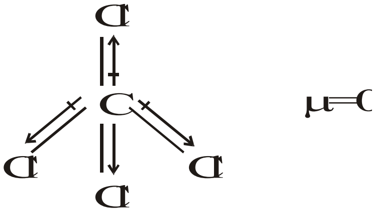


Q.17 Which of the following molecules will be polar or non-polar, sketch the structures and justify your answer:

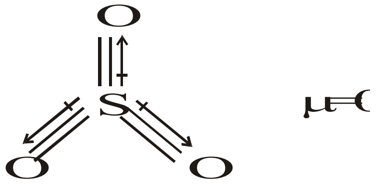
(i) CCl_4 (ii) SO_3 (iii) SF_4 (iv) NF_3 (v) PF_5
(vi) SO_2 (vii) SF_6 (viii) IF_7

Ans.

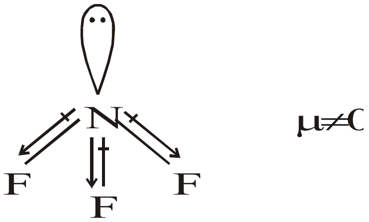
(i) **CCl_4:** It is a non-polar molecule. Individual bonds are polar. Due to perfectly tetrahedral geometry, all the dipole moments cancel the effect of each other. As a result the net dipole moment is zero.



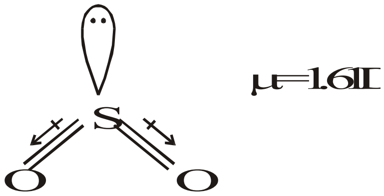
(ii) **SO_3:** It is a non-polar molecule. Individual bonds are polar. Due to triangular planner geometry, all the dipole moments are cancelled out and net dipole moment is zero.



(iii) **NF_3:** It is a polar molecule. Its geometry is pyramidal. Due to which there is no cancellation effect. It is also due to lone pair of electrons. hence, net dipole moment is not zero.



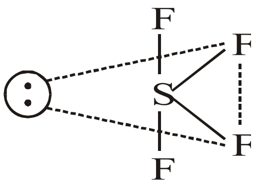
(iv) **SO_2:** It is a polar molecule. It has two dipole moments which do not cancel each other due to non-linear (angular) geometry. Hence, net dipole moment is not zero.



(v) **SF_4:**

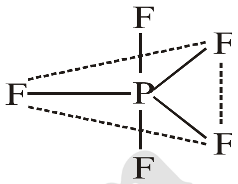
$M \neq 0$

Due to one lone pair, SF_4 has distorted trigonal bi-pyramidal shape.



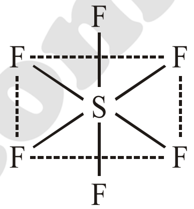
(vi) **PF_5:** It has trigonal bi-pyramidal shape.

$M = 0$



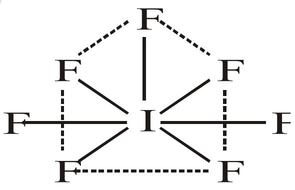
(vii) **SF_6:** It has octahedral structure S – F bond angles are equal = 90°.

Dipole moment = 0



(viii) **IF_7:** Its structure is pentagonal bi-pyramidal. It is non-polar.

$M = 0$



Q.18 **Explain the following with reason:**

(i) Bond distance is the compromise distance between two atoms.

(ii) The distinction between a co-ordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+, H_3O^+ and $CH_3NH_3^+$.

(iii) The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4. Although O – and N – atoms are sp^3 hybridized.

(iv) π-bonds are more diffused than σ-bonds.

(v) The abnormality of bond length and bond strength in HI is less prominent than that of HCl.

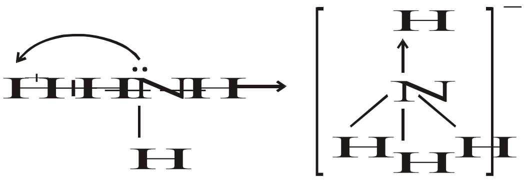
(vi) Dipole moment of CO_2 and CS_2 is zero and of SO_2 is not zero why?

(vii) The melting points, boiling points, heat of vaporization and heats of sublimation of electrovalent compounds are higher as compared with those of covalent compounds.

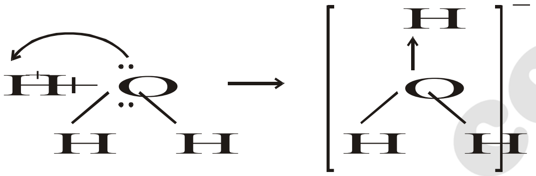
Ans.

(i) When two atom approach each other to form a bond, they attract each other and the energy of the system is lowered. When they reach at a certain distance, their forces of attractions are maximum. On further coming close they start repelling each other and thus the energy of the system increases. Now the two atoms try to remain at a compromising distance whereas the energy of the system is minimum. This is called bond distance or compromise distance between the two atoms.

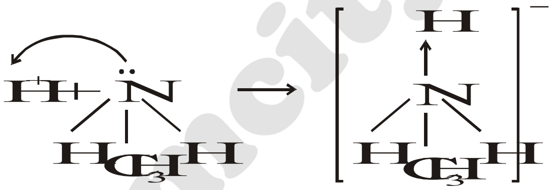
(ii) There are four bonds between nitrogen and hydrogen atoms in $\overset{+}{NH_4}$. No doubt one of the bonds is coordinate covalent and three bonds are covalent but every bond has 25% coordinate covalent bond character and 75% covalent bond character.



In H_3O^+, each bond has 33% coordinate covalent bond character and 66% covalent bond character.



In $CH_3N^+H_3$, there remains no difference between two types of bonds between N-atom and three hydrogen atoms.



In CH_4 all the electron pairs are bonded and have equal repulsion.

(iii) H_2O and NH_3 are not perfectly tetrahedral because there is one lone pair of electrons on the nitrogen atom and two lone pair of electrons on the oxygen atom.

In NH_3 there are three bond pairs and one lone pair. According to VSEPR theory lone pair – bond pair repulsions reduce the angle from 109.5° to 107.5°.

In case of H_2O, there are two lone pairs and two bond pairs. Due to increased repulsions, the bond angle is further reduced to 104.5°.

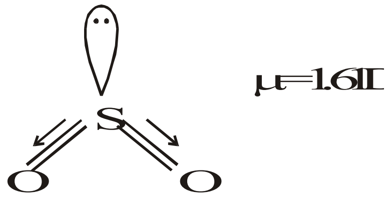
(iv) σ-bond is formed by head to head overlap of two half filled orbitals. The electronic cloud density is symmetrically distributed along the bond axis.

π-bond is formed due to the side way or parallel overlap of two half filled p-orbitals. The electronic cloud density is not symmetrical along the bond axis. It has two regions of electron cloud density, above and below the bond axis.

(v) The decrease in polarity from HCl to HI indicates a trend of equal sharing of electrons. It is due to decreasing electronegativity from Cl to I. Electronegativity of Cl is more than iodine. Therefore the bond length and bond strength of HCl is more prominent in its abnormality than that of HI.

(vi) In case of CO_2 and CS_2 and molecules with linear geometry, the two dipole moments are cancelled out by each other and resultant is zero.

When there are molecules like SO_2 with two dipole moments. These dipole moments cannot cancel each other due to non-linear (angular) geometry. Hence, resultant dipole moment is not zero and in SO_2 it is 1.61D.



(vii) Electrovalent (ionic) compounds have high melting and boiling points due to close packing of oppositely charged ions. The positively charged ions are surrounded by negatively charged ions and vice versa. Therefore ionic compounds have high melting points, boiling points, heat of sublimation and heat of vaporization than the covalent compounds.

KNOW?

1. The tendency of an atom to attain a maximum of two electrons in the valence shell is called duplet rule.
2. The tendency of an atom to attain a maximum of eight electrons in the valence shell is called octet rule.
3. The bond length of H_2 is 75.4 pm.
4. The average distance between the nucleus of the atom and its outer most shell is called atomic size.
5. The one half distance between the nuclei of two alike bonded atoms is called atomic radius.
6. Half of the single bond length between two covalently bonded atoms in a molecule is called covalent radius.
7. L. Pauling was awarded a Nobel Prize in 1954 for his work in chemical bonding.
8. Coordinate covalent bond is also called Dative bond or Semi polar bond.
9. O_2 is paramagnetic but N_2 is diamagnetic O_2^{+2} and O_2^{-2} are also diamagnetic.
10. The shared pair of electrons restricted to the region between two bonded nuclei of atoms is called localized electron.

11. The shared pair of electrons extended over more than two bonded atomic nuclei are called delocalised electrons.

12. The common region along the imaginary line between two bonded nuclei is called bond axis.

13. The substance which is not attracted by the magnet is called diamagnetic. In this substance, all the electrons are paired.

14. The substance which is attracted by the magnet is called paramagnetic. Such a substance has unpaired electrons in it.

15. The orbital formed by mixing the atomic orbitals of an atom are called hybrid orbitals e.g., sp^3, sp^2, sp.

16. The orbital which has only one electron in it is called half-filled or partially filled orbital.

17. The orbital which is extended over two or more atomic nuclei is called molecular orbital. For example: σ-orbital, π-orbital, σ*-orbital, π*-orbital.

18. VSEPR stand for valence shell electron pair repulsion.

19. AB_2 type of molecules have linear structure with a bond angle of 180°. ($BeCl_2$)

20. AB_3 type of molecules (BF_3) have triangular planar structure with a bond angle of 120°.

21. AB_4 type of molecules (CH_4) with no lone pair have tetrahedral structure with a bond angle of 109.5°.

22. AB_5 type of molecules (PCl_5) have triangular bipyramidal structure.

23. AB_6 type of molecules (SF_6) have octahedral geometry.

24. HF is the weakest of all halogen acid.

25. The distance between the nuclei of two atoms forming a covalent bond is called bond length.

26. The S.I unit of dipole moment is coulomb meter (Cm).

27. $1\ \text{Debye} = 3.336 \times 10^{-30}$ C.m.

28. Dipole moment of CO_2 is zero but the dipole moment of CO is 0.12 D.

29. Bond order of H_2^+ is 0.5.

30. Atomic size of Na = 186 pm and
Ionic radius of Na^+ = 95 pm
Similarly atomic size of Cl = 99 pm
and ionic radius of Cl^- = 181 pm

Chapter 7

THERMOCHEMISTRY

THERMOCHEMISTRY

"The branch of chemistry which deals with the study of heat changes during a chemical reaction is called **thermo–chemistry**."

It is noticed that energy in the form of heat is either evolved or absorbed as a result of a chemical change. This is mostly, due to the breaking of bonds in the reactants and formation of new bond in the products. **Bond breaking absorbs energy but bond making release it**. The overall energy change that occurs, results from the difference between energy supplied for the breaking of reactant bonds and that evolved in the making of product bonds. Different substances have different amounts of energy associated with them. Due to this reason, the **total energy** of the products is **never equal** to that of reactants. Hence, in a chemical change, the energy in the form of heat will either be evolved or absorbed and this is called **heat of reaction**.

Definitions:

Temperature:

"The measure of average kinetic energy of the all particle of a system is called temperature."

If we transfer energy to a system, the kinetic energy of particles in system increases and temperatures rises. It is a state function.

Heat:

"The transfer of energy caused by the difference of temperature between two objects is called **heat**."

Heat transfer is denoted by q. Heat is proportional to the mass m of a system and temperature change ΔT.

$$q \; \alpha \; m\Delta T$$

or $$q = ms\Delta T$$

Where s = specific heat of a substance (Heat is not state function)

Specific Heat:

The amount of energy required to raise the temperature of one kilogram of the substance by one Kelvin. For example, the specific heat of water is 4184 J kg^{-1} K^{-1} or 4.184 kJ K^{-1}.

Units of Energy:

Mostly Joule and calorie are used for the measurement of energy.

Calorie:

The amount of energy required to raise the temperature of one gram of water through 1°C from 14.5^oC to 15.5^oC is called one **calorie**.

1000 cal = 1 k cal. (1 calorie = 4.184 Joules)

BTU:

The amount of energy required to raise the temperature of one pound of water through $1F^o$.

(12000 BTU = 1 ton)

Joule:

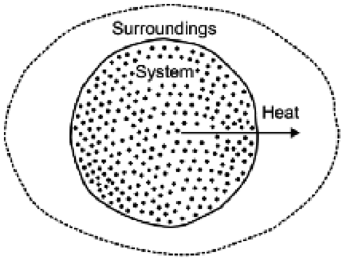
The energy expended when a force of one Newton move an object one meter in the direction in which force is applied.

$$\begin{aligned} \text{Energy} &= \text{force} \times \text{distance moved} \\ &= kg\ m\ s^{-2} \times m = kgm^2\ s^{-2} \\ &= 1000\ J = 1\ kJ \\ 1J &= 10^7\ \text{ergs} \end{aligned}$$

Joule is also defined as, the kinetic energy possessed by an object having mass of 2kg traveling at 1m/s.

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

$$J = \frac{1}{2}(2kg)\,(m/s)^2 = Kgm^2\ s^{-2}$$



Exothermic reaction

Exothermic Reactions:

"Those reactions is which heat is evolved from system to surrounding, are called as **exothermic reactions**."

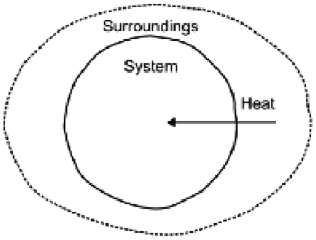
For example,

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.7\ kJ/mole.$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -285.58\ kJ/mole.$$

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -41.6\ kJ\ mole^{-1}$$

Endothermic Reactions:



Endothermic reaction

"Those reactions in which heat is absorbed from surrounding to system are called **endothermic reactions**."

For examples,

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \quad \Delta H = +180.51\ kJ$$

$$H_2O_{(l)} \longrightarrow H_{2(g)} + \frac{1}{2}O_{2(g)} \quad \Delta H = +285.58\ kJ\ mole^{-1}$$

Difference of between Exothermic and Endothermic Reactions:

Exothermic Reactions	Endothermic Reactions
1. Heat is evolved from the system.	1. Heat is absorbed in the system.
2. Temperature of the system rises.	2. Temperature of the system decreases.
3. Enthalpy of products is less than the enthalpy of reactants.	3. Enthalpy of products is high than the enthalpy of reactants.
4. Sign of enthalpy change is negative.	4. Sign of enthalpy change is positive.
5. Generally exothermic reactions are spontaneous.	5. Generally endothermic reactions are non–spontaneous.
6. More bonds are formed than the bonds broken.	6. More bonds are broken than the bonds formed.
7. Example $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -285.58\ kJ\ mole^{-1}$ $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7\ kJ\ mole^{-1}$	7. Example $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.51\ kJ$ $H_2O_{(l)} \longrightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$ $\Delta H = +285.58\ kJ\ mole^{-1}$

Practical Utility of Thermo–chemistry:

The subject matter of thermo–chemistry is based on the fist law of thermodynamics. The subject has an important practical utility as it gives us information about the energy or heat contents of compounds, a knowledge of which necessary for the study of chemical bonding and chemical equilibrium. The scope of thermo–chemistry is limited mainly because only a few of many chemical reactions are such whose heat of reaction can be accurately measured.

Spontaneous Process of Reaction:

"A process which occurs itself without any outside assistance and moves from a non–equilibrium state towards an equilibrium state is known as spontaneous process or natural process."

It is unidirectional, irreversible and a real process. Some examples of spontaneous processes are given below.

(i) Water flows from higher level to the lower level. The flow cannot be reversed without some external aid.

(ii) Neutralization of a strong acid with a strong base is a spontaneous acid base reaction.

$$NaOH_{(aq)} + HCl_{(aq)} \xrightarrow{\qquad} NaCl_{(aq)} + H_2O_{(l)}$$

(iii) When a piece of zinc is added to the copper sulphate solution, blue–colour of the solution disappears due to the spontaneous redox reaction.

$$CuSO_{4(aq)} + Zn_{(s)} \xrightarrow{\qquad} ZnSO_{4(aq)} + Cu_{(s)}$$

(iv) A reaction will also be called a **spontaneous process** if it needs energy to start with, but once it is started, then it proceeds on its own. Burning of coal and hydrocarbon in air are examples of such spontaneous reaction. A piece of coal does not burn in air on its own rather the reaction is initiated by a spark and once coal starts burning, then the reaction goes spontaneously, to completions. Burning of candle is also spontaneous.

SPONTANEOUS AND ENDOTHERMIC REACTION

Our common experience shows that spontaneous processes proceed with a decrease in energy. We might except, therefore, that a chemical reaction would proceed spontaneously if the reaction system decreases in energy by transferring heat to its surroundings. In other words, we might except all **exothermic reactions to be spontaneous**. This is usually true but **not always**. There are many endothermic changes that proceed spontaneously although they absorb heat.

For example,

$$H_2O_{(l)} \xrightarrow{\qquad} H_2O_{(g)} \qquad \Delta H = 44.0 \text{ kJ mole}^{-1}$$

Ammonium chloride dissolves in water and this process is also endothermic.

$$NH_4Cl_{(s)} \xrightarrow{\qquad} \overset{+}{NH}_{4(aq)} + \overset{-}{Cl}_{(aq)} \qquad \Delta H = 15.1 \text{ kJ mole}^{-1}$$

Thus, energy change alone cannot help us to predict whether a reaction will occur spontaneously or not. To predict whether a reaction will occur spontaneously or not, it is necessary to study the free energy of the system, a discussion of which is outside the scope of this book.

NON–SPONTANEOUS REACTIONS

"The process which does not occur itself with any outside assistance is called **non–spontaneous process**."

Non–spontaneous process does not occur in nature. Reversible processes constitute a limiting case between spontaneous and non–spontaneous processes. Some non–spontaneous processes can be made to take place by supplying energy to the system from external source. Some examples of non–spontaneous processes are given below.

(i) Pumping of water uphill.

(ii) Transfer of heat from cold interior part of the refrigerator to the hot surroundings.

(iii) When nitrogen reacts with oxygen, nitric oxide is formed. This reaction takes place by the absorption of heat. Although N_2 and O_2 are present in air but they do not react chemically at ordinary conditions. The reaction takes place when the energy is provided by lighting.

$$N_{2(g)} + O_2 \rightleftharpoons 2NO_{(g)} \quad \text{(Non–spontaneous reaction)}$$

System:

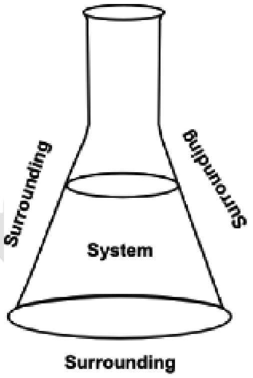
"The substance or mixture of substance which is under experiment or under consideration is called **system**."

Surrounding:

"Everything which is not part of the system is called **surrounding**."

Boundary:

"The real or imaginary surface separating the system from surrounding is called **boundary**."



For example, consider a reaction between Zn and $CuSO_4$ solution. The reaction mixture is system and the vessel in which this solution is present and everything around it is surrounding.

State of System:

"The condition of a system like temperature, pressure, volume, enthalpy etc are **state of a system**."

Initial State:

"The initial condition of system is called **initial state**. It is the state which is before change."

Let us consider water in a beaker. It has some temperature and volume, which is its initial state.

Final State:

"The condition of system after change is called **final state**."

Suppose we heat the water which is present in beaker, its temperature changes, it is its final state.

Change in State:

"Final state minus initial state is called **change in state**."

Let T_1 and T_2 denote the temperature of water before and after heating respectively. The change in temperature ΔT, may be represented as:

$$\Delta T = \text{Final State} - \text{Initial State}$$

$$\Delta T = T_2 - T_1$$

STATE FUNCTION OR STATE VARIABLE

"A state function is a macroscopic property of a system which has some definite values for initial and final state and which is independent of the path adopted to bring about a change."

By convention, we use capital letters as symbols for a state function, e.g. pressure (P) temperature (T), volume (V), internal energy (E), enthalpy (H), are all state functions.

State function is a quantity, whose value depends only on the current state of the system and not on the system's prior history. The magnitude of change in state function depends only on the initial and final states of the system and is independent of the path followed between these states.

Change in State Function:

The difference between final state function and initial state function is called **change in state functions** e.g.

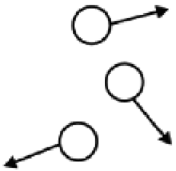
$\Delta E = E_2 - E_1$, $\Delta H = H_2 - H_1$

$\Delta P = P_2 - P_1$, $\Delta T = T_2 - T_1$

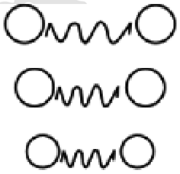
Condition "2" is final and condition "1" is initial.

Internal Energy of a Chemical System:

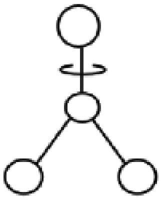
"The sum of all kinds of kinetic and potential energies of all atoms, molecules or ions in the system is called **internal energy**."



(a)
Translational motion of He gas molecules



(b)
A diatomic molecule is vibrating



(c)
A molecule is rotating on an axis

Internal energy depends upon motion of molecules, their arrangement, and intermolecular and interamolecular forces.

In other words, total kinetic energy of molecules is due to translational, vibrational and rotational motions.

$$\boxed{E_{totoal} = E_{translation} + E_{vibration} + E_{rotation}}$$

Potential energy is due to intermolecular and intramolecular forces of attraction with in the particles. So sum of total kinetic energy and potential energy is the internal energy of the system.

The absolute value of internal energy of a system cannot be determined. However, change in internal energy can be and calculated.

$\Delta E = E_{(final)} - E_{initial}$

The internal energy change ΔE of a system is the amount of energy exchange with the surroundings, during a chemical or physical changes of a systems.

Transfer of Energy:

There are two fundamental methods for transfer of energy.

(i) Heat (ii) Work

(i) Heat:

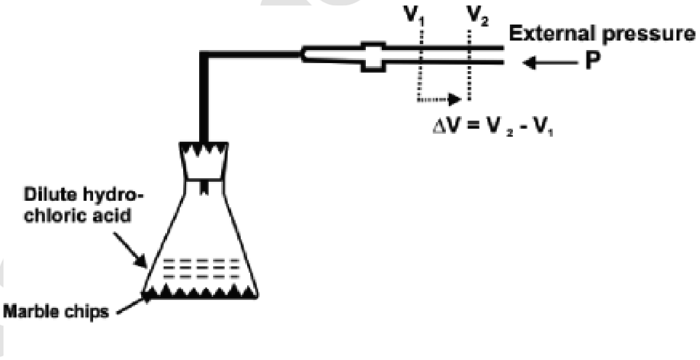
The transfer of energy caused by the difference of temperature between two objects is called heat.

(ii) Work:

The product of force and distance moved is called **work**.

$W = f \times d$

Where f is force and d is distance moved. The SI unit of work is Joule. There are different kinds of work. In chemistry we mostly deal with the pressure volume work. For example, expansion takes, place when a CO_2 gas is evolved during a chemical reaction of dilute HCl and marble chips.



The work done by this chemical system – PΔV

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$

Work done by this chemical system is

W = force x distance moved

$W = -P \times \Delta V$

In pressure volume work, force becomes pressure, distance moved is ΔV or change is volume.

THERMODYNAMICS

"The study of flow of heat or any other form of energy into or out of the system, as it undergoes a physical or chemical transformation is called **thermodynamics**."

FIRST LAW OF THERMODYNAMICS

This law is also called **law of conservation of energy**. This law is stated as, "energy of universe is constant".

or "Energy can neither be created nor destroyed but can change from one form to another."

In other words, a system cannot destroy or create energy. However, it can exchange energy with its surrounding in the form of heat or work. Thus the energy change is the sum of both heat and work so that the total energy of the system and its surroundings remains constant.

Consider a gas enclosed in a cylinder having a piston. Suppose the internal energy of the system is E_1. A quantity of heat q is given to the system and work W is done on the piston to keep it in its original position. During these operations, the internal energy of the system changes to E_2, the change in internal energy ΔE is given by the following equation, which is the mathematical from of first law of thermodynamics.

$$E_2 - E_1 = \Delta E = q + W$$

$$\Delta E = q + W$$

Sign of q will be positive when heat is supplied to the system and q is negative when heat flows out side across the boundary. W is negative when **work is done by the system** and W is positive when work is done in the system. Pressure volume work is given mathematically as:

$$\text{Work} = \text{force} \times \text{distance}$$

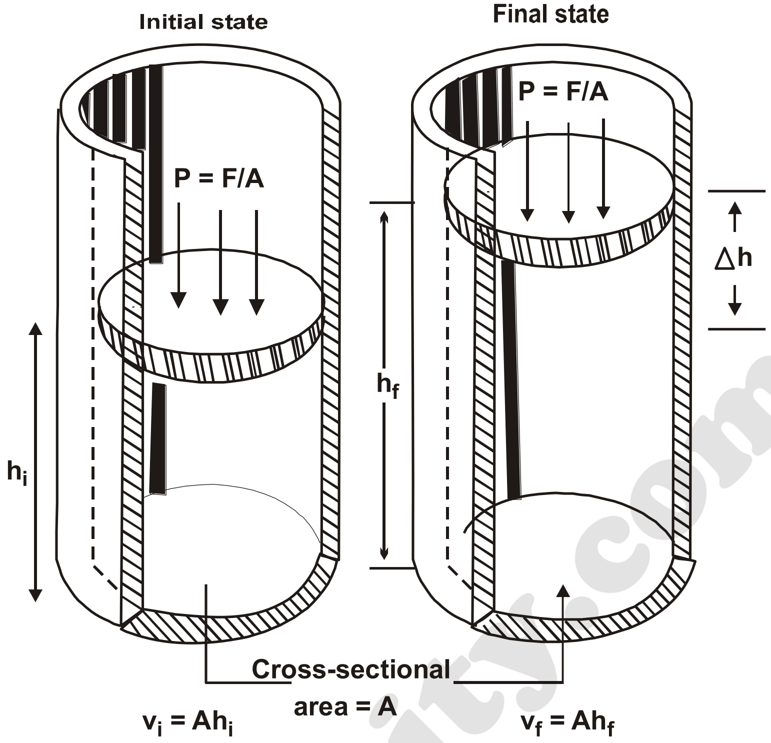
An external pressure P exerted by a force F, spreads over the area A, as pressure is force per unit area.

$$P = \frac{F}{A} \quad \text{or} \quad F = P \times A$$

Volume of the gas in the cylinder is equal to cross–section area A multiplied by the height of the column of the gas h.

$$V = A \times h$$

Now, let us assume that the gas expands and does work by pushing the piston against external pressure, "A" remains same but "h" changes.



(Pressure - volume work)

$\Delta V = V_2 - V_1$

$\Delta V = Ahf - Ahi$

$\Delta V = A(h_f - h_i)$

$\Delta V = A\,\Delta h$

Work done by expansion of gas against constant pressure is given by.

$W = -F \times \Delta h$

$W = -P \times A \times \Delta h$

$W = -P\,\Delta V$

The negative sign indicate that work is done by the system on the surrounding. So first law of thermodynamics can be written as:

$\Delta E = q - P\,\Delta V$

Energy Changes at Constant Volume:

It volume of gas does not change, no work is done, ($\Delta V = 0$). By applying first law of thermodynamics.

$\Delta E = q_v - P\,\Delta V$

$\Delta E = q_v - 0 \qquad (\Delta V = 0)$

$\Delta E = q_v$

So the increase of heat at constant volume (qv) increases only the internal energy (ΔE) of the system and work done is zero.

ENERGY CHANGES AT CONSTANT PRESSURE

Enthalpy of the System:

Consider a gaseous system at constant pressure. q heat is given to the system at constant pressure. this heat is utilized to increase the internal energy of the system and rest is used to do work, on the surrounding. This work is done by the gas when it expands against a constant pressure.

"The increase in the internal energy of a system plus work done is enthalpy."

It is the total heat contents of a system. it is denoted by H. In general, enthalpy is equal to pressure and volume (PV).

$H = E + PV$

Enthalpy is a state function. It is measured in Joules. It is not possible to measure the enthalpy of a system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system. A change in enthalpy of a system can be written as:

$\Delta H = \Delta E + \Delta (PV)$

or $\Delta H = \Delta E + V\,\Delta P + P\,\Delta V$

since the gas is kept at constant pressure, $\Delta P = 0$.

Hence

$$\Delta H = \Delta E + P\,\Delta V \qquad (1)$$

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. $\Delta H \approx \Delta E$.

According to first law of thermodynamics.

$\Delta E = q + W$

If W is pressure – volume work done by the system, then:

$W = -P\,\Delta V$

So
$$\Delta E = q - P\,\Delta V \qquad (2)$$

Putting the value of ΔE in Equation (1) from Equation (2) we get:

$\Delta H = q - P\,\Delta V + P\,\Delta V$

$\Delta H = q$

Since the pressure is constant, therefore,

$$\Delta H = q_p \qquad (3)$$

This shows that changes in enthalpy is equal to heat of reaction at constant pressure. since the reactions are carried out at constant pressure more frequently than at constant volume, usually working with ΔH rather than ΔE is more convenient.

Example 1:

When 2.00 moles of H_2 and 1.00 mole of O_2 at 100°C and 1 torr pressure react to produce 2.00 moles of gaseous water, 484.5 kJ of energy are evolved.

What are (a) ΔH and (b) ΔE for the product of one mole of $H_2O_{(g)}$?

Solution:

(a) The reaction is occurring at constant pressure.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

Enthalpy for one mole.

$$q_p = \Delta H = \frac{-484.5 \text{ kJ}}{2 \text{ moles of } H_2O} = -242.2 \text{ kJ mol}^{-1}$$

The minus sign shows that the reaction is exothermic for the production of 1 mole of water.

(b) Calculate ΔE from ΔH, we use the Equation (4).

Let us first calculate the value of $P\,\Delta V$ using the ideal gas equation.

$$PV = n\,RT$$

or $$P\,\Delta V = \Delta n\,RT$$

Now, Δn = No. of moles of the products – No. of moles of the reactants

$$= 2 \text{ mole} - 3 \text{ mole} = -1 \text{ mole}$$

$$R = 8.314 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$T = 373 \text{ K}$$

$$P\,\Delta V = n\,RT$$

$$P\,\Delta V = -1 \text{ mole} \times 8.314 \text{ J mole K}^{-1} \times 373 \text{ K}$$

$$= -3100 \text{ J} = -3.10 \text{ kJ}$$

This is the value for 2 moles of water. For the formation of 1 mole of water,

$$P\,\Delta V = \frac{-3.10}{2} = -1.55 \text{ kJ}$$

On substituting these values into equation $\Delta H = \Delta E + P\,\Delta V$.

$$\Delta E = \Delta H - P\,\Delta V$$

$$\Delta E = -242.2 - (-1.55)$$

$$\Delta E = -242.2 + 1.55 = -240.6 \text{ kJ mol}^{-1}$$

Standard Enthalpy of Reaction (ΔH_r^0):

"It is the amount of enthalpy change which occurs when number of moles of reactants react together as specified in a balance equation at standard state."

It is denoted by ΔH_r^0. The standard state for enthalpy change is 25°C (298 K) and 1 atmosphere. All the reactants and products must be present in standard physical state e.g.

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} \qquad (\Delta H_r^0 = -285.8 \text{ kJ mol}^{-1})$$

(i) Enthalpy Change Exothermic Reactions:

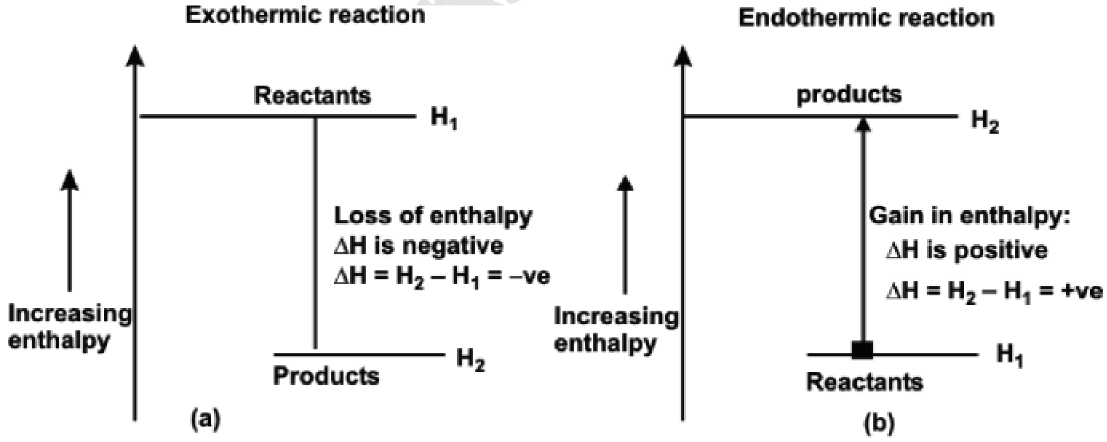
In an exothermic reaction, the heat content or enthalpy of the products, H_2 is less than that of the reactants H_1. Since the system has lost heat, we can say the enthalpy change for the reaction ΔH is negative.

$$H_2 - H_1 = -\Delta H_r^0$$

(ii) Enthalpy Change for Endothermic Reactions:

In an endothermic reaction, the enthalpy of products H_2, is greater than that of the reactants H_1 and the enthalpy change, ΔH is positive. These enthalpy changes are represented in Figure.

$$H_2 - H_1 = +\Delta H_r^0$$



Enthalpy changing thermo chemical reactions

Enthalpy of Formation (ΔH_f^0):

"The enthalpy change when one mole of compound is formed from its elements at standard state is called **standard enthalpy of formation**."

It is denoted by ΔH_f^0. It is measured in $kJ\ mol^{-1}$. The standard state for enthalpy is 25^oC (298 K) and one atmosphere, for example

$$Mg_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow Mg\,O_{(s)} \quad \Delta H_f^0 = -692\ kJ\ mol^{-1}$$

When carbon reacts with oxygen to form CO_2, $393.7\ kJ\ mol^{-1}$ energy is released, it is ΔH_f^0 of CO_2.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_f^0 = -393.7\ kJ\ mol^{-1}$$

Enthalpy of Atomization (ΔH^0_{atm}):

"The standard enthalpy of atomization H^0_{atm} of an element is defined as the enthalpy change when one mole of gaseous atoms are formed from the element under standard conditions."

For example the standard enthalpy of atomization of hydrogen is given below.

$$\frac{1}{2} H_{2(g)} \longrightarrow H_{(g)}$$

$$\Delta H^0_{atm} = 218\ kJ\ mol^{-1}$$

A wide range of experimental techniques are available for determining enthalpies of atomization of elements.

Standard Enthalpy of Neutralization (ΔH^0_n):

"The standard enthalpy of neutralization H^0_n is the amount of heat evolved when one mole of hydrogen ions from an acid react with one mole of hydroxide ions from a base to from one mole of water."

For example, the enthalpy of neutralization of sodium hydroxide by hydrochloride acid is $-57.4\ kJ\ mol^{-1}$. Note that a strong acid e.g. HCl and a strong base e.g. $NaOH$ ionize completely in dilute solutions as follows.

$$HCl_{(aq)} \longrightarrow \overset{+}{H}_{(aq)} + \overset{-}{Cl}_{(aq)}$$

$$NaOH_{(aq)} \longrightarrow \overset{+}{Na}_{(aq)} + \overset{-}{OH}_{(aq)}$$

When these solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, the enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components,

$$\overset{+}{H}_{(aq)} + \overset{-}{Cl}_{(aq)} + \overset{+}{Na}_{(aq)} + \overset{-}{OH}_{(aq)} \longrightarrow \overset{+}{Na}_{(aq)} + \overset{-}{Cl}_{(aq)} + H_2O_{(l)}$$

or $$\overset{+}{H}_{(aq)} + \overset{-}{OH}_{(aq)} \longrightarrow H_2O_{(l)}$$

$$\Delta H^0_n = -57.4\ kJ\ mol^{-1}$$

Enthalpy of neutralization for any strong acid with a strong base is approximately the same i.e. $-57.4\ kJ\ mol^{-1}$.

Enthalpy of Combustion (ΔH_c^0):

"The standard enthalpy of combustion of a substance, ΔH_c^0 is defined as the enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions."

For example, standard enthalpy of combustion of ethanol ΔH_c^0 is – 1368 kJ mol^{-1}. The reaction is represented by the following equation.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H_c^0 = -1368 \text{ kJ mol}^{-1}$$

Enthalpy of Solution (ΔH_{sol}^0):

"The standard enthalpy of a solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change."

$$NH_4Cl_{(s)} \longrightarrow NH_4Cl_{(aq)} \qquad \Delta H = +15.1 \text{ kJ mol}^{-1}$$

$$Na_2CO_{3(s)} \longrightarrow Na_2CO_{3(aq)} \qquad \Delta H = -25.0 \text{ kJ mol}^{-1}$$

For example, enthalpy of solution ΔH_{sol}^0 of ammonium chloride is + 15.1 kJ mol^{-1} and that of sodium carbonate is – 25 kJ mol^{-1} in the first case, heat absorbed from the surroundings is indicated by cooling of the solvent (water), an endothermic process. While in the second case, the temperature of the solvent rises showing that the process is exothermic.

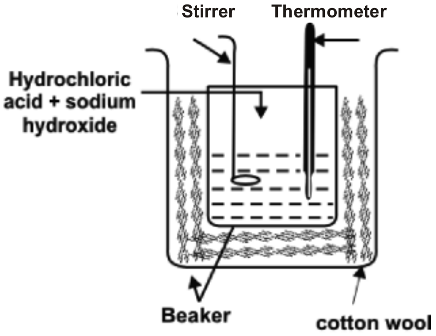
Measurement of Enthalpy of a Reaction:

Exothermic and endothermic reactions can easily be detected by observing the temperature of the reaction vessel before and after the reaction, as long as the heat of reaction evolved or absorbed is considerable. More accurate values of ΔH can be determined by using calorimeters as described below.

(i) GLASS CALORIMETER
(MEASUREMENT OF ΔH AT CONSTANT PRESSURE)

For most purposes, an ordinary glass calorimeter can be used to determine the value of ΔH_r. This usual type of calorimeter is basically an insulated container with a thermometer and a stirrer.

Reactants in stiochiometric amounts are placed in the calorimeter. When the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system.



Glass Calorimeter

The temperature of the system is recorded before and after the chemical reaction. Knowing the temperature change, the mass of reactants present and the specific heat capacity of the reaction mixture, we can calculate the quantity of heat q evolved or absorbed during the reaction. Thus:

The reaction is carried out at **constant pressure** so we can write as:

$q_p = m \times s \times \Delta T$

where m = mass of reactants

s = specific heat of reaction mixture

ΔT = change in temperature

The reactions is carried out at constant pressure so,

$q = m \times s \times \Delta T$

where $q_p = \Delta H$

Example 2:

Neutralization of 100 cm^3 of 0.5 M NaOH at 25^oC with 100 cm^3 of 0.5 M HCl at 25^oC raised the temperature of the reaction mixture to 28.5^oC. Find the enthalpy of neutralization. Specific heat of water = $4.2 \text{ J g}^{-1} \text{ K}^{-1}$.

Solution:

Specific heat of water, $s = 4.2 \text{ J g}^{-1} \text{ K}^{-1}$.

Density of H_2O is around 1g cm^{-3}, 200 cm^3 of solution is 200 g.

Total mass of the reaction mixture = 200 g

Rise is temperature, $\Delta T = 28.5 - 25.0 = 3.5^oC = 3.5 \text{ K}$.

100 cm^3 of 0.5 M NaOH = 100 cm^3 of 0.5 M HCl.

$M = n/V$

$n \Rightarrow M \times V$

$n = 0.5 \times 0.1 = 0.05$ moles

= 0.05 mole of each HCl and NaOH reacts to form 0.05 mole of H_2O.

Total heat evolved, $q = m \times s \times \Delta T$

$= 200 \text{ g} \times 4.2 \text{ J g}^{-1} \text{ K}^{-1} \times 3.5 \text{ K} = 2940 \text{ J}$

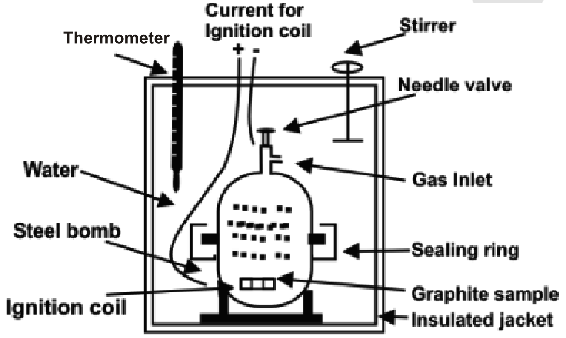
$= -2.94 \text{ kJ}$ (Exothermic reaction)

Enthalpy of neutralization, $\Delta H_n^0 = \dfrac{-2.94 \text{ kJ}}{0.05 \text{ mol}} = -58.8 \text{ J mol}^{-1}$

The minus sign indicates that heat is evolved.

(ii) BOMB CALORIMETER
(MEASUREMENT OF ΔE AT CONSTANT VOLUME)

A bomb calorimeter is usually used for the accurate determination of **enthalpy of combustion for food**, fuel and other compounds. A bomb calorimeter is shown in the Figures. It consists of strong cylindrical steel vessel usually lined with enamel to prevent corrosion. A known mass (about one gram) of the test substance is placed in a platinum crucible inside the bomb. The lid is screwed on tightly and oxygen is provided in through a valve and the pressure inside is **about 20 atmosphere**. After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well–insulated calorimeter and allowed to attain a steady temperature. The initial temperature is measured by using the thermometer, present in the calorimeter. The test substance is then ignited electrically by passing the current through the ignition coil. The temperature of water, which is stirred continuously, is **recorded at 30 sec** intervals in order to find the maximum temperature attained. Knowing the heat capacity of the whole system (calorimeter water, thermometer and stirrer) the rise in temperature and heat generated by ignition, it is possible to calculate the heat of combustion as follows.



Bomb calorimeter

$q = c \times \Delta T$

c = specific heat capacity of whole system (bomb, water etc) and its unit is kJ K^{-1}.

ΔT = rise in temperature.

This measurement takes place at constant volume, so the energy released is called internal energy change.

The heat capacity of a body or a system is defined as the quantity of heat required to change its temperature by 1 Kelvin.

Example 3:

If 10.16 g of graphite is burnt in a bomb calorimeter and the temperature rise recorded is 3.87 K. Calculate enthalpy of combustion of graphite if the specific heat capacity of the calorimeter (bomb, water etc) is 86.02 kJ K^{-1}.

Solution:

$$\text{No. of moles of graphite} = \frac{10.16}{12} = 0.843 \text{ mole}$$

Specific heat capacity of system = 86.02 kJ K^{-1}

Rise in temperature, ΔT = 3.87 K

Enthalpy of combustion of graphite, ΔH_c^0

$$q = c \times \Delta T$$

$$= 86.02 \text{ kJ K}^{-1} \times 3.87 \text{ K}$$

$$= 332.89 \text{ kJ} = -332.89 \text{ kJ (Exothermic reaction)}$$

The minus sign indicates that the heats evolved. Combustion process is always exothermic in nature.

$$\Delta H_c = \frac{-332.89 \text{ kJ}}{0.843 \text{ mole}} = -394.8 \text{ kJ mol}^{-1}$$

LAWS OF THERMOCHEMISTRY

(i) FIRST LAW OF THERMOCHEMISTRY (LAVOISER – LAPLAC'S LAW)

"The heat of decomposition of a compound is equal to the heat of formation of that compound."

For example, Heat of formation of H_2O is – 285.8 kJ mol^{-1}. Heat of decomposition of H_2O also + 285.8 kJ mol^{-1} and law of energy is also conserved.

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H_f = -285.8 \text{ kJ mol}^{-1}$$

$$H_2O_{(l)} \longrightarrow H_{2(g)} + \frac{1}{2} O_{2(g)} \quad \Delta H_{(d)} = +285.8 \text{ kJ mol}^{-1}$$

HESS'S LAW OF CONSTANT HEAT SUMMATION (SECOND LAW)

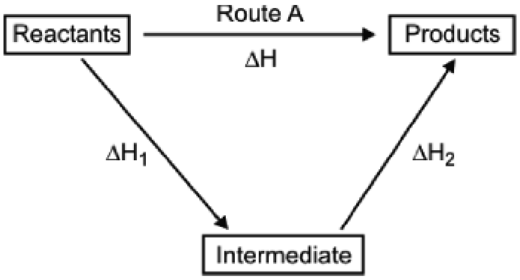
This law was stated by G.H. Hess in 1840. It states that "The amount of heat evolved or absorbed in a chemical reaction is same, whether the reaction take place in one step or in several steps."

or "Net heat of reaction depends only on the initial and final states and not on the intermediate states through which a system may pass."

The Hess's law often called **the law of constant heat summation**. It is direct application of law of conservation of energy or first law of thermodynamics.

Explanation of Hess's Law:

Suppose in a process some reactants change to products and the enthalpy change is ΔH. Now this reaction can also takes place in two steps. First an intermediate is formed and enthalpy change is ΔH_1. Now this intermediate change to the product and enthalpy change is ΔH_2.



According the Hess's law.

$\Delta H = \Delta H_1 + \Delta H_2$

$\Sigma\, \Delta H_{(cycle)} = 0$

Hess's law of constant heat summation can be explained by the following examples.

Example 1:

The formation of sodium carbonate is another example for the verification of Hess's law. The formation of sodium carbonate may be studied as a single step process, or in two steps as via sodium hydrogen carbonate.

Single Step Process:

$2NaOH_{(aq)} + CO_{2(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H_1 = -89.08\ kJ$

Two Steps Process:

$NaOH_{(aq)} + CO_{2(aq)} \longrightarrow NaHCO_{3(aq)} \qquad \Delta H_2 = -48.06\ kJ$

and $NaHCO_{3(aq)} + NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H_3 = -41.02\ kJ$

According to Hess's law.

$\Delta H_1 = \Delta H_2 + \Delta H_3$

Putting the values of $\Delta H_1, \Delta H_2$ and ΔH_3

$-89.08 = -48.06 - 41.02$

$-89.08 = -89.08$

This illustrates how heats of reactions may be added algebraically which proves Hess's law.

Example 2:

If the enthalpy of combustion for graphite to form CO_2 and the enthalpy of combustion of CO to form CO_2 are known, we can determine the enthalpy of formation for CO. The oxidation of carbon (graphite) can be written as follows.

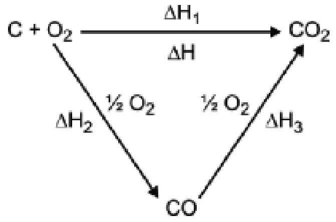
1. $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_1\ (graphite) = -393.7\ kJ\ mol^{-1}$
2. $C_{(graphite)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H_2\ (CO) = ?$
3. $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_3\ (CO) = -283\ kJ\ mol^{-1}$

$\Delta H_1 = \Delta H_2 + \Delta H_3$

$\Delta H_2 = \Delta H_1 - \Delta H_3$

$\Delta H_2 = -393.7 - (-283)$

$= -393.7 + 283 = -110.7\ kJ\ mol^{-1}$



So Hess's is simply an application of law of conservation of energy. We know that,

$\Delta H_1 = \Delta H_2 + \Delta H_3$

Put the value in above equation, we get

$-393.7 = -110.7 - 283$

$-393.7 = -393.7$

Thus this prove Hess's law.

Applications of Hess's Law:

The enthalpy of many reactions cannot be measured directly with the help of calorimeter. Enthalpy of such reactions can be measured indirectly with the help of Hess's law. For example,

(i) Some compounds like CCl_4 cannot be prepared directly by combining graphite and Cl_2. It does not decompose easily into its constituent elements. So its enthalpy of formation can be determined indirectly with the help of Hess's law.

(ii) Boron oxide (B_2O_3) and aluminum oxide (Al_2O_3), provide problems for the measurement of standard enthalpies of their formation. In these cases, it is difficult to burn these elements completely in oxygen, because a **protective layer of oxides** covers the surface of the un–reacted element. So enthalpy cannot be measured because all reactants are not completely consumed.

(iii) Similarly heat of formation of CO cannot be measured directly due the formation of CO_2.

Step 1: $C_{(s)} + O_{2(g)} \xrightarrow{\qquad} CO_{2(g)},\ \Delta H_1$

Step 2: $C_{(s)} + \frac{1}{2} O_{2(g)} \xrightarrow{\qquad} CO_{(g)},\ \Delta H_2$

Step 3: $CO_{(g)} + \frac{1}{2} O_{2(g)} \xrightarrow{\qquad} CO_{2(g)},\ \Delta H_3$

If enthalpy of step 1 and step 3 are known then with the help of Hess's law enthalpy of step 2 can be calculated.

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$\Delta H_2 = \Delta H_1 - \Delta H_3$$

LATTICE ENERGY

"The amount of energy required to break the solid into its isolated ions in the gas phase in called **lattice energy**."

$NaCl_{(s)} \xrightarrow{\qquad} Na^{+}_{(g)} + Cl^{-}_{(g)} \quad \Delta H_{(l)} = +787\ \text{kJ mol}^{-1}$

or The amount of energy evolved when gaseous ions of opposite charge combine to form one mole of ionic solid is called **lattice energy**.

$Na^{+}_{(g)} + Cl^{-}_{(g)} \xrightarrow{\qquad} NaCl_{(s)} \quad \Delta H_{(l)} = -787\ \text{kJ mol}^{-1}$

BORN – HABER CYCLE

Direct determination of lattice energy is difficult. However, Hess's law is helpful to determine the lattice energy of binary ionic compound such as $M^{+}X^{-}$. Binary ionic compound consists of two ions.

The method, to calculate the lattice energy was device by Max Born and Fritz Haber in 1919, and called **Born – Haber Cycle**.

Direct Rout:

According to this solid NaCl is formed from two different routes from their elements these routes are shown in the Figure.

NaCl is formed directly from the elements Na and $\frac{1}{2}Cl_2$. The enthalpy change is called ΔH_f^0 (heat of formation).

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \text{ direct route } NaCl_{(s)}\ \Delta H_f^0 = -411 \text{ kJ mol}^{-1}$$

Second Route:

The second route consists of following five steps.

1. Sublimation or Atomization of Na:

Solid sodium changes to vapours, and it is called sublimation. It is an endothermic process.

$$Na_{(s)} \xrightarrow{\hspace{2cm}} Na_{(g)} \qquad \Delta H_{(s)}^0 = 108 \text{ kJ mol}^{-1}$$

2. Ionization of Sodium:

Sodium atom ionizes to Na^+ and enthalpy change is called **ionization**. It is an endothermic process.

$$Na_{(g)} \xrightarrow{\hspace{2cm}} Na^+_{(g)} + 1e^- \qquad \Delta H_i = 496 \text{ kJ mol}^{-1}$$

3. Dissociation of Chloride:

In this step Cl_2 molecule dissociate to atoms. Enthalpy change of dissociation is 121 kJ mol^{-1}. It is an endothermic process. It is also called “Atomization”.

$$\frac{1}{2}Cl_{2(g)} \xrightarrow{\hspace{2cm}} Cl_{(g)} \qquad \Delta H_{(d)} = +121 \text{ kJ mol}^{-1}$$

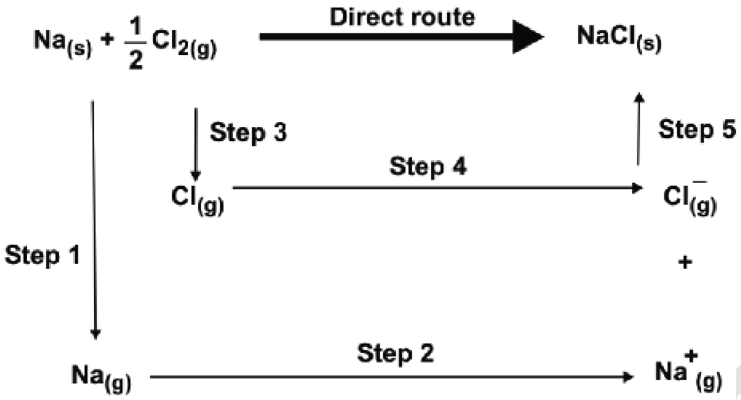
4. Formation of Chloride Ion:

Chlorine atom absorb one electron which was released from Na atom. The amount of energy released is called **electron affinity**. It is an exothermic process.

$$Cl_{(g)} + 1e^- \xrightarrow{\hspace{2cm}} Cl^-_{(g)} \qquad \Delta He = -349 \text{ kJ mol}^{-1}$$

5. Formation of NaCl from Ions:

Na^+ and Cl^- ions which are formed in step 2 and step 4 respectively combine to from solid NaCl. It is just reverse of the lattice energy (breaking of solid into ions). Say the enthalpy change of step 5 is ΔH_1. Heat of formation of a compound is the sum of all these steps.



(Borm-Haber cycle)

$\Delta H_f = \Delta H_{(s)} + \Delta H_i + \Delta H_d + \Delta H_e + \Delta H_l$

Put the values of all enthalpies in the above equation.

$-411 = 108 + 496 + 121 - 349 + \Delta H_l$

$-411 = 725 - 349 + \Delta H_l$

$-411 = 376 + \Delta H_l$

$\Delta H_l = -376 - 411 = -787 \text{ kJ mol}^{-1}$

So the lattice energy of NaCl is – 787 kJ mol^{-1}. It is the amount of energy released when gaseous ions (Na^+ and Cl^-) combine to form solid NaCl. It is the force of attraction between Na^+ and Cl^- ions in an ionic crystalline solid.

Lattice energy of some ionic compounds in kJ mol^{-1}			
LiF	–1030	KF	–808
LiCl	–833	KCl	–690
NaF	–895	KBr	–665
NaCl	–787	CsCl	–657
NaBr	–728	CsI	–600
NaI	–690	$MgCl_2$	–2326
		$SrCl_2$	–2127

EXERCISE

Q.1 Select the suitable answer from the given choice:

(i) If an endothermic reaction is allowed to take place very rapidly in the air, the temperature of the surrounding air:

(a) remains constant (b) increases
(c) decreases (d) remain unchanged

(ii) In endothermic reactions, the heat content of the:

(a) Products is more than that of reactants
(b) reactants is more than that of products
(c) both (a) and (b)
(d) reactants and products are equal.

(iii) Joule is equivalent to:

(a) 0.329 cal (b) 0.923 cal
(c) 0.239 cal (d) 0.932 cal

(iv) The change in heat energy of chemical reaction at constant temperature and pressure is called:

(a) enthalpy change (b) heat of sublimation
(c) bond energy (d) internal energy change

(v) Which of the following statements is contrary to the first law of thermodynamics?

(a) Energy can neither be created nor destroyed.
(b) One form of energy can be transferred into an equivalent amount of other kinds of energy.
(c) In an adiabatic process, the work done is independent of its path.
(d) Continuous production of mechanical work without supplying an equivalent amount of heat is possible.

(vi) For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as:

(a) $q_p = q_v$ (b) $q_p < q_v$
(c) $q_p > q_v$ (d) $q_p = pv/s$

(vii) For the reaction: $NaOH + HC1 \rightarrow NaCl + H_2O$ the change in enthalpy called:

(a) heat of reaction (b) heat of formation
(c) heat of neutralization (d) heat of combustion.

(viii) The net heat change in a chemical reaction is same, whether it is brought about in two or more different ways in one or several steps. It is know as:

(a) Henry's law (c) Joule's principle
(b) Hess's law (d) Law of conservation of energy

(ix) Enthalpy of neutralization of all the strong acids and strong bases has the same value because:
  (a) neutralization leads to the formation of salt and water.
  (b) strong acids and bases are ionic substances.
  (c) acids always give rise to H^+ ions and bases always furnish $O\bar{H}$ ions.
  (d) the net chemical change involve the combination of H^+ and $\bar{O}H$ ions to form water.

ANSWERS

Answers	Explanation
(i) (c)	During endothermic reaction heat is absorbed by the system from surrounding and temperature of surrounding air is decreased.
(ii) (a)	In endothermic reaction, the products are formed with the absorption of heat. So heat contents of products will be greater than reactants.
(iii) (c)	1 J = 0.239 cals Calorie is bigger unit of energy than joule.
(iv) (a)	The change in heat energy of a chemical reaction at constant temperature and pressure is called enthalpy change.
(v) (d)	It is not possible to get continuous mechanical work without supplying of heat because according to first law of thermodynamics the amount of work done is equal to the amount of supplied heat.
(vi) (c)	At constant pressure, heat supplied (q_p) is used in expansion (work done) as well as in increasing internal energy of the system. But at constant volume, heat supplied (q_v) only increases the internal energy. Hence value of q_p is greater than q_v.
(vii) (c)	When acid base reaction takes place, it leads to formation of neutral compounds (water and salt). That's why this reaction is called as neutralization reaction and heat evolved during this reaction is called heat of neutralization.
(viii) (b)	The statement is the definition of Hess's law.
(ix) (d)	Strong acids and bases are completely dissociated in water and during neutralization H^+ and OH^- combine to form H_2O, which is an exothermic process and 57.4 kJ/mol of energy is evolved. This value is always same for strong acids and bases.

Q.2 Fill in the blanks with suitable words:

(i) The substance undergoing a physical or chemical change forms a chemical ——————.

(ii) The change in internal energy —————— be measured.

(iii) Solids which have more than one crystalline forms posses —————— values of heats of formation.

(iv) A process is called —————— if it takes place on its own without any external assistance.

(v) A —————— is a macroscopic property of a system which is —————— of the path adopted to bring about that change.

ANSWERS

(i)	**system**	(ii)	**can**	(iii)	**different**
(iv)	**spontaneous**	(v)	**state function, independent**		

Q.3 Indicate the true or false as the case may be:

(i) It is necessary that a spontaneous reaction should be exothermic.

(ii) Amount of heat absorbed at constant volume is internal energy change.

(iii) The work done by the system is given the positive sign.

(iv) Enthalpy is a state function but internal energy is not.

(v) Total heat content of a system is called enthalpy of the system.

ANSWERS

Answers	Correct Statement
(i) False	No, it is not necessary that all the spontaneous processes should be exothermic because. There are some spontaneous reactions which are endothermic as well. e.g., (a) evaporation, (b) dissolution of NH_4Cl and KI.
(ii) True	At constant volume, no expansion takes place. Hence heat supplied is equal to internal energy change.
(iii) False	The work done by the system is given in negative sign (because it leads to decrease in internal energy of the system).
(iv) False	Enthalpy is a state function and internal energy is also a state function (because internal energy also has initial and final states).
(v) True	

Q.4 Define the following terms and give three examples of each:

(i) System

(ii) Surroundings

(iii) State function

(iv) Units of energy

(v) Exothermic reaction

(vi) Endothermic reaction

(vii) Internal energy of the system

(viii) Enthalpy of the system

Ans.

(i) **System:** A substance undergoing a physical or chemical change is called system.

Examples:

1. A sample of melting ice.
2. A sample of burning coal.
3. A sample of acid base mixture undergoing a reaction.

(ii) **Surrounding:** The environment containing the system is called “Surrounding”.

Examples:

1. Air
2. Beaker
3. Flask

(iii) **State Function:** A macroscopic property of a system which has definite initial and final state and is independent of the path adopted to bring the change.

Examples:

1. Temperature (T)
2. Pressure (P)
3. Volume (V)

(iv) **Units of Energy:** The SI unit of energy is joule and is defined as the amount of energy expended when a force of one Newton moves an object 1m in the direction of the force.

Examples:

$1\ J = 1\ Nm$

$1\ J = kg\ m^2s^{-2}$

$1\ J = 10^7$ ergs

Another important unit of energy is calorie which is defined as the amount of energy required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C is called 1 calorie.

Examples:

1 cal = 4.18 J

1 cal = 4.18 Nm

1 cal = 4.18×10^7 ergs

(v) **Exothermic Reactions:** A chemical reaction during which heat is released is called exothermic reaction.

Examples:

1. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393$ kJ/mole
2. $2H_{(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -285.58$ kJ/mole
3. $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -1368$ kJ/mole

(vi) **Endothermic Reactions:** A chemical reaction during which heat is absorbed is called endothermic reaction.

Examples:

1. $N_{2(g)} + O_{2(g)} \longrightarrow 2NO$ $\Delta H = +180.5$ kJ/mole

2. $PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$ $\Delta H = +90$ kJ/mole

(vii) **Internal Energy of the System:** The sum of kinetic energy and potential energy of molecules present in a system is called internal energy of the system.

(viii) **Enthalpy of the System:** Total heat contents of a system is called its enthalpy.

OR

The sum of internal energy and product of pressure and volume of the system.

Q.5 (a) Differentiate between the following:

(i) Internal energy and enthalpy.

(ii) Internal energy change and enthalpy change.

(iii) Exothermic and endothermic reaction.

(b) Define the following enthalpies and give two examples of each:

(i) Standard enthalpy of reaction.

(ii) Standard enthalpy of combustion.

(iii) Standard enthalpy of atomization.

(iv) Standard enthalpy of solution.

Ans.

(i) Difference between internal energy and enthalpy:

Internal Energy	Enthalpy
1. It is the sum of kinetic energy and potential energy of the system.	1. It is the sum of internal energy and product of pressure and volume of the system.
2. It is represented by 'E'.	2. It is represented by 'H'.
3. Mathematically it is $E = K.E + P.E$	3. Mathematically it is: $H = E + PV$
4. Its units are joule or calorie.	4. Its units are kilojoule or kilocalorie.

(ii) Difference between internal energy change and enthalpy change:

Internal Energy Change	**Enthalpy Change**
1. It is the amount of heat evolved or absorbed by the system at constant volume. i.e., $\Delta E = q_V$	1. It is the amount of heat evolved or absorbed at constant pressure. i.e., $\Delta H = q_p$
2. It is represented by ΔE.	2. It is represented by ΔH.
3. Mathematically it is $\Delta E = q + w$ or $\Delta E = q + P\Delta V$ $\Delta V = 0$ $\Delta E = q - 0$ $\Delta E = q_v$	3. Mathematically it is $\Delta H = \Delta E + P\Delta V$ or $\Delta H = q - P\Delta V + P\Delta V$ $\Delta H = q_p$

(b) (i) **Standard Enthalpy of Reaction:** Enthalpy change when certain moles of reactants as indicated by balanced equation reacts completely under standard conditions to give products is called standard enthalpy of reaction. It is represented by $\Delta H°$.

Examples:

1. $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H° = -285.8$ kJ/mol
2. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H° = -393.7$ kJ/mol

(ii) **Standard Enthalpy of Combustion:** Enthalpy change when one mole of substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion. It is denoted by ΔH^o_c.

Examples:

1. $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H^o_c = -1368$ kJ/mol
2. $2C_2H_{2(g)} + 5O_{2(g)} \longrightarrow 4CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H^o_c = -1296$ kJ/mol

(iii) **Standard Enthalpy of Solution:** Enthalpy change when one mole of substance is dissolved in so much solvent that further dilution results in no detectable heat change. It is represented by ΔH^o_s.

OR

Enthalpy change when one mole of a substance is dissolved in solvent to form infinitely dilute solution.

Examples:

1. $NH_4Cl_{(s)} + aq\ H_2O \rightleftharpoons NH_4Cl_{(aq)}$ $\Delta H^o_s = 16.2$ kJ/mol

2. $Na_2CO_{3(s)} + aq\ H_2O \rightleftharpoons Na_2CO_{3(aq)}$ $\Delta H^o_s = -25$ kJ/mol

(iv) **Standard Enthalpy of Atomization:** Enthalpy change when one element is converted in one mole of gaseous atoms under standard conditions is called standard enthalpy of atomization. It is represented by ΔH^o_{at}.

Examples:

1. $\frac{1}{2} H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H^o_{at} = 218$ kJ/mol

2. $\frac{1}{2} Cl_{2(g)} \longrightarrow Cl_{(g)}$ $\Delta H^o_{at} = 121$ kJ/mol

Q.6 (a) What are spontaneous and non-spontaneous process. Give examples.

(b) Explain that burning of a candle is a spontaneous process.

(c) Is it true that a non-spontaneous process never happens in the universe? Explain it.

Ans.

(a) **Spontaneous Process:** A process that takes place on its own without any external assistance and moves from non-equilibrium to equilibrium state is called spontaneous process. It is unidirectional, irreversible and real process.

Examples:

1. Spreading fragrance from one corner to another.
2. Neutralization reaction of strong acid and strong base.

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

Non-spontaneous Process: A process that requires external assistance to take place is called non-spontaneous process.

Examples:

1. Reaction between N_2 and O_2 to form NO.
2. Flow of heat from cold body to hot body.

(b) All the processes that proceeds with the decrease in energy of the system (exothermic) are spontaneous.

Burning of candle requires some energy to initiate (from burning matchstick) and burning proceeds further spontaneously to completion. Hence, it is a spontaneous process because all those reactions that requires external assistance to start and proceeds further at their own are spontaneous.

(c) No, it is not true non-spontaneous process sometime happens whenever there is a source of energy naturally.

For example: combination of N_2 and O_2 is non-spontaneous. But this reaction does happen when electric current produced by thunder storms passes through the air.

$$N_2 + O_2 \xrightarrow[\text{current}]{\text{electric}} 2NO$$

Q.7 (a) What is the first law of thermodynamics. How does it explain that:

(i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

(b) How will you differentiate between ΔE and ΔH? It is true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

Ans.

(a) **First Law of Thermodynamics:** It states that:

“Energy can neither be created nor be destroyed but it can be changed from one form to another”.

OR

“Internal energy change of the system (ΔE) is equal to the sum of (i) heat evolved or absorbed (q) (ii) work done by or on the system.

$$\Delta E = q + w$$

or $$\Delta E = q + P\Delta V$$

1. $qv = \Delta E$: Consider the heat supplied to the system at constant volume.

$$\Delta E = q + P\Delta V$$

$$\Delta E = qV \quad \text{(at constant volume } \Delta V = 0 \text{ and } P\Delta V = 0)$$

At constant volume heat supplied is equal to internal energy change.

2. **$q_p = \Delta H$:** For this, consider the enthalpy change at constant pressure. Enthalpy is the sum of internal energy and product of pressure and volume as

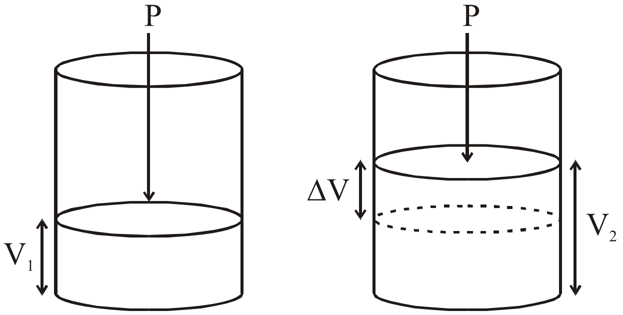
$$H = E + PV$$

Enthalpy change will be:

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

$$\Delta H = \Delta E + P\Delta V \quad \text{(Since P = Constant } \Delta P = 0 \text{ and } \Delta PV = 0)$$



Initial state Final state

For liquids and solids $\Delta V = 0$ and $P\Delta V = 0$.

$$\Delta H = \Delta E$$

For gases:

$$\Delta H = \Delta E + P\Delta V \qquad \text{...... (1)}$$

(Since $\Delta V \neq 0$ volume changes for gases by supplying heat)

Put the value of $\Delta E = q - w$

$$\Delta E = q - P\Delta V \qquad \text{...... (2)}$$

(w = –ve since, at constant pressure work is done by the system when heat is supplied)

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q_p$$

Heat supplied to system at constant pressure is used to do work as well as in increasing the internal energy of the system. Thats why it is called as enthalpy.

(b) ΔH is the amount of heat evolved or absorbed at constant pressure whereas ΔE is the amount of heat evolved or absorbed at constant volume.

$$\Delta E = qV \quad \text{and} \quad \Delta H = \Delta E + P\Delta V$$

Consider equation for ΔH

$$\Delta H = \Delta E + P\Delta V$$

For reactions taking place in solution form, heat supplied brings insignificant (negligible) volume change. Hence $\Delta V = 0$ and $P\Delta V = 0$ and equation for ΔH becomes

$$\Delta H = \Delta E + P(0) \quad \text{since,} \quad P\Delta V = 0$$

$$= \Delta E + 0$$

$$\boxed{\Delta H = \Delta E}$$

Q.8 (a) What is the difference between heat and temperature? Write a mathematical relationship between these two parameters.

(b) How do you measure the heat of combustion of substance by bomb calorimeter?

Ans. Difference between heat and temperature

Heat	Temperature
1. Measure of total kinetic energy of a substance.	1. Measure of average kinetic energy of a substances.
2. It is measured by calorimeter.	2. It is measured by thermometer.
3. It is denoted by ‘q’.	3. It is denoted by ‘T’.
4. Its units are kJ/mole Kcal mole^{-1}.	4. Its units are kelvin, centigrade (°C) or Fahrenheit (°F).
5. It depends upon quantity of substance. e.g., 2 kg of water at 70°C has twice the heat as 1 kg of water.	5. It is independent of quantity of substance. e.g., 2 kg of water at 70°C will have same temperature as that for 1 kg of water.
6. Heat is not state function.	6. Temperature is a state function.

Mathematical Relationship between Heat and Temperature:

Formula for calculating heat is:

$$q = C \times \Delta T$$

$$q \propto \Delta T \quad \text{(Since C = Constant for one substance)}$$

This relationship shows that heat and temperature are directly proportional. Greater the amount of heat supplied to specific amount of substance, greater will be rise in temperature (ΔT) and vice versa.

(b) Descriptive question, consult text book.

Q.9 Define heat of neutralization. When a dilute solution of a strong acid is neutralized by a dilute solution of strong base, the heat of neutralization is found to be nearly the same in all the cases. How do you account for this?

Ans. **Heat of Neutralization:** The amount of heat evolved when one mole of H^+ ions from an acid and one mole of $\overset{-}{O}H$ ions from a base form one 1 mole of water is called heat of neutralization.

$$HCl_{(aq)} \rightleftharpoons \overset{+}{H}_{(aq)} + \overset{-}{Cl}_{(aq)}$$

$$NaOH_{(aq)} \rightleftharpoons \overset{+}{Na}_{(aq)} + \overset{-}{OH}_{(aq)}$$

Neutralization reaction:

$$\overset{+}{H}_{(aq)} + OH^- \rightleftharpoons H_2O_{(l)} \qquad \Delta H_n^o = -57.4 \text{ kJ/mol}$$

Strong acids and strong bases are the species that undergo complete ionization. This ionization is further facilitated in dilute form.

When 1 mole of strong acid and 1 mole of strong base is taken in dilute solution form, they will ionize to 100% and will produce exactly 1 mole of H^+ ions and 1 mole of OH^- ions. They will combine to produce same amount of heat always for all the strong acids and bases.

Q.10 (a) State the laws of thermochemistry and show how are they based on the first law of thermodynamics.

(b) What is a thermochemical equation. Give three examples. What information do they convey?

(c) Why is it necessary to mention the physical states of reactants and products in a thermochemical reaction? Apply, Hess's law to justify your answer.

Ans. **First Law of Thermochemistry:** The amount of heat required to decompose a compound into its elements is equal to amount of heat evolved when compound is formed from its elements. e.g., (Lavoiser – Laplace law).

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H° = -285.58$ kJ/mol

$2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}$ $\Delta H° = 285.58$ kJ/mol

Second Law of Thermochemistry (Hess's Law): Heat change during a reaction is same and depends upon the initial and final state regardless of the path followed for reaction. e.g.,

1. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7$ kJ/mole
2. $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$ $\Delta H = -110$ kJ/mole
3. $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -283$ kJ/mole

Total heat = –393 kJ/mole

The comparison of above two paths for the formation of CO_2 shows that heat is same.

First Law of Thermodynamics (Law of conservation of energy): It states that energy can neither be created nor be destroyed but it can be changed from one form to another.

Both the laws of thermochemistry follow energy conservation principle i.e. The energy difference between two states (initial and final) is same.

For endothermic reaction, when we go from low energy state (reactant) to high energy state (products), the energy is absorbed. The same amount of energy is released in reverse manner.

$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.5$ kJ/mol

$2NO \longrightarrow N_2 + O_2$ $\Delta H = -180.5$ kJ/mol

(b) **Thermochemical Equation:** A balanced chemical equation that shows heat change during a chemical reaction is called thermochemical equation.

Examples:

1. $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -285.58$ kJ/mol
2. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7$ kJ/mol
3. $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.5$ kJ/mol

Information: A thermochemical equation tells us that whether a reaction is endothermic or exothermic i.e. It will require heat or it will release heat. From these informations, worker can maintain the conditions in the laboratory to carry out reaction.

(c) The energy possessed by the particles of a substance is according to its physical state. If a substance is formed from its element in different physical states in two reactions, then enthalpy change will also be different.

Consider the following reactions:

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H = -241.5$ kJ/mol

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -285.8$ kJ/mol

In both the cases H_2 and O_2 reacts to form H_2O when water is formed in gaseous state (in which particles posses greater energy) the enthalpy change is less in comparison to the case when H_2O is formed in liquid state (in which particles posses less energy). In later case enthalpy change is more.

Hence, physical states of reactants and products is necessary to mention because it directly correlates to enthalpy change.

Applying Hess's Law:

Two Step Process:

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H = -241.5$ kJ/mol

$2H_2O_{(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -44.3$ kJ/mol

Single Step Process:

$2H_{(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -285.8$ kJ/mol

In both paths, enthalpy changes are same. This is Hess's law.

Q.11 (a) Define and explain Hess's Law of constant heat summation. Explain it with examples and give its applications.

(b) Hess's law help us, to calculate the heat of those reactions.

Ans.

(a) Descriptive question, consult text book.

(b) For those reactions whose heat of reaction cannot be measured directly, Hess's law gives us an indirect measurement of enthalpy of reaction. For example enthalpy of formation of CO is calculated as follows:

First path:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393 \text{ kJ/mole}$$

Second path:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{(g)}$ $\qquad \Delta H_1 = ?$

(ii) $CO_{(g)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\qquad \Delta H_2 = -283$ kJ/mole

According to Hess's law:

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 \\ -393 &= \Delta H_1 - 283 \\ \Delta H_1 &= -393 + 283 \\ \Delta H_1 &= -110 \text{ kJ/mole} \end{aligned}$$

This is indirect measurement of enthalpy of CO.

Q.12 (a) What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

(b) Justify that heat of formation of compound is the sum of all the other enthalpies.

Ans.

(a) Descriptive question, consult text book.

(b) Enthalpy of formation of a compound is equal to the sum of its enthalpy of combustion and enthalpies of combustion of elements from which it is formed. For example:

Formation of ethyl alcohol:

$$2C + 3H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow C_2H_5OH_{(l)} \qquad \Delta H = ?$$

Enthalpies of combustion of carbon, hydrogen and C_2H_5OH.

(i) $C + O_2 \longrightarrow CO_2$ $\qquad \Delta H = -394$ kJ/mole

(ii) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$ $\qquad \Delta H = -285.8$ kJ/mole

(iii) $C_2H_5OH + O_2 \longrightarrow 2CO_2 + 3H_2O$ $\qquad \Delta H = -1368$ kJ/mole

Multiply eq. (i) by 2 and eq. (ii) by 3 and add then. From this adduct, subtract equation (iii).

$$\begin{array}{lll}
\text{(i)} & 2C_{(g)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} & \Delta H = -788 \text{ kJ/mole} \\
\text{(ii)} & 3H_{2(g)} + \frac{3}{2} O_{2(g)} \longrightarrow 3H_2O_{(g)} & \Delta H = -857.4 \text{ kJ/mole} \\
\text{(iii)} & \underset{-}{}C_2H_5OH + \underset{-}{3O_2} \longrightarrow \underset{-}{2CO_2} + \underset{-}{3H_2O} & \Delta H = \underset{+}{-}1368 \text{ kJ/mole} \\
\hline
 & 2C_{(s)} + 3H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow C_2H_5OH_{(l)} & \Delta H = -277.4 \text{ kJ/mole}
\end{array}$$

$\Delta H = -277.4$ kJ/mole is enthalpy of formation of C_2H_5OH.

Q.13 50 cm^3 of 1.0 HM HCl is mixed with 50 cm^3 of 1.00 M NaOH in a glass calorimeter. The temperature of the resultant mixture increases from 21.0°C to 27.5°C. Assume, that calorimeter losses of heat are negligible. Calculate the enthalpy change $mole^{-1}$ for the reactions. The density of solution to be considered is 1 gcm^{-3} and specific heat is 4.18 $Jg^{-1}k$.

Ans. Initial temperature of solution = 21°C

= 21°C + 273 = 294 K

Final temperature = 27.5°C

= 27.5°C + 273 = 300.5 K

Difference of temperature = 300.5 – 294 = 6.5 K

Volume of HCl = 50 cm^3

Volume of NaOH = 50 cm^3

Total volume of solution = 50 + 50 = 100 cm^3

As density of solution = 1 g/cm^3

Total mass of solution = 100 g

Heat evolved can be calculated by the relation:

$$\begin{aligned} q &= m \times s \times \Delta T \\ &= 100 \times 4.18 \times 6.5 \\ &= -2717 \text{ J or } -2.717 \text{ kJ} \end{aligned}$$

No of moles of HCl in 1000 cm^3 = 1 mole

No of moles of HCl in 50 cm^3 $= \dfrac{1}{1000} \times 50 = 0.05$ mol

The amount of heat evolved per mol $= \dfrac{-2.717}{0.05}$

$\Delta H_n = -54.34$ kJ/mol

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

$$\begin{array}{ccc} H^+ & + OH^- \longrightarrow & H_2O \\ 0.05 \text{ mol} & 0.05 \text{ mol} & 0.05 \text{ mol} \end{array}$$

Heat evolved per 0.05 mol of H_2O = –54.34 kJ/mol

Q.14 Hydrazine (N_2H_4) is rocket fuel. It burns in O_2 to give N_2 and H_2O.

$$N_2H_{4(l)} + O_{2(g)} \xrightarrow{\quad} N_{2(g)} + 2H_2O_{(g)}$$

1.00 g of N_2 H_4 is burned in a bomb calorimeter. An increase of temperature. 3.51°C is recorded. The heat capacity of calorimeter is 5.5 $Jg^{-1}K^{-1}$. Calculate the quantity of heat evolved. Also, calculate the heat of combustion of 1 mole of N_2H_4.

Ans. Mass of hydrazine burnt= 1 g

Heat capacity of bomb calorimeter = 5.5 kJ $K^{-1}g^{-1}$

Rise in temperature = ΔT = 3.51°C

Enthalpy of combustion = ΔH_C = ?

$q = m \times s \times \Delta T$

$= 1 \times 5.5 \times 3.51$

$= 19.3$ kJ

Amount of heat for 1 g of N_2H_4 = −19.3 kJ

(−ve sign is used because it is a combustion reaction and heat is evolved)

Molar mass of N_2H_4 = 32 g/mol

Heat evolved by 32 g of N_2H_4 = -19.3×32 = −617.6 kJ/mol

Q.15 Octane (C_8H_{18}) is a motor fuel. 1.0 g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJ k^{-1}. The temperature of the calorimeter increases from 21.36°C to 28.78°C. Calculate the heat of combustion for 1 g of octane. Also, calculate the heat for 1 mole of octane.

Ans. Mass of octane burned = 1.0 g

Molar mass of octane = 114 g/mole

Rise of temperature ΔT = $T_2 - T_1$

= 28.78 − 21.36 = 7.42°C

Heat capacity of bomb calorimeter = 11.66 kJ/K

Heat of combustion by a Bomb Calorimeter.

As $q = C \times \Delta T$

Therefore $q = 11.66 \times 7.42$

= 86.51 kJ/mole

Hence amount of heat for 1 g of octane will be = −86.51 kJ/g

Amount of heat for 114 g (1 mole) of octane = -86.51×114

= −9862.14 kJ/mole

Q.16 By applying, Hess's law calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl. The results for various reactions and pressures are as follows.

(i) $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H = -35.16$ kJ mol

(ii) $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H = -72.41$ kJ mol

(iii) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48$ kJ mol

Ans. Add the given three equations and the total enthalpy will be equal to the formation of aq. NH_4Cl from NH_3 and HCl gas.

$$\begin{array}{ll} NH_{3(g)} + aq \longrightarrow NH_{3(aq)} & \Delta H_1 = -35.16 \text{ kJ mol}^{-1} \\ HCl_{(g)} + aq \longrightarrow HCl_{(aq)} & \Delta H_2 = -72.41 \text{ kJ mol}^{-1} \\ HCl_{(aq)} + NH_{3(aq)} \longrightarrow NH_4Cl_{(aq)} & \Delta H_3 = -51.48 \text{ kJ/mol}^{-1} \\ \hline NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(aq)} & \Delta H = -159.05 \text{ kJ/mol}^{-1} \end{array}$$

As according to Hess's law:

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -35.16 - 72.41 - 51.48 \\ &= -159.05 \text{ kJ/mol} \end{aligned}$$

Q.17 Calculate the heat of formation of ethyl alcohol from the following information:

(i) Heat of combustion of ethyl alcohol is -1368 kJ mole^{-1}

(ii) Heat of formation of carbon dioxide is -393.7 kJ mol^{-1}

(iii) Heat of formation of water is -285.8 kJ mol^{-1}

Ans. Formation of ethyl alcohol is given by equation:

$$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH \qquad \Delta H_f^o = ?$$

(i) Combustion of ethyl alcohol is given as:

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \qquad \Delta H_C^o = -1368 \text{ kJ mol}^{-1}$$

(ii) Formation of carbon dioxide:

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H_C^o = -393.7 \text{ kJ/mol}$$

(iii) Formation of water:

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H_f^o = -285.8 \text{ kJ/mol}$$

Invert equation (i), multiply equation (ii) by 2 and equation (iii) by 3 and then add these equations in inverted equation (i).

(i) $2CO_2 + 3H_2O \xrightarrow{\qquad} C_2H_5OH + 3O_2$ $\qquad \Delta H^o_C = 1368 \text{ kJ mol}^{-1}$

(ii) $2C + 2O_2 \xrightarrow{\qquad} 2CO_2$ $\qquad \Delta H^o_f = -787.4 \text{ kJ/mol}$

(iii) $3H_2 + \frac{3}{2}O_2 \xrightarrow{\qquad} 3H_2O$ $\qquad \Delta H^o_f = -857.4 \text{ kJ mol}^{-1}$

$2C + 3H_2 + \frac{1}{2}O_2 \xrightarrow{\qquad} C_2H_5OH$ $\qquad \Delta H^o_f = -276.8 \text{ kJ/mol}$

Q.18 If the heat of combustion of C_2H_2, H_2 and C_2H_6 are –337.2, 68.3 and –372.8 K calories respectively, then calculate the heat of the following reaction.

$$C_2H_2 + 2H_2 \xrightarrow{\qquad} C_2H_{6(g)}$$

Ans. $C_2H_2 + 2H_2 \xrightarrow{\qquad} C_2H_6$

(i) Combustion of C_2H_2:

$C_2H_2 + \frac{5}{2}O_2 \xrightarrow{\qquad} 2CO_2 + H_2O$ $\qquad \Delta H = -337.2 \text{ K Cal}$

(ii) Combustion of H_2:

$H_2 + \frac{1}{2}O_2 \xrightarrow{\qquad} H_2O$ $\qquad \Delta H = -68.3 \text{ K Cal/mol}$

(iii) Combustion of C_2H_6:

$C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\qquad} 2CO_2 + 3H_2O$ $\qquad \Delta H = -372.8 \text{ K Cal/mol}$

Multiply equation (ii) by 2 and add in eq. (i)

(i) $C_2H_2 + \frac{5}{2}O_2 \xrightarrow{\qquad} 2CO_2 + H_2O$ $\qquad \Delta H = -337.2 \text{ K Cal/mol}$

(ii) $2H_2 + O_2 \xrightarrow{\qquad} 2H_2O$ $\qquad \Delta H = -136.6 \text{ K Cal/mol}$

(iv) $C_2H_2 + 2H_2 + \frac{7}{2}O_2 \xrightarrow{\qquad} 2CO_2 + 3H_2O$ $\qquad \Delta H = -473.8 \text{ K Cal/mol}$

Now subtract eq. (iii) from eq. (iv), we get:

(iv) $C_2H_2 + 2H_2 + \frac{7}{2}O_2 \xrightarrow{\qquad} 2CO_2 + 3H_2O$ $\qquad \Delta H = -473.8 \text{ K Cal/mol}$

(iii) $\underset{-}{C_2H_6} + \underset{-}{\frac{7}{2}O_2} \xrightarrow{\qquad} \underset{-}{2CO_2} + \underset{-}{3H_2O}$ $\qquad \Delta H = -372.8 \text{ K Cal/mol}$

$C_2H_2 + 2H_2 \xrightarrow{\qquad} C_2H_6$ $\qquad \Delta H = -101 \text{ K Cal/mol}$

Q.19 Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is –395.51 kJ mol^{-1} and that of diamond is –395.41 kJ mol^{-1}.

What is the enthalpy change of the process? Graphite → Diamond at the same temperature?

Ans.

(i) $C_{(graphite)} + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.5 \text{ kJ/mol}$

(ii) $C_{(diamond)} + O_2 \longrightarrow CO_2 \qquad \Delta H = -395.41 \text{ kJ/mol}$

Now subtract equation (ii) from equation (i):

$$C_{(graphite)} + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.51 \text{ kJ/mol}$$

$$\underset{-}{C_{(diamond)}} \underset{-}{+} O_2 \longrightarrow \underset{-}{CO_2} \qquad \Delta H = -395.41 \text{ kJ/mol}$$

$$C_{(graphite)} \longrightarrow C_{(diamond)} \qquad (-393.51) - (-395.41)$$

$$\Delta H = 1.9 \text{ kJ/mol}$$

Q.20 What is the meaning of the term enthalpy of ionization? If the heat of neutralization of HCl and NaOH is –57.3 kJ mol^{-1} and heat of neutralization of CH_3COOH with NaOH is –55.2 kJ mol^{-1}, calculate the enthalpy of ionization of CH_3COOH.

Ans. Enthalpy of Ionization: In case of HCl and NaOH.

$$HCl + NaOH \longrightarrow NaCl + H_2O \qquad \Delta H = -57.3 \text{ kJ mol}^{-1}$$

$$H^+ + OH^- \longrightarrow H_2O$$

In case of CH_3COOH and NaOH.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O \quad \Delta H = -55.2 \text{ kJ mol}^{-1}$$

$$H^+ + OH^- \longrightarrow H_2O$$

In both cases same type of reaction, takes place.

Heat of neutralization of both equations must be same, but they are not equal, actually the difference of enthalpies is of 2.1 kJ/mol.

Because acetic acid is a weak acid and 2.1 kJ/mol of energy is required for the ionization of this acid. Therefore in this case less amount of energy is released.

Enthalpy of ionization of CH_3COOH is:

$$(-55.2 \text{ kJ}) - (-57.3 \text{ kJ}) = 2.1 \text{ kJ/mol}$$

Q.21 (a) Explain what is meant by the following terms:

(i) Atomization energy (ii) Lattice energy

(b) Draw a complete, fully labeled Born-Haber cycle for the formation of potassium bromide.

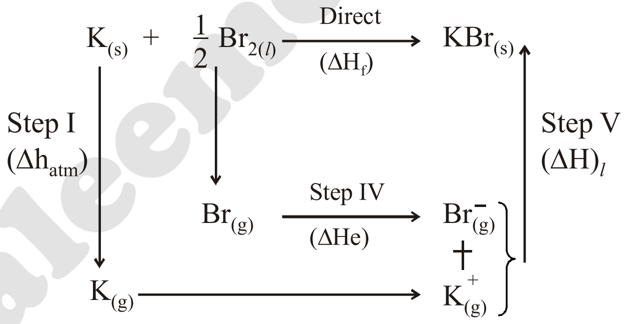
(c) Using the information given in the table below, calculate the lattice energy of potassium bromide.

Reactions	**ΔH/kJ mol^{-1}**
$K_{(s)} + ½ Br_{2(l)} \longrightarrow K^+Br^-_{(s)}$	–923
$K_{(s)} \longrightarrow K_{(g)}$	+90
$K_{(g)} \longrightarrow K^+_{(g)} + e$	+420
$½ Br_{2(l)} \longrightarrow Br_{(g)}$	+112
$Br_{(g)} + e \longrightarrow Br^-_{(g)}$	–342

Ans.

(a) Consult text book.

(b) Draw a complete Born Haber cycle for formation of KBr.



(c) $K_{(s)} + \frac{1}{2} Br_{2(l)} \longrightarrow KBr_{(s)}$ $\Delta H_f = -392$ kJ mol^{-1}

$K_{(s)} \longrightarrow K_{(g)}$ $\Delta H_{at} = +90$ kJ mol^{-1}

$K_{(g)} \longrightarrow K^+ + e^-$ $\Delta H_i = +420$ kJ mol^{-1}

$\frac{1}{2} Br_{2(l)} \longrightarrow Br^-_{(g)}$ $\Delta H_d = +112$ kJ mol^{-1}

$Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$ $\Delta H_e = -342$ kJ mol^{-1}

ΔH_l = ? (lattice energy)

Heat of formation of a compound is equal to the sum of all these processes (atomization, ionization, dissociation, electron affinity and lattice energy).

$$\Delta H_f = \Delta H_{at} + \Delta H_i + \Delta H_d + \Delta H_e + \Delta H_l$$

$$-392 = 90 + 420 + 112 - 342 + \Delta H_l$$

$$-392 = 280 + \Delta H_l$$

$$\Delta H_l = -392 - 280$$

$$\Delta H_l = -672 \text{ kJ/mol}$$

−672 kJ/mol is the lattice energy of potassium bromide (KBr)

[illegible] KNOW?

1. 1 Cal = 4.184 J
1 J = 0.239 Cal

2. The energy expended when a force of 1N moves an object 1m in the direction of the force
1 J = 1 N × 1 m

3. The amount of heat required to raise the temperature of one gram of water through 1°C is called one calorie.

4. The amount of heat required to raise the temperature of one pound of water through 1°F is called one BTU (British thermal unit). (12000 BTU = 1 ton)

5. 1 Joule = 10^7 ergs

6. Burning of candle is spontaneous process.

7. The substance or mixture of substances which is under experiment or under discussion for sake of argument is called a system.

8. Every thing which is not part of the system or the environment containing the system is called surrounding.

9. The real or imaginary surface separating the system from the surrounding is called boundary.

10. The conditions of the system like temperature pressure, volume, enthalpy are called state of the system.

11. The amount of enthalpy change which occurs when number of moles of reactant react together as specified in the balanced chemical equation at standard states is called standard enthalpy of reaction.

12. The enthalpy change when 1 mol of compound is formed from its elements at standard state is called standard enthalpy of formation.

13. The enthalpy change when one mole of gaseous atoms are formed from the elements under standard states is called enthalpy of atomization.

14. The amount of heat evolved when 1 mol of H^+ from the acid react with 1 mol of the OH^- from the base to form 1 mol of H_2O at the standard states is called standard heat of neutralization.

15. The enthalpy change when 1 mol of a substance is completely burnt in excess of oxygen at standard conditions is called standard heat of combustion.

16. The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change at standard conditions is called standard heat of solution.

17. Bomb calorimeter is used for the accurate determination of enthalpy of combustion of food and fuel or other compounds.

18. Born-Haber cycle is another form of Hess's law.

19. The amount of energy required to break the solid into the isolated ions in the gas phase is called Lattice energy.

20. $q_p > q_v$

Chapter 8

CHEMICAL EQUILIBRIUM

IRREVERSIBLE REACTION

"The reaction which proceeds only in one direction and product formed cannot be converted to reactants is called **irreversible reaction**."

For example, sodium metal reacts with water to form sodium hydroxide and H_2 gas.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

H_2 reacts with O_2 to form H_2O in electric spark.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

This reaction is represented as single head arrow (→). If reactants are taken in stiochiometric amounts (as specified in balance equation) no reactant is left behind and it is totally converted to product. For example, when 4g of H_2 and 32g of O_2 reacts together, no residual will be present in the presence of electric spark. However, if H_2O is heated at $1500^{\circ}C$ some molecules decompose to form again H_2 and O_2.

REVERSIBLE REACTIONS

"The reactions that do not proceed to completion and take place in both directions are called **reversible reactions**."

Reversible reactions are denoted by the sign $\rightleftharpoons$.

For example, when N_2 reacts with H_2 at $450^{\circ}C$, under high pressure in the presence of a catalyst, following reaction takes place.

$$N_{2(g)} + 3H_{2(g)} \underset{\text{High Pressure}}{\overset{450^{\circ}C}{\rightleftharpoons}} 2NH_{3(g)}$$

The reaction mixture, after some time, will contain all the three species i.e. nitrogen, hydrogen and ammonia. No matter, how long the reaction is allowed to continue, the percentage composition of species present remains constant. The conditions are favorable for the forward as well as for a reverse reaction to occur to a measurable extent.

Other examples, of reversible reactions.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

STATE OF CHEMICAL EQUILIBRIUM

"The state of chemical reaction at which rate of forward reaction is exactly equal to the rate of backward reaction is called **equilibrium state**."

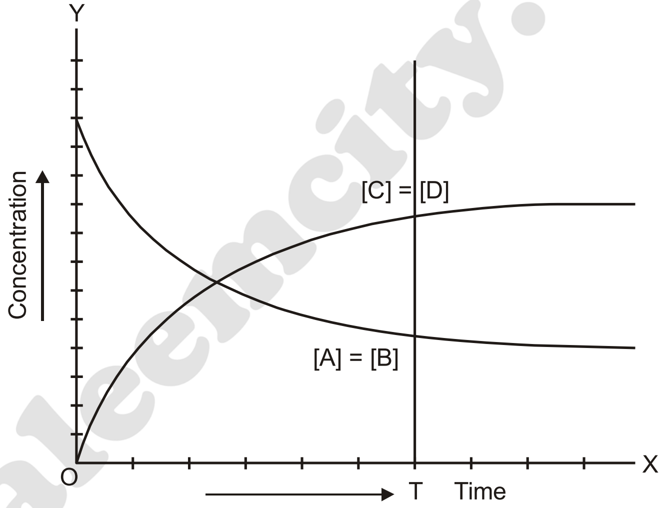
Rate of forward reaction = Rate of backward reaction.

If a reversible reaction is allowed to continue for a considerable long time, without changing the conditions, there is no further change in composition of the reaction mixture. The reaction is said to have attained a state of chemical equilibrium. Once this equilibrium has been established, it will last forever if undisturbed.

To illustrate an example of the attainment of equilibrium, let use consider a general reaction, in which A reacts with B to produce C and D.

$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$

All the substances are in gaseous form.



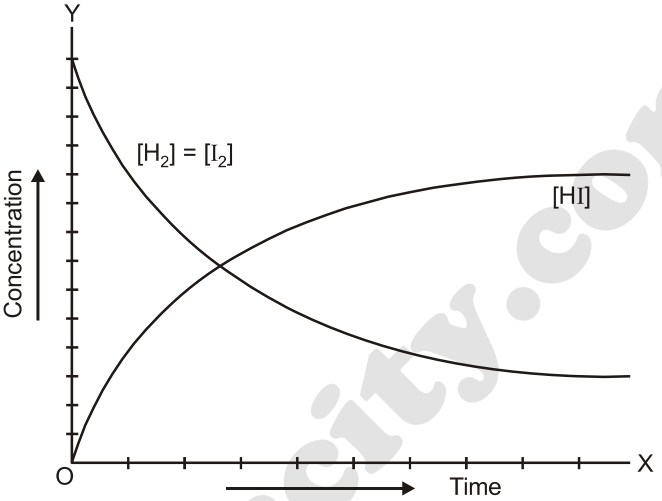
Reversible reaction and state of equilibrium

Let the initial concentrations of A and B be equal. As time goes on, concentrations of A and B decrease, at first quite rapidly but later slowly. Eventually the concentrations of A and B decreases and become constant. The initial concentrations of C and D are zero. As the time passes the products C and D are formed. Their **concentrations increase rapidly at first** and then decreases. At time T_{eq}, the concentrations become constant. This is how the chemical equilibrium is attained, i.e. state of equilibrium is reached. At equilibrium line the products and reactant are parallel to each other.

Consider an example of reversible reaction between H_2 gas and I_2 vapours to for HI at 450°C.

$$H_{2(g)} + I_{1(g)} \overset{450^\circ C}{\rightleftharpoons} 2HI_{(g)}$$

The same equilibrium mixture is obtained irrespective whether the reaction starts by mixing hydrogen and iodine or by decomposition of hydrogen iodide. The situation suggests two possibilities of the state of reaction at equilibrium; either all reactions cease at equilibrium so that the system becomes stationary or the **forward and reverse reactions** are taking place simultaneously at **exactly the same rate**. It is now universally accepted that the later conditions prevail in a reversible reaction at equilibrium. It is known as the state of **dynamic equilibrium**. At equilibrium product and reactant lines are parallel to each other.



State of dynamic equilibrium

LAW OF MASS ACTION

This law was given by C.M. Guldberg and P. Waage in 1864.

This law states as:

"The rate of a chemical reaction is directly proportional to the product of active masses of reactants." (active mass means molar concentration)

The **active mass** is the amount of a substance which changes into products in a chemical reaction. Initial concentration of a substance is not always an active mass. For dilute solution, active mass is usually the concentration of reactants in mole dm^{-3}.

Now, consider a general reaction in which A and B are the reactants and C and D are the products. The reaction is represented by the following chemical equation.

$$A + B \rightleftharpoons C + D$$

The equilibrium concentrations 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}. According to the law of Mass Action, the rate of the forward reaction, i.e. the formation of products C and D, is proportional to the product of molar concentrations of A and B.

Rate of forward reaction $\propto$ [A] [B]

$$R_f = k_f [A] [B]$$

k_f is the proportionality constant and is called **rate constant** for forward reaction and R_f is the rate of forward reaction. Similarly, the rate of reverse reaction (R_r) is given by

$$R_r = k_r [C] [D]$$

Where k_r is the proportionality constant and is called **the rate constant for backward reaction**. At **equilibrium both rates**, forward and reverse and **equal**.

$$R_f = R_r$$

$$k_f = [A] [B] = k_r [C] [D]$$

On rearranging, we get

$$K_c = \frac{k_f}{k_r} = \frac{[C] [D]}{[A] [B]}$$

The constant K_c is called **the equilibrium constant of the reaction**. Conventionally, while writing equilibrium constant, the products are written as numerator and reactants as denominator.

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

and $$K_c = \frac{\text{Rate constant for forward step}}{\text{Rate constant for backward step}}$$

For a more general reaction

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c and d are the coefficients or the number of moles of A, B, C and D respectively which are present at the equilibrium.

The equilibrium constant is given by

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The coefficients in the equation appear as exponents of the terms of concentrations in the equilibrium constant expression.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2] [H_2]^3}$$

2. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3] [Cl_2]}{[PCl_5]}$$

Units of Equilibrium Constants:

Equilibrium constant is the ratio of the products of the concentrations of the products to the product of concentrations of the reactants. If the reaction has **equal number of moles** on the reactant and product sides, then equilibrium constant has **no unit**. When the number of moles is unequal then it has units related to the concentration or pressure. But it is a usual practice that we don't write the units with K_p or K_c values.

Following are some important reversible reactions, their K_c are expressed as

(i) $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$K_c = \frac{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]} = \textbf{no units}$$

(ii) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]^3} = \frac{\text{mol}^2\,\text{dm}^{-6}}{(\text{mol dm}^{-3})(\text{mol}^3\,\text{dm}^{-9})}$$

$$K_c = \text{mol}^{-2}\,\text{dm}^{+6}$$

In the expression of K_c, we have ignored the physical states for the sake of convenience.

Example 1:

The following reaction was allowed to reach the state of equilibrium.

$$2A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)}$$

The initial amounts of the reactants present in one dm^3 of solution were 0.50 mole of A and 0.60 mole of B. At equilibrium the amounts were 0.20 mole of A and 0.45 mole of B and 0.15 mole of C. Calculate the equilibrium constant, K_c.

Solution:

K_c for the reaction is given by

$$K_c = \frac{[C]}{[A]^2\,[B]}$$

	$2A_{(aq)}$ +	$B_{(aq)}$ $\rightleftharpoons$	$C_{(aq)}$
Initial conc.	0.50	0.60	0.00
Eq. conc.	0.20	0.45	0.15

K_c of a reaction is calculated from the equilibrium concentration only.

Since $K_c = \frac{[C]}{[A]^2\,[B]}$

So, $K_c = \frac{0.15}{(0.20) \times (0.20) \times (0.45)}$

$$= \frac{0.15}{0.04 \times 0.45} = \frac{0.15}{0.018} = 8.3$$

EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME IMPORTANT REACTIONS

1. Formation of Ester from an Organic Acid and Alcohol (Esterification):

This is a well known reversible reaction in the solution state.

Let us suppose 'a' moles of CH_3COOH and 'b' moles of C_2H_5OH are initially taken in a vessel in the presence of small amount of a mineral acid as a catalyst.

The progress of the reaction can be studied by finding out the concentrations of acetic acid after regular intervals. A very small portion of the reaction mixture is withdrawn, and the concentration of acetic acid is determined by titrating it against a standard solution of sodium hydroxide. The concentration of acetic acid will decrease until the attainment of state of equilibrium, when it will become constant. At equilibrium stage, x moles of ester and 'x' moles of H_2O are produced. The number of moles of acid and alcohol left behind are 'a – x' moles and 'b – x' moles respectively. If the volume of reaction mixture at equilibrium stage is 'v' dm^3, then

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

a moles	b moles	0 moles	0 moles	t = 0 sec
(a – x) moles	(b – x) moles	x moles	x moles	t = eq.

When number of moles are divided by total volume of the reaction mixture, we get concentration in moles dm^{-3}.

$$\left(\frac{a-x}{v}\right)\text{moles dm}^{-3}\ \left(\frac{b-x}{v}\right)\text{moles dm}^{-3}\ \left(\frac{x}{v}\right)\text{moles dm}^{-3}\ \left(\frac{x}{v}\right)\text{moles dm}^{-3}$$

Since $K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$

Putting concentrations at equilibrium

$$K_c = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{a-x}{v}\ \frac{b-x}{v}}$$

$$K_c = \frac{x^2}{(a-x)\,(b-x)}$$

In this expression of K_c the factor of volume has been cancelled out. So the change of volume at equilibrium stage does not effect the K_c value or value or equilibrium position of reaction.

2. Dissociation of PCl_5:

The dissociation of PCl_5 into PCl_3 and Cl_2, is a well known homogeneous gaseous phase reaction, with unequal number of moles of reactants and products.

Let 'a' moles of PCl_5 present initially are decomposed by 'x' moles. At equilibrium stage, a – x' moles of PCl_5 are left behind while 'x' moles of PCl_3 and 'x' moles of Cl_2 are produced. If the volume of equilibrium mixture is 'v' litres, then

$$\begin{array}{lllll} PCl_{5(g)} & \rightleftharpoons & PCl_{3(g)} \quad + & Cl_{2(g)} & \\ \text{a moles} & & \text{0 moles} & \text{0 moles} & t = 0 \text{ sec} \\ (a - x) \text{ moles} & & \text{x moles} & \text{x moles} & t = \text{equilibrium} \end{array}$$

Dividing the number of moles by total volume of reactants.

$$\left(\frac{a-x}{v}\right) \text{moles dm}^{-3} \left(\frac{x}{v}\right) \text{moles dm}^{-3} + \left(\frac{x}{v}\right) \text{moles dm}^{-3}$$

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{a-x}{v}}$$

$$K_c = \frac{x^2}{v\,(a-x)}$$

The final expression is not independent of the factor of volume. The change of volume at equilibrium stage disturbs the equilibrium position of the reaction. We will discuss this reaction in Le–Chatelier's principle with reference to effect of volume change and its effect on change of equilibrium position.

3. Decomposition of Dinitrogen Tetra Oxide (N_2O_4):

N_2O_4 on heating at 100°C changes to NO_2.

$$\begin{array}{llll} N_2O_4 & \rightleftharpoons & 2NO_{2(g)} & \\ \text{a mole} & & \text{0 mole} & t = 0 \text{ sec} \\ a - x & & 2x & t = \text{equilibrium} \end{array}$$

'a' is the initial number of moles of N_2O_4, 'x' is number of moles of NO_2 at equilibrium and 'v' is total volume of N_2O_4 and NO_2 at equilibrium stage.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)}$$

$$= \frac{4x^2}{v^2} \times \frac{v}{a-x}$$

$$K_c = \frac{4x^2}{v\,(a-x)}$$

4. Synthesis of NH_3:

Nitrogen combine with hydrogen at 450°C and high pressure to form NH_3.

$$\begin{array}{llll} N_{2(g)} & + \quad 3H_{2(g)} & \rightleftharpoons & 2NH_{3(g)} \\ \text{a moles} & \quad\;\; \text{0 moles} & & \text{0 moles} \quad t = 0\text{ sec} \\ a-x & \quad\;\; b-3x & & 2x \quad t = \text{equilibrium} \end{array}$$

Where 'a' and 'b' are the initial number of moles of N_2 and H_2 and 'x' is number of moles of N_2 decomposed at equilibrium stage. 'v' is the total volume of N_2, H_2 and NH_3 at equilibrium. The final expression involves v^2 in the numerator:

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$= \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3}$$

$$= \frac{4x^2 \,.\, v \,.\, v^3}{v^2\,(a-x)\,(b-3x)^3}$$

$$K_c = \frac{4x^2 \,.\, v^2}{(a-x)\,(b-3x)^3}$$

Relationship Between Equilibrium Constants:

The expressions of equilibrium constants depend upon the concentration units used. Mostly the concentrations are expressed in mole dm^{-3}. Let us consider the following reversible reaction.

$$aA + bB \rightleftharpoons cC + dD \qquad (1)$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \quad \text{or} \quad K_c = \frac{C_C^c\,D_D^d}{A_A^a\,B_B^b}$$

The square brackets represent the concentration of species in moles dm^{-3}.

Relation Between K_c and K_p:

(i) When moles are equal on both side:

If the reactants A, B and the products C, D of the reaction under consideration are ideal gases, molar concentration of each gas is proportional to its partial pressure. When the concentrations are expressed in terms of partial pressure the expression of K_p is,

$$K_p = \frac{P_C^c\, P_D^d}{P_A^a\, P_B^b}$$

Here P_A, P_B, P_C and P_D are partial pressures of A, B, C and D respectively at equilibrium position. As long as the number of moles of products and reactants, which are in the gaseous state, are equal, the values of K_C and K_P remain the same.

(ii) When moles are not equal on both side:

If moles are not equal, this relation between K_c and K_p is determined by the equation

$$PV = nRT$$

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

$$P = CRT$$

Where C is molar concentration of reactants and products. Apply this in a general equation.

$$K_p = \frac{[C]^c\,[RT]^c\,[D]^d\,[RT]^d}{[A]^a\,[RT]^a\,[B]^b\,[RT]^b}$$

$$K_p = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}\;[RT]^{(c+d)-(a+b)}$$

$$K_p = K_c \times (RT)^{\Delta n} = K_c\,.\,(RT)^{\Delta n}$$

When $\Delta n = (c + d) - (a + b)$

Δn = moles of products minus moles of reactants. R is gas constant and T is absolute temperature. K_p value increases by increasing the temperature of reaction.

If $\Delta n = 0$ than K_c is equal to K_p.

If Δn is negative, K_c is greater than K_p.

If Δn is positive, K_c is smaller than K_p.

Example 2:

$N_{2(g)}$ and $H_{2(g)}$ combine to give $NH_{3(g)}$. The value of K_c in this reaction at 500°C is 6.0×10^{-2}. Calculate the value of K_p for this reaction.

Solution:

The reaction for the synthesis of NH_3 is

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

This reaction takes place with decrease in the number of moles. The relationship for this purpose is

$K_p = K_c (RT)^{\Delta n}$

Now $K_c = 6.0 \times 10^{-2}$

Temperature = 500 + 273 = 773 K

Δn = moles of products – moles of reactants

$\Delta n = 2 - 4 = -2$

$R = 0.0821\ dm^3$ atmosphere $K^{-1}\ mol^{-1}$

Substituting these values in the expression.

$$K_p = 6.0 \times 10^{-2} (773 \times 0.0821)^{-2}$$

$$= 6.0 \times 10^{-2} (63.5)^{-2}$$

$$K_p = \frac{6.0 \times 10^{-2}}{(63.5)^2}$$

$$K_p = 1.5 \times 10^{-5}$$

In this case the value of K_p is smaller then K_c. Those reactions, which take place with increase in the number of moles, have greater K_p than K_c values.

APPLICATIONS OF EQUILIBRIUM CONSTANT

The value of equilibrium constant is specific and remains constant at particular temperature. The study of equilibrium constant provides us the following information's:

1. Prediction of direction of reaction.
2. Extent of reaction.
3. Effect of various factors on equilibrium constant at equilibrium position.

1. Prediction of Direction of Reaction:

Direction of a reaction can be predicted at any time by means of the ratio of products / reactants before the reaction attains equilibrium.

This ratio of products / reactants is called **reaction quotient Q**. For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

For prediction of direction, we put the concentration of substances into reaction quotients and compare its value to K_c. The reaction quotient, Q has the same form as equilibrium expression, but the concentration substituted are those of a mixture, that is not necessarily at equilibrium.

If $Q > K_c$, the reaction will go to the left.

If $Q < K_c$, the reaction will go to the right.

If $Q = K_c$, the reaction mixture is at equilibrium.

Example 3:

Esterification reaction between ethanol and acetic acid was carried out by mixing definite amounts of ethanol and acetic acid along with some mineral acid as a catalyst. Samples were drawn out of the reaction mixture to check the progress of the esterification reaction. In one of the samples drawn after time t, the concentrations of the species were found to be $[CH_3COOH] = 0.025$ mol dm^{-3}, $[C_2H_5OH] = 0.032$ mol dm^{-3}, $[CH_3COOC_2H_5] = 0.05$ mol dm^{-3}, and $[H_2O] = 0.04$ mol dm^{-3}. Find out the direction of the reaction if K_c for the reaction at 25^{o}C is 4.

Solution:

Esterification reaction is represented by the following stiochiometric equation.

$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

All the substances are present in the same volume of solution, therefore K_c is given by

$$Q = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

By substituting the value in the expression, we get

$$Q = \frac{0.05 \times 0.04}{0.025 \times 0.032}$$

$$Q = 2.50$$

The given value of K_c for this reaction is 4 and ratio 2.5 is less than K_c. Therefore, the reaction will proceed in the forward direction to attain the equilibrium.

2. Extent of a Chemical Reaction:

extent of a chemical reaction can be determined by the value of K_c.

(i) K_c – very large:

If value of K_c equilibrium constant is very large, this indicate the reaction is almost complete.

For example, the K_c for this reaction is very large.

$$2O_3 \rightleftharpoons 3O_2$$

$$K_c = \frac{[O_2]^3}{[O_3]^2} = 1 \times 10^{55} \text{ at } 25^oC$$

We conclude from this value that at room temperature O_3 is very unstable and changes rapidly to O_2.

(ii) K_c – very small:

If value of equilibrium constant, K_c is very small, it reflects that reaction does not proceed forward. Almost backward reaction is complete. For example,

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$$

$$K_c = \frac{[H_2]\,[F_2]}{[HF]^2} = 1 \times 10^{-13} \text{ at } 2000^oC$$

This value indicates that this compound does not decomposed rapidly even at 2000^oC.

(iii) K_c – Neither very large nor small:

If value of K_c is slightly greater than or less than one, it is a moderate value. At moderate value, appreciable amount of both reactants and product are present. For example, formation of ester from alcohol and acetic acid has $K_c = 4$.

THE EFFECT OF CONDITIONS ON THE POSITION OF EQUILIBRIUM

Equilibrium Constant:

"The rate ratio of forward constant and reverse constant is called **equilibrium constant**."

$$K_c = \frac{K_f}{K_r}$$

Every reaction has a fix value of K_c at constant temperature.

Position of Equilibrium:

"The ratio of products/reactants in equilibrium mixture is called **position of the equilibrium**."

The position of equilibrium changes by changing the condition like concentration, pressure temperature etc. If K_c is large, the position of equilibrium lies toward left. If K_c is small the position of equilibrium lies toward right, for a reversible reaction. Change in condition can be studied by Le–Chatelier's principles.

LE–CHATELIER'S PRINCIPLE

"If a system in physical or chemical equilibrium is altered by a change of some condition, the system will shift so as to minimize or undo the effect of that change."

Let us explain the application of this principle in the following changes.

(a) Effect of Change in Concentration:

In order to understand the effect of change in concentration on the reversible reaction, consider the reaction in which $BiCl_3$ reacts with water to give a white insoluble compound BiOCl (artificial milk).

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The equilibrium constant expression for above reaction can be written as

$$K_c = \frac{[BiOCl]\,[HCl]^2}{[BiCl_3]\,[H_2O]}$$

Aqueous solution of $BiCl_3$ is cloudy because of hydrolysis and formation of BiOCl. 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.

$$BiCl_3 + H_2O \longleftarrow BiOCl + 2HCl$$

However, if water is added to the above solution, the system will move in forward direction and solution again becomes cloudy.

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

1. **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**.
2. Similarly 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 therefore increase the yield of a reversible reaction. The value of K_c however remains constant. This concept is extensively applied in common ion effect and in many industries to increase the yield.

(b) Effect of Change in Pressure or Volume:

This effect will be present in those equilibrium systems which are gases.

Those reaction in which number of **moles** of reactants and products are **equal**, they are **not affected** by change in pressure. For example,

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K_c = \frac{\left[\frac{NO}{V}\right]^2}{\left[\frac{N_2}{V}\right]\left[\frac{O_2}{V}\right]}$$

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$$

Change in volume or pressure is important only for those reversible reactions where number of moles of reactants are not equal to the number of moles of products.

(i) The reactions in which moles of products are less than reactants:

Take the example of formation of SO_3 gas from SO_2 gas and O_2 gas.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

This gas phase reaction proceeds with the decrease in the number of moles and hence decreases in volume. 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 will move to the forward direction. 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.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

a mol	b mol	0 mol	t = 0
a – 2x	b – x	2x	t = equilibrium

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-2x}{v}\right)^2\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{4x^2\,v}{(a-2x)^2\,(b-x)}$$

Where v is the volume of reaction mixture at equilibrium stage, a and b are the number of moles of SO_2 and O_2 present initially and x is the number of moles of oxygen which has reacted at equilibrium. According to the above equation when volume is increased then x has to decrease 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.

Similarly increasing the pressure on the above reaction at equilibrium will decrease the volume and hence 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.

In the formation of NH_3 from N_2 and H_2, more product is formed by increasing pressure.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(ii) The reaction in which number of moles of products are greater than reactants:

In the same way, we can also explain the effect of change of pressure on the equilibrium positions for the following reactions.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

a	0 mol	0 mol	t = 0
a – x	x	x	t = equilibrium

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left[\frac{a-x}{v}\right]}$$

$$K_c = \frac{x^2}{(a-x)\,v}$$

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

a mol	0 mol	t = 0
a – x	2x	t = equilibrium

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{\left[\frac{2x}{v}\right]^2}{\left[\frac{a-x}{v}\right]}$$

$$K_c = \frac{4x^2}{(a-x)\,v}$$

Both these reactions have the factor of volume present in the denominator. 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.

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 either liquids or solids.

(c) Effect of Change in Temperature:

According to Le–Chatelier's principle, the direction of reaction can be predicted b the change in temperature at equilibrium state.

(a) In exothermic reactions, increase in temperature will favour the reverse reaction and decrease in temperature will favour the forward reaction.

(b) In endothermic reactions, increase in temperature will favour the forward reaction and decrease in temperature will favour the reverse reaction.

Most of the reversible reactions are disturbed by changing temperature because, they are either exothermic or endothermic.

If we consider heat as a component of equilibrium system, a rise in temperature adds heat to the system and a drop in temperature removes heat from the system. According to Le–Chatelier's principle, therefore, a temperature increase, favour the endothermic reaction and temperature decrease, favours the exothermic reaction.

The equilibrium constant changes by the change of temperature because the equilibrium position shifts without any substance being added or removed.

Consider the following reaction in gas phase at equilibrium at a known temperature.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \quad \Delta H = -41.84 \text{ kJ mol}^{-1}$$

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**. Thus, 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. On the contrary, heating the reaction at equilibrium will shift the reaction to the backward direction because the reaction is exothermic.

Formation of NO from N_2 and O_2 is an endothermic process. By absorbing heat this reaction move in forward direction.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad \Delta H = +180.5 \text{ kJ/mol.}$$

Solubility of salts increases by increasing temperature because majority of the such reaction are endothermic.

Consider a salt such as KI. It dissolves in water and absorbs heat.

$KI_{(s)} \rightleftharpoons KI_{(aq)} \quad \Delta H = +21.4 \text{ kJ/mol.}$

If we have saturated salt solution of KI in water at a given temperature, a **rise in temperature** favours **more dissolution** of the salt. Equilibrium is shifted to the forward direction. On the other hand, cooling will favour crystallization of salt. Hence the solubility of salt must increase with increase in temperature.

For some salts the **heat of solution** is close to **zero** (heat is neither evolved or absorbed). The solubility of these salts in water is **not affected by the change in temperature**. Formation of aqueous solution of NaCl is an example of such salts.

(d) Effect of Catalyst on Equilibrium Constant:

"The substance which increase the rate of a chemical reaction but does not take part in chemical reaction is called **catalyst**."

In most of the reversible reactions the equilibrium is not always reached within a suitable short time. So an appropriate catalyst is added. 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.

APPLICATION OF CHEMICAL EQUILIBRIUM IN INDUSTRY

(a) Synthesis of Ammonia by Haber's Process:

This process was developed by a German chemist F – Haber in 1933. Synthesis of NH_3 is an exothermic process.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad (\Delta H = -92.46 \text{ kJ})$

The best yield is obtained at low temperature because as temperature rise, reverse reaction takes place. Unfortunately rate of reaction is very low at low temperature. A slow rate of reaction means slow production.

Yield of ammonia can be increased by the following ways.

(i) By continual **withdrawal of ammonia** after intervals, the equilibrium will shift to forward direction in accordance with Le–Chatelier's principle.

(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 to the forward direction according to Le–Chatelier's principle.

Therefore high pressure, low temperature and continual removal of ammonia will give the maximum yield of ammonia.

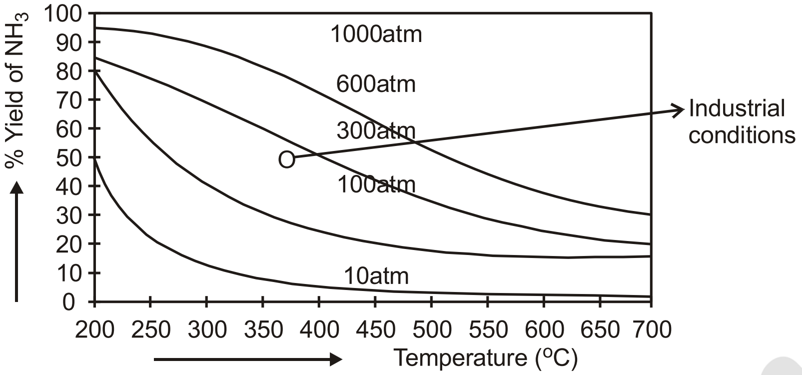


Figure shows, percent yield of ammonia vs. temperature (°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield of NH_3 is high but the rate of formation is low. Industrial conditions, (circle) are between 200 and 300 atmospheres and at about 400°C.

No doubt, the yield of NH_3 is favoured at **low temperature**, but the rate of its formation does not remain favourable. The **rate become so slow** and the process is rendered uneconomical. One needs a compromise to optimize the yield and the rate. The temperature is raised to a moderate level and a catalyst is employed to increase the rate. If one wants to achieve the same rate without a catalysts, then it requires much higher temperature, which lowers the yield. Hence the optimum conditions are the pressure of **200 – 300 atmosphere** and temperature around **673 K (400°C)**. The catalyst is the pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

The equilibrium mixture has 35% by volume of ammonia. The mixture is cooled by refrigeration coils, ammonia condenses (B.P = – 33.4°C) and is removed. Since boiling points of nitrogen and hydrogen are very low, they remain in the gaseous state and are recycled into the reaction chamber.

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tonnes 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.

(b) Synthesis of Sulphur Trioxide:

In the contact process for manufacture of H_2SO_4, the conversion of SO_2 to SO_3 as achieved in a reversible reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad (\Delta H = -97.9 \text{ kJ})$$

The temperature and pressure are the most essential factors for controlling the rate of this reaction. The principles involves here are the same is those discussed previously for Haber's process.

1. **At low temperature**, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly. As the temperature is raised the rate increases but the yield of SO_3 drops according to Le–Chatelier's principle.

2. **High pressure** tends to increase yield of SO_3. However instead of using high pressure, the concentration of O_2 (air) is increased to increase the yield of SO_3. Table helps to understand the effect of different conditions on the yield of SO_3. During the process, pressure is kept at one atmosphere.

TABLE

Effect of Temperature on the Yield of SO_3

Temperature (^oC)	200	300	400	500	600	700
K_c	5500	690	160	55	25	13
Mole % of SO_3	98	91	75	61	46	31

3. To have the best possible yield of SO_3 within a reasonable time, a mixture of SO_2 and O_2 (air) at **1 atmospheric pressure** is passed over a solid catalyst at 650°C. The equilibrium mixture is then recycled at lower temperature, 400 to 500°C, to increase the yield of SO_3. The most effective catalysts are V_2O_5 and finely divided platinum. 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. A country's industrial progress in measured by the amount of H_2SO_4 manufactured each year.

IONIC PRODUCT OF WATER AND CONCEPT OF pH

Pure water is a very poor conductor of electricity but its conductance is measurable. Water undergoes self ionization as follows:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant for this reaction can be written as follows:

$$K_c = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

$$K_c\,[H_2O] = [H^+]\,[OH^-]$$

$$K_c = \frac{[H^+]\,[OH^-]}{[H_2O]} = 1.8 \times 10^{-16}\ \text{mol dm}^{-3}$$

The concentration of $[H_2O]$ in pure water may be calculated to be 1000 g dm^{-3} divided by 18 g mol^{-1} giving 55.5 mol dm^{-3}.

$$\frac{1000\ \text{g dm}^{-3}}{18\ \text{g mol}^{-1}} = 55.5\ \text{mol dm}^{-3}\ \text{or}\ 55.5\ \text{M}.$$

Since, water is present in large excess and very few molecules undergo ionization so its concentration remains effectively constant.

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$$[H^+][OH^-] = K_c[H_2O]$$

$$K_w = 1.8 \times 10^{-16} \times 55.5 = 1.01 \times 10^{-14} \text{ (at } 25^oC)$$

K_w is called **ionic product of water or dissociation constant of water**. The value of K_w depends upon temperature as shown in the Table.

TABLE

Temperature (^oC)	K_w
0	0.10×10^{-14}
10	0.30×10^{-14}
25	1.01×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

Data shows that ionization of water increases 75 times when we increase the temperature from 0^oC to 100^oC. However, this increases in ionization is not regular.

$$\frac{\text{Ionization at } 100^oC}{\text{Ionization at } 0^oC} = \frac{7.5 \times 10^{-14}}{0.1 \times 10^{-14}} = 75$$

Whenever some quantity of acid or base is added in water, then K_w remains the same, but $[H^+]$ and $[OH^-]$ are no more equal. Anyhow, in neutral water

$$[H^+] = [OH^-]$$

or $[H^+][H^+] = 10^{-14}$

$$[H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7} \text{ moles dm}^{-3}$$

and $[OH^-] = 10^{-7}$ moles dm^{-3}

This means that out of 55.5 moles of pure water in one dm^{-3} of it, only 10^{-7} moles of it have dissociated into ions. This shows that water is very weak electrolyte. At 40^oC, $[H^+] = [OH^-]$ but the values are less than 10^{-7} mole dm^{-3} and pure water is again neutral at 40^oC. Similarly pure water is neutral at 100^oC, although $[H^+]$ and $[OH^-]$ are greater than at 40^oC but are equal.

Water is neutral. The solution which has H^+ ions concentration 1×10^{-7} will be neutral.

If $H^+ > 1 \times 10^{-7}$ solution will be acidic.

If $H^+ < 1 \times 10^{-7}$ solution will be basic.

pH AND pOH SCALE

pH scale was introduced by **S.P.L. Sorenson (Danish biochemist)**.

"The concentration of $[H^+]$ ions of a solution can be expressed in term of pH scale."

"The pH of solution is the logarithm of the reciprocal of the hydrogen ions concentration."

$$pH = \log \frac{1}{[H^+]}$$

or $$pH = -\log [H^+]$$

Similarly pOH which expresses the OH^- ion concentration of a solution and is given by

$$pOH = \log \frac{1}{[OH^-]}$$

or $$pOH = -\log [OH^-]$$

From ionic product of water it is clear that

$$[H^+][OH^-] = 10^{-14}$$

Taking logarithm of each value, we get

$$\log [H^+] + \log [OH^-] = \log 10^{-14}$$

Multiple equation by – 1, we get

$$(-\log [H^+]) + (-\log [OH^-]) = -\log 10^{-14}$$

$$pH + pOH = 14$$

Similarly pK_w is the reciprocal of K_w

$$pK_w = \log \frac{1}{K_w}$$

$$pK_w = -\log K_w$$

or $$pK_w = -\log 1 \times 10^{-14}$$

$$K_w = 1 \times 10^{-14} \text{ at } 25^oC$$

$$pK_w = 14$$

pH scale is from (O – 14). The solution which has pH 7 is neutral. The solution which has greater pH than 7 is basic while the solution which has less pH than 7 is the acidic.

Solutions have usually value in between 0 to 14. However, solutions of negative pH and more than 14 are also known.

TABLE

Relationship of $[H_3O^+]$ $[OH^-]$ pH and pOH					
		$[H_3O^+]$	pH	$[OH^-]$	pOH
	Basic	1×10^{-14}	14.0	1×10	0.0
More basic		1×10^{-13}	13.0	1×10^{-1}	1.0
		1×10^{-12}	12.0	1×10^{-2}	2.0
		1×10^{-11}	11.0	1×10^{-3}	3.0
		1×10^{-10}	10.0	1×10^{-4}	4.0
		1×10^{-9}	9.0	1×10^{-5}	5.0
		1×10^{-8}	8.0	1×10^{-6}	6.0
	Neutral	1×10^{-7}	7.0	1×10^{-7}	7.0
More acidic		1×10^{-6}	6.0	1×10^{-8}	8.0
		1×10^{-5}	5.0	1×10^{-9}	9.0
		1×10^{-4}	4.0	1×10^{-10}	10.0
		1×10^{-3}	3.0	1×10^{-11}	11.0
	Acidic	1×10^{-2}	2.0	1×10^{-12}	12.0
		1×10^{-1}	1.0	1×10^{-13}	13.0
		1×10^{-0}	0.0	1×10^{-14}	14.0

The pH values of some familiar aqueous solutions are shown in Table.

TABLE

Approximate pH of some common materials at 25°C			
Material	**pH**	**Materials**	**pH**
1.0 M HCl	0.1	Bread	5.5
0.1 M HCl	1.1	Potato	5.8
0.1 M CH_3COOH	2.9	Rainwater	6.2
Gastric juice	2.0	Milk	6.5

Lemon	2.3	Saliva	6.5 – 6.9
Vinegar	2.8	Pure water	7.0
0.1 M $NaHCO_3$	8.4	Egg	7.8
Soft drink	3.0	Apple	3.1
Cherries	3.6	Seawater	8.5
Tomato	4.2	Milk of magnesia	10.5
Banana	4.6	0.1 M NH_3	11.1
Grapefruit	3.1	0.05 M Na_2CO_3	11.6
Orange	3.5	0.1 M NaOH	13.0

IONIZATION CONSTANTS OF ACIDS (K_a)

"The acid which ionizes partially in water is called **weak acid**. e.g., CH_3COOH, C_6H_5COOH. The acid which ionizes completely in water is called **strong acid**." e.g., H_2SO_4, HCl, HI.

Many acids are weak electrolytes and they ionize to an extent which is much less than 100%. The value of $\mathbf{K_a}$ called the **dissociation constant of acid**, is the quantitative measure of the strength of the acid. Suppose we have an acid HA dissolved in water.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c for the reversible reaction will be written as follows.

$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

Water is in excess and its concentration remains almost constant.

$$K_c\,[H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Let $K_c \times [H_2O] = K_a$

Hence $K_a = \dfrac{[H_3O^+]\,[A^-]}{[HA]}$

K_a is called **ionization constant or the acidity constant**. The acids which have high value of K_a are more stronger than those which have low value of K_a.

When $K_a < 10^{-3}$ acid is weak

$K_a = 1$ to 10^{-3} acid is moderately strong

$K_a > 1$ acid is strong

Percentage Ionization of Acids:

We can calculate the percentage ionization of weak acid and the formula is as follows:

$$\% \text{ ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

The percentage ionization of weak acids depends upon the extent of dilution of their aqueous solutions. Ionization increases by increasing dilution. Value of ionization constant and percentage ionization of Acetic acid is given in the Table.

TABLE

Dissociation Constants of Some Acids at 25^{o}C and their Relative Strength

Acid	Dissociation	K_a	Relative Strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	Very large	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	Very large	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large	Very strong
HSO_4^-	$HSO_4^- \rightleftharpoons H^+ + SO_4^{-2}$	1.3×10^{-4}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1.8×10^{-5}	Weak
$(H_2O + CO_2)$ H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.4×10^{-7}	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Weak
NH_4^+	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Weak
HCO_3^-	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	Very weak

TABLE

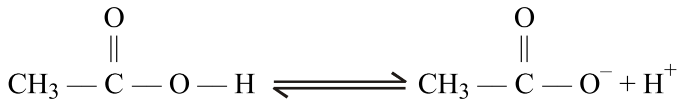
Percentage Ionization and Ionization Constants of Acetic Acid at 25^{o}C

Molarity	% Ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.1	1.33	0.001330	0.098670	1.79×10^{-5}

0.05	1.89	0.000945	0.049060	1.82×10^{-5}
0.01	4.17	0.000417	0.009583	1.81×10^{-5}
0.001	12.60	0.000126	0.000874	1.72×10^{-5}

Example 3:

What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been dissolved per dm^3 of the solution.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \rightleftharpoons CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H^+$$

$$K_a = 1.8 \times 10^{-5}$$

Solution:

Concentration (M)	**CH_3COOH**	**CH_3COO^-**	**H^+**
Initial value	0.1	0	0
Change	– x	x	x
At equilibrium	0.1 – x	x	x

Since CH_3COOH is very weak acid, it slightly ionizes. We expect x to be significantly smaller than 0.1 M. Assume x is small as compared to 0.1 M.

$$\therefore \quad 0.1 - x = 0.1$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.1}$$

$$x^2 = 0.1 \times 1.8 \times 10^{-5} = 1.8 \times 10^{-6}$$

$$x = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3} \text{ moles dm}^{-3}$$

$$x = 1.3 \times 10^{-3} \text{ mol dm}^{-3} \text{ (amount of acid ionized)}$$

$$\% \text{ ionization} = \frac{\text{Concentration of ionized acid}}{\text{Original concentration}} \times 100$$

$$= \frac{1.3 \times 10^{-3}}{0.1} \times 100 = 1.3\ \%$$

Hence, out of 1000 molecules of acetic acid only 13 are dissociated into ions when 0.1 M solution is prepared. The degree of dissociation increases by increasing the dilution of solution, which is called **Oswald dilution laws**.

IONIZATION CONSTANT OF BASES (K_b)

Unlike strong bases, weak Bronsted bases usually consist of molecules or ions which react with water, remove a proton from it, and generate a OH^- ion. Take the example of NH_3 and CO_3^{2-}.

$$NH_{3(aq)} + H_2O \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$CO_3^{-2} + H_2O \rightleftharpoons HCO^{1-}_{3(aq)} + OH^-_{(aq)}$$

NH_3 and CO_3^{2-} have different abilities to accept protons from water molecules. We compare these abilities of bases by knowing the equilibrium K_b, which is called **ionization constant of base**. Let the base is 'B' then

$$B_{(aq)} + H_2O \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Water is in excess and its concentration almost remains constant, so

$$K_c \times [H_2O] = K_b$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Greater will be the value of K_b stronger will the base and smaller will be the value of K_b, weaker will be the base.

TABLE

Some Weak Bases and their Aqueous Solution Equilibrium K_b Values for Some Bases

Base	Dissociation	K_b	Relative Strength
NaOH	$NaOH \rightleftharpoons Na^+ + OH^+$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	High	Strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

pK_a AND pK_b

We know that the value of K_a and K_b for weak acids and bases are small numbers usually expressed in exponential form. It is convenient to convert them into whole number by taking their negative log. Thus we obtain pKa and pK_b values of acids and bases.

$$pK_a = \log \frac{1}{K_a}$$

$$pK_b = \log \frac{1}{K_b}$$

or

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

Larger the pK_a weaker is the acid and vice versa. Similarly, larger the pK_b, weaker is the base. If the different of pK_a values of the two acids is one, then acid with smaller pK_b is ten times stronger than the other.

LOWRY BRONSTED ACID BASE CONCEPT

"According to this concept, the species which donate protons is called an acid and which accept the protons is called **a base**."

Whenever, a weak acid or weak base is dissolved in water, the conjugate acid base pair is produced. Let us have an acid HA, when it is dissolved in water, it gives protons H_3O^+ or H^+ in reversible manner and a conjugate base A^-.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+} + \underset{\text{conjugate base}}{A^-}$$

$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

or $$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + \underset{\text{conjugate base}}{A^-}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

The equation for hydrolysis of conjugate base A^- is,

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_c = \frac{[HA]\,[OH^-]}{[A^-]\,[H_2O]}$$

$$K_c \times [H_2O] = K_b$$

So $$K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

Let us multiply two expression $K_a \times K_b$.

$$K_a \,.\, K_b = \frac{[H^+]\,[A^{-1}]}{[HA]} \times \frac{[HA]\,[OH^-]}{[A^{-1}]}$$

or $$K_a \,.\, K_b = [H^+]\,[OH^-]$$

or $$K_a \,.\, K_b = K_w$$

This equation is useful in the sense that if we known K_a of the acid, we can calculate K_b for the conjugate base and vice versa. The value of K_w is constant at given temperature. The value of K_w is 14 at 25^oC and less than 14 at higher temperature.

Let us take the log of above equation.

$$\log (K_a \times K_b) = \log (K_w)$$

or $$\log K_a + \log K_b = \log K_w$$

Multiply both sides by '– 1'

$$-\log K_a - \log K_b = -\log K_w$$

or $$pK_a + pK_b = pK_w$$

Since $pK_w = 14$ at 25^oC hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25^oC$$

This equation proves the following facts.

(a) Conjugate base of a very weak acid is relatively very strong base.

(b) Conjugate acid of a very strong base is relatively very weak acid.

So $$K_a \propto \frac{1}{K_b}$$

Common Ion Effect:

"The phenomenon in which degree of ionization of an electrolyte is suppressed by the addition of another electrolyte, having common ion in it, is called **common ion effect**."

For example, sodium chloride can be purified by this process. Make the saturated solution of $NaCl$ in water.

(1) In saturated solution of $NaCl$, there is an equilibrium between ionized and unionized salt.

$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

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

When HCl gas is passed through this solution, equilibrium is disturbed according to Le–Chatelier's principle, the equilibrium position shift toward left, to re–establish the equilibrium by passing HCl, the ionized sodium chloride precipitates out. In this way impurities of $NaCl$ are removed.

(2) The solubility of a less soluble salts $KClO_3$ in water suppressed by the addition of a more soluble salt KCl by common ion effect.

$$KClO_{3(s)} \rightleftharpoons K^{+}_{(aq)} + ClO^{-}_{3(aq)}$$

$$KCl \rightleftharpoons K^{+}_{(aq)} + Cl^{-}_{(aq)}$$

(3) Similarly the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl.

$$H_2S_{(g)} \rightleftharpoons 2H^{+}_{(aq)} + S^{2-}_{(aq)}$$

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

(4) 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^{+}.

$$NH_4Cl_{(aq)} \rightleftharpoons NH^{+}_{4(aq)} + Cl^{-}_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH^{+}_{4(aq)} + OH^{-}_{(aq)}$$

Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

BUFFER SOLUTION

"The solution which resists the change in pH when

(i) small amount of acid or base is added to it

(ii) on dilute

(iii) on keeping for a long time

is called **"buffer solution"**.

COMPOSITION OF BUFFERS

Buffer solutions are prepared by mixing two solutions.

1. By mixing a weak acid and its conjugate base.

(weak acid and salt of it with strong base).

(i) $CH_3COOH + CH_3COONa$

$C_6H_5COOH + C_6H_5COONa$

$H_3PO_4 + NaH_2PO_4$

$H_2CO_3 + NaHCO_3$

Such solution give acidic buffer with pH less than 7.

2. By mixing a weak base and its conjugate acid e.g.

(weak base and salt of it with strong acid).

(ii) $NH_4OH + NH_4Cl$

Such solution give basic buffer with pH greater than 7.

Why do we need BUFFER solution?

1. It is common experience that the pH of the human blood is maintained at 7.35. If it goes to 7.00 or 8.00, a person may die. Some protein buffers control the pH of blood.
2. Sometimes one wants to study and reaction under conditions that would suffer any associated change in the pH of the reaction mixture. So, by suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if a small amount of strong acid or a strong base is added.
3. Buffer are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

How do the BUFFER acts?

Suppose your have a buffer of CH_3COOH and CH_3COONa with equal amounts. If a strong acid is added to the buffer, it supplies hydrogen ions that react with the conjugate base CH_3COO^-.

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(aq)}$$

On the other hand, if a strong base is added to the buffer, it supplies hydroxyl ions. These ions react with acid (CH_3COOH).

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} + CH_3COO^-$$

Thus buffer solution resists changes in pH by the ability to combine with H^+ ions and OH^- ions.

pH OF BUFFER CHANGES BY CHANGING COMPOSITION OF SALT AND ACID

Let us consider the example of CH_3COOH and CH_3COONa.

Acetic acid dissociate as

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

When a strong electrolyte $CH_3COONa_{(aq)}$ is added to CH_3COOH solution, then dissociation of CH_3COOH is suppressed due to common ion effect of CH_3COO^-.

Table shows how the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increase. This table also tell us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid, lesser is its pH.

Solution:

TABLE

$[CH_3OOH]$	**$[CH_3COO^-]$**	**% Dissociation**	**pH**
Mol/dm^3	Mol/dm^3		
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

pH OF A BUFFER

Consider a weak acid HA and its salt with a strong base NaA. The reversible reactions are as follows:

$$HA \rightleftharpoons H^+ + A^-$$

The dissociation constant of a weak acid HA will be given by:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

$$[H^+] = \frac{K_a\,[HA]}{[A^-]}$$

The concentration of A in the reaction mixture is predominantly being supplied by NaA which is a stronger electrolyte than HA, and the ionization of HA is being suppressed by common ion effect (A^- is the common ion).

$$\log [H^+] = \log \frac{K_a [HA]}{[A^-]}$$

$$\log [H^+] = \log (K_a) + \log \frac{[HA]}{[A^-]}$$

Multiplying with (negative) on both sides.

$$-\log [H^+] = -\log (K_a) - \log \frac{[HA]}{[A^-]}$$

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

Since $[A^-]$ refers to the concentration of the salt so

Hence $pH = pK_a - \log \frac{[acid]}{[salt]}$

or $pH = pK_a + \log \frac{[salt]}{[acid]}$

This equation is called **Henderson equation**.

TWO FACTORS CONTROL THE pH OF A BUFFER

(1) pK_a of the acid used.

(2) Ratio of the concentration of salt and acid.

The **best buffer** is prepared by taking the salt and acid concentrations equal.

So pH controlled by pK_a of the acid. For example, for acetic acid–sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log 1$$

then $pH = pK_a + O$

$$pH = pK_a$$

so $pH = 4.74$

It means that the pH of this buffer is just equal to the pK_a of the acid.

Similarly for formic acid–sodium format buffer, if

$$[HCOOH] = [HCOONa]$$

then $pH = pK_a + O = pK_a$

so $pH = 3.78$

To prepare a buffer of definite pH, we need a suitable acid for that purpose. We can also manage the buffer of our own required pH by suitably selecting the concentration ratio of the salt and the acid.

Example:

What is the pH of buffer, if concentration of CH_3COOH is 0.1 mol dm^{-3} and CH_3COONa is 1.0 mol dm^{-3}. (pK_a of CH_3COOH is 4.74).

Solution:

$CH_3COOH = 0.1\ M \quad pK_a = 4.74$

$CH_3COONa = 1.0\ M$

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$pH = 4.74 + \log\left(\frac{1.0}{0.1}\right)$$

$$pH = 4.74 + 1$$

$$pH = 5.74$$

Example:

What is the pH of buffer, if concentration of CH_3COOH is 1.0 mole dm^{-3} and CH_3COONa is 0.1 mol dm^{-3}. (pK_a of CH_3COOH is 4.74).

Solution:

$CH_3COOH = 1.0\ M \quad pK_a = 4.74$

$CH_3COONa = 0.1\ M$

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$pH = 4.74 + \log\left(\frac{0.1}{1.0}\right)$$

$$pH = 4.74 - 1$$

$$pH = 3.74$$

pOH OF BUFFER

Just like acidic buffer, the basic buffer have their own shape of Henderson equation. For this purpose, let us the mixture of NH_4OH and NH_4Cl. NH_4OH is a solution of NH_3 in water and it can be represent as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[NH_4^+]\,[OH^{-1}]}{[NH_3]}$$

Taking the log, multiplying with negative sign and rearranging, we get

$$pOH = pK_b + \log\frac{[salt]}{[base]}$$

Using the relationship, we can prepare a basic buffer of the required pH by suitably selecting a base and adjusting the ratio of $\frac{[salt]}{[base]}$.

Example 4:

Calculate the pH of a buffer solution in which 0.11 M CH_3COONa and 0.09 M acetic acid solutions are present. K_a for CH_3COOH is 1.8×10^{-5}.

Solution:

$$[CH_3COONa] = 0.11\ M$$

$$[CH_3COOH] = 0.09\ M$$

$$K_a \text{ of } CH_3COOH = 1.8 \times 10^{-5}$$

$$pK_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pH = 4.74 + \log \left(\frac{0.11}{0.09} \right)$$

$$pH = 4.74 + 0.087$$

$$pH = 4.83$$

Since the concentration of CH_3COONa is more than that of CH_3COOH, therefore pH of buffer is greater than 4.74.

BUFFER CAPACITY

"The amount of acid or base, which a buffer solution can absorb without significant change in pH is called **buffer capacity**."

Buffer capacity of a solution is the capability of a buffer to resist the change is pH. Buffer capacity depends upon the **actual molarities of the component**. A chemist must decide before making the buffer solution, what outer limits of change in its pH can be tolerated.

Let us do some calculations to check the effectiveness of a buffer system. Consider a buffer having 0.11 M CH_3COONa and 0.09 M acetic acid. Its pH will be 4.83. Let us add **0.01 M NaOH** in one dm^3 of the buffer solution remember that addition of 0.01 M NaOH per dm^3 of solution will change the pH from **(7.00 to 12.00 in pure water)**. Since NaOH is a strong base and it is 100% dissociated, it generates 0.01 M OH^-. Out of 0.09 M of CH_3COOH 0.01 M will react with OH^- and 0.08 M of CH_3COOH is left behind in one dm^3 of solution. This neutralization, of course makes the identical change in the amount of CH_3COONa and its concentration will increase from 0.11 M to 0.12 M.

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pH = 4.74 + \log \left(\frac{0.12}{0.08} \right)$$

pH = 4.74 + log 1.5

pH = 4.74 + 0.176

pH = 4.92

It means that there is a very small change in pH from 4.83 to 4.92, that is only a difference of 0.09. So we reach the conclusion that the buffer does not hold the pH exactly constant. But it does a very good job in limiting the change in pH to a very small amount.

Saturated Solution:

"The solution in which no more amount of solute can dissolve at given temperature is called **saturated solution**."

Solubility:

"The amount of solute which is required to saturate 100 g of solvent at given temperature is called **solubility**."

EQUILIBRIUM OF SLIGHTLY SOLUBLE IONIC COMPOUNDS (SOLUBILITY PRODUCT)

When a sparingly soluble salt such as lead chloride ($PbCl_2$) is placed in water, it dissolve until a saturated solution in formed. An equilibrium is established between the resulting saturated solution, ions and un–dissolved solid phase.

Equilibrium is present between Pb^{2+} ions, Cl^- ions and solid $PbCl_2$.

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

The equilibrium for the reaction is given as

$$K_c = \frac{[Pb^{2+}]\,[Cl^-]}{[PbCl_2]}$$

For a sparingly soluble salt, the amount of solid, remains almost constant.

$$[PbCl_2] \times K_c = K_{sp}$$

K_{sp} is called **solubility product constant**.

K_{sp} is defined as;

"The product of molar concentration of negative and positive ions, in equilibrium state with solid salt, at given temperature is called **solubility product constant**."

Value of K_{sp} is usually small and depends upon temperature.

Other Examples:

(1) $PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

$$K_c = \frac{[Pb^{2+}]\,[SO_4^{2-}]}{[PbSO_4]}$$

$$K_{sp} = [Pb^{2+}]\,[SO_4^{2-}]$$

(2) $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$K_c\,[AgCl] = K_{sp}$$

$$K_{sp} = [Ag^+][Cl^-]$$

(3) $Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)}$

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$

(4) For a general sparingly soluble substance. $A_x\,B_y$

$$A_x\,B_y \rightleftharpoons x\,A^{+y} + yB^{-x}$$

$$K_{sp} = [A^{+y}]^x\,[B^{-x}]^y$$

So the solubility product is the product of the concentrations of ions raised to an exponent equal to the co–efficient of the balanced equation. The value of K_{sp} is a measure of how for the right dissolution proceeds at equilibrium (saturation). The following table shows us the K_{sp} values of slightly soluble ionic compounds.

TABLE

K_{sp} Values For Some Ionic Compounds					
Salt	**Ionic Product**	K_{sp}	**Salt**	**Ionic Product**	K_{sp}
Ag_2S	$[Ag^+][S^{2-}]$	1.6×10^{-49}	MnS	$[Mn^{2+}][S^{2-}]$	2.5×10^{-13}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	1.3×10^{-33}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	1.1×10^{-10}	$MnCl_2$	$[Mn^{+2}][Cl^-]^2$	1.9×10^{-4}
CdS	$[Cd^{2+}][S^{2-}]$	8.0×10^{-27}	PbS	$[Pb^{2+}][S^{2-}]$	8×10^{-28}

APPLICATIONS OF SOLUBILITY PRODUCT

(a) Determination of K_{sp} from Solubility:

From the solubility of the compounds, we can calculate K_{sp} of the salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since the quantity of solute is very small, so 100 g of water solution is consideration to be 100 cm^3 of solution. Hence we get the concentration in moles. The number of moles of solute per dm^3 of the solution is calculated and then by using the balanced equation, we find the molarity of each ion and then find K_{sp}.

Example 5:

The solubility of PbF_2 at 25^oC is 0.64 g dm^{-3}. Calculate K_{sp} of PbF_2.

Solution:

Mass of PbF_2 dissolved dm^{-3} = 0.64 g

Molecular mass of PbF_2 = 245.2 mol^{-1}

$$\text{No. of mole of } PbF_2 = \frac{0.64 \text{ g dm}^{-3}}{245.2 \text{ g mol}^{-1}} = 2.6 \times 10^{-3} \text{ mol dm}^{-3}$$

	$PbF_{2(s)}$	$\rightleftharpoons$	$Pb^{2+}_{(aq)}$	+	$2F^{1-}_{(aq)}$
Initial conc.:	2.6×10^{-3}		0	+	0
Change:	2.6×10^{-3}		2.6×10^{-3}		$2 \times 2.6 \times 10^{-3}$
Equilibrium conc.:	2.6×10^{-3}				5.2×10^{-3}

$K_{sp} = [Pb^{2+}] [F^-]^2$

$K_{sp} = [2.6 \times 10^{-3}] [5.2 \times 10^{-3}]^2$

$K_{sp} = 7.0 \times 10^{-8}$

(b) Determination of Solubility from K_{sp}:

From the K_{sp} value we can calculate the solubility of a substance and concentration of ions.

Example 6:

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

Solution:

Let the solubility is represented by S in terms of moles dm^{-3}.

$$Ca(OH)_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

Concentration of OH^- is double than Ca^{2+}

$K_{sp} = [Ca^{2+}] [OH^-]^2$

$6.5 \times 10^{-6} = [S] [2S]^2$

$6.5 \times 10^{-6} = S \times 4S^2$

$$6.5 \times 10^{-6} = 4S^3$$

$$\frac{6.5 \times 10^{-6}}{4} = S^3$$

$$\sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = S$$

$$S = 1.175 \times 10^{-2} \text{ mole dm}^{-3}$$

Solubility of $Ca(OH)_2$ is 1.175×10^{-2} mol/dm^3. The concentration of Ca^{+2} is 1.175×10^{-2} mol/dm^3. The concentration of OH^- is double than Ca^{2+}. It is

$$1.175 \times 10^{-2} \times 2 = 2.35 \times 10^{-2} \text{ mol/dm}^3$$

This solubility of $Ca(OH)_2$ can be calculated in grams/100 cm^3.

Formula mass of $Ca(OH)_2$ = 40 + 16 x 2 + 2 = 74 g

$$\text{Solubility of grams} = 74 \text{ g mol}^{-1} \times 1.175 \times 10^{-2} \text{ mol/dm}^3$$

$$= 0.8695 \text{ g dm}^{-3}$$

$$\text{Solubility in 100 cm}^3 = \frac{0.8695 \times 100}{1000} = 8.695 \times 10^{-2} \text{ g/100 cm}^3$$

(c) Prediction of Precipitation Formation:

Solubility product can be used to predict whether precipitation will occur or not. Suppose you mix dilute solutions of $BaCl_2$ and dilute solution of sodium sulphate.

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$

Solubility product is given by

$$BaSO_{4(s)} \longrightarrow Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

K_{sp} for $BaSO_4$ at 25°C is 1.1×10^{-10}.

If the product of the concentration of the Ba^{2+} and SO_4^{2-} ions in the two solution which are mixed are together exceed the solubility product, then precipitation occurs until the product of the concentration has been reduced the solubility product. If ionic concentration is less than K_{sp}, no precipitation will occur. We can write as

If $[Ba^{2-}]\,[SO_4^{2-}] > K_{sp}$ precipitation occurs.

Until $[Ba^{2-}]\,[SO_4^{2-}] = K_{sp}$

But if $[Ba^{2-}]\,[SO_4^{2-}] < K_{sp}$ precipitation does not occur.

The term $[Ba^{2-}]\,[SO_4^{2-}] =$ is called **ionic product**.

Effect of Common Ion on Solubility:

The presence of a common ion decrease the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

Now add Na_2CrO_4, which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

EXERCISE

Q.1 Multiple choice questions:

(i) For which system does the equilibrium constant, K_c has units of $(\text{concentration})^{-1}$?

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $H_2 + I_2 \rightleftharpoons 2HI$

(c) $2NO_2 \rightleftharpoons N_2O_4$ (d) $2HF \rightleftharpoons H_2 + F_2$

(ii) Which statement about the following equilibrium is correct

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -188.3\ \text{kJ mol}^{-1}$

(a) The value of K_p falls with a rise in temperature

(b) The value of K_p falls with increasing pressure

(c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide

(d) The value of K_p is equal to K_c

(iii) The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is:

(a) 3.0 (b) 2.7

(c) 2.0 (d) 1.5

(iv) The solubility product of AgCl is 2.0×10^{-10} mol^2 dm^{-6}. The maximum concentration of Ag^+ ions in the solution is:

(a) 2.0×10^{-10} mol dm^{-3} (b) 1.41×10^{-5} mol dm^{-3}

(c) 1.0×10^{-10} mol dm^{-3} (d) 4.0×10^{-20} mol dm^{-3}

(v) An excess of aqueous sliver nitrate is added to aqueous barium chloride and precipitate is removed by filtration. What are the main ions in the filtrate?

(a) Ag^+ and NO_3^{-1} only (b) Ag^+ and Ba^{2+} and NO_3^-

(c) Ba^{2+} and NO_3^{-1} only (d) Ba^{2+} and NO_3^- and Cl^-

ANSWERS

Answers	Reasons
(i) (c)	$2NO_2 \rightleftharpoons N_2O_4$ $K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{[Conc.]^1}{[Conc.]^2} = [Conc.]^{-1}$ For reaction in option 'b' and 'd', K_C has no units since number of moles of products and reactants are equal. For reaction in option 'a' number of moles of reactants are greater than products by 2. Hence, K_c for this reaction has units $[Conc.]^{-2}$.
(ii) (a)	Negative enthalpy of this reaction shows that reaction is endothermic in backward reaction. Rise of temperature will speed up the backward reaction, with the increasing concentration of reactants, their partial pressures increase in the denominator of equilibrium expression. Hence value of K_P will fall. $K_P = \frac{[P_{SO_3}]^2}{[P_{SO_2}]^2 [P_{O_2}]}$
(iii) (b)	$H_2SO_4 \longrightarrow 2H^+ + SO_4^{-2}$ 10^{-3} moles 2×10^{-3} 10^{-3} moles From the above ionization, it is clear that H^+ ion concentration is 2×10^{-3}. $[H^+] = 2 \times 10^{-3}$ Hence, $pH = -\log [H^+]$ $pH = -\log 2 \times 10^{-3}$ $pH = 2.7$
(iv) (b)	Ionization of AgCl is $AgCl \rightleftharpoons Ag^+_{(s)} + Cl^-_{(s)}$ If 'S' moles of AgCl are soluble, it produce 'S' moles of Ag^{+1} ions and 'S' moles of Cl^- ions and $K_{sp} = [Ag^+][Cl^-]$. $K_{sp} = S \times S = S^2$ $S^2 = K_{sp}$ $S^2 = 2 \times 10^{-10}$ $\sqrt{S^2} = \sqrt{2 \times 10^{-10}}$ $S = 1.41 \times 10^{-5}$ moles/dm^3 The maximum concentration of Ag^+ ion will be 1.41×10^{-5} moles/dm^3.
(v) (b)	When $AgNO_3$ reacts with $BaCl_2$, $Ba(NO_3)_2$ and AgCl is formed. AgCl is precipitated. $Ba(NO_3)_2$ is soluble as Ba^{+2} and NO_3^{-1}. As $AgNO_3$ is used in excess, Ag^+ ion and NO_3^{-1} ions will also be present. Hence, filtrate will have soluble Ba^{+2}, NO_3^{-1} and excess Ag^+ ion.

Q.2 Fill in the blanks:

(i) Law of mass action states that the ―――――― at which a reaction proceeds, is directly proportional to the product of the active masses of the ――――――.

(ii) In an exothermic reversible reaction, ―――――― temperature will shift the equilibrium towards the forward direction.

(iii) The equilibrium constant for the reaction $2O_3 \rightleftharpoons 3O_2$ is 10^{55} at 25°C′, it tells that ozone is ―――――― at room temperature.

(iv) In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of the products, K_c of the reaction is ―――――― to the K_p.

(v) Buffer solution is prepared by mixing together a weak base and its salt with ―――――― or a weak acid and its salt with ――――――.

ANSWERS

Answers	**Explanation**
(i) Rate, reactants	This statement of law of mass action is evident from fact that rate of reaction is faster at the start. When concentration of reactant is maximum. As the reaction proceeds rate slows down with the decreasing concentration of reactants.
(ii) Decrease	For exothermic reversible reaction, the reaction is exothermic in forward direction and endothermic in backward direction. Rise of temperature speed up backward direction and decrease of temperature speed up forward reaction.
(iii) Unstable	Very high value of K_C for a reaction tells us that reactants are highly unstable and reaction is appreciable in forward direction.
(iv) Equal	The relation between K_P and K_C is $K_P = K_C (RT)^{\Delta n}$ When $\Delta n = n_P - n_R = 0$, Since, $n_P = n_R$ $K_P = K_C(RT)^{\circ}$ When no. of moles products are equal $n_P = n_R$. Then $\Delta n = n_P - n_R = 0$. $K_P = K_c \quad (\Delta n = 0)$ Since, $(RT)^{\circ} = 1$
(v) Strong acid, Strong base	

Q.3 Label the sentences as True or False.

(i) When a reversible reaction attains equilibrium both reactants and products are present in a reaction mixture.

(ii) The K_c of the reaction

$$A + B \rightleftharpoons C + D$$

is given by

$$K_c = \frac{[C][D]}{[A][B]}$$

therefore it is assumed that:

$$[A] = [B] = [C] = [D]$$

(iii) A catalyst is a compound which increases the speed of the reaction and consequently increase the yield of the product.

(iv) Ionic product K_w of pure water at 25°C is 10^{-14} $mol^2\ dm^{-6}$ and is represented by an expression $K_w = [H^+][OH^-] = 10^{-14}$ $mol^2\ dm^{-6}$.

(v) AgCl is a sparingly soluble ionic solid in water. Its solution produces excess of Ag^+ and Cl^- ions.

ANSWERS

Answers	Reasons
(i) True	As the reaction proceeds in both the directions at equilibrium, both reactants and products are present.
(ii) False	K_c is the ratio of concentration of products to concentration of reactants at equilibrium. Concentration of reactants and products does not become equal at equilibrium, rather become constant due to equal rate of two opposing reactions.
(iii) False	A catalyst increases the rate of reaction but does not increases the yield of product.
(iv) True	
(v) False	AgCl is sparingly soluble ionic solid in water. Its solution produces least number of Ag^+ and Cl^- ions.

Q.4 (a) Explain the terms “reversible reaction” and “state of equilibrium”.

(b) Define and explain the Law of mass action and derive the expression for the equilibrium constant (K_c).

(c) Write K_c for the following reactions:

(i) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(ii) $Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

(iii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(iv) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(v) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Ans.

(a) **Reversible Reaction:** A type of chemical reaction that proceeds in both the directions i.e., forward and backward is called reversible reaction. e.g., formation of NH_3 from H_2 and N_2.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

State of Equilibrium: A state of reversible chemical reaction at which two opposing reaction i.e., forward and backward proceeds at equal rate and concentration of reactant and products becomes constant is called state of equilibrium.

$$A + B \rightleftharpoons C + D$$

At the start of reversible reaction, the rate of forward reaction is maximum due to high concentration of reactants. And rate of backward reaction is minimum. As the reaction proceeds, the concentration of reactants decreases and rate of reaction also slows down. But the concentration of products increases and rate of backward reaction also increases with the decreasing rate of forward reaction and increasing rate of backward reaction, a stage reaches where both reactions proceeds at equal rate i.e., equilibrium.

(b) Descriptive question, consult text book.

(c) (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)

$$Ag^{+1}_{(aq)} + Fe^{+2}_{(aq)} \rightleftharpoons Fe^{+3}_{(aq)} + Ag_{(s)}$$

$$K_c = \frac{[Fe^{+3}_{(aq)}][Ag_{(s)}]}{[Ag^{+1}_{(aq)}][Fe^{+2}_{(aq)}]}$$

(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$$K_c = \frac{[NO_{(g)}]^2}{[N_{2(s)}][O_{2(g)}]}$$

(iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

$$K_c = \frac{[NO_{(g)}]^4[H_2O_{(g)}]^6}{[NH_{3(g)}]^4[O_{2(g)}]^5}$$

(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_{3(g)}][Cl_{2(g)}]}{[PCl_{5(g)}]}$$

Q.5 (a) Reversible reactions attain the position of equilibrium which is dynamic in nature and not static. Explain it.

(b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage.

Ans.

(a) At equilibrium state, the two opposing reactions are proceeding at equal rate. Thats why we call equilibrium as dynamic one. For equilibrium to be static the two opposing reaction should stop. Since, reactions are proceeding at equal rate in opposite direction, hence the equilibrium is dynamic not static.

(b) Rate of reaction is directly proportional to molar concentrations (active masses) of reactants. At start, concentration of reactants is maximum and rate of reaction is faster. When equilibrium is approached, the concentration of reactants is small as most of it is converted to products. Hence, the rate of forward reaction is slow due to low concentration of reactants.

Q.6 When a graph is plotted between time on x-axis and the concentrations of reactants and products on y-axis for a reversible reaction, the curves become parallel to time axis at a certain stage.

(a) At what stage the curves become parallel?

(b) Before the curves become parallel, the steapness of curves falls? Give reasons.

(c) The rate of decrease of concentrations of any of the reactants and rate of increase of concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Ans.

(a) & (b) Descriptive questions, consult textbook.

(c) CASE-I: Rate of change of concentration of reactants and products are equal: For all those reactions in which number of moles of reactants and products are equal in balanced equation, their rate of change of concentrations are also equal.

Example:

$H_2 + I_2 \rightleftharpoons 2HI$

For this reaction, two moles of reactants form two moles of products. Hence, change in concentration is same.

CASE-II: For all those reactions in which number of moles of reactants and products are unequal, their rate of change of concentration are also unequal.

Example:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In this reaction one mole of reactant produces two moles of product. Hence, rate of change of concentration is unequal.

Q.7 (a) Write down the relationship of different types of equilibrium constants i.e. K_c and K_p for the following general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

(b) Decide the comparative magnitudes of K_c and K_p, for the following reversible reactions.

(i) Ammonia synthesis (ii) Dissociation of PCl_5

Ans.

(a) K_c for the above mentioned reaction is:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

or
$$K_c = \frac{C_C^c \, C_D^d}{C_A^a \, C_B^b}$$

For gaseous reaction, we can also write:

$$K_p = \frac{P_C^c \, P_D^d}{P_A^a \, P_B^b}$$

Relation between K_p and K_c:

$K_p = K_c (RT)^{\Delta n}$

$\Delta n = n_P - n_R$

n_R = No. of moles of reactants

n_P = No. of moles of products

R = General gas constant

T = Absolute temperature

(b) (i) Ammonia synthesis:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

General relation between K_p and K_c is:

$$K_p = K_c (\Delta T)^{\Delta n}$$

$$K_p = K_c (RT)^{-2}$$

$$K_p = \frac{K_c}{(RT)^2}$$

$$K_p (RT)^2 = K_c$$

For this reaction

$n_P = 2$, $n_R = 4$

$\Delta n = 2, -4$

$\Delta n = -2$

For this reaction $K_c > K_p$. This, is true for all those reactions which proceeds with decrease in number of moles.

(ii) Dissociation of PCl_5:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

General relation between K_p and K_c is:

$$K_p = K_c (RT)^{\Delta n}$$

For this reaction:

$$n_p = 2 \quad , \quad n_R = 1$$

$$\Delta n = 2 - 1$$

$$\Delta n = 1$$

$$K_p = K_c (RT)^1$$

$$K_p = K_c (RT)$$

For this reaction $K_p > K_c$.

This is true for those reactions which proceeds with the increase in no. of moles.

Note: $K_p = K_c$ for those reactions in which number of moles of reactants and products are equal in balance equation e.g.,

$$N_2 + O_2 \longrightarrow 2NO$$

Q.8 (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm^3 at equilibrium stage:

(i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
(ii) $H_2 + I_2 \rightleftharpoons 2HI$
(iii) $2HI \rightleftharpoons H_2 + I_2$
(iv) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(v) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) How do you explain that some of the reactions mentioned above are affected by change of volume at equilibrium stage.

Ans.

(a) (i)

$$\begin{array}{llllll} & CH_3COOH & + \; CH_3CH_2OH & \rightleftharpoons \; CH_3COOC_2H_5 & + \; H_2O & \\ & \text{a moles} & \text{b moles} & \text{0 moles} & \text{0 moles} & t = 0 \\ \text{moles} & (a-x) & (b-x) & x & x & t = eq \\ \text{mole/dm}^3 & \frac{(a-x)}{v} & \frac{(b-x)}{v} & \frac{x}{v} & \frac{x}{v} & \end{array}$$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\frac{(a-x)}{v}\,\frac{(b-x)}{v}}$$

$$= \frac{\frac{x^2}{v^2}}{\frac{(a-x)(b-x)}{v^2}}$$

$$\boxed{K_c = \frac{x^2}{(a-x)(b-x)}}$$

(ii)

$$\begin{array}{lllll} & H_2 & + \; I_2 & \rightleftharpoons \; 2HI & \\ & a & b & 0 & t = 0 \\ \text{moles} & (a-x) & (b-x) & 2x & t = eq \end{array}$$

mol/dm^3 $$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\frac{(a-x)}{v}\,\frac{(b-x)}{v}}$$

$$K_c = \frac{\frac{4x^2}{v^2}}{\frac{(a-x)(b-x)}{v^2}}$$

$$K_c = \frac{4x^2}{(a-x)(b-x)}$$

(iii) $$2HI \rightleftharpoons H_2 + I_2$$

	a	0	0	$t = 0$
moles	$(a - 2x)$	x	x	$t = eq$
mol/dm^3	$\frac{(a-2x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$	

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{a-2x}{v}\right)^2}$$

$$K_c = \frac{\frac{x^2}{v^2}}{\frac{(a-2x)^2}{v^2}}$$

$$\boxed{K_c = \frac{x^2}{(a-2x)^2}}$$

(iv) $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	a	0	0	$t = 0$
moles	$(a - x)$	x	x	
mol/dm^3	$\frac{(a-x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$	

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\frac{(a-x)}{v}}$$

$$= \frac{\frac{x^2}{v^2}}{\frac{(a-x)}{v}}$$

$$\boxed{K_c = \frac{x^2}{v(a-x)}}$$

(v)

$$\begin{array}{lcccl} & N_2 & +\,3H_2 & \rightleftharpoons\ 2NH_3 & \\ & a & b & 0 & t = 0 \\ \text{moles} & (a - x) & (b - x) & 2x & t = eq \\ \text{mol/dm}^3 & \dfrac{(a - x)}{v} & \dfrac{(b - 3x)}{v} & \dfrac{2x}{v} & \end{array}$$

$$K_c = \frac{\left(\dfrac{2x}{v}\right)^2}{\left(\dfrac{a - x}{v}\right)\left(\dfrac{b - x}{v}\right)^3}$$

$$= \frac{\dfrac{4x^2}{v^2}}{\left(\dfrac{a - x}{v}\right)\left(\dfrac{b - 3x}{v}\right)^3}$$

$$= \frac{\dfrac{4x^2}{v^2}}{\dfrac{(a - x)(b - 3x)^3}{v \,.\, v^3}}$$

$$= \frac{4x^2 \,.\, v^4}{(a - x)(b - 3x)^3 \,.\, v^2}$$

$$\boxed{K_c = \frac{4x^2 \times v^2}{(a - x)(b - 3x)^3}}$$

(b) For first three reactions volume change does not affect equilibrium stage due to following:

Reasons:

(a) First reaction is in liquid state.

(b) First three reactions have equal no. of moles of reactants and products in balanced equation.

(c) For first three reactions equilibrium expression does not involve volume term i.e., independent of volume change.

For last two reactions, volume change effects equilibrium stage due to following:

Reasons:

(a) They have different number of moles of reactants and products in balanced equation.

(b) They involve the volume term in equilibrium expression i.e., depends upon volume change.

Q.9 Explain the following two applications of equilibrium constant. Give examples:

(i) Direction of reaction (ii) Extent of reaction

Ans. Descriptive question, consult text book.

Q.10 Explain the following with reasons:

(a) The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant.

(b) The change of temperature disturbs both the equilibrium position and the equilibrium constant of a reaction.

(c) The solubility of glucose in water is increased by increasing the temperature.

Ans.

(a) Consider following reaction and its equilibrium expression:

$$\begin{array}{cccc} 2SO_{2(g)} + & O_{2(g)} & \rightleftharpoons & 2SO_{3(g)} & \\ a & b & & 0 & t = 0 \\ \frac{(a-2x)}{v} & \frac{(b-x)}{v} & & \frac{2x}{v} & t = eq \end{array}$$

$$K_c = \frac{4x^2v}{(a-2x)^2\,(b-x)}$$

When we decrease the volume for this reaction, equilibrium position will shift in forward direction (where lesser no. of moles are being formed). As a result of that value of ‘x’ increases (the no. of moles of O_2 reacted at equilibrium). The decrease of term ‘V’ in equilibrium expression causes the increase of term ‘x’ and value of K_c remains constant. Hence, the equilibrium position shifted but value of equilibrium constant remains the same.

Note: Change of volume affects the equilibrium position of only those reactions in which no. of moles of reactants and products are different.

Increase of volume shifts equilibrium in a direction where more no. of moles are formed and vice versa.

(b) Increase of temperature favours endothermic reaction because it requires heat and decrease of temperature favours exothermic reaction.

For example consider the following exothermic reversible reaction.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad \Delta H = -41.84\ KJ/mol$$

It is endothermic in backward direction increase of temperature favours the backward endothermic reaction and equilibrium is shifted to left. This shift continues until new equilibrium position is established with new concentration of reactants (increased) and that of products (decreased). Hence, the value of K_c is also changed at new equilibrium position because.

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Note: The value of K_c for endothermic reversible reaction increases with the rise of temperature and reverse is true for exothermic reversible reactions.

(c) The solubility of glucose in water is endothermic process. It requires heats to be dissolved when temperature is increased, it absorbs heat and become more soluble. Hence, the solubility of sugar increases with the rise of temperature.

Q.11 (a) What is an ionic product of water? How does this value vary with the change in temperature? Is it true that its value increase 75 times when the temperature of water is increased form 0°C to 100°C.

(b) What is the justification for the increase of ionic product with temperature?

(c) How would you prove that at 25°C 1 dm^3 of water contains 10^{-7} moles of H_3O^+ and 10^{-7} moles of OH^-.

Ans.

(a) **Ionic Product of Water:** The product of molar concentration of H^+ and OH^- in pure water is called ionic product of water. It is represented by K_w and its value is 10^{-14} at 25°C.

$$K_w = [H^+][OH]$$

$$\boxed{K_w = 10^{-14}}$$

K_w and Change of Temperature: The value of K_w is directly proportional to the temperature. Higher the temperature, greater will be the value of K_w, because at high temperature ionization of water increases and ionic concentration of water is more e.g.,

$$K_w = 0.1 \times 10^{-14} \text{ at } 0°C$$

and $$K_w = 1 \times 10^{-14} \text{ at } 25°C$$

K_w at 0°C and 100°C: Yes, it is true that value of K_w increases 75 times when temperature of water is raised from 0°C to 100°C. The value of $K_w = 0.1 \times 10^{-14}$ at 0°C and $K_w = 7.5 \times 10^{-14}$. This can be shown as.

$$(\text{Ionic product of water at } 0°C) \times (75) = \text{Ionic product of water at } 100°C$$

$$0.1 \times 10^{-14} \times 75 = 7.5 \times 10^{-14}$$

This comparison verifies that ionic product of water at 100°C is 75 times of the value of 0°C.

(b) When temperature increases, then ionic concentration of water increases with the increasing ionic concentration, ionic product of water (K_W) also increases.

(c) Ionic product of water is:

$$K_w = [H^+][OH^-]$$

$$10^{-14} = [H^+][OH^-] \quad \ldots\ldots (1)$$

Water ionizes as $H_2O \rightleftharpoons H^+ + OH^-$.

It shows that in case of pure water:

$$[H^+] = [OH]^-$$

Hence, we can write eq. (1) as:

$$10^{-14} = [H^+][H^+] \qquad \text{since,} \quad [H^+] = [OH]^-$$

$$10^{-14} = [H^+]^2$$

Taking square root on both sides:

$$10^{-7} = [H^+] \text{ moles/dm}^3 \qquad \text{since,} \quad [H^+] = [H_3O^+]$$

Hence, $10^{-7} = [OH^-]$ moles/dm^3

Q.12 (a) Define pH and pOH. How are they related with pK_w.

(b) What happens to the acidic and basic properties of aqueous solutions when pH varies from zero to 14?

(c) Is it true that sum of pK_a and pK_b is always equal to 14 at all temperatures for any acid? If not, why?

Ans.

(a) **pH:** It is the negative logarithm of hydrogen ion concentration.

$$pH = -\log [H^+]$$

pOH: The negative logarithm of hydroxide ion concentration is called pOH.

$$pOH = -\log [OH^-]$$

Relation of pH and pOH wih pK_w: From the concept of ionic product of water we have

$$K_w = [H+][OH^-]$$

Taking log:

$$\log K_w = \log [H^+] + \log [\bar{O}H]$$

Now multiply with (–1)

$$-\log K_w = -\log [H^+] + (-\log [\bar{O}H])$$

$$pK_w = pH + pOH \quad \ldots\ldots (1)$$

$$pH + pOH = 14 \text{ at } 25°C \qquad (\text{Since, } pK_w = 14 \text{ at } 25°C)$$

Equation (1) shows that the sum of pH and pOH is equal to pK_w i.e., 14 at 25°C.

(b) When pH value varies from zero to 7, acidic properties of aqueous solution decreases. And when it varies from 7 to 14 to basic properties of aqueous solution increases.

The solution is acidic when pH value is between zero and 7 and is basic when pH value is between 7 and 14.

(c) No, it is not true always. Lets understand it at two different temperatures.

(i) Sum of pK_a and pK_b at 25°C.

$$pK_a + pK_b = pK_w \qquad -\log K_w = pK_w$$

$$K_w = 10^{-14} \text{ at } 25°C$$

$$pK_a + pK_b = -\log K_w$$

$$pK_a + pK_b = -\log 10^{-14}$$

$$pK_a + pK_b = 14 \qquad \log 10 = 1$$

It is true at 25°C.

(ii) Sum of pK_a and pK_b at 100°C.

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = -\log K_w$$

$$pK_a + pK_b = -\log (7.5 \times 10^{-14}) \qquad K_w = 7.5 \times 10^{-14} \text{ at } 100°C$$

$$pK_a + pK_b = -[(\log 7.5) + (\log 10^{-14})]$$

$$pK_a + pK_b = -[0.875 + (-14 \log 10)] \qquad \log 10 = 1$$

$$pK_a + pK_b = -[0.875 - 14] = -0.875 + 14$$

$$pK_a + pK_b = 13.125$$

Hence at 100°C, the sum of pK_a and pK_b is less than 14.

The reason for this is that the value of ionization constant (K_w) of water has greater value and its –log (pK_w) has lesser value than at 25°C.

Another reason is that at 100°C, ionization constant (K_a) for acids have high value and –log (pK_a) have low value than 25°C. Hence, the sum of pK_a and pK_b at 100°C is less than that at 25°C.

Q.13 (a) What is Lowry Bronsted idea of acids and bases: Explain conjugate acid and bases.

(b) Acetic acid dissolves in water and gives proton to water, but when dissolved in H_2SO_4, it accepts protons. Discuss the role of acetic acid in both cases.

Ans.

(a) **Lowry Bronsted Concept:**

Acid: Hydrogen ion (proton) donar in water is called acid.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{Cl^-}$$

According to this concept, acid after donating a proton forms negative ion. This negative ion is called conjugate base, since it has tendency to accept proton again.

Base: Hydrogen ion acceptor in water is called base.

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+} + \underset{\text{Conjugate base}}{OH^-}$$

According to this concept, base accepts a proton and forms positive ion. This ion is called conjugate acid, since, it has tendency to release proton again.

The strength of conjugate acid and base is inverse of each other.

(b) When acetic acid is dissolved in water, it undergo dissociation as:

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{CH_3COO^-} + \underset{\text{Conjugate acid}}{H_3O^+}$$

Acetic acid donates a proton to water and acts as an acid whereas water accepts a proton from acetic acid and acts as base.

When acetic acid is dissolved in H_2SO_4, it undergoes association as:

$$\underset{\text{Base}}{CH_3COOH} + \underset{\text{Acid}}{H_2SO_4} \rightleftharpoons CH_3COO^+H_2 + HSO_4^-$$

H_2SO_4 being more stronger acid donates a proton to acetic acid and acts as an acid whereas CH_3COOH being weak acid accepts a proton from sulphuric acid and behaves as a base.

Q.14 In the equilibrium:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\ kJ\ mol^{-1}$$

What is the effect on:

(a) the position of equilibrium (b) equilibrium constant? if

(i) temperature increased (ii) volume of the container is decreased

(iii) catalyst is added (iv) chlorine is added

Explain your answer.

Ans. Equilibrium of:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\ KJ/mol$$

the effect on.

(a) Position of equilibrium (b) Equilibrium constant

If:

(i) **Temperature is Increased:** Temperature change will affect both equilibrium position and equilibrium constant.

This is endothermic reaction, the increase of temperature shifts equilibrium position in forward direction to re-establish equilibrium. Hence, the value of K_c increases.

(ii) **Volume is Decreased:** The volume change affects equilibrium position only. When volume is decreased, reaction moves in backward direction to establish equilibrium again. Equilibrium constant is not affected.

(iii) **Catalyst is Added:** Catalyst has no effect on the equilibrium position and equilibrium constant. When catalyst is added at equilibrium, it enhances both the rates equally. Hence, equilibrium is not affected.

(iv) **Chlorine is Added:** The addition of a substance at equilibrium affects the equilibrium position only. Equilibrium constant remains the same.

When Cl_2 is added at equilibrium, equilibrium position is shifted in backward direction and is re-established.

Q.15 Synthesis of ammonia by Haber's process is an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46\ \text{kJ}$$

(a) What should be the possible effect of change of temperature at equilibrium state?

(b) How does the change of pressure or volume shifts the equilibrium position of this reaction?

(c) What is the role of the catalyst in this reaction?

(d) What happens to equilibrium position of this reaction if NH_3 is removed from the reaction vessel from time to time?

Ans.

(a) Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shifts the equilibrium to right and yield of NH_3 will increase.

(b) Increase of pressure decreases the volume and equilibrium position is shifted in forward direction. As a result yield of ammonia increases and vice versa.

(c) Catalyst have no effect on the position of equilibrium. However, it helps the equilibrium to establish earlier. The most important role of catalyst is that it increases the overall rate of reaction at optimum temperature. And we obtain the maximum yield of ammonia at faster rate.

(d) Continuous removal of NH_3 from reaction vessel from time to time, completely shifts reaction in forward direction. And we get maximum yield of NH_3.

Q.16 Sulphuric acid is the king of chemicals. It is produced by the burning of SO_2 to SO_3 through an exothermic reversible process.

(a) Write the balanced reversible reaction.

(b) What is the effect of pressure change on this reaction?

(c) Reaction is exothermic but still the temperature of 400-500 °C is required to increase the yield of SO_3. Give reasons.

Ans.

(a)

$$2SO_2 + O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3 \qquad (\Delta H = -97.9\ \text{kJ})$$

(b) Increase of pressure shifts the reaction in forward direction (less no. of moles are produced) and vice versa.

Hence, increase of pressure increases the yield of SO_3.

(c) For this exothermic reaction, if the temperature is kept low, the reaction will be slow but yield of SO_3 will be high. Due to slow rate of reaction, it becomes uneconomical. To make the process economical temperature is maintained at 400 – 500°C so that SO_3 is obtained at faster rate. In this way we get maximum yield of SO_3 in short time which is economical.

Q.17 (a) What are buffer solutions? Why we do need them in daily life?

(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?

(c) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer.

(d) How do you justify that the greater quantity of CH_3COONa in acetic acid decreases the dissociating power of acetic acid and so the pH increases.

(e) Explain the term buffer capacity.

Ans.

(a) **Buffer Solutions:** A solution that resists a change in pH, when a small amount of acid or base is added to it is called buffer solution. A buffer solution may be:

(i) **Acidic Buffer:** Mixture of weak acid and its salt with strong base.

e.g., $CH_3COOH + CH_3COONa$

(ii) **Basic Buffer:** Mixture of weak base and its salt with strong acid.

e.g., $NH_4OH + NH_4Cl$

Need of Buffer in Daily Life:

(i) Many chemical processes in the laboratory are accompanied by pH change. Buffer solutions are added to them to maintain pH.

Examples:

(i) Preparation of paper pulp.

(ii) Preparation of dyes.

(iii) The pH of our blood is maintained at 7.35. It is naturally buffered at this value.

(iv) While ignoring bacterial culture, buffer solutions are used to maintained the pH of medium.

(b) Both the species in the mixture ionizes as follows:

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

$$CH_3CONa \rightleftharpoons CH_3COO^- + Na^+$$

Since this mixture produces H^+ ion in the solution, makes it acidic and is called acidic buffer solution.

(c) Both the species in the mixture ionizes as follows:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Since, this mixture produces OH^- ion in the solution makes it basic and is called basic buffer solution.

(d) Acetic acid ionizes as:

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

When sodium acetate is added to above solution it ionizes as:

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

It suppresses the ionization of acetic acid by common ion effect of CH_3COO^- ions. In other words association of CH_3COO^- and H^+ increases. Due to which H^+ ion concentration decreases and pH value increases.

Hence, greater is the quantity of CH_3COONa in the mixture, lesser will be H^+ ion concentration and increased value of pH.

(e) **Buffer Capacity:** The ability of a buffer to resist a change in pH is called buffer capacity.

It is the ability of a buffer to absorb no. of moles/dm^3 of acid or base to change its pH by one unit. It is quantitative measurement of the amount of acid or base absorbed by solution before it is essentially destroyed.

Q.18 (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, AgCl, Ag_2CrO_4 and $PbCl_2$.

(b) How do you determine the solubility product of a substance when its solubility is provided in grams / 100 g of water?

(c) How do you calculate the solubility of a substance from the value of solubility product?

Ans.

(a) **Solubility Product:** Solubility product is the product of the concentration of ions raised to an exponent equal to the coefficient of the balanced equation.

Solubility Product Expression for:

(i) AgCl (ii) Ag_2CrO_4 (iii) $PbCl_2$

(i) AgCl:

$$AgCl_{(s)} \rightleftharpoons \overset{+}{Ag}_{(aq)} + \overset{-}{Cl}_{(aq)}$$

$$K_c = \frac{[\overset{+}{Ag}_{(aq)}][\overset{-}{Cl}_{(aq)}]}{[AgCl_{(s)}]}$$

$$K_c\,[AgCl_{(s)}] = [\overset{+}{Ag}_{(aq)}][\overset{-}{Cl}_{(aq)}]$$

$$K_{sp} = [\overset{+1}{Ag}_{(aq)}][\overset{-}{Cl}_{(aq)}]$$

Since, $[AgCl_{(s)}] = \text{Constant}$

(ii) Ag_2CrO_4:

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^{+1}_{(aq)} + CrO^{-2}_{4(aq)}$$

$$K_c = \frac{[Ag^{+1}_{(aq)}]^2[CrO^{-2}_{4(aq)}]}{[Ag_2CrO_{4(s)}]}$$

$$K_c\,[Ag_2CrO_{4(s)}] = [Ag^{+1}_{(aq)}]^2\,[CrO^{-2}_{4(aq)}]$$

$$K_{sp} = [Ag^{+1}_{(aq)}]^2\,[CrO^{-2}_{4(aq)}]$$

Since $[Ag_2CrO_4]$ = Constant

(iii)

$$PbCl_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$$

$$K_c = \frac{[Pb^{+2}_{(aq)}][Cl^{-}_{(aq)}]^2}{[PbCl_{2(s)}]}$$

$$K_c\,[PbCl_{2(s)}] = [Pb^{+2}_{(aq)}][Cl^{-}_{(aq)}]^2$$

$$K_{sp} = [Pb^{+2}_{(aq)}][Cl^{-}_{(aq)}]^2$$

Since $[PbCl_{2(s)}]$ = Constant

(b) Descriptive question, consult text book.

(c) Descriptive question, consult text book.

Q.19 K_c value for the following reaction is 0.016 at 520°C

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Equilibrium mixture [HI] = 0.08 M, $[H_2]$ = 0.01 M, $[I_2]$ = 0.01 M. To this mixture more HI is added so that its new concentration is 0.096 M. What will the concentration of [HI], $[H_2]$ and $[I_2]$ when equilibrium is re-established.

Ans. $K_c = 0.016$

Chemical equation = $2HI \rightleftharpoons H_2 + I_2$

Initial conc. in moles dm^{-3} $0.08 \rightleftharpoons 0.01 + 0.01$ t = eq.

On adding more HI : $0.096 \rightleftharpoons 0.01 + 0.01$

Change in conc. in moles dm^{-3}.

$$(0.096 - 2x) \rightleftharpoons (0.01 + x)(0.01 + x) \qquad t = \text{new eq.}$$

Concentrations of HI, H_2 and I_2 at new equilibrium = ?

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:

$$0.016 = \frac{(0.01 + x)(0.01 + x)}{(0.096 - 2x)^2}$$

$$0.016 = \frac{(0.01 + x)^2}{(0.096 - 2x)^2}$$

Taking square root on both sides:

$$\sqrt{0.016} = \sqrt{\frac{(0.01 + x)^2}{(0.096 - 2x)^2}}$$

$$0.126 = \frac{0.01 + x}{0.09 - 2x}$$

$$\begin{aligned} 0.126(0.096 - 2x) &= 0.01 + x \\ 0.012 - 0.252\,x &= 0.01 + x \\ 1.252\,x &= 0.0021 \\ x &= \frac{0.0021}{1.252} = 0.00168 \end{aligned}$$

Hence, the equilibrium concentration of H_2 = (0.01 + 0.00168) = 0.01168 M

The equilibrium concentration of I_2 = (0.01 + 0.00168) = 0.01168 M

The equilibrium concentration of HI = (0.096 – 2 × 0.00168) = 0.0926 M

Q.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 one mole of C_2H_5OH is allowed to come to equilibrium. Calculate the amount of ethyl acetate at equilibrium stage in number of moles and grams. Also calculate the masses of reactants left behind.

Ans. Equilibrium constant K_c = 4

Initial conc. of acetic acid, (CH_3COOH) = 3 moles

Initial conc. of ethyl alcohol, (C_2H_5OH) = 1 mole

Amount of ethyl acetate present at equilibrium = ?

Let the no of moles of ethyl acetate of equilibrium = X moles

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initial conc. 3 + 1 0 + 0

in moles

Equilibrium conc. in moles dm^{-3}.

$(3 - x) \quad + \quad (1 - x) \qquad\qquad x \quad + \quad x \qquad (t = eq.)$

Equilibrium constant expression for the reaction can be written as:

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Putting the values:

$$4 = \frac{(x) \times (x)}{(3 - x) \times (1 - x)}$$

$$4 = \frac{x^2}{x^2 - 4x + 3}$$

By cross multiplying:

$$4(x^2 - 4x + 3) = x^2$$

$$4x^2 - 16x + 12 = x^2$$

$$4x^2 - x^2 - 16x + 12 = 0$$

$$3x^2 - 16x + 12 = 0$$

To find value of 'x' following formula is applied.

Since, $$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here $a = 3$, $b = -16$ and $c = 12$

Putting these values:

$$x = \frac{+16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2(3)}$$

$$x = \frac{+16 \pm \sqrt{256 - 144}}{6}$$

$$x = \frac{16 \pm \sqrt{112}}{6}$$

$$x = 4.43 \text{ or } 0.9 \text{ mole}$$

The value, $x = 4.43$ moles is not possible as it is greater than the concentrations of the reactants. Thus 0.9 mole of ethyl acetate is present at equilibrium.

No of moles of ethyl acetate of equilibrium = 0.9 moles

Mass of ethyl acetate = 0.9×88 = 79.46 g

No. of moles of water produced = 0.9 moles

Mass of water produced = 0.9×18 = 16.2 g

Moles of acetic acid left behind = $3.0 - 0.9$ = 2.1 moles

Mass of acetic acid left behind = 2.1×60 = 126 g

Moles of alcohol left behind = $1.0 - 0.9$ = 0.1

Mass of alcohol left behind = 0.1×46 = 4.6 g

Q.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 units of K_p.

Ans.

(a) This is a reversible reaction and all the reactants and products are in the gaseous state. It is homogeneous equilibrium. So the value of K_p can be written in terms of partial pressures of gases at equilibrium stage.

$$K_p = \frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}}$$

(b)

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

$$1.00 + 1.00 \rightleftharpoons 0 + 0 \qquad t = 0 \text{ sec.}$$

$$(1 - x) + (1 - x) \rightleftharpoons x + x \qquad t = \text{equilibrium}$$

Total no of moles of reactants and products at equilibrium stage is 2. The no. of moles of H_2 i.e., 'x' = 33.3% of mixture.

$$\frac{\text{Number of moles of } H_2}{\text{Total moles of mixture}} = \frac{33.3}{100}$$

So, $$\frac{x}{2} = \frac{33.3}{100}$$

$$x = \frac{66.6}{100} = 0.666$$

Hence, at equilibrium stage the no. of moles of hydrogen is 0.666.

Equilibrium concentrations:

$$[H_2O] = 1 - 0.66 = 0.33$$

$$[CO] = 1 - 0.66 = 0.33$$

$$[H_2] = 0.66$$

$$[CO_2] = 0.66$$

$$K_p = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

Putting the values:

$$K_p = \frac{0.66 \times 0.66}{0.33 \times 0.33} = 4$$

K_p has no units.

Q.22 Calculate the pH of:

(a) 10^{-4} mole dm^{-3} of HCl

(b) 10^{-4} mole dm^{-3} of $Ba(OH)_2$

(c) 1.0 mole dm^{-3} of H_2X, which is only 50% dissociated.

(d) 1.0 mole dm^{-3} of NH_4OH which is 1% dissociated.

Ans.

(a) HCl is a strong electrolyte. It is 100% dissociated. So, the concentration of HCl which is 10^{-4} mol dm^{-3} gives H^+ ion having concentration 10^{-4} mol dm^{-3}.

$$\begin{array}{lcll} HCl & \rightleftharpoons & H^+ + Cl^- & \\ 10^{-4}\ mol.dm^{-3} & \rightleftharpoons & 0 + 0 & t = 0\ sec. \\ 0 & \rightleftharpoons & 10^{-4} + 10^{-4} & t = equilibrium \end{array}$$

$$[H^{\oplus}] = 10^{-4}$$

$$pH = ?$$

$$pH = -\log [H^{\oplus}]$$

Putting the values:

$$pH = -\log 10^{-4}$$

$$pH = +4 \log 10$$

$$pH = 4$$

(b)

$$Ba(OH)_2 \rightleftharpoons Ba^{+2} + 2OH^-$$

$$10^{-4}\ mol/dm^3 \rightleftharpoons 0 \quad + \quad 0$$

$$0 \rightleftharpoons 10^{-4} + 2(10^{-4}) \qquad t = equilibrium$$

So, $[OH^-] = 2(10^{-4}) = 2 \times 10^{-4}$

$pOH = -\log [OH^{\ominus}]$

Putting the values:

$pOH = -\log 2 \times 10^{-4}$

$pOH = 3.69$

Since, $pH + pOH = 14$

Therefore,

$pH = 14 - pOH$

$pH = 14 - 3.69 = 10.31$

(c) H_2X is a dibasic acid. One molecule of H_2X gives two ions of H^+. So one mole of H_2X will give 2 moles of H^+. But the acid is weak and it is 50% dissociated. So the concentration of H^+ is 1 mol dm^{-3}.

$[H^{\oplus}] = 1\ mol\ dm^{-3}$

$pH = ?$

$pH = -\log [H^{\oplus}]$

$pH = -\log 1$

$pH = 0$

100 contains $= 50$

1 contains $= \dfrac{50}{100}$

2.0 contains $= \dfrac{50}{100} \times 2$

$= 1.0$

(d) NH_4OH is a weak electrolyte and is 1% dissociated only. From one mole dm^{-3} only 1% is dissociated.

$$[OH^{\ominus}] = 1 \times \frac{1}{100} = 0.01 = 10^{-2}\ mol\ dm^{-3}$$

$pH = ?$

$pOH = -\log [OH^{\ominus}]$

$pOH = -\log 10^{-2}$

$pOH = 2$

100 contains $= 1$

1 contains $= \dfrac{1}{100}$

$= 10^{-2}$

Since, $pH + pOH = 14$

$pH = 14 - 2$

$pH = 12$

Q.23 (a) Benzoic acid, C_6H_5COOH, is a weak mono-basic acid ($K_a = 6.4 \times 10^{-5}$ mol dm^{-3}). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm^3 of 0.02 mole dm^{-3} benzoic acid.

(b) A buffer solution has been prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate the pH of solution. pKa of acid = 4.74 at 25°C. How the values of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl separately.

Ans.

(a) Benzoic acid and sodium benzoate give a buffer solution.

Mass of sodium benozoate = 7.2 g dm^{-3}

Molar mass of sodium benzoate = 144 g mol^{-1}

No. of moles of sodium benzoate = $\frac{7.2}{144}$ = 0.05 moles dm^{-3}

Number of moles of benzoic acid = 0.2 moles dm^{-3}

K_a of benzoic acid = 6.4×10^{-5}

pK_a of benzoic acid = $-\log(6.4 \times 10^{-5}) = 4.2$

$$pH = pK_a + \log\frac{[\text{Sodium benzoate}]}{[\text{Benzoic acid}]}$$

$$pH = 4.2 + \log\frac{[0.05\ M]}{[0.02\ M]}$$

$$pH = 4.2 + 0.39$$

$$pH = 4.59$$

(b) $[CH_3COOH] = 0.5$ M

$[CH_3COONa] = 0.2$ M

$pK_a = 4.74$

$pH = ?$

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acids}]}$$

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{pH} = 4.74 + \log \frac{[0.2\ \text{M}]}{[0.5\ \text{M}]}$$

$$\text{pH} = 4.74 + \log (0.4)$$

$$\text{pH} = 4.74 + (-0.4)$$

$$\text{pH} = 4.74 - 0.4$$

$$\text{pH} = 4.34$$

Addition of 0.1 mole of NaOH: Since, NaOH is a strong base therefore it is 100% dissociated. It generates 0.1 moles of OH^- ions. Out of 0.5 moles of CH_3COOH, 0.1 will react with OH^- ions and 0.4 moles of CH_3COOH is left behind in one dm^3 of solution. This neutralization makes identical change in the amount of CH_3COONa and its concentration will also increase from 0.2 moles to 0.3 moles. Now putting new values in Henderson equation, we get new value of pH.

$$\text{pH} = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{pH} = 4.74 + \log \frac{[0.3\ \text{M}]}{[0.4\ \text{M}]}$$

$$\text{pH} = 4.74 + \log (0.75)$$

$$\text{pH} = 4.62$$

Addition of 0.1 mole of HCl: Since HCl is a strong acid therefore it is 100% dissociated. It generates 0.1 moles of Cl^- ions. Out of 0.2 moles of CH_3COONa, 0.1 moles will react with Cl^- ions and 0.1 moles of CH_3COONa is left behind in one dm^3 of the solution. This reaction makes identical change in the amount of CH_3COOH and its concentration will also increase from 0.5 moles to 0.6 moles.

Now putting these new values in Henderson equation, we get new value of pH.

$$\text{pH} = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

Substituting the value of pK_a, $[CH_3COONa]$ and $[CH_3COOH]$ we get:

$$\text{pH} = 4.74 + \log \frac{[0.1]}{[0.6]}$$

$$= 4.74 + (-0.78)$$

$$= 4.74 - 0.78$$

$$= 3.96$$

New value of pH shows that a minor change has taken place. On addition of NaOH its basic strength increases slightly but when HCl is added to the solution its acidic strength increases slightly.

Q.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?

Ans. CaF_2 is a sparingly soluble salt. In order to know the concentration of the ions. Lets us write down the following equation:

$$CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$$

The concentration of Ca^{+2} at equilibrium stage = 2.05×10^{-4} mol dm^{-3}

The concentration of F^- at equilibrium stage = 4.1×10^{-4} mol dm^{-3}

Solubility product K_{sp} at 25°C = ?

$$K_{sp} = [Ca^{+2}][F^{-1}]^2$$
$$K_{sp} = (2.05 \times 10^{-4})(4.1 \times 10^{-4})^2$$
$$K_{sp} = 2.05 \times 10^{-4} \times 16.8 \times 10^{-8}$$
$$K_{sp} = 34.46 \times 10^{-12}$$
$$K_{sp} = 3.446 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

Q.25 The solubility product of Ag_2CrO_4 is 2.6×10^{-2} at 25°C. Calculate the solubility of the compound.

Ans.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$
$$K_{sp} = 2.6 \times 10^{-2}$$

Solubility of the compound (s) = ?

$$K_{sp} = [Ag^+]^2\,[CrO_4^{-2}]$$

Suppose that molar solubility of the Ag_2CrO_4 is s.

The concentration of Ag^+ is two times than CrO_4^{-2} ions.

Putting the values in above formula.

$$2.6 \times 10^{-2} = (2s)^2 \times s$$
$$2.6 \times 10^{-2} = 4s^3$$
$$4s^3 = 2.6 \times 10^{-2}$$
$$s^3 = \frac{2.6 \times 10^{-2}}{4} = 0.0065$$

Taking cube root on both sides.

$$s = \sqrt[3]{0.0065}$$
$$s = 0.1866 \text{ mol dm}^{-3}$$

Formula mass of Ag_2CrO_4 = 332g mol^{-1}

Amount in grams = 0.1866×332

= 61.752g dm^{-3}

Amount of Ag_2CrO_4 in 100g of solvent.

$$= \frac{61.752 \times 100}{1000}$$
$$= 6.1752\text{g}$$

[illegible] KNOW?

1. Law of mass action is also called Guldberg and Waag's law.
2. At equilibrium, the rate of forward reaction becomes equal to the rate of reverse reaction.
3. If the reaction has equal number of moles of the reactants and the products, the equilibrium constant has no units.
4. BiOCl is called artificial milk.
5. In case of exothermic reaction, decrease of temperature will favour the formation of the product.
6. In case of endothermic reaction the increase of temperature will favour the formation of the product.
7. The optimum temperature in the synthesis of NH_3 is 400 – 450°C and optimum pressure is 200 – 300 atm.
8. K_W at 0°C is 0.1×10^{-14} and at 25°C $K_W = 1.0 \times 10^{-14}$ but at 100°C $K_W = 7.5 \times 10^{-14}$.
9. pH scale was introduced by Sorenson.
10. pH of pure water is 7.
11. pH + POH = 14.
12. pH of milk is 6.5.
13. pH of Bread is 5.5.
14. pH of Banana is 4.6.
15. pH of Cherries is 3.6.
16. pH of soft drinks is 3.0.
17. pH of orange is 3.5.
18. pH of potato is 5.8.
19. pH of egg is 7.8.
20. pH of apple is 3.1.
21. pH of milk of magnesia is 10.5.
22. pH of sea water is 8.5.
23. pH of saliva is 6.5 – 6.9.
24. pH of rain water is 6.2.
25. The acid which ionizes partially in H_2O is called weak acid.
26. The acid which ionizes completely in H_2O is called strong acid.
27. According to the Lewis concept the species which donate the electrons are called bases.
28. According to the Lowery Bronsted acid base concept. The species which donate protons are called acids and those which accept protons are called bases.
29. The solution which resists the change in pH on the addition of small amount of the acid or base into it is called Buffer solution.
30. pH of human blood is 7.35.
31. The amount of solute required to saturate 100 g of the solvent at a given temperature is called solubility.

Chapter

9

SOLUTION

SOLUTION

"Any mixture with only a single phase is called **homogeneous mixture or solution**."

Binary Solution:

"The solution which contains two components only, is called **binary solution**."

For example, mixture of sugar in water. Binary solution consists of solute and solvents.

Solvent and Solute:

"The substance which is present in large quantity in solution is called **solvent and the substance in small quantity is solute**."

In above example sugar is solute and water is solvent.

Concentration of Solution:

"The amount of solute dissolved in a unit volume of solution or solvent is called **concentration of solution**."

Dilute Solution and Concentrated Solution:

Solutions containing relatively lower concentrations of solute are called **dilute solutions**, whereas those containing relatively higher concentrations of solutes are called **concentrated solutions**.

CONCENTRATION UNITS

"The quantity of solute or solvent is generally measured in term of volume, mass, or moles, are usually called **concentration unit**."

The concentration of solution can be expressed by molarity, molality, percentage, and mole fraction.

1. Percentage Composition:

The amount of solute and solvent can be expressed in % age of four ways.

(a) Percentage weight/weight

(b) Percentage weight/volume

(c) Percentage volume/weight

(d) Percentage volume/volume

(a) Percentage weight/weight:

"It is the weight of a solute dissolved per 100 parts by weight of solution."

5% w/w sugar solution will contain 5 g of sugar dissolved in 100 g of solution in water.

$$\% \text{ by weight} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Example 1:

Calculate the percentage by weight of NaCl, if 2.0 g of NaCl is dissolved in 20 g of water.

Weight of NaCl = 2.0 g

Weight of solvent = 20.0 g

Weight of solution = 20 + 2 = 22 g

$$\% \text{ of NaCl by weight} = \frac{2.0\text{ g}}{22.0\text{ g}} \times 100$$

$$= 9.09\ \%$$

(b) Percentage weight/volume:

"It is the weight of solute dissolved per 100 parts by volume of solution."

10 g of glucose dissolved in 100 cm^3 of solution is 10% w/v solution of glucose. **The quantity of the solvent is not exactly known**. In such solutions, the total volume of the solutions is under consideration.

(c) Percentage volume/weight:

"It is number of cm^3 of a solute dissolved per 100 g of the solution."

If we dissolve 10 cm^3 of alcohol in water and the total weight of the solution is 100 g then it is 10% v/w solution of alcohol in water. In such type of solutions **we don't know the total volume of the solution**.

(d) Percentage volume/volume:

"It is the volume of a solute dissolved per 100 cm^3 of the solution."

This unit of concentration is best applicable to the solutions of liquids in liquids. A 12% alcohol beverage is 12 cm^3 of alcohol and 88 cm^3 of water is present. Total volume of solution will be 100 cm^3, if solution is ideal. If solution is non ideal, total volume of solution is not equal to the volume of solute and volume of solvent.

2. MOLARITY (M)

"The number of moles of solute dissolved per dm^3 of solution is called **molarity**."

It is denoted by "M".

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in dm}^3}$$

$$\text{No. of moles} = \frac{n}{v} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}}$$

$$M = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3)}$$

For example:

One molar glucose contains 180 g of $(C_6H_{12}O_6)$ glucose dissolved per dm^3 of solution. One molar (1M) $C_{12}H_{22}O_{11}$ sucrose contains 342 g of sucrose per dm^3 of solution. This solution is **prepared in measuring** flask. Measuring flask of different volumes are available.

However, 1M $C_6H_{12}O_6$ and 1M $C_{12}H_{22}O_{11}$ have same number of solute particles but volume of solvent is different. Volume of solvent is greater in 1M $C_6H_{12}O_6$ and less in 1M $C_{12}H_{22}O_{11}$.

To calculate the volume of solvent we need to know the density of solute.

Example 2:

Calculate the molarity of a solution containing 20.7 g of K_2CO_3 dissolved in 500 cm^3 of the given solution.

Solution:

Mass of K_2CO_3 = 20.7 g

Molar mass of K_2CO_3 = 138 g mol^{-1}

Volume of solution = 500 cm^3 = 0.5 dm^3

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3)}$$

$$= \frac{20.7\text{ g}}{138\text{ g mol}^{-1}} \times \frac{1}{0.5\text{ dm}^3}$$

$$= 0.3\text{ mole dm}^{-3} = 0.3\text{ M}$$

MOLALITY (m)

"The number of moles of solute dissolved per kilogram of solvent is called **molality**."

It is denoted by "m".

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (kg)}}$$

$$\text{No. of moles} = \frac{n}{w} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

$$m = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

For Example:

One molar glucose contains 180 g of $(C_6H_{12}O_6)$ present [in one kg of water (solvent)]. Total mass of solution is (1000 g solvent + 180 g solute) 1180 g. In this case to calculate volume of solution, we need density of solution.

1m NaOH contains 40 g of NaOH in 1 kg of water.

1m sucrose ($C_{12}H_{22}O_{11}$) contains 342 g of solute in 1 kg of solvent.

Example 3:

What is the molality of a solution prepared by dissolving 5 g of toluene (C_7H_8) in 250 g of benzene.

Solution:

Mass of toluene = 5 g

Mass of benzene = 250 g

Molar mass of toluene = 12 x 7 + 1 × 8 = 92

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

$$= \frac{5\text{ g}}{92\text{ g of mol}^{-1}} \times \frac{1}{0.250\text{ kg}}$$

$$= \frac{5}{92 \times 0.25}\text{ mole kg}^{-1}$$

$$= 0.217\text{ mole kg}^{-1} = 0.217\text{ m}$$

Molality of solution does not change by changing temperature. However, molarity of solution decreases by increasing temperature. Volume of liquid is affected by temperature but mass is not affected by variation of temperature.

TABLE

Comparison of Molarity and Molality:	
Molarity (1M)	**Molality (1m)**
1. The number of moles of solute dissolved per dm^3 of solution.	1. The number of moles of solute dissolved per kg of solvent.
2. It is denoted by "M".	2. It is denoted by "m".
3. Quantity of solvent is less than molal solution so it is concentrated than molal solution with values.	3. Quantity of solvent is greater than molar solution so it is dilute as compared to molar solution with same values.
4. Molarity changes by changing the temperature because volume or solvent is affected.	4. Molality does not changes by changing the temperature because mass of solvent is not affected.
5. **Example:**	5. **Example:**

1M glucose contain 1 mole of $C_6H_{12}O_6$ (180 g) per dm^3 of solution.	1m glucose contain 1 mole of $C_6H_{12}O_6$ (180 g) per kg of solvent.

3. Mole Fraction (x):

"The ratio of number of mole of a component to the total number of moles in a solution is called **mole fraction**."

It is denoted by "x".

The important features of mole fraction is

(i) This unit of concentration may be used for any solutions of gas in gas, liquid in liquid, and liquid in solid.

(ii) This unit of also applicable when more than two components are present in the solution.

(iii) There are no formal units of mole fraction. Anyhow we sometimes multiply mole fraction by 100 to get mole percent.

Let there be many components A, B and C making a solution. The number of moles are n_A, n_B and n_C respectively. If the mole fraction of A, B and C are denoted by X_A, X_B and X_C respectively then.

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

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

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

The **sum of the mole fractions** of all the components of a solution must be equal to **one**.

$$X_A + X_B + X_C = 1$$

$$\text{Mole percent} = \frac{\text{Mole of one component}}{\text{Total moles}} \times 100$$

In the case of mixture of gases, one can determine the mole fraction from the partial pressure data of the mixture. Hence

$$X_A = \frac{P_A}{P_A + P_B + P_C}$$

$$X_B = \frac{P_B}{P_A + P_B + P_C}$$

$$X_C = \frac{P_C}{P_A + P_B + P_C}$$

$$\text{Mole fraction of any gas} = \frac{\text{Partial pressure of that gas}}{\text{Total pressure of the mixture of gases}}$$

Example 4:

Calculate the mole fraction and mole percent of each component in a solution having 92 g of ethyl alcohol, 96 g of methyl alcohol and 90 g of water.

$$\text{No. of moles of the substance} = \frac{\text{Mass of grams of the substance}}{\text{Molecular mass}}$$

$$\text{No. of moles of ethyl alcohol} = \frac{92\text{ g}}{46\text{ g mol}^{-1}} = 2\text{ moles}$$

$$\text{No. of moles of methyl alcohol} = \frac{96\text{ g}}{32\text{ g mol}^{-1}} = 3\text{ moles}$$

$$\text{No. of moles of water} = \frac{90\text{ g}}{18\text{ g mol}^{-1}} = 5\text{ moles}$$

$$X_{\text{ethyl alcohol}} = \frac{2}{2+3+5} = \frac{2}{10} = 0.2$$

$$X_{\text{methyl alcohol}} = \frac{3}{2+3+5} = \frac{3}{10} = 0.3$$

$$X_{H_2O} = \frac{5}{2+3+5} = \frac{5}{10} = 0.5$$

Mole % of alcohol = 0.2 x 100 = 20

Mole % of CH_3OH = 0.3 x 100 = 30

Mole % of H_2O = 0.5 x 100 = 50

4. PARTS PER MILLION (ppm)

"The number of parts (by mass or volume) of a solute per million parts (by mass or by volume) of the solution is called **ppm**."

This unit is used for very low concentrations of solutions, e.g. to express the impurities of substances in water.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Example 5:

Seawater has 5.65×10^{-3} g of dissolved oxygen is one kg of water. Calculate the concentration of oxygen in seawater in parts per million.

Solution:

$$\text{ppm of oxygen in seawater} = \frac{5.65 \times 10^{-3}\ \text{g}}{1000\ \text{g}} \times 10^{6}$$

$$= 5.65\ \text{ppm}$$

INTER–CONVERSION OF VARIOUS CONCENTRATION UNITS OF SOLUTION

Sometimes we get prepared solutions form the chemical supply houses. For example, we are working with a solution whose molarity is given by the supplier, but we need to know its molarity or w/w percentage. For such purpose, we need to convert one unit of concentration into other. These conversions are usually done if we known the formula masses and the densities of the solutes or solutions.

Example 6:

Percentage to Molality:

Calculate the molality of 8% w/w NaCl solution.

Solution:

8% w/w NaCl solution means that 8 g of NaCl is dissolved in 100 g of solutions.

So, mass of water in the solution = 100 – 8 = 92 g.

$$\text{Mass of solvent in kg} = \frac{92}{1000} = 0.092\ \text{kg}$$

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

$$= \frac{8\ \text{g}}{58.5\ \text{g mol}^{-1}} \times \frac{1}{0.092\ \text{kg}}$$

$$= 1.487\ \text{mole kg}^{-1}$$

Example 7:

Percentage to Molarity:

Hydrochloric acid available in the laboratory is 36% (w/w). The density of HCl solutions is 1.19 cm^{-3}. Determine the molarity of HCl solution.

Solution:

Mass of HCl = 36 g

Mass of solution = 100 g

$$\text{Volume of solution} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{100\ \text{g}}{1.19\ \text{g cm}^{-3}} = 84.03\ \text{cm}^{3}$$

$$\text{Volume in dm}^{3} = \frac{84.03\ \text{cm}^{3}}{1000} = 0.084\ \text{dm}^{3}$$

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3\text{)}}$$

$$= \frac{36\text{ g}}{36.5\text{ g mol}^{-1}} \times \frac{1}{0.084\text{ dm}^3}$$

$$= 11.73\text{ mole dm}^{-3} \text{ or } 11.73\text{ M}$$

Example 8:

Molarity to Percentage:

9.2 molar $HClO_4$ is available from the market. The density of this solution is 1.54 cm^{-3}. What is the percentage by weight of $HClO_4$.

Solution:

Molarity of $HClO_4$ = 9.2 mole dm^{-3}

Mass = v x d

Mass of 1000 cm^3 solution = 1000 cm^3 x 1.54 g cm^{-3}

= 1540 g

Molar mass of $HClO_4$ = 100.5 g mol^{-1}

Mass = molar mass x mole

Mass of $HClO_4$ = 100.5 g mol^{-1} x 9.2 mol dm^{-3}

= 924.6 g dm^{-3}

Mass of H_2O = 1540 g – 924.6 g = 615.4 g

$$\text{Mass \%} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$\text{\% of } HClO_4 \text{ by mass} = \frac{924.6\text{ g}}{1540\text{ g}} \times 100 = 60.013\%$$

$$\text{\% of } H_2O \text{ by mass} = \frac{615.4\text{ g}}{1540\text{ g}} \times 100 = 39.99\%$$

TYPES OF SOLUTIONS

There are nine types of solution on the bases of physical states of solutes and solvents. These types are given in the Table.

TABLE

Common Types and Examples of Solutions

No.	State of Solute	State of Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	O_2 in water, CO_2 in water (aerated water, soft drinks, fizzy drinks, soda water).
3.	Gas	Solid	H_2 absorbed by palladium (occlusion).
4.	Liquid	Gas	Mist, fog, clouds, liquid air pollutant.
5.	Liquid	Liquid	Alcohol in water, milk.

6.	Liquid	Solid	Mercury in silver (amalgam), butter, cheese.
7.	Solid	Liquid	Sugar in water, jellies, paints.
8.	Solid	Gas	Dust particles or smoke in air.
9.	Solid	Solid	Metal alloy (brass, bronze, German silver) pearls, opals, carbon in iron (steel).

1. SOLUTION OF SOLIDS IN LIQUIDS

When a solid comes in contact with a suitable liquid, it dissolves forming a solution i.e. a homogenous mixture. This process of dissolution can be explained in terms of attraction between the particles of a solute and that of a solvent. The molecules or ions in solids are arranged in such a regular pattern that the inter–molecular or inter–ionic forces are at a maximum. The process of dissolution is to overcome these forces of attraction holding together the solute molecules or ions in the crystal lattice, by the solute–solvent forces.

The principle of solubility is that "**like dissolved like**". Polar solutes are soluble in polar solvents while non–polar solutes soluble in non–polar solvents.

(a) Molecular Crystals are Soluble in Non–Polar Solvents:

In molecular crystals, the inter–molecular forces of attraction are either dipole–dipole or London dispersion type, so are relatively weak and can easily be overcome. Non–polar or less polar molecular crystals usually dissolve in non–polar solvents like benzene.

(b) Ionic–Crystals and Highly Polar Crystals are Soluble in Polar Solvents:

In the crystal lattice, the inter–molecular or inter–ionic forces of attraction between highly polar molecules or ions are quite strong, hence the polar solids fail to dissolve in non–polar solvents. These strong electrostatic forces cannot be overcome or shattered by the weak solute–solvent attractions. Take the case of cane sugar, due to hydrogen bonding, it has tightly bonding molecules, so it will not be dissolved by solvents like kerosene oil, petrol, benzene, etc. but will be dissolved readily in water because water attracts sugar molecules almost in the same way as the sugar molecules attract one another.

The inter–ionic forces of attraction are very strong in ionic solids. Equally strong polar solvents are needed to dissolve them. Such solids cannot be dissolved by moderately polar solvents like acetone. A moderate polar solvent, fails to dissolve ionic solids like NaCl.

2. Solution of Liquids in Liquids:

The solutions of liquids in liquids may be divided into three classes.

1. Practically Immiscible Liquids:

Those liquids which do not dissolve into each other in any proportion are immiscible.

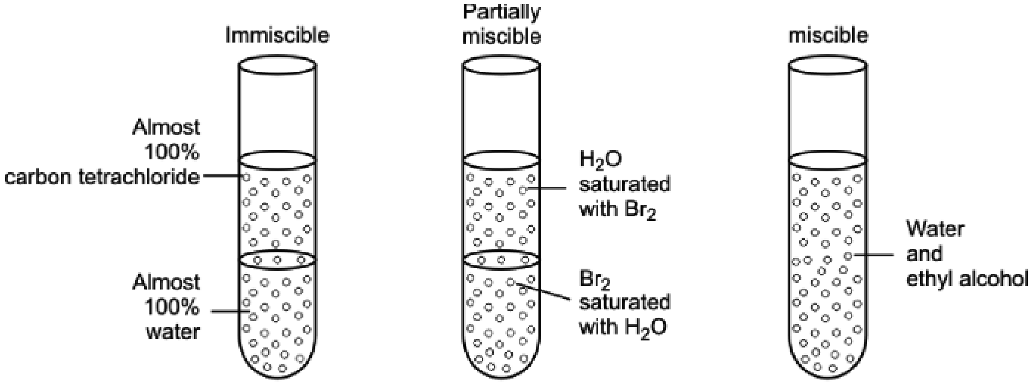
Example:

(i) Water and Benzene
(ii) Carbon disulphide and water
(iii) Carbon tetrachloride and water

2. Completely Miscible Liquids:

"Such liquids are miscible in all proportions."

Liquids like alcohol and water or alcohol and ether mix in all proportions. However, the properties of such solutions are not strictly additive. Generally, the volume decrease on mixing but in some cases it increase. Heat may be evolved or absorbed during the formation of such solutions. These types of solutions can usually be separated by fractional distillation.



Immiscible, partially miscible, and miscible liquids

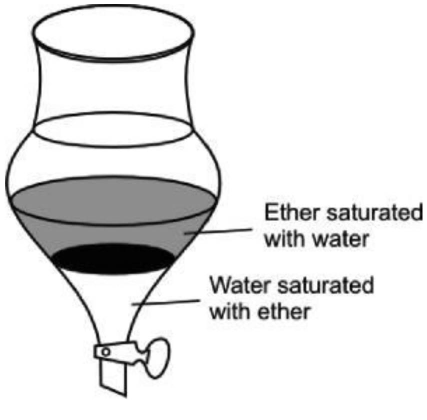
Example:

(i) Water and ethyl alcohol
(ii) Ethyl alcohol and ether
(iii) Benzene and toluene

3. PARTIALLY MISCIBLE LIQUIDS

"The liquid which dissolves into another liquid upto a limited extent is called **partially miscible liquid**."

For example, when ether and water are shaken together in separating funnel and layers allowed to separate. Some ether is present in water layer (1.2%). Presence of water in ether can be seen by igniting it. some water vapours are present in ether layer (6.5%). Presence of water vapour in ether layer can be seen, by dissolving some anhydrous $CuSO_4$ in this layer. $CuSO_4$ is not soluble in pure ether.



Each liquid layer is a saturated solution of the other liquid. Such solutions are called **conjugate solutions**. The mutual solubility of these conjugate solutions is affected by temperature changes. Typical example of such systems are:

(i) Phenol–water system

(ii) Tri–ethylamine–water system
(iii) Nicotine–water system

PHENOL–WATER SYSTEM

If equal volumes of water and phenol are mixed together they show partial miscibility. 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 phenol giving us the lower layer.

As 25°C the **upper layer is 5% solution of phenol in water and the lower layer is 30% water** in phenol. 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. When the temperature of water–phenol system is increased, the compositions of both layers change. Water starts traveling from upper to the lower layer and phenol travels from lower to the upper layer. When the temperature of this system approaches **65.9°C**, a homogenous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water.

"The temperature at which two conjugate solutions merge into one another, is called **critical solution temperature or upper consulate temperature**."

Critical solution temperature for water–phenol system is 65.9°C.

Some other partially miscible pairs of liquids have their own consulate temperature with definite compositions. For example, water–aniline system has a single layer at 167.0°C with 15% water. Methanol–cyclohexane system has consulate temperature of 49.1°C with 29% methanol.

Ideal and Non–Ideal Solutions:

When two or more than two liquid substances are mixed, the solutions may be ideal or non–ideal. To distinguish between such solutions we look at the following aspects:

TABLE

Ideal Solution	Non–Ideal Solution
1. The force of interaction between the molecules of different components are same as they were in the pure state. $A - A,\ B - B = A - B$	1. The force of interaction between the molecules of different components are not same as they were in the pure state. $A - A,\ B - B \neq A - B$
2. Volume of solution is sum of the volumes of solute and solvent and change in volume is zero, $\Delta V = 0$. $V_{solvent} + V_{solute} = V_{solution}$	2. Volume of solution is sum of the volumes of solute and solvent and change in volume is not zero, $\Delta V \neq 0$. $V_{solvent} + V_{solute} \neq V_{solution}$
3. Ideal solutions have zero enthalpy change as their heat of solution, $\Delta H = 0$.	3. Non–ideal solutions have endothermic or exothermic enthalpy as their heat of solution, $\Delta H \neq 0$.
4. Temperature does not change, when solution is formed.	4. Temperature increases or decreases, when solution is formed.
5. Ideal solution obey the Raoult's law.	5. Non–ideal solution does not obey the

$P = P^oX_1$	Raoult's law. $P = P^oX_1$
6. Ideal solutions obey Vant-Hoff's equation $\pi v = n_2RT$.	6. Non-ideal solutions do not obey Vant-Hoff's equation.
Example: (i) Benzene and ether (ii) Chlorobenzene and bromobenzene.	**Example:** (i) Acetone–water (ii) Ethanol–hexane.

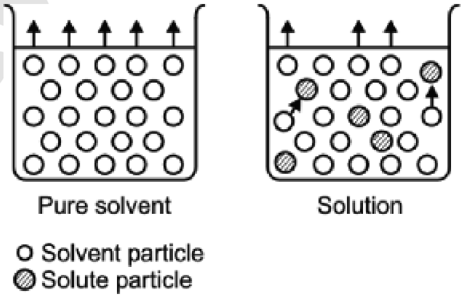
RAOULT'S LAW

(When solute in non–volatile and solvent is volatile)

(a) Vapour pressure of a solvent above solution is equal to the product of vapour pressures of pure solvent and mole fraction of solvent in a solution.

Mathematically it is can be written as

$$p = p^o x_1 \qquad (1)$$



Where p^o is vapour pressure pure of solvent p is vapour pressure of solvent in solution x_1 is mole fraction of solvent. p is always less than P^o, because surface area for the solvent decreases in solutions form. Some solute particles are also present at the surface, which are non–volatile, so $P < P^o$.

(b) This law can be written as $\Delta P = P^o X_2$. **Lowering of vapour pressure is directly proportional to mole fraction of solute**. We know that $x_1 + x_2 = 1$ $\quad x_1 = 1 - x_2$

Putting the value of x_1 in Equation (1).

$$p = p^o (1 - x_2)$$

or $\quad p = p^o - p^o x_2$

or $\quad p^o - p = p^o x_2$

or $\quad \Delta p = p^o x_2$ or $\Delta p \propto x_2 \qquad (2)$

(c) "Relative lowering of vapour pressure $\left(\frac{\Delta p}{p^o}\right)$ is equal to the mole fraction of solute."

We know that

$$\Delta p = p^o x_2$$

by rearranging $\frac{\Delta p}{p^{o}} = x_2$ (3)

The 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.

Example 9:

The vapour pressure of water of $30^{o}C$ is 28.4 torr. Calculate the vapour pressure of a solution containing 70 g of cane sugar $(C_{12}H_{22}O_{11})$ in 1000 g of water at the same temperature.

Solution:

$$\text{No. of moles of } C_{12}H_{22}O_{11}\ (n_2) = \frac{70\ \text{g}}{342\ \text{g/mol}} = 0.20 \text{ moles}$$

$$\text{No. of moles of } H_2O\ (n_1) = \frac{1000\ \text{g}}{18.02\ \text{g/mol}} = 55.49 \text{ moles}$$

$$\text{Total no. of moles} = 0.20 + 55.49 = 55.69$$

$$\text{Mole fraction of } H_2O\ (x_1) = \frac{n_1}{n_1 + n_2}$$

$$= \frac{55.49}{55.69} = 0.9964$$

$$\text{Applying the formula} = p = p^{o}\, x_1$$

$$= (28.4)\,(0.9964) = 28.29 \text{ torr}$$

So, vapour pressure of solution = 28.29 torr.

RAOULT'S LAW

When both components are volatile:

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. Consider two liquids 'A' and 'B' with vapour pressures p_A^o and p_B^o 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.

Applying Raoult's law to both components

$$p_A = p_A^o\, X_A$$

$$p_B = p_B^o\, X_B$$

$$P_t = p_A + p_B = p_A^o\, X_A + p_B^o\, X_B$$

Since $X_A + X_B = 1$

$$X_B = 1 - X_A$$

$$P_t = p_A^o\, X_A + p_B^o\,(1 - X_A)$$

$$P_t = p^o_A X_A + p^o_B - p^o_B X_A$$

$$P_t = p^o_A X_A - p^o_B X_A + p^o_B$$

$$P_t = (p^o_A - p^o_B) X_A + p^o_B \qquad (4)$$

Equation (4) is a straight line. The equation of straight line is $y = mx + c$. Where y and x are variable, m is slope and c is constant.

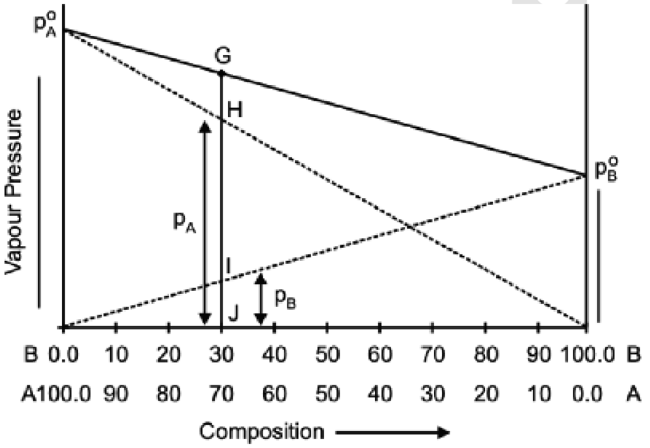
$$P_t = (p^o_A - p^o_B) X_A + p^o_B$$

↑ ↑ ↑ ↑

y m x c

If we plot a graph between P_t at y–axis and, X_A or $(1 - X_B)$ at x–axis, a straight line is obtained. Liquid A is more volatile than liquid B.

Only those pairs of liquids give straight lines which form ideal solutions. So Raoult's law is one of the best criterion to judge whether a solution is ideal or not.



Graph between composition and vapour pressure

All the possible solutions of two components A and B have their vapour pressures on the straight line connecting p^o_A with p^o_B. All such solutions will be ideal. 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 component with increase in its mole fraction in solution.

In order to explain it, consider a point G on the straight line. This point represents the vapour pressure of solution with 30% contribution of the component B and 70% of A. 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. Similarly 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^o_A to p^o_B.

The total vapour pressure of the solution (P_t) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components $(p_A + p_B)$ as shown in Figure.

Vapour Pressures of Liquid – Liquid Solutions:

The study of vapour pressures of miscible liquids is of great help in the separation of liquids by fractional distillation.

Binary mixtures of miscible liquids may be classified as (i) Ideal (ii) Non–ideal or real solutions.

The vapour pressures of solutions provide a simple picture about their behaviour. Let us consider the vapour pressures of ideal and real solutions.

(i) IDEAL SOLUTIONS

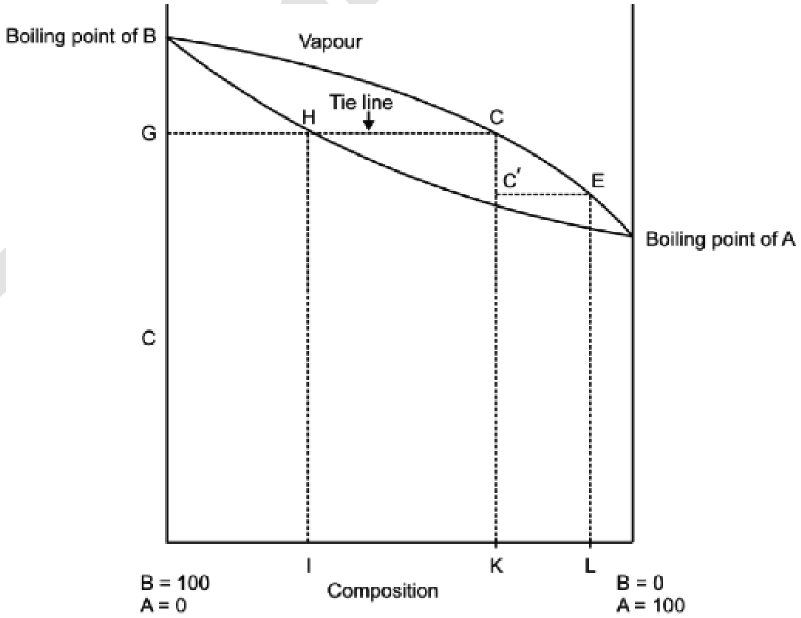
An ideal solution is that which obeys Raoult's law."

Some typical ideal solution forming liquid pairs are: benzene–toluene, benzene–ether, chlorobenzene–bromobenzene, ethyl iodide–ethyl bromide, etc.

FRACTIONAL DISTILLATION OF IDEAL MIXTURE OF TWO LIQUIDS

Liquid–vapour phase diagram at constant pressure is important to study the fractional distillation. Fractional distillation is a technique by which different liquids are separated from each other on the basis of their different boiling points.

Let us have two liquids A and B in mixture, which forms a completely miscible solution. A is more volatile and has less boiling point, while B is less volatile and has greater boiling point. If we plot a boiling point of liquid mixture against its composition and the composition of vapour in contact with it, we get two separate curves of each type of solutions.



Constant-pressure phase diagram showing composition of both liquid and vapour

Consider the temperature corresponding to point G. It meets liquid curve at point H and vapour curve at point C. This CH curve is called **tie line**. Composition of liquid mixture correspond to point H is shown at point I. At point I the percentage of have high percentage of A and less percentage of B. These vapours rise in fractional column, its temperature decreases until it condenses. This temperature drop is represented by vertical line CK in the phase diagram. At point C', a new equilibrium is established between the condensate descends the column while the vapour ascends. Thus, at various stages in the column, the descending liquid and ascending vapours are in equilibrium. These equilibrium are represented by tie lines. As the vapours rise in the column through each successive equilibrium, they become richer in more volatile component A. Eventually, they pass out the column at the top are condensed and collected. At the same time, liquid in the flask becomes richer in the less volatile component and consequently its boiling point increases. So we can completely separate the liquid mixture by fractional distillation.

"The liquid mixture which distil with a change in composition are called a **Zeotropic mixture**."

For example, methyl alcohol water solution can be separated by fractional distillation.

Fractional distillation technique is also used

(1) In the refining of petroleum.

(2) Manufacture of O_2, N_2 and noble gases from liquid air.

(3) Production of whisky and other alcoholic products.

(ii) Non–Ideal Solutions (Azeotropic Mixtures):

Many solutions do not behave ideally as they show deviations from Raoult's law due to differences in their molecular structures i.e. size, shape and inter–molecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy. The vapour pressure deviations may be positive or negative in such solutions.

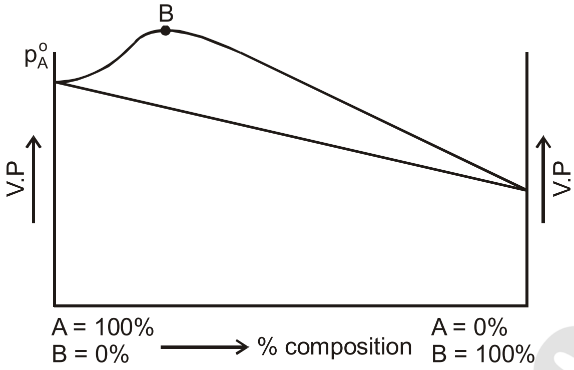
AZEOTROPIC MIXTURE

"The liquid mixture which boils at constant temperature and distills over without change in composition at any pressure like a chemical compound is called **azoetropic mixture**."

(a) POSITIVE DEVIATION

When the vapour pressure of mixture is greater than that predicted by the Raoult's law, exhibit a positive deviation. When **attractive forces** between the solute molecules or between solvent molecules, neither the solute nor the solvent held as tightly in the solution as they are in pure state. The escaping tendency of each is therefore greater in the solution than in the solute or solvent alone. As a result, **partial pressures** of both of them over the solution are **greater** than predicted by the Raoult's law.

The liquids which have greater vapour pressure have **low boiling points**. The liquid mixtures which have highest vapour pressure have lowest boiling points. On distilling this type of solution, the first fraction will be constant boiling mixture (azoetropic mixture) having a fixed composition. For such mixture, it is impossible to bring about complete separation of components by fractional distillation. Ethanol–water is an example of positive deviation. The composition which have 95% alcohol by volume is a azoetropic mixture and 5% water cannot be removed from it by fractional distillation.



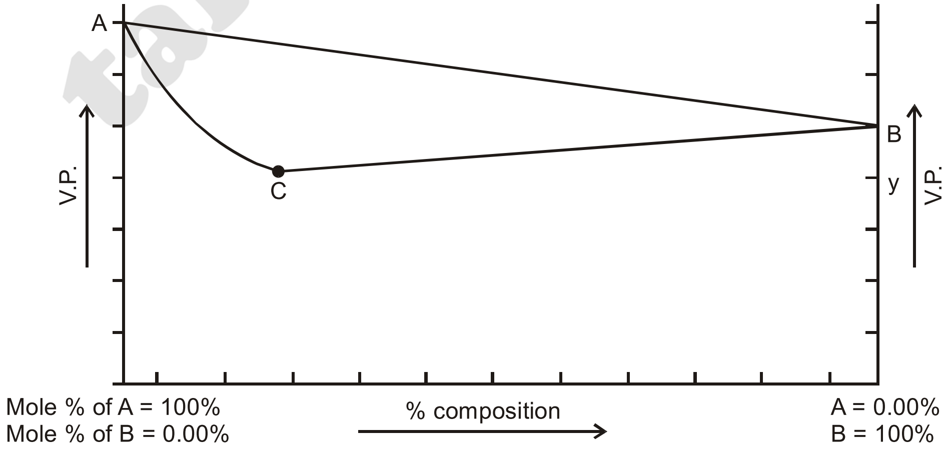
A pair of components showing positive deviation from Raoult's law.

NEGATIVE DEVIATION

"When the vapour pressure of liquid mixture is less than the predicted value of Raoult's law, it shows negative deviation."

When solute–solvent **interaction is stronger** than solute–solute or solvent–solvent interaction opposite effect is seen. Each substance in the presence of other is held more tightly then in the pure material and their **partial pressure are less**, as predicted by the Raoult's law. Doted line in the graph shows the ideal behaviours. The liquid mixture which have lowest vapour pressure have **highest boiling points**. It is also impossible to separate completely such mixtures by fractional distillation.

We can give the example of hydrochloric acid solution in water for this type of solutions. HCl forms an azeotropic mixture with water which boils at 110°C and containing 20.24% of the acid. Similarly figure shows that the pair of liquids showing the negative deviation form azeotropic mixture with maximum boiling point corresponding to G in comparison with pure components.



A pair of components showing negative deviation from Raoult's law.

TABLE

Summary of Solution Properties

Relative attractive forces	$\Delta H_{(sol)}$	Temp. change when solution is formed	Deviation from Raoult's laws	Volume Change
A – A, B – B = A – B	Zero	None	None (ideal sol)	$\Delta V = 0$
A – A, B – B < A – B	Negative (exothermic)	Increase	Negative	Slightly decreases
A – A, B – B > A – B	Positive (endothermic)	Decrease	Positive	Slightly increases

SOLUBILITY AND SOLUBILITY CURVE

Solubility:

"The concentration of the solute in solution, when it is in equilibrium with solid substance, at particular temperature is called **solubility**."

Whenever a solid solute is put in a liquid solvent then the molecules or ions breakaway from the surface of the solid and pass into the solvent. These particles of solid are free to diffuse throughout the solvent to give a uniform solution. The solute and solvent molecules are constantly moving about in the solution phase because of kinetic energy possessed by them. This process is called **dissolution**.

Some of the particles of the solute come back towards the solid due to collisions. These molecules or ions are entangled in its crystal lattice and get deposited on it. This is called **re–crystallization or precipitation**.

If excess solid is present in the solution than the rate of dissolution and rate of crystallization becomes equal. This is the state of dynamics equilibrium.

Dissolution $\rightleftharpoons$ Crystallization.

The concentration of the solute at equilibrium with the solution is constant for a particular solvent and at a fixed temperature. The solution thus obtained is called **saturated solution of the solid substance** and the concentration of this solution is termed as its solubility.

Unit of Solubility:

Solubility is expressed in terms of number of grams of solute in 100 g of solvent. At a particular temperature saturated solution of $NaCl$ in water at 0^oC contains 37.5 g of $NaCl$ in 100 g of water. Similarly the solubility of $CuSO_4$ in water at 0^oC is 14.3 g/100 g while at 100^oC it is 75.4 g/100 g.

Determination of Solubility:

To determine the solubility of substance, a saturated solution of a solid is prepared at a constant temperature. Then this solution is filtered. A known volume of this solution is evaporated in a china dish and from the mass of the residue, the solubility can be calculated.

Effect of Temperature on Solubility:

Temperature °C

Substance	0°	20°	40°	60°	80°	100°
NaCl	35.7	35.9	36.4	37.1	38.0	39.2
$NaNO_3$	73	87.6	102	122	148	180
KCl	28.0	34.2	40.1	45.8	51.3	56.3
KI	128	144	162	176	192	206
KNO_3	13.9	31.6	61.3	106	167	245
Li_2CO_3	1.54	1.33	1.17	1.01	0.85	0.72
$AgNO_3$	122	216	311	440	585	733
$Ba(OH)_2$	1.67	3.89	8.22	20.9	101	
$C_{12}H_{22}O_{11}$	179	204	238	287	362	487
$Ca(OH)_2$	0.189	0.173	0.141	0.121	0.094	0.07

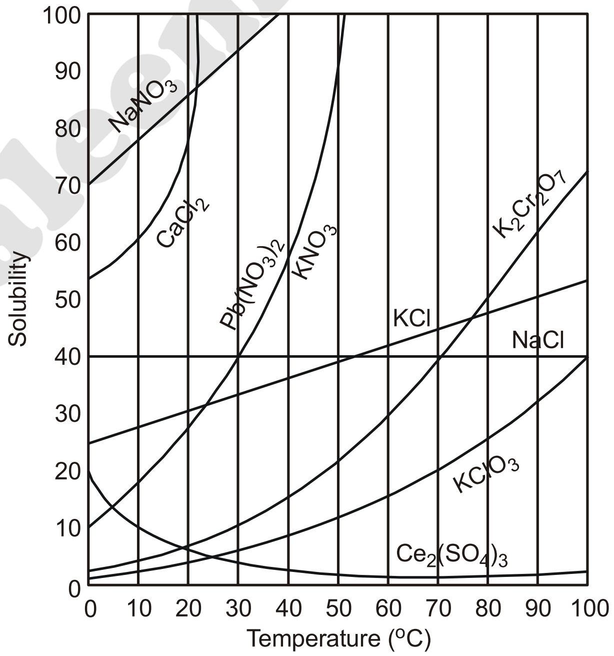
SOLUBILITY CURVE

Temperature has a marked effect on the solubility of many substances. A curve between solubility and temperature is called **solubility curve**. There are two types of solubility curves.

1. Continuous solubility curves
2. Discontinuous solubility curves

1. Continuous Solubility Curves:

Continuous solubility curves don't show breaks anywhere. According to figure $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCl_2$ are showing continuous solubility curves.



Continuous solubility curves

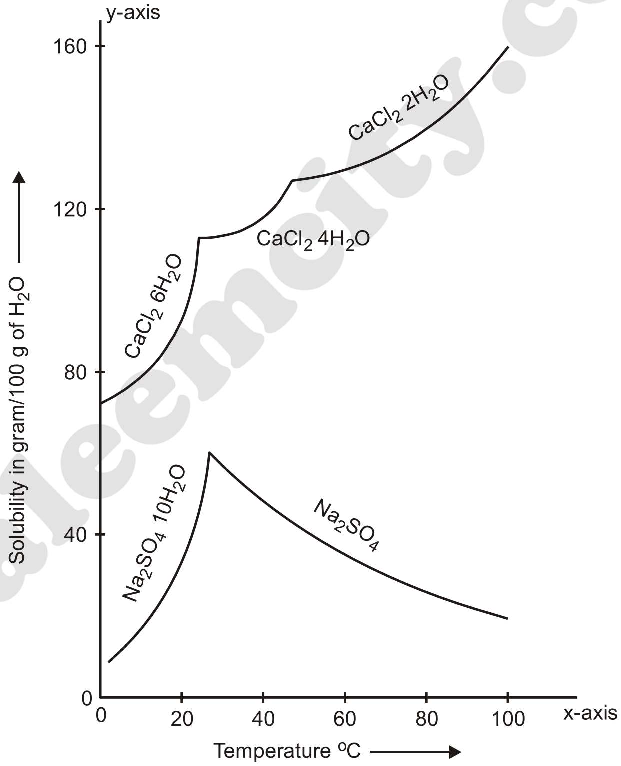
The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines. NaCl shows a very small change of solubility from 0^oC to 100^oC increase of temperature.

$Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40^oC onwards. Anyhow, it shows continuous solubility curve.

2. Discontinuous Solubility Curves:

Sometimes the solubility curves shows sudden changes of solubilities and these curves are called **discontinuous solubility curves**. The best examples in this reference are Na_2SO_4 $10H_2O$, $CaCl_2$ $6H_2O$. Actually these curves are combination of two or more solubility curves. At the break, a new solid phase appears the another solubility curve of that new phase begins.

For example, in case of **Glauber's salt (Na_2SO_4 $10H_2O$)** solubility increase upto 32.4^oC, it loses water of crystallization and changes to anhydrous Na_2SO_4 32.4^oC is the transition temperature between Na_2SO_4 $10H_2O$ and Na_2SO_4. Above this point, curve for Na_2SO_4 starts and represents the effect of rise of temperature on Na_2SO_4.



Discontinuous solubility curves

Fractional Crystallization:

"Separation of solid substances from their solution one by one depending upon their solubilities at different temperatures is called **fractional crystallization**."

A procedure for purifying the substance in which the impure solid is dissolved in a minimum amount of hot solvent. The solution is then gradually cooled, which cause crystals of pure substance to precipitate. These are collected by filtration while impurities remain in the solution.

The solubility curve shows that solubility changes by variation of temperature.

For example, the change in solubility, in case of KNO_3, is very rapid with changing temperature, while such a change is more gradual in other cases like KBr, KCl. These differences in the behaviour of compounds provide the basis for fractional crystallization, which is a technique for the separation of impurities from the chemical products.

Method of Separation:

By using the method, the impure solute is dissolved in a hot solvent in which the desired solute is less soluble than impurities. As the hot solution is cooled, the desired solute being comparatively less soluble, separates out first from the mixture, leaving impurities behind in solution. In this way pure desired product crystallizes out from the solution.

COLLIGATE PROPERTIES OF SOLUTIONS

"The properties of solutions that depends upon the number of solute particles in given quantity of solvent but not on the nature of solute, are called **colligate properties**."

Colligate properties are given below:

(1) Lowering of the vapour pressure
(2) Elevation of boiling point (Ebullioscopy)
(3) Depression of freezing point (Cryoscopy)
(4) Osmotic pressure

First three properties are discussed here.

(a) LOWERING OF VAPOUR PRESSURE

The reason for these properties to be called colligate can be explained by considering three solutions. Let us take 6 g of urea, 18 g of glucose and 34.2 g of sucrose and dissolve them separately in 1 kg of H_2O. This will produce 0.1 molal solution of each substance. Pure H_2O has certain value of vapour pressure at a given temperature. In these three solutions, the vapour pressures will be lowered. The reason is that the molecules of a solute, present upon the surface of a solution decrease the evaporating capability. Apparently it seems that sucrose solution show the maximum lowering of vapour pressure while urea should have minimum lowering of vapour pressure. the reality is that the lowering of vapour pressure in all these solutions will be same at a given temperature. Actually the number of particles of the solute in all the solutions are equal. We have added 1/10th of Avogadro's number of particles (6.02×10^{22}). The lowering of vapour pressure depends upon the number of solute particles and not upon their molar mass and structures. It should be kept in mind that these three **solutes are non-volatile and non-electrolyte**.

(b) ELEVATION OF B.P. AND DEPRESSION OF F.P.

The boiling points of these solutions are higher than that of pure solvent. It is observed that the boiling point elevation of these three solutions is $0.052^{\circ}C$. Similarly freezing points will be depressed for these solutions and the value of depression in these three cases is $0.186^{\circ}C$. The reason again is that the elevation of boiling point and the depression of freezing point depend upon number of particles of solute.

Now let us deduce the values of elevation of the boiling point and the depression of the freezing point of water for 1 molal solutions. For that purpose, try to dissolve 60 g of urea, 180 g of glucose and 342 g of sugar separately of freezing point of water will be 0.52^{o}C and 1.86^{o}C respectively. All the three solutions will boil at 100.52^{o}C and freeze at – 1.86^{o}C. These values of elevation of boiling point and depression of freezing are called **molal boiling point constant** and molal freezing point constant of H_2O denoted by K_b and K_f. These are also named as **ebullioscopic constant and cryoscopic constant** respectively. These constants depend upon the **nature of solvent and not upon the nature of solute**. Following table give the values of K_b and K_f for some common solvents.

TABLE

K_b and K_f Values for Some Solvents

Solvent	B.P. ^{o}C	K_b (^{o}C/m)	F.P. ^{o}C	K_f (^{o}C/m)
H_2O	100	0.52	0	1.86
Ether	34.4	2.16	– 116.3	1.79
Acetic acid	118	3.07	17	3.90
Ethanol	79	1.75	– 114.5	1.99
Benzene	80	2.70	5.5	5.10

To observe the colligate properties, following condition should be fulfilled by the solutions.

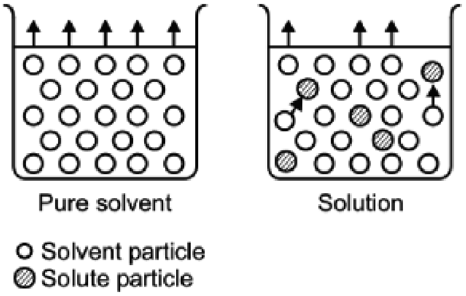
(a) Solution should be dilute.

(b) Solute should be non–volatile.

(c) Solute should be non–electrolyte.

1. LOWERING OF VAPOUR PRESSURE

In a pure solvent, particles can escape from all over the surface of the liquid. However, if some non–volatile, solute is added to the solvent, escaping tendency of the solvent decreases. In this way, vapour pressure of solution is less than the vapour pressure of pure solvent.



Non-voltaic solute particles inhibit solvent particles from escaping from the surface and thus lower vapour pressure

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.

Relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta p}{p^o} = x_2$$

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then

$$x_2 = \frac{n_2}{n_1 + n_2}$$

So, $$\frac{\Delta p}{p^o} = \frac{n_2}{n_1 + n_2}$$

For a dilute solution n_2 can be ignored in denominator because n_2 is very small.

Hence, $$\frac{\Delta p}{p^o} = \frac{n_2}{n_1}$$

The number of moles of solute and solvent are obtained by dividing their masses in grams with their respective relative molecular masses. If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses respectively, then

$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^o} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \times \frac{M_1}{W_1} \qquad (1)$$

or $$M_2 = \frac{p^o}{\Delta p} \cdot \frac{W_2 M_1}{W_1} \qquad (2)$$

The molecular mass (M_2) of a non–volatile solute can be calculated from the equation.

Example 10:

Pure benzene has a vapour pressure of 122.0 torr at 32.°C. When 20 g of a non–volatile solute were dissolved in 300 g of benzene, a vapour pressure of 120 torr was observed. Calculate the molecular mass of the solute the molecular mass of benzene being 78.1.

Solution:

Let the molecular mass of the solute be = M_2

Mass of solute dissolved (W_2) = 20 g

Vapour pressure of pure solvent (p^o) = 122.0 torr

Vapour pressure of solution (p) = 120.0 torr

Lowering of vapour pressure (Δp) = 122.0 – 120.0
= 2.0 torr

Mass of solvent (W_1) = 300 g

Molar mass of solvent (M_1) = 78.1

Formula applied $\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \text{ x } \frac{M_1}{W_1}$

$$M_2 = \frac{p^o}{\Delta p} \frac{W_2 M_1}{W_1}$$

Putting the values

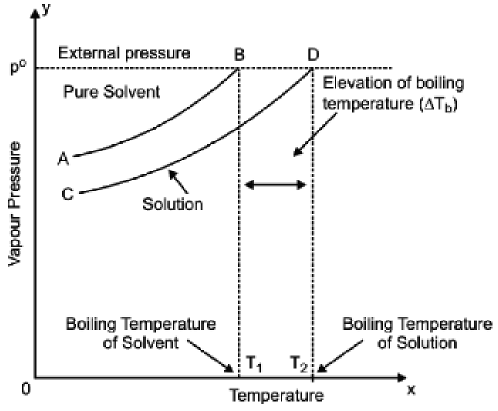
$$M_2 = \frac{122.0}{2.0} \text{ x } \frac{20 \text{ x } 78.1}{300}$$

$$M_2 = 317.6 \text{ g mol}^{-1}$$

2. ELEVATION OF BOILING POINT (EBULLIOSCOPY)

"Boiling point of a liquid depends upon the vapour pressure when some non–volatile and non–electrolyte solute is added to a solvent, the boiling point of solution increases called **elevation of boiling point**."

In order to understand it, determine the vapour pressure of a solvent at various temperatures. Plot a graph between temperature on x–axis and vapour pressures on y–axis. 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^o.



Elevation of boiling temperature curve

When the solute is added in the solvent and vapour pressures are plotted vs temperatures, then a curve CD is obtained. This curve is lower than the curve AB because vapoure pressures of solution are less than those of pure solvent. Solution will boil at higher temperature T2 to equalize its pressure to p^o. The difference of two boiling points give the elevation of the boiling point ΔT_b.

The higher the concentration of solute, the greater will be the lowering in vapour pressure of solution and hence higher will be its boiling point. So elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m \qquad (1)$$

Where K_b is called **the ebullioscopic constant or molal boiling point constant**.

$$\Delta T_b = T_2 - T_1$$

Molal boiling point constant or Ebullioscopic constant (K_b):

"The elevation in boiling point when 1 mole of solute is dissolved to the one kilogram of solvent is called **molal boiling point constant or ebullioscopy constant**."

$$\Delta T_b = K_b m$$

When $m = 1$, $\Delta T_b = K_b$

The unit of K_b is $^oC\ kg\ mol^-$

Equimolar solution of different non–electrolytes **increase the boiling point equally**. For example, 6 g of Urea 18 g of glucose and 34.2 g of $C_{12}H_{22}O_{11}$ when dissolved in 1 kg of solvent, increases the boiling point equally because, the molality is same.

We know that

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1000}{\text{Mass of solvent in grams}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} \qquad (2)$$

Where W_1 = mass of solvent in grams

W_2 = mass of solute

M_2 = molar mass of solute

Put the value of Equation (2) in Equation (1).

$$\Delta T_b = K_b \frac{W_2\ 1000}{M_2 \times W_1}$$

By rearranging we get

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000 \qquad (3)$$

This Equation (3) can be used to determine the molar mass of non–electrolyte solute.

MEASUREMENT OF BOILING POINT ELEVATION (LANDSBERGER'S METHOD)

This is one of the best methods for the measurement of boiling elevation of a solution. 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 gradual tube through a rose head.

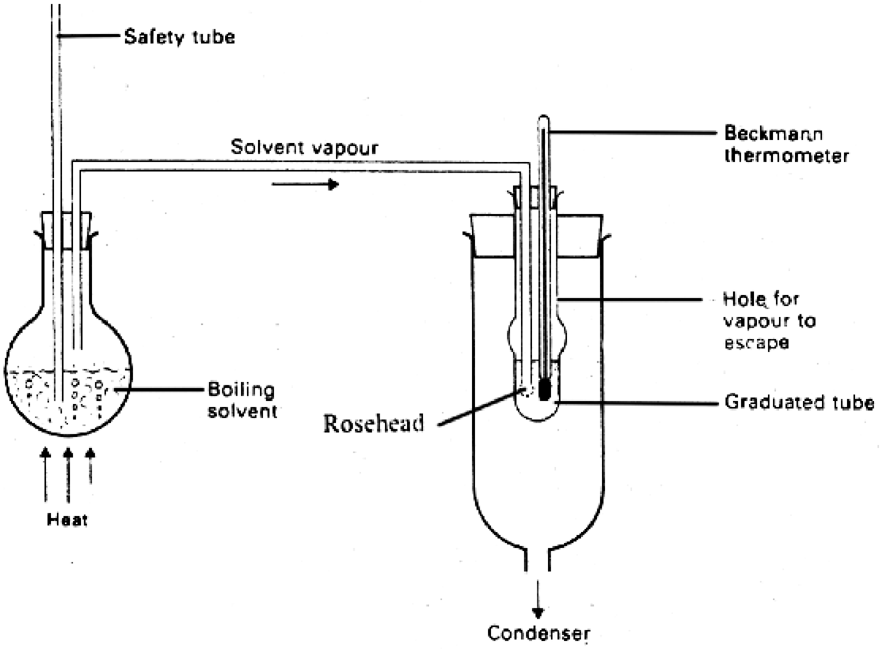
(c) An outer tube, which receives hot solvent vapours coming from side hole of the inner tube.

(d) A thermometer which can read up to 0.01 K.

The solvent is placed in the inner tube. Some solvent is also taken separate flask and its vapour are sent into this tube. These vapours cause the solvent in the tube to boil by its **latent heat of condensation**. This temperature is the boiling point of the pure solvent.

The supply of the vapours is temporarily cut off and a weighed pellet of solute is dropped in the inner tube. The vapours of the solvent are again pass through it until the solution is boiled. This temperature is again noted.

Now the supply of the solvent vapours is cut off, the thermometer and the rose head are removed and the volume of the solution is measured. The difference of the two boiling points gives the value ΔT_b. The following formula is used to calculated the molecular mass of solute.



$$M_2 = \frac{K_b}{\Delta T_b} \frac{1000\ W_2}{W_1} \qquad (1)$$

Latent Heat of Condensation:

"The amount of heat evolved when one mole of vapours are condensed to a liquid at constant temperature is called **latent heat of condensation**."

It is an exothermic process

$$\text{Vapour} \longrightarrow \text{Liquid} \qquad \Delta H = -\text{heat}$$

Example 11:

The boiling point of water is 99.725°C. To a sample of 600 g of water are added 24.0 g of a solute having molecular mass of 58 g mol^{-1} to form a solution. Calculate the boiling point of the solution.

($K_b = 0.52^oC\ kg\ mol^{-1}$)

Solution:

Boiling point of pure H_2O = 99.725°C

Mass of solvent (H_2O) W_1 = 600 g

Mass of solute (W_2) = 24.00 g

Molar mass of solute (M_2) = 58 g mol^{-1}

The molar boiling point constant of H_2O (K_b) = $0.52^oC\ kg\ mol^{-1}$

$$\Delta T_b = K_b \times \frac{1000\ W_2}{W_1 \times M_2}$$

$$= \frac{0.52 \times 1000 \times 24.00}{600 \times 58} = 0.358^oC$$

Boiling point of solution = boiling point of pure solvent + elevation of boiling point

= 99.725 + 0.358

= 100.083°C

3. DEPRESSION IN FREEZING POINT (CRYOSCOPY)

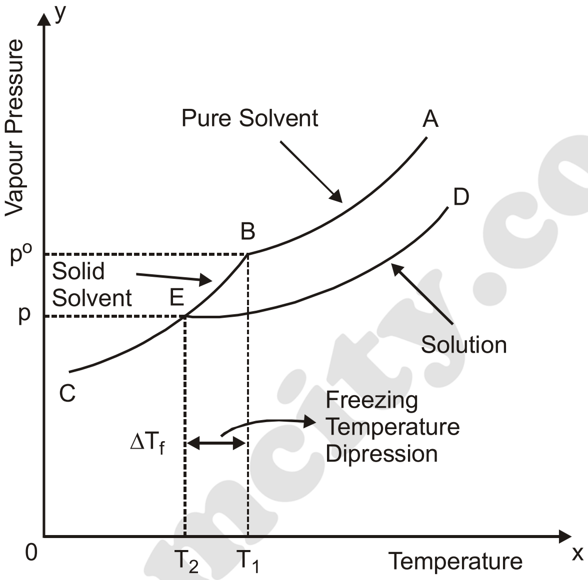
The **freezing point** of a substance is the temperature at which the solid and liquid phases of the substance co–exist.

Freezing point is also defined as that temperature at which its solid and liquid phases have the **same vapour pressures**.

When a non–volatile solute is added to a solvent, its vapour pressure is decreased. At the freeing point there are liquid solution and the solid solvent in the vessel. The **solution will freeze** at that temperature at which the **vapour pressures of both liquid solution and solid solvent are same**. It means that a solution should freeze at lower temperature than the pure solvent.

In order to understand it, plot a graph between vapour pressure and T_1 temperature of pure solvent and that of solution. The curve ABC is for the pure solvent. The solvent freezes at temperature T_1 corresponding to the point B when the vapour pressure of freezing solvent is p^o. The portion of the curve BC is for the solid solvent. This portion has a greater slope showing that the change of vapour pressure with the change of temperature is more rapid.

The curve DEC for the solution will meet the curve BC at the point E. This is the freezing point of solution T_2 and corresponds to the vapour pressure p which is lower than p^o. The reason is that vapour pressure of solution is less than the pure solvent.



Depression of freezing point curve

Depression of freezing point = freezing point of pure solvent – freezing point of solution

So $\Delta T_f = T_1 - T_2$

This depression of freezing point ΔT_f when a solute is added to a solvent is related to the molality (m) of the solution. The relationship is similar to that of elevation of the boiling point.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \qquad (1)$$

K_f is called the **molal freezing point constant** or the cryoscopic constant and m is the molality of the solution.

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1000}{\text{Mass of solvent gram}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

Where W_2 = mass of solute in grams

W_1 = mass of solvent

and M_2 = molar mass of solute

Put the value of this molality in Equation (1).

$$\Delta T_f = K_f \frac{1000\ W_2}{M_2 \times W_1}$$

$$\text{Molar mass of solute } (M_2) = \frac{K_f}{\Delta T_f}\,\frac{1000\ W_2}{W_1} \qquad (2)$$

Molal Freezing Point Constant or Cryoscopic Constant (K_f):

"The depression in freezing point when one mole of solute is dissolved to one kilogram of solvent is called **cryoscopic constant or molal freezing point constant**."

$$\Delta T_f = K_f\, m$$

when $m = 1,\ \Delta T_f = K_f$

Units:

$$K_f = \frac{\Delta T_f}{m} = \frac{^oC}{\text{mol kg}^{-1}} = {}^oC\ \text{kg mol}^{-1}$$

MEASUREMENT OF FREEZING POINT DEPRESSION (BECKMAN'S FREEZING POINT APPARATUS)

There are many methods but Beckman's method is easy to perform.

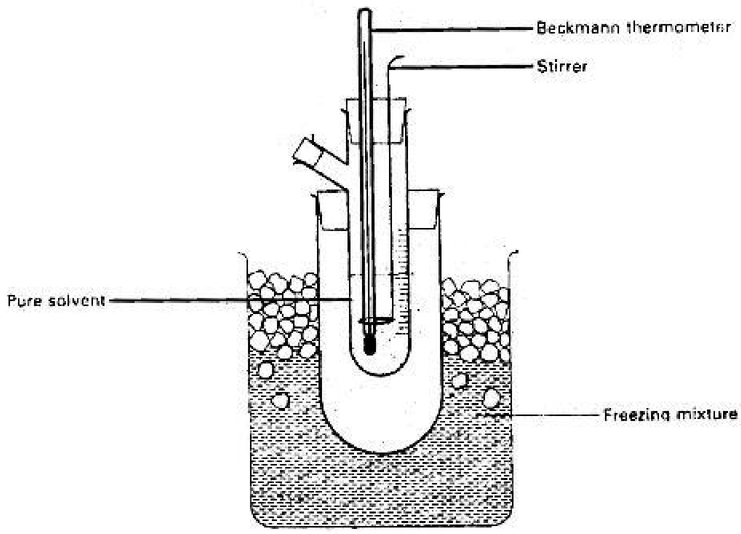
The apparatus consists of three major parts.

(a) **A freezing tube with a side arm**. It contains solvent or solution and is fitted with a stirrer and a Beckman thermometer.

(b) **An outer larger tube** into which the freezing tube is adjusted. The air jacket in between these tubes help to achieve a slower and more uniform rate of cooling.

(c) **A larger jar containing a freezing mixture**.

Around 20 to 25 g of the solvent is taken in the freezing tube. The bulb of the thermometer is immersed in the solvent. First of all approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.



Apparatus for determining depression of freezing point

The freezing tube is then put in the air jacket and cooled slowly. In this way accurate freezing point of the solvent is determined. Now the solvent is re–melted by removing the tube from the bath and weighed amount (0.2 to 0.3 g) of the solute is introduced in the side tube. The freezing point of the solution is determined while stirring the solution. The difference of the two freezing points gives the value of ΔT_f and the following formula is used to calculate the molar mass of solute.

$$M_2 = \frac{K_f}{\Delta T_f} \frac{1000\, W_2}{W_1}$$

Example 12:

The freezing point of pure camphor is 178.4^{o}C. Find the freezing point of a solution containing 2.0 g of a non–volatile compound, having molecular mass 140, in 40 g of camphor. The molal freezing point constant of camphor 37.7^{o}C kg mol^{-}1.

Solution:

Freezing point of camphor = 178.4^{o}C

Mass of solute (W_2) = 2.00 g

Mass of solvent (W_1) = 40 g

Molar mass of solute (M_2) = 140 g mol^{-1}

The molal freezing point constant of solvent = 37.7^{o}C kg mol^{-1}

Freezing point of solution = ?

Applying the equation $\Delta T_f = K_f \dfrac{1000\, W_2}{W_1 \times M_2}$

We have to calculate the freezing point of solution, so first we get the depression in freezing point ΔT_f then subtract it from freezing point pure solvent.

$$\Delta T_f = \frac{37.7 \times 1000 \times 2}{40 \times 140} = 13.46^oC$$

Freezing point of solution = 178.4 – 13.46 = 164.94°C

APPLICATION OF BOILING POINT ELEVATION AND FREEZING POINT DEPRESSION PHENOMENA

(1) These phenomena are used to determine the molecular masses of the compounds.

(2) This phenomenon find use as antifreeze in the radiator of an automobile. In radiators of automobiles, ethylene glycol ($C_2H_6O_2$) is added. It is completely miscible in water but have very low vapour pressure because it is non–volatile. When mixed with water, it lowers the freezing point as well as raises the boiling point. During winter it protects a car by preventing the liquid in the radiator from freezing, as water alone. In hot summer the antifreeze solution also protects the radiator from boiling over.

(3) Another common application is the use of NaCl or KNO_3 to lower the melting point of ice. One can prepare freezing mixture for use in an ice cream machine.

(4) In some countries NaCl is sprayed over roads for de–icing of road.

ENERGETIC OF SOLUTIONS

The heat of solution of a substance depends upon the relative magnitude of two processes.

First Process:

When a solid is dissolved in a liquid, a **change in the physical state** of liquid takes place. **Energy is absorbed** in overcoming the intrinsic or intermolecular forces, that holds the particles of substance in their crystal lattices. On the other hand the distance between solute and solvent molecules or ions increases, as compared to their pure state. This increase in distance of solvent molecule also required energy. It is also an **endothermic** process and change is physical change.

Second Process:

In second process a **chemical reaction** between solute molecule or ion and solvent molecule takes place. New forces are established between the solute and solvent molecules. The second change is **usually an exothermic process**.

If heat evolved in chemical change is greater than that absorbed in the physical change the heat of solution is negative and net process is exothermic. If heat evolved in chemical change is lesser than that absorbed in the physical change, the heat of solution is positive and net process is endothermic.

"The quantity of heat absorbed or evolved when one mole of a substance is dissolved in specific amount of solvent at given temperature, is called **heat of solution**."

When **potassium nitrate** is dissolved in water, the temperature of the solution decreases indicating an **endothermic process**, while solution of **lithium chloride** in water produces heat, showing that the process of dissolution is **exothermic**. The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution.

It is given the symbol $\Delta H_{(sol)}$. The $\Delta H_{(sol)}$ gives the difference between the energy possessed by the solution after its formation and the original energy of the components before their mixing i.e.

$$\Delta H_{(sol)} = H_{solution} - H_{components}$$

Here $H_{(sol)}$ is the energy content of solution **after its formation** while $H_{components}$ represents the energy contents of components **before their mixing**. However, both these factors cannot actually be measured, only their difference i.e., the change $\Delta H_{(sol)}$ is practically measurable. If the value of $\Delta H_{(sol)}$ is negative, it would mean that the solution is having less energy than the components from which it was made, hence the dissolution process is an exothermic one. On the other hand an endothermic process would have a positive $\Delta H_{(sol)}$ value.

TABLE

Heats of Solution of Some Ionic Solids at Infinite Dilution

Substance	**Heat of Solution (kJ mol^{-1} of solute)**	**Substance**	**Heat of Solution (kJ mol^{-1} of solute)**
NaCl	4.98	NH_4Cl	16.0
NH_4NO_3	26.0	LiCl	– 37.0
KCl	17.2	$AlCl_3$	– 321.0
KI	20.3		

The magnitude of heat of solution gives **information** regarding the **strength of intermolecular forces of attraction** between components which mix to form a solution.

When one mole (58.5 g) of sodium chloride is dissolved in 10 moles (180 g) of water 2.008 kJ of energy is absorbed.

$$NaCl + 10H_2O \longrightarrow NaCl\,(10H_2O) \quad \Delta H = +2.008\text{ kJ}$$

On diluting a concentrated solution there is a further heat change. This heat change depends on the amount of water used for dilution. The heat of dilution gradually decreases, so that eventually increasing the dilution produces no further heat change. This occurs when there are 800 – 1000 moles of water to one mole of solute. This stage is called **infinite dilution** and the heat of solution is expressed as:

$$NaCl_{(s)} + \text{Water} \longrightarrow NaCl_{(aq)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)} \; \Delta H = +4.98\text{ kJ mol}^{-1}$$

HYDRATION AND HYDROLYSIS

Hydration:

"The process in which water molecules surround and interact with solute particles is called **hydration**."

Salvation:

"The process in which solvent molecules surround and interact with solute particles is called **salvation**."

When ionic compounds are dissolved in water, they are dissociated into ions. Negative ions are surrounded by water molecules. The partial positively charged hydrogen atoms of water surround and attract the anions with electrostatic forces of attraction. Similarly, positive ions of solute, create attractions with partial negative oxygen atoms of water molecules. In this way, all the ions in the aqueous solution are hydrated.

The ions, which are surrounded by water molecules, are called **hydrated ions**. The number of water molecules which surround a given ion depends upon the size of the ions and the magnitude of its charge. If the size of the ion is small and is highly charged positive ion then greater number of water molecules will surround it. negatively charged ions have smaller number of water molecules surrounding them. Hence the ions with high **charge density** (charge/unit area) has a greater ability to attract polar water molecules than ions with smaller charge density.

Hydrates:

"The crystalline substances which have water of crystallization in them are called **hydrates**."

In hydrates, mostly water molecules are attached with cations rather than anions due to their greater charge density. Formation of hydrates takes place in salts, acids, bases and some elements.

When aqueous solution of many soluble salts are evaporated the salt separates as crystals that contain the salt and water combined in a definite proportion.

For example, copper sulphate is penta hydrated $CuSO_4\ 5H_2O$. Four water molecules are attached with Cu^{2+} and one molecule with SO_4^{2-} Cu^{2+} has greater charge density than anion. Some other examples of hydrates are given below:

$(COOH)_2 . 2H_2O$

$MgCl_2 . 6H_2O$

$MgSO_4 . 7H_2O$

$FeSO_4 . 7H_2O$

$BaCl_2 . 2H_2O$

$Na_2B_4O_7 . 10H_2O$

$AlCl_3 . 6H_2O$

$FeSO_4 . (NH_4)_2SO_4 . 6H_2O$

$Na_2CO_3 . 10H_2O$

$CaSO_4 . 2H_2O$

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

$(NH_4)_2C_2O_4 . H_2O$

Energies of Hydrations:

When a crystal is added to a solvent, the solvent molecules start attaching themselves to the lattice. Some interaction usually takes place between liquid and solid releasing energy of salvation which causes the affected crystal particles to oscillate vigorously and break from the lattice. The energy of salvation must exceed the energy used to disrupt the lattice and separates its constituent particles. This process will continue all over the surface of the crystal. When potassium iodide (KI) is added to water hydration takes place in two steps.

1. Separation of Ions:

The first step breaks the lattice to separate the ions. Since energy is required to accomplish this step, so this step is **endothermic**. The amount of energy needed to separate a crystalline compound into isolated ions (or atoms) is known as **lattice energy**. The lattice energy of ionic solids is always higher than molecular solids.

$$KI_{(s)} \longrightarrow K^{+}_{(g)} + I^{-}_{(g)}$$

2. Hydration Energy of Ions:

In the second step, the ions are brought into water and get hydrated (solvated). A hydrated ions is attracted by the solvent dipoles and energy is released, so this step is exothermic. The energy given out by this step is known as the hydration energy (or salvation energy).

$$K^{+}_{(g)} + I^{-}_{(g)} + H_2O \longrightarrow K^{+}_{(aq)} + I^{-}_{(aq)}$$

The overall change that takes place when KI dissolves in water can be represented as:

1st Step:

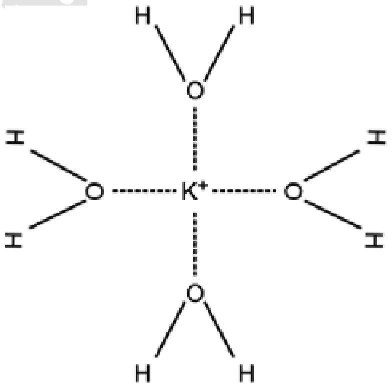
$$KI_{(s)} \longrightarrow K^{+}_{(g)} + I^{-}_{(g)}$$

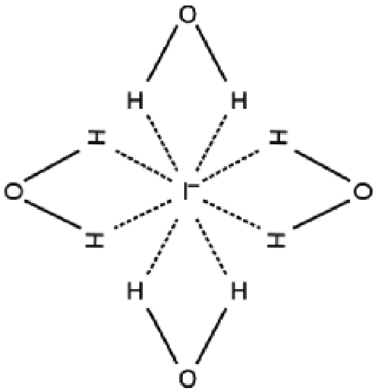
2nd Step:

$$\underline{K^{+}_{(g)} + I^{-}_{(g)} + H_2O \longrightarrow K^{+}_{(aq)} + I^{-}_{(aq)}}$$

$$KI_{(s)} + H_2O \longrightarrow K^{+}_{(aq)} + I^{-}_{(aq)}$$

The values of hydration energies of individual ions i.e. cations and anions are given in Table. It is interesting to compare these values with the ionic radii of the ions. Greater the size of monovalent cation lesser is the heat of hydration. Divalent and trivalent cations have higher values due to high charge densities. Anions also show definite trend of heat of hydration.





TABLE

Hydration Energies of Common Ions					
Ion	**kJ mol^{-1}**	**Ion**	**kJ mol^{-1}**	**Ion**	**kJ mol^{-1}**
H^+	– 1075	K^+	– 305	F^-	– 457
Li^+	– 499	Mg^+	– 1891	Cl^-	– 384
Na^+	– 390	Cu^+	– 1562	Br^-	– 351
Ag^+	– 464	NH_4^+	– 281	OH^-	– 460
		Al^{+++}	– 4613		

Hydrolysis of Salt:

"Some cations or anions of salts reacts with water and form acidic or basic solution respectively, is called **hydrolysis**."

The concentration of each of H^+ and OH^- ions are equal to 10^{-7} M, as in pure water. But this balance between H^+ and OH^- ions can be disturbed with resulting change in the pH of solution when other salts are dissolved in water.

For example;

(1) NaCl is dissolved in water, no change in pH takes place.

(2) Na_2CO_3 is dissolved in water, solution becomes basic and pH of solution is greater than 7.

(3) $CuSO_4$ is dissolved in water, solution becomes acidic and pH of solution is less than 7.

There are some cations or anions which undergoes chemical reactions with water (hydrolytic reaction) and concentration of H^+ and OH^- becomes unbalanced in water.

Cations which undergo hydrolysis:

Usually cations of large size undergo hydrolysis e.g. Cu^{2+}, Zn^{2+} Al^{3+}, NH_4^+, etc.

Anions which undergo hydrolysis:

Conjugates bases of weak acids, undergo hydrolysis. These are weak bases and reacts with water to produce OH^- ions.

$$CH_3COO^- + HOH \longrightarrow CH_3COOH + OH^-$$

Example:

$CH_3COO^-, CN^-, C_2O_4^{2-}, S^{2-}, HCO_3^{-1}, CO_3^{-2}$

1. Hydrolysis of salt of strong acids with strong bases:

Such salts do not hydrolysis in water and pH of water remain unchanged. For example, NaCl, KCl, K_2SO_4, Na_2SO_4, KBr, NaBr, NaI, etc.

The positive ions Na^+, K^+, are not hydrolyzed in water. Similarly, Cl^-, Br^-, SO_4^{2-}, I^- are also not hydrolyzed by water.

2. Hydrolysis of salt of strong acids with weak bases:

Such salts when dissolved in water, they produces strong acids and weak bases. Due to greater ionization of acids, they have higher value of Ka. The solution will be acidic and pH of solution will be less than 7 e.g.

$$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + 3H^+ + 3Cl^-$$

$$NH_4Cl + H_2O \longrightarrow NH_4OH + H^+ + Cl^-$$

$$CuSO_4 + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + SO_4^{2-}$$

3. Hydrolysis of salt of weak acids with strong bases:

Salt of weak acids with strong basis on hydrolysis produce basic solution and pH of solution is greater than 7. Such salts form strong bases by reacting with water e.g.

$$CH_3COONa + H_2O \longrightarrow CH_3COOH + Na^+ + OH^-$$

$$Na_2S + 2H_2O \longrightarrow H_2S + 2Na^+ + 2OH^-$$

$$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + Na^+ + OH^-$$

$$Na_2CO_3 + 2H_2O \longrightarrow H_2CO_3 + 2Na^+ + 2OH^-$$

$$Na_3PO_4 + 3H_2O \longrightarrow H_3PO_4 + 3Na^+ + 3OH^-$$

4. Hydrolysis of salt of weak acids with weak bases:

Salt of weak acids with bases also undergo hydrolysis. Acidic or basic nature depends upon the values of K_a and K_b respectively e.g.

$$CH_3COO\,NH_4 + H_2O \longrightarrow NH_4OH + CH_3COOH$$

If $K_a = K_b$ solution will be neutral.

If $K_a > K_b$ solution will be acidic.

If $K_a < K_b$ solution will be basic.

EXERCISE

Q.1 Chose the correct answer for the given ones:

(i) Molarity of pure water is:

(a) 1 (b) 18

(c) 55.5 (d) 6

(ii) 18 g glucose is dissolved in 90 g of water. The relative lowering of vapour pressure is equal to:

(a) $\frac{1}{5}$ (b) 5.1

(c) $\frac{1}{51}$ (d) 6

(iii) A solution of glucose is 10 percent. The volume in which 1 g mole of it is dissolved will be:

(a) 1 dm^3 (b) 1.8 dm^3

(c) 200 Cm^3 (d) 900 Cm^3

(iv) An aqueous solution of ethanol in water may have vapour pressure:

(a) Equal to that of water (b) Equal to that of ethanol

(c) More than that of water (d) Less than that of water

(v) An azeotropic mixture of two liquids boils at a lower temperature than either of them when:

(a) It is saturated

(b) It shows positive deviation from Raoult's law

(c) It shows negative deviation from Raoult's law

(d) It is metastable.

(vi) An azeotropic mixture showing positive deviation from Raoult's law, the volume of the mixture is:

(a) Slightly more than the total volume of the components

(b) Slightly less than the total volume of the components

(c) Equal to the total volume of the components

(d) None of these

(vii) Which of the following solutions has the highest boiling point:

(a) 5.85 percent solution of sodium chloride

(b) 18.0 percent solution of glucose

(c) 6.0 percent solution of urea

(d) All have the same boiling point

(viii) Two solutions of NaCl and KCl are prepared separately by dissolving same amount of the solute in water. Which of the following statements is true for these solutions:

(a) KC1 solution will have higher boiling point than NaCl solution

(b) Both of the solutions have different boiling points

(c) KC1 and NaCl solution possess same vapour pressure

(d) KCl solution possesses lower freezing point than NaCl solution

(ix) The molal boiling constant is the ratio of the elevation in boiling point to:

(a) Molarity (b) Molality

(c) Mole fraction of solvent (d) Mole fraction of solute

(x) Colligative properties are the properties of:

(a) Dilute solution which behave as nearly ideal solutions

(b) Concentrated solutions which behave as nearly non-ideal solutions

(c) Both (a) and (b)

(d) Neither (a) nor (b)

ANSWERS

Answers	Reasons
(i) (c)	Molarity is the number of moles per litre (1 dm^3). And density of water is g/cm^3 $1\ g = 1\ cm^3$ $1000\ g = 1000\ cm^3 = 1\ dm^3$ The mass of 1 dm^3 is 1000 g. We can calculate the no. of moles in 1000 g (1 dm^3) of pure water $n = \frac{m}{M} = \frac{1000}{18} = 55.5$ moles

(ii)	(b)	The relative lowering of vapour pressure is equal to mole fraction of solute $\frac{\Delta P}{P^o} = x_2$ Mole fraction of solute (x_2) can be calculated by knowing the no. of moles of solute and solvent. No. of moles of glucose in 18 g $= \frac{18}{180} = \frac{1}{10} = 0.1$ moles. No. of moles of water in 90 g $= \frac{90}{18} = 5$ moles. Hence, mole fraction of solute (x_2) is the ratio of no. of moles of solute to the total no. of moles $x_2 = \frac{0.1}{0.1 + 5} = \frac{0.1}{5.1} = \frac{1}{51}$ and $\boxed{\frac{\Delta P}{P^o} = \frac{1}{51}}$
(iii)	(b)	10% w/v glucose solution means 10 g of glucose = 100 cm^3 of solution 1 g of glucose $= \frac{100}{10}$ cm^3 of solution and 180 g (1 g mole) of glucose $= \frac{100}{10} \times 180$ cm^3 of solution = 1800 cm^3 = 1.8 dm^3 of solution (1 dm^3 = 1000 cm^3) Hence, the volume of solution in which 1 g mole (180 g) of glucose is present is 1800 cm^3 (1.8 dm^3)
(iv)	(c)	The solution ethanol in water shows positive deviation from Raoult's Law. It means that vapour pressure of solution is greater and boiling point is lesser than either of the two component. Boiling point of water = 100°C Boiling point of ethanol = 78.5°C Boiling point of solution = 78.1°C
(v)	(b)	An azeotropic mixture of two liquids that boils at lower temperature than either of them, then its vapour pressure is higher than either of them. And a solution whose vapour pressure is greater than either of two components.
(vi)	(a)	When azeotropic mixture shows positive deviation from Raoult's law, then its vapour pressure is greater than either of the two components. Increase of vapour pressure is only possible when there is decrease of intermolecular force between solute and solvent molecules. The decrease of forces leads to increase of volume of two components.

(vii)	(a)	5.85% NaCl solution means 5.85 g (0.1 mole) of NaCl in 100 g of solution. 18.0% glucose solution means 1.8 g (0.1 mole) of glucose in 100 g of solution. 6.0% urea solution means 6 g (0.1 mole) of urea 100 g of solution. All the solutions contains 0.1 moles of respective species per 100 g of solution. 0.1 moles of both glucose and urea produces 6.02×10^{23} particles in solution whereas 0.1 moles of NaCl produces $2 \times 6.02 \times 10^{23}$ particles in solution because NaCl ionizes and produces twice the no. of ions than formula. Unit 5.85% NaCl solution will have highest boiling point than other two species because it contain twice no. of particles than other two.
(viii)	(b)	The molar mass of NaCl is 5.85 g/mole and that of KCl is 74.5 g/mole. 1 formula unit of both the species produces two ions in the solution. If we consider the same amount (mass) i.e., 58.5 g of both the species, then 58.5 g of NaCl (equal to its 1 mole) produces twice the Avogadro's number of particles (ions). Whereas 58.5 g KCl (less than its one mole) produce less than twice the N_A of ions. Hence, the 58.5 g of NaCl solution containing greater number of particles (ions) have higher boiling point than KCl solution. In other words, both have different boiling point. Note: (For this case only) 1. The boiling point of NaCl solution is higher and its freezing point is lesser than KCl solution. 2. The vapour pressure of NaCl solution is lower than KCl solution.
(ix)	(b)	The boiling point elevation of a solution is directly proportional to molality of the solution. $\Delta T_b \propto m$ $\Delta T_b = K_b m$ $\boxed{K_b = \frac{\Delta T_b}{m}}$ Hence, molal boiling point constant is the ratio of boiling point elevation to molality of the solution.
(x)	(a)	Dilute solutions are usually ideal. Colligative properties are the properties of dilute solutions. For concentrated solutions, there are large numbers of solute particles very close to each other. Due to which attraction starts and particles associate. As a result, no. of particles reduces and effect on the property is also less. Hence concentrated solution do not behave ideally.

Q.2 Fill in the blanks with suitable words:

(i) Number of molecules of sugar in 1 dm^3 of 1 M sugar solution is ————.

(ii) 100 g of a 10% aqueous solution of NaOH contains 10 g of NaOH in ———— g of water.

(iii) When an azeotropic mixture is distilled, it ———— remains constant.

(iv) The molal freezing point constant is also known as ———— constant.

(v) The boiling point of an azeotropic solution of two liquids is lower than either of them because the solution show ———— from Raoult's law.

(vi) Among equimolal aqueous solutions of NaCl, $BaC1_2$ and $FeC1_3$, the maximum depression in freezing point is shown by ———— solution.

(vii) A solution of ethanol in water shows ———— deviation and show azeotropic solution with ———— boiling point than other components.

(viii) Colligative properties are used to calculate ———— of compound.

(ix) The hydration energy of Br^- ion is ———— than that of F^- ion.

(x) The aqueous solution of NH_4Cl is ————while that of Na_2SO_4 is ————.

ANSWERS

Answers	Explanation
(i) 6.02×10^{23}	1 dm^3 of 1M sugar solution contains 1 mole of sugar. And there 6.02×10^{23} molecules of sugar in the solution.
(ii) 90 g	10% NaOH solution means 10 g of NaOH and 90 g of water to make total 100 g of solution.
(iii) Composition	Azeotropic mixture (corresponding to specific composition distil without change in composition and have constant boiling point.
(iv) Cryoscopic	
(v) Positive deviation	When Azeotropic solution have boiling point less than either of the component, then its vapour pressure will be higher than either of two components and is said to show positive deviation from Raoult's law.
(vi) $FeCl_3$	Freezing point depression is a colligative property and depends upon number of solute particles. 1 molal solution of NaCl have twice the Avogadro's no. of ions, and 1 molal solution of $BaCl_2$ have thrice the Avogadro's no. of ions and 1 molal solution of $FeCl_3$ have, four times the Avogadro's no. of ions when dissolved in water. Amongst the equimotal. (1 molal) solutions of all the three species, $FeCl_3$ produced greatest no. of ions in the solution. Hence, it has maximum depression in freezing point.

(vii)	Less	Ethanol solution in water shows positive deviation i.e., have higher vapour pressure and low boiling point than component.
(viii)	Molar mass	Mathematical form at the end of each colligative property gives us basis for molar mass calculation of unknown compound e.g., mathematical equation for lowering of vapour pressure. $\frac{\Delta P}{P^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$ $\boxed{M_2 = \frac{P^\circ}{\Delta P} \times \frac{W_2}{W_1} M_1}$ M_2 is a molar mass of unknown compound.
(ix)	Lesser	The value of hydration energy depends upon charge to size ratio or charge density of ions. Greater the charge density, greater will be the Hydration energy. The charge on Br^- and F^- ion is same but the size of Br^- ion larger. Hence, Br^- ion will have low charge density and less hydration energy.
(x)	Acidic, neutral	NH_4Cl undergo hydrolytic reaction as $NH_4Cl + H_2O \longrightarrow NH_4OH + H^+ + Cl^-$ This produces weak base NH_4OH and Cl^- ion which is not hydrolysed. As a result H^+ ions are set free and solution becomes acidic. Na_2SO_4 ionizes as: $Na_2SO_4 + H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + H^+ + OH^-$ Na^+ ion and SO_4^{2-} are not hydrolysed by water. As a result, H^+ ion and OH^- concentration remains same and solution remains neutral.

Q.3 Indicate True or False from the given statement:

(i) At a definite temperature the amount of solute in a given saturated solution is fixed.

(ii) Polar solvents readily dissolve non-polar covalent compounds.

(iii) The solubility of substance decreases with increases in temperature if the heat of solution in negative.

(iv) The rate of evaporation of liquid is inversely proportional to the intermolecular forces of attraction.

(v) The molecular mass of an electrolyte determined by lowering of vapour pressure is less than the theoretical molecular mass.

(vi) Boiling point elevation is directly proportional to the molality of the solution and inversely proportional to boiling point of solvent.

(vii) All solutions containing 1 g of non-volatile non-electrolyte solutes in same solvent will have same freezing point.

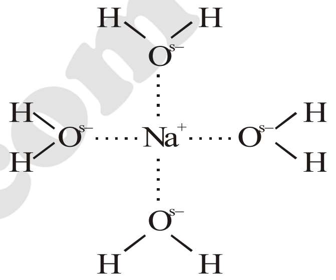
(viii) The freezing point of a 0.05 molal solution of a non-volatile non-electrolyte solute in water is $-0.93^{o}C$.

(ix) Hydration and hydrolysis are different process for Na_2SO_4.

(x) The hydration energy of an ion only depends upon its charge.

ANSWERS

Answers	Explanation
(i) True	
(ii) False	Polar solvents readily dissolve polar covalent compounds. The principle of dissolution is, like dissolve like i.e. Polar compounds are soluble is polar solvents whereas non-polar compounds are soluble in non-polar solvents. e.g., Sugar is soluble in water and I_2 is soluble in CCl_4.
(iii) True	If the dissolution of a compounds is exothermic (heat of solution is negative), then rise of temperature will favour its crystallization which is endothermic. Hence, solubility decreases.
(iv) True	If intermolecular forces of attraction between the molecules of liquid are stronger, then there are less chances for the molecules to escape from the surface. Hence, evaporation and intermolecular forces are inversely proportional.
(v) True	
(vi) False	Boiling points elevation is directly proportional to molality of the solution and is independent of boiling point of solvent. $\boxed{\Delta T_b \propto m}$ In this relationship, boiling point elevation has no relation with the boiling point of solvent.
(vii) False	All the solutions containing 1 g of non-volatile, non-electrolyte solutes in same solvent will have different freezing point. 1g of all the electrolytes have different number of moles and molecules, since their molar masses are different. For example: 1 g of glucose will have moles $= \frac{1}{180}$ and 1 g of sucrose will have moles $= \frac{1}{342}$ Hence their no. of molecules will be different and freezing points also be different because it depends upon no. of solute particles.

(viii)	False	The freezing point of a 0.05 molal solution of a non-volatile and non-electrolyte solute in water is −0.093°C. The molal freezing point of non-electrolyte solute in water is −1.86°C. Mean: Freezing point of 1 molal solution = $-1.86°C$ Freezing point of 0.1 molal solution = $-0.186°C$ Freezing point of 0.05 $\left(\frac{0.1}{2}\right)$ molal solution = $\left(-\frac{0.186}{2}\right) = -0.093°C$
(ix)	True	Hydration is the surrounding of ions by water molecules with their oppositely charged ends whereas hydrolysis is the interaction of salt and water as a result of which salt dissociates in ions.  $Na_2SO_4 \xrightleftharpoons{H_2O} 2Na^+ + SO_4^{-2}$
(x)	False	Hydration energy of an ion depends upon charge / size ratio (charge density) of ions. Greater the charge density of ion, greater will be its hydration energy.

Q.4 Define and explain the following with examples:

(a) A homogeneous phase

(b) A concentrated solution

(c) A solution of solid in a solid

(d) A consulate temperature

(e) A non-ideal solution

(f) Zeotropic solution

(g) Heat of hydration

(h) Water of crystallization

(i) Azeotropic solution

(j) Conjugate solution

Ans.

(a) **A Homogeneous Phase:** A mixture of two or more substances with uniform composition and properties throughout the sample is called homogeneous phase.

Example: Sugar solution.

Note: If small amount of sugar is added to water, sugar is dissolved and the whole mixture is in liquid state with sweet taste. These properties remain uniform throughout the sample. Hence, sugar solution is said to be homogeneous phase.

(b) **A Concentrated Solution:** A solution containing relatively large amount of solute dissolved in solvent is called concentrated solution.

Example: 1 dm solution containing 50 g dissolved sugar is concentrated than 1 dm^3 solution containing 20 g dissolved sugar.

(c) **A Solution of Solid in Solid:** A solution in which both solute and solvent are in solid phase is called solution of solid in solid.
Example: Metal alloys (homogeneous mixture of two or more metals).

(d) **A Consulate Temperature:** The temperature at which two conjugate solutions completely merge into each other is called consulate temperature or upper consulate temperature. It is also called critical solution temperature. OR
The temperature at which two polarity miscible liquids forms homogeneous mixture (a true solution) is called consulate temperature.
Example: The consulate temperature for phenol-water system is 65.9°C.

(e) **A Non-ideal Solution:** The solution that shows deviations from Raoult's law due to differences in molecular structures (i.e., size, shape, and intermolecular forces) of the components are called non-ideal solutions.
Example: Solution of ethanol in water, solution of HCl in water.

(f) Zeotropic Solution: A solution that distill with the change in composition and do not have constant boiling point is called zeotropic solution. Its components can be separated by fractional distillation. It is ideal solution that obeys Raoults law.

(g) **Heat of Hydration:** The amount of heat evolved or absorbed when one mole of gaseous ions or solute particles dissolve in water to form an infinite dilute solution.
For Ex; When 1 mole of gaseous hydrogen ions are dissolve in water forming an infinitely dilute solution, a large amount of heat is evolved.

$$H^{+}_{(g)} + \text{Water} \longrightarrow H^{+}_{(aq)} \qquad \Delta H = -1075 \text{ kJ/mol}$$

Heat of hydration depends upon the charge to size ration. In IA, heat of hydration decreases. In this group size of ions increases but charge remains the same.
In the VII A, heat of hydration decreases due to decrease in the ratio of charge to size.

(h) **Water of Crystallization:** The water molecules which combine with the compounds as they are crystallized from aqueous solution are called water molecules of crystallization or simply water of crystallization or water of hydration.
Example: $Na_2CO_3 . 10H_2O$.

(i) **Azeotropic Solution:** A solution that distills without change in composition and have constant boiling point is called azeotropic solution. Its components cannot be separated by fractional distillation. It is non-ideal solution that shows either positive or negative deviation from Raoult's law.
Example: Solution of HCl in water or solution of ethanol in water.

(j) **Conjugate Solution:** Two partially miscible liquids remain as separate layers but small quantities of these layers dissolve into each other forming solution of one another called conjugate solutions or two layers of partially miscible liquids which are solution of each other are called conjugate solutions.

Q.5 (a) What are the concentration units of solutions. Compare molar and molal solutions.
(b) One has one molal solution of NaCl and one molal solution of glucose:
(i) Which solution has greater number of particles of solute?
(ii) Which solution has greater amount of solvent?
(iii) How do we convert these concentration into weight by weight percentage?

Ans.

(a) **Concentration Units of Solution:** The units used to measure the concentration of solutions are called concentration units of solutions which are listed below:

(i) Percentage composition (%)
(ii) Molarity (M)
(iii) Molality (m)
(iv) Mole-fraction (X)
(v) Parts per million (ppm)

Comparison of Molar and Molal Solution:

Molar Solution	Molar Solution
(i) The solution having no. of moles of solute per dm^3 of the solution.	(i) The solution having no. of moles of solute per kg of the solvent.
(ii) Molar solution of a substance (say sugar) is concentrated.	(ii) Molal solution of a substance (say sugar) is dilute.
(iii) The concentration of molar solution vary with the temperature because volume of solution is considered which depends upon temperature.	(iii) The concentration of molal solution do not vary with the temperature because masses of solute and solvent are considered which do not depend upon temperature.
(iv) The concentration of molar solution is calculated by formula.	(iv) The concentration of molal solution is calculated by formula.
$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in dm}^3}$	$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$

(b) (i) 1 molal NaCl solution has greater number of particles than 1 molal glucose solution.

1 molal solution means that the solutions contain one mole of solute per kg of the solvent. 1 mole of NaCl has Avogadro's no. of formula units and twice the Avogadro's no. of particles (ions) and 1 mole of glucose has Avogadro's no. of molecules. Avogadro's no. of formula unit of NaCl (being electrolyte) produces twice the Avogadro's no. of ions (particles) in solution. Avogadro's no. of molecules of glucose (1 mole) being non-electrolyte do not dissociate or ionize in solution and as a result its no. of molecules (particles) remains the same i.e., Avogadro's no.

Hence, 1 molal NaCl solution has greater number of particles than 1 molal glucose solution.

(ii) Both the solutions are molal and for molal solution we consider 1 kg of the solvent. So, both the solutions have equal amount of solvent.

(iii) For weight by weight percentage, we need mass of solute and total mass of solution and formula used is:

$$\text{Percentage of solution} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

(a) w/w % of 1 molal NaCl solution:

Mass of NaCl (solute) = 58.5 g (1 mole)

Mass of water (solvent) = 1000 g (1 kg)

Total mass of solution = 1000 + 58.5 = 1058.5 g

$$\text{Percentage of NaCl solution} = \frac{\text{Mass of NaCl}}{\text{Total mass of solution}} \times 100$$

$$= \frac{58.5\text{ g}}{1058.5\text{ g}} \times 100 = 5.52\%$$

(b) w/w % of 1 molal solution of glucose:

Mass of glucose (solute) = 180 g (1 mole)

Mass of water (solvent) = 1000 g (1 kg)

Total mass of solution = 1000 + 180 = 1180 g

$$\text{Percentage of glucose solution} = \frac{\text{Mass of glucose}}{\text{Total mass of solution}} \times 100$$

$$= \frac{180}{1180} \times 100 = 15.2\%$$

Q.6 Explain the following with reason?

(i) The concentration in terms of molality is independent of temperature but molarity depends upon temperature.

(ii) The sum of mole fractions of all the components is always equal to unity for any solution.

(iii) 100 g of 98% H_2SO_4 has volume of 54.34 cm^3 of H_2SO_4 because its density is 1.84 gcm^{-3}.

(iv) Relative lowering of vapour pressure is independent of the temperature.

(v) Colligative properties are obeyed when the solute is non-electrolyte and also when the solutions are dilute.

(vi) The total volume of the solution by mixing 100 cm^3 of water with 100 cm^3 of alcohol may not be equal to 200 cm^3 Justify it.

(vii) One molal solution of urea, in water is dilute as compared to one molar solution of urea. But the number of particles of the solute is same. Justify it.

(viii) Non-ideal solution don't obey the Raoult's law.

Ans.

(i) In case of molarity, we consider masses of solute and solvent. Mass is a temperature independent quantity. Hence, molality is also a temperature independent quantity.

Whereas, for molarity volume of the solution is taken and volume is a temperature dependent quantity. Hence molarity also depends upon temperature.

Note: Molar solution of a substance is concentrated at higher temperature than at lower temperature.

(ii) We have solution with two components i.e., A = solvent and B = solute. For example:

No. of moles of solvent (A) = n_A = 98 moles

No. of moles of solute (B) = n_B = 2 moles

Total no. of moles of solution = $n_A + n_B$ = n_t = 100 mole

Mole fraction of a component = No. of moles of that components÷Total no. of moles

Mole fraction of solvent (A) = X_A

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

$$= \frac{98}{100} = 0.98$$

Mole fraction of solute (B) = X_B

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

$$= \frac{2}{100} = 0.02$$

Sum of mole fraction ‘A’ and ‘B’ = $X_A + X_B$

$= 0.98 + 0.02$

$= X_A + X_B$

$= 1.00$

Note: (i) The mole fraction of one component in a mixture is always less than unity.

(ii) The sum of mole fractions of all the components is always equal to unity.

(iii) The mole fraction multiplied by 100 gives mole percent.

(iv) The mole percent of one component in a mixture is always than 100.

(v) The sum of mole percents of all the components in a mixture is always equal to 100.

(iii) Mass of H_2SO_4 solution = 100 g

Density of H_2SO_4 solution = $1.84\ g\ cm^{-3}$

Volume of H_2SO_4 solution = ?

We know that:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

or

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{Volume} = \frac{100}{1.84}$$

$$\boxed{\text{Volume} = 54.34\ cm^3}$$

(iv) The relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{\Delta P}{P^\circ} = X_2$$

Mole fraction of the solute is a temperature independent quantity. Mole fraction of a solute is ratio of no. of moles of solute to the total no. of moles of solute and solvent. And no. of moles does not depend upon temperature. Hence, relative lowering of vapour pressure does not depend upon temperature.

(v) **Colligative properties when solute is non-electrolyte:** Colligative properties depends upon number of solute particles in solution. Non-electrolyte solute do not ionize in solution and its number of particles remain the same. e.g., 1 mole of urea-produces 6.02×10^{23} particles in solution.

When solute is electrolyte, it ionizes in the solution and its no. of particles increases. As a result of that Raoult's law and colligative properties are not obeyed e.g., 1 mole of NaCl produces $2(6.02 \times 10^{23})$ particles (6.02×10^{23} Na^+ ions and 6.02×10^{23} Cl^- ions) in the solution.

Colligative properties when solution is dilute: When solution is dilute, less number of solute particles far away from each other and they behave independently. And colligative properties are obeyed.

For a concentrated solution, there are greater number of solute particles which are closer to each other. Due to which attraction dominate and particles may associate. As a result of which lowering of vapour pressure is less than the ideal value.

Hence colligative properties are not obeyed for concentrated solution.

(vi) When 100 cm^3 of water and 100 cm^3 of alcohol are mixed together, the volume of the solution is slightly more than 200 cm^3. This is because forces of attraction between water-alcohol in mixture are weaker than that between water and alcohol in their pure state. Also, that is the reason why this solution shows deviation from Raoult's law.

This solution is not ideal and shows positive deviation from Raoult's law.

(vii) In one molal solution of urea, 60 g of urea is dissolved in 1000 g of water. 1000 g of water is approximately equal to its 1000 cm^3. In 1 molal solution, volume of solvent (H_2O) will be 1000 cm^3 whereas, 1 molar solution contains 60 g urea dissolved per 1000 cm^3 of solution. Means in the later solution the volume of water is less than 1000 cm^3, because solute is also included in 1000 cm^3 of solution.

Hence, number of solute particles are same in both the solutions but molal solution of urea containing greater amount of solvent (water) is dilute as compared to its molar solution.

(viii) During the formation of non-ideal solution, there is either decrease or increase of attraction between solute and solvent particles. As a result, of which the values of vapour pressure of the individual components are not proportional to their mole fraction. This is against the Raoult's law. Therefore, we say that non-ideal solutions do not obey Raoult's law.

Q.7 What are non-ideal solution? Discuss their types and give three examples of each.

Ans. Descriptive question, consult text book.

Q.8 (a) Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.

(b) The solutions showing positive and negative deviations cannot be fractionally distilled at their specific compositions. Explain it.

Ans.

(a) Descriptive question, consult text book.

(b) Descriptive question, consult text book.

Q.9 (a) What are azeotropic mixtures? Explain them with the help of graphs.

(b) Explain the effect of temperature on phenol- water system.

Ans.

(a) Descriptive question, consult text book.

(b) Descriptive question, consult text book.

Q.10 (a) What are the colligative properties? Why are they called so?

(b) What is the physical significant of K_b and K_f values of solvents?

Ans.

(a) Descriptive question, consult text book.

(b) **Molal Boiling Point Constant (K_b):** If we have one molal solution of different non-volatile and non-electrolyte solutes in H_2O, then the boiling point elevation for all the solutions will be same i.e., 0.52°C. This is called molal boiling point constant. Its value is different for different solvents but is independent of nature of solute. It units are C° kg mol^{-1}.

Molal Freezing Point Constant (K_f): Freezing point depression for 1 molal solution of non-volatile and non-electrolyte solute in H_2O is same i.e., 1.86°C and is called molal freezing point constant. Its value depends upon the nature of solvent and is independent of nature of solute. Its units are C° kg mol^{-1}.

(b) Descriptive question, consult text book.

Q.11 How do you explain that the lowering of vapour pressure is a colligative property? How do we measure the molar mass of a non-volatile, non-electrolyte solute in a volatile solvent?

Ans. Descriptive question, consult text book.

Q.12 How do you justify that?

(a) Boiling points of the solvents increase due to the presence of solutes.

(b) Freezing points are depressed due to the presence of solutes.

(c) The boiling point of one molal urea solution is 100.52°C but the boiling point of two molal urea solution is less than 101.04°C.

(d) Beckmann's thermometer is used to note the depression in freezing point.

(e) In summer the antifreeze solutions protect the liquid of the radiator from boiling over.

(f) NaCl and KNO_3 are used to lower the melting point of ice.

Ans.

(a) When solute is added to solvent, some of the solute molecules come to lie on the surface of solvent as well. They do not allow the solvent molecules to escape from the surface as quickly as in pure state. As a result of that vapour pressure decreases and boiling point increases.

Increase in boiling point depends upon the concentration of solute. Greater the amount of solute, greater will be the increase of boiling temperature.

(b) When solute is added into a solvent solute particles come to the lie in between solvent molecules and solution. As a result of that, distance between solvent molecules increases and forces of attraction between solvent molecules decreases. Hence solvent in solution freeze at lower temperature than pure solvent and freezing point decreases.

Therefore, we can easily say that the freezing point is depressed due to presence of solute.

(c) Two molal urea solution is concentrated than one molal urea solution. No. of molecules in two molal urea solution is twice the Avogadro's no. Due to high concentration, molecules are closer together and there are dominant forces of attraction between them and molecules may associate. Due to which number of molecules which are free to move are less than twice the Avogadro's no. Hence, elevation in boiling is not doubled (101.4°C).

(d) Beckmann's thermometer can measure upto $\frac{1}{100}$ th of a degree i.e., 0.01 K. Since depression in freezing point for a dilute solution is small. Hence, Beckmann's thermometer can read very small changes of temperature during depression in freezing point.

(e) Ethylene glycol is an anti-freeze solutions in the water of car radiator. Due to the addition of ethylene glycol in water, its freezing point decreases and boiling point increases. In winter, it prevents water from freezing and in summer, it prevents water from boiling over.

(f) NaCl and KNO_3 being electrolytes and highly soluble in water. They dissolve and produces double the number of ions than formula units. Due to which freezing point is depressed to greater extent. This mixture is also used to melt the ice from roads in winter.

Q.13 What is Raoult's law? Give its three statements. How this law can help us to understand the idealility of a solution.

Ans. Descriptive question, consult text book.

Q.14 Give graphical explanation for elevation of boiling point of a solution. Describe one method to determine the boiling point elevation of a solution.

Ans. Descriptive question, consult text book.

Q.15 Freezing points of solutions are depressed when non-volatile solutes present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also give one method to record the depression of freezing point of a solution.

Ans. Detailed question. For answer, consult text book.

Q.16 Discuss the energetics of solution. Justify the heats of solutions as exothermic or endothermic properties.

Ans. Descriptive question, consult text book.

Q.17 (a) Calculate the molarity of glucose solution when 9g of it is dissolved in 250 cm^3 of solution.

(b) Calculate the mass of urea in 100 g of water in 0.3 molal solution.

(c) Calculate the concentration of solution in molality kg^{-1} which is obtained by mixing 250 g of 20% solution of NaC1 with 200 g of 40% solution of NaCl.

Ans.

(a) The volume of solution has to be taken in dm^3.

Mass of glucose dissolved (W_2) = 9.0 g
Volume of solution = 250 cm^3
= 0.25 dm^3
Molar mass of glucose = 180.0 g mol
Molarity of solution = ?

Molarity (M) = $\frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$

Substituting the values:

Malarity (M) = $\frac{9.00 \text{ g}}{180.0 \text{ g/mol}} \times \frac{1}{0.25 \text{ dm}^3}$

Molarity (M) = $\frac{9}{180 \times 0.25}$ moles dm^{-3}

Molarity (M) = 0.2 M

(b) We need the mass of solvent in kg.

Mass of water as a solvent = 100.00 g

Mass of solvent in kg = $\frac{100}{1000}$ = 0.1 kg

Molality of solution (m) = 0.3 m

Molar mass of urea = 60.0 g mol^{-1}

Mass of urea dissolved = ?

Molality (m) = $\frac{\text{Mass of urea}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in (kg)}}$

Putting values:

0.3 mol kg^{-1} = $\frac{\text{Mass of urea}}{60.00 \text{ g mol}^{-1}} \times \frac{1}{0.1 \text{ kg}}$

Mass of urea = 0.3 × 60.00 × 0.1

Mass of urea = 1.8 g

(c) 1st solution:

% of NaCl solution = 20%

Mass of 20% solution = 250 g

Concentration of solution = ?

20% of NaCl solution means that:

100 g of solution has NaCl = 20 g

1 g of solution has NaCl = $\frac{20}{100}$ g

= $\frac{20}{100} \times 250$ g

250 g of solution has NaCl = 50 g

2nd solution:

% of NaCl solution = 40

Mass of 40% NaCl solution = 200 g

100 g of solution has NaCl = 40 g

1 g of solution has NaCl = $\frac{40}{100}$ g

200 g of solution has NaCl = $\frac{40}{100} \times 200$

= 80 g

Mass of NaCl in both solutions = 50 + 80 = 130 g

Total mass of both the solutions = 200 + 250 = 450 g

Mass of solvent = 450 – 130 = 320 g = 0.32 kg

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass}} \times \frac{1}{\text{Mass of solvent in kg}}$$

Putting the values:

$$\text{Molality} = \frac{130}{58.5} \times \frac{1}{0.32} = 0.71 \text{ m}$$

Q.18 (a) An aqueous solution of sucrose has been labeled as one molal. Find the mole fraction of the solute and the solvent.

(b) You are provided with 80 % H_2SO_4 w/w having density 1.8 g cm^{-3}. How much volume of this sulphuric acid sample is required to obtain 1 dm^3 of 20% w/w H_2SO_4 whose density is 1.25 g cm^{-3}.

Ans.

(a) Name of compound = Sucrose ($C_{12}H_{22}O_{11}$)

Molar mass of sucrose = 342 g mol^{-1}

Since, the solution is 1 molal, so 342 g is dissolved in 1000 g of H_2O.

Hence Mass of sucrose dissolved = 342 g

Mass of H_2O taken = 1000 g

Number of moles of sucrose = 1

Mole fraction of solvent = ?

Mole fraction of solute = ?

First of all calculate no. of moles of water.

$$\text{Number of moles of } H_2O = \frac{\text{Mass of water taken}}{\text{Molar mass of water}}$$

Putting values:

$$\text{No. of moles of } H_2O = \frac{1000}{18} = 55.55$$

And no. of moles of sucrose is 1.

Now we calculate mole fraction of sucrose.

$$\text{Mole fraction of sucrose } (X_{sucrose}) = \frac{\text{No. of moles of sucrose}}{\text{Total no. of moles}}$$

Putting the values:

$$\text{Mole fraction of sucrose } (X_{sucrose}) = \frac{1}{55.51 + 1} = \boxed{0.0176}$$

Similarly calculate mole fraction of H_2O.

$$\text{Mole fraction of water } (X_{H_2O}) = \frac{\text{Number of moles of } H_2O}{\text{Total no. of moles}}$$

Putting the values:

$$\text{Mole fraction of water } (X_{H_2O}) = \frac{55.55}{55.55 + 1} = \boxed{0.9823}$$

(b) The solution of this numerical is to be done in two stages:

(i) Conversion of 80% H_2SO_4 to molarity:

% of concentrated H_2SO_4 = 80.00

Density of concentrated H_2SO_4 = $1.8\ g\ cm^{-3}$

It means:

$1\ cm^3$ of H_2SO_4 has mass = 1.8 g

$1000\ cm^3$ of H_2SO_4 has mass = 1.8×1000 = 1800 g

1800 g of concentrated H_2SO_4 is 80% of H_2SO_4.

100 g of concentrated solution of H_2SO_4 contains H_2SO_4 = $\frac{80}{100} \times 1800$ = 1440 g

$$\text{Number of moles of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar mass of } H_2SO_4}$$

Putting the values:

$$\text{Number of moles of } H_2SO_4 = \frac{1440\ g}{98\ g\ mol^{-1}} = 14.7\ \text{mole}$$

It means 14.7 moles of H_2SO_4 is present in $1000\ cm^3$ of solution, hence, it is 14.7 molar H_2SO_4.

Conversion of 20% H_2SO_4 in molarity:

% of dilute H_2SO_4 = 20

Density of dilute H_2SO_4 = $1.25\ g\ cm^{-3}$

It means:

$1\ cm^3$ of H_2SO_4 has mass = 1.25 g

$1000\ g\ cm^3$ of H_2SO_4 has mass = 1.25×1000 = 1250 g

1250 g of dilute H_2SO_4 is 20% H_2SO_4.

100 g of dilute solution contains H_2SO_4 = 20 g

1 g of dilute solution of H_2SO_4 has H_2SO_4 = $\frac{20}{100}$ g

1250 g of dilute solution of H_2SO_4 has H_2SO_4 = $\frac{20}{100} \times 1250$ = 250 g

$$\text{No. of moles of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar mass}}$$

Putting the values:

$$\text{No. of moles of } H_2SO_4 = \frac{250\ g}{98\ g\ mol^{-1}} = 2.55\ \text{mol}$$

Now, we have to dilute 14.7 M solution to 2.55 M H_2SO_4. For this purpose, use the dilution formula.

(ii) Conc. H_2SO_4 = Dil. H_2SO_4

$$M_1V_1 = M_2V_2$$

Putting the values:

$$14.7 \times V_1 = 2.55 \times 1000$$

$$V_1 = \frac{2.55 \times 1000}{14.7}$$

$$V_1 = 173.5 \text{ cm}^3$$

So, 173.5 cm^3 of conc. H_2SO_4 is diluted up to 1000 cm^3 to get the solution of required molarity. In this way 14.7 M H_2SO_4 is converted to 2.55 M H_2SO_4.

Q.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.

Ans. 250 cm^3 of 0.2 molar K_2SO_4 solution has 0.4 moles $K^{\oplus}$ ion. Because each formula unit of K_2SO_4 has two $K^{\oplus}$ ions.

250 cm^3 of 0.2 molar KCl solution has 0.2 moles $K^{\oplus}$ ion.

Because one formula unit of KCl has one $K^{\oplus}$ ion.

When two solutions are mixed then 0.6 moles $K^{\oplus}$ ions may be present if the volume remains 250 cm^3. Since after mixing 500 cm^3 volume is obtained, so the conc. of $K^{\oplus}$ ions become half of 0.6 molar i.e., 0.3 molar.

Q.20 5 g of NaCl is dissolved in 1000 g of water, the density of resulting solution is 0.997 gcm^{-3} Calculate the Molarity and mole fractions of this solution. Assume that the volume of the solution is equal to that of solvent.

Ans.

(i) Calculation of molality (m):

Mass of NaCl = 5 g

Mass of H_2O = 1000 g = 1 kg

$$\text{Molality of NaCl (m)} = \frac{\text{Mass of NaCl}}{\text{Molar mass of NaCl}} \times \frac{1}{\text{Mass of solvent in (kg)}}$$

$$\text{Molality of NaCl (m)} = \frac{5}{58.5} \times \frac{1}{1 \text{ kg}} = 0.0854 \text{ molal}$$

(ii) Calculations of molarity (M):

Density of solution = 0.997 g cm^{-3}

Total mass of solution = 1005 g

$$d = \frac{m}{V}$$

$$V = \frac{m}{d}$$

Putting the values:

$$V = \frac{1005}{0.997} = 1008.02 \text{ cm}^3$$

Volume of solution in dm^3 = 1.00802 dm^3

$$\text{Molarity (M)} = \frac{\text{Mass of NaCl}}{\text{Molar mass}} \times \frac{1}{1.00802}$$

Molar mass of NaCl = 58.5 mol^{-1}

Putting the values:

$$\text{Molarity (M)} = \frac{5}{58.5} \times \frac{1}{1.00802} = \boxed{0.084}$$

(iii) Calculation of Mole Fraction:

$$\text{No. of moles of NaCl} = \frac{5}{58.5} = 0.0854$$

$$\text{No. of moles of } H_2O = \frac{1000}{18} = 55.55$$

$$X_{NaCl} = \frac{\text{No. of moles of NaCl}}{\text{No. of moles of NaCl + No. of moles of } H_2O}$$

Putting the values:

$$X_{NaCl} = \frac{0.0854}{0.0854 + 55.5}$$

$$= \frac{0.0854}{55.5854} = \boxed{0.000153}$$

$$X_{H_2O} = \frac{55.55}{55.5854} = \boxed{0.999}$$

Q.21 4.675 g of a compound with empirical formula C_3H_3O, was dissolved in 212.5 g of pure benzene. The freezing point of the solution was found 1.02°C less than that of pure benzene. The molal freezing point constant of benzene is 5.1°C. Calculate:

(i) the relative molar mass

(ii) the molecular formula of the compound

Ans. Mass of solute dissolved (W_2) = 4.675 g

Mass of solvent benzene (W_1) = 212.5 g

Depression of F.P. of solution (ΔT_f) = 1.02°C

Molar F.P constant of solvent (K_f) = 5.1°C

(i) Relative molar mass of solute (M_2):

$$M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{1000\ W_2}{W_1}$$

$$= \frac{5.1°C \times 1000 \times 4.675\ g}{1.02\ C° \times 212.5\ g}$$

$$= \frac{5.1 \times 1000 \times 4.675}{1.02 \times 212.5}$$

$$M_2 = \frac{23842.5}{216.75} = 110\ g\ mol^{-1}$$

(ii) Empirical formula = C_3H_3O

Empirical formula mass = 36 + 3 + 16 = 55

Molar mass = n(E.F. mass)

110 = n(55)

$$n = \frac{110}{55} = 2$$

Molecular formula of the compound = 2(E.F.)

= 2(C_3H_3O)

Hence, the molecular formula of the compound= $\boxed{C_6H_6O_2}$

Q.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.

Ans. Mass of the solute A (W_2) = 0.2 g

Mass of the solvent ether (W_1) = 20.0 g

Elevation of B.P. of solution (ΔT_b) = 0.17 k

Molal B.P. constant of ether (K_b) = 2.16 k

Molar mass of A (M_2) = ?

$$M_2 = \frac{K_b}{\Delta T_b} \cdot \frac{1000\ W_2}{W_1}$$

$$= \frac{2.16\ K \times 1000 \times 0.2\ g}{0.17\ K \times 20\ g}$$

$$M_2 = \frac{132}{3.4} = \boxed{127.0\ g\ mol^{-1}}$$

Q.23 3 g of a non-volatile, non-electrolyte solute 'X' is dissolved in 50 g of ether (molar mass 74) at 293 K. The vapour pressure of ether falls from 442 torr to 426 torr under these conditions. Calculate the molecular mass of the solute X.

Ans. Mass of solute 'X' dissolved (W_2) = 3.00 g

Mass of solvent ether (W_1) = 50.00 g

Molar mass of ether (M_1) = 74.00 g mol^{-1}

Vapour pressure of pure ether (P°) = 442 torr

Vapour pressure of solution (P°) = 426 torr

Lowering of vapour pressure (ΔP) = 442 – 426 = 16 torr

Molar mass of 'X' (M_2) = ?

$$\frac{\Delta P}{P^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{W_2 \times M_1 \times P^\circ}{\Delta P \times W_1}$$

$$= \frac{3.0 \text{ g} \times 74 \text{ g mol}^{-1} \times 442 \text{ torr}}{16 \text{ torr} \times 50.0 \text{ g}}$$

$$= \frac{3 \times 74 \times 442}{16 \times 50} \text{ g mol}^{-1}$$

$$= \frac{98124}{800} \text{ g mol}^{-1}$$

$$M_2 = \boxed{122.6 \text{ g mol}^{-1}}$$

DID YOU KNOW?

1. Any mixture having uniform composition and single phase is called solution.
2. The solution which contains two components is called Binary solution.
3. The substance which is present in large quantity in solution is called solvent and the substance present in small quantity is called solute.
4. The number of moles of solute dissolved per dm^3 of solution is called molarity.
5. The number of moles of solute dissolved per kg of solvent is called molality.
6. One molar solution of sugar is sweeter than one molal solution.
7. The sum of the mole fraction of all components of a solution must be equal to one (unity).
8. The number of parts by mass or volume of solute per million parts by mass or volume of solution is called ppm.
9. Phenol and water are partially miscible whereas alcohol and water are completely miscible.
10. Benzene and water are immiscible.
11. Raoults law is obeyed in case of dilute solutions.
12. The temperature at which two conjugate solutions merge into one another is called critical solution temperature or consulate temperature.
13. The liquid mixture which distills with a change in composition is called zeotropic mixture.
14. The liquid mixture which boils at constant temperature and distills over without change in composition at any pressure like a chemical compound is called azeotropic mixture.
15. The elevation of the boiling point when 1 mole of solute is dissolved in one kg of solvent is called molal boiling point constant or Ebullioscopic constant.
16. Equimolal solution of different non-electrolytes increase the boiling point equally.
17. The amount of heat evolved when one mole of vapours are condensed to a liquid at constant temperature is called latent heat of condensation.
18. The depression in the freezing point when 1 mole of solute is dissolved in one kg of solvent is called molal freezing point constant or cryoscopic constant.
19. Units of $K_b = \text{C}^\circ \text{ kg mol}^{-1}$.

20. Units of K_f = C° kg mol^{-1}.

21. The process in which solvent molecules surround and interact with the solute particles is called solvation.

22. The process in which water molecules surround and interact with the solute particles is called hydration.

23. Copper sulphate is penta hydrated.

24. Washing soda is deca hydrated.

25. Epsom salt is hepta hydrated.

Chapter 10

ELECTROCHEMISTRY

ELECTROCHEMISTRY

Electrochemistry is the conversion of electrical energy into chemical energy in electrolytic cells as well the conversion of chemical energy into electrical energy in galvanic or voltaic cells.

IMPORTANT DEFINITIONS

Current:

"The flow of electric charge is called **current**." It is measured in amperes.

Conductor:

"The substance through which electricity can pass is called **conductor**."

All metals are good conductor of electricity due to the presence of free electrons in them. Conductor are of two types.

(i) Electronic Conductor:

The flow of charge in an electronic conductor is due to flow of electrons. Metals are electronic conductor.

(ii) Electrolytic Conductor:

The flow of charge in an electrolytic conductor is due to movement of ions. Electrolytic conductors are called **electrolytes**.

For example aqueous solution of NaCl, molten NaCl, some salts, acids or bases in water.

Ionization:

The process in which an ionic compound when fused or dissolved in water split into negative ions and positive ions.

Examples:

$$PbBr_{2(s)} \xrightarrow{H_2O} Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)}$$

$$NaCl_{(s)} \xrightarrow{H_2O} Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$NaCl_{(s)} \xrightarrow{\text{Heat}} Na^{+}_{(l)} + Cl^{-}_{(l)}$

Electrolysis:

"A chemical change caused by the passage of electricity through a molten compound or through a solution that contains ions."

Electrode:

"The surface of a cell at which electron transfer reaction takes place."

Electrolyte:

The substance that give ions in aqueous solution and then solution conduct electricity. For example, aqueous NaCl, aqueous $CuSO_4$ solutions.

Spontaneous Reaction:

"The reaction, that takes place itself without changing the condition of reaction is called **spontaneous reaction**."

$Zn + CuSO_4 \longrightarrow CuSO_4 + Zn$

Non–Spontaneous Reaction:

"The reaction, which does not take place and completed without applying external force is called **non–spontaneous reaction**."

$2NaCl \xrightarrow{\text{Electrolysis}} 2Na + Cl_2$

$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2 + Cl_2$

OXIDATION

In **oxidation** process, **increase** in oxidation state and **loss** of electrons take place. In galvanic or electrolytic cell, oxidation takes place at anode.

$Na \longrightarrow Na^{+1} + 1e^{-}$

$Pb \longrightarrow Pb^{2+} + 2e^{-}$

$Zn \longrightarrow Zn^{2+} + 2e^{-}$

$2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

REDUCTION

In **reduction** process, **decrease** in oxidation state and **gain** of electrons take place. In galvanic or electrolytic cell, reduction takes place at cathode.

$Cu^{2+} + 2e^{-} \longrightarrow Cu$

$2H^{+} + 2e^{-} \longrightarrow H_2$

Oxidizing Agent or Oxidant:

"The substance which gains electrons in chemical reaction, is called **oxidizing agent or oxidant**." An oxidizing agent itself reduces.

$Cu^{2+} + 2e^{-} \xrightarrow{\qquad} Cu^{0}$ (Oxidizing agent)

Reducing Agent or Reductant:

"The substance which loses electrons in chemical reaction, is called **reducing agent or reductant**." A reducing agent is itself oxidized.

$Zn^{0} \xrightarrow{\qquad} Zn^{2+} + 2e^{-}$ (Reducing agent)

Redox Reaction:

"The reaction in which transfer of electrons takes place from one substance to another substance is called **redox reaction**." Zn is oxidized and act as reducing agent. Cu^{2+} is reduced to Cu. $CuSO_4$ is an oxidizing agent.

$Zn + CuSO_4 \xrightarrow{\qquad} ZnSO_4 + Cu$

Oxidation Number of Oxidation State:

"The apparent charge which would be present in an atom of an element in a molecule or is called **oxidation state**." It many be positive or negative or zero.

Rules for Assigning Oxidation Number:

(1) Oxidation of all element in free state is zero.

For example, $O_2^0, N_2^0, H_2^0, F_2^0, Cl_2^0, Br_2^0, O_3^0, P_4^0, S_8^0, Na^0, K^0, Fe^0, Cu^0, Zn^0$ etc.

(2) The oxidation number of hydrogen is + 1 except in the case of metal hydrides where it is – 1 e.g.

$\overset{+1}{Na}\overset{-1}{H}$, $\overset{+1}{Li}\overset{-1}{H}$ $\overset{+2}{H_2}\overset{-2}{O}$, $\overset{+1}{H}\overset{-1}{Cl}$

(3) The oxidation number of oxygen is – 2 except in the case of peroxide where it is – 1 e.g.

$\overset{+2}{Na_2}\overset{-2}{O_2}$, $\overset{+2}{H_2}\overset{-2}{O_2}$

and super oxide where it is $-\frac{1}{2}$ e.g. $\overset{+1}{K}\overset{-1}{O_2}$.

The oxidation number of oxygen is + 2 in the case of $\overset{+2}{O}\overset{-2}{F_2}$.

(4) The oxidation number of halogens (VII A group) is – 1 in binary compounds. (The compounds which have only two elements in them are called **binary compounds**). For example,

$\overset{+1}{Na}\overset{-1}{Cl}$, $\overset{+2}{Ca}\overset{-2}{Cl_2}$, $\overset{+2}{Fe}\overset{-2}{Cl_2}$, $\overset{+1}{K}\,\overset{-1}{I}$

(5) Oxidation of number of an ion consisting of single element is same as the charge on the ion e.g.

$Na^{+}, K^{+}, Ca^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$, etc.

(6) The oxidation number of IA group (Li, Na, K, Rb, Cs) is + 1. IIA group (Be, Mg, Ca, Sr, Ba) is + 2 and IIIA group B. Al, is + 3.

(7) The sum of oxidation state of all the element in a neutral compound is zero.

$\overset{+1}{K}\overset{+7}{Mn}\overset{-8}{O_4}$, $\overset{+2}{K_2}\overset{+6}{Cr}\overset{-8}{O_4}$, $\overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4}$, $\overset{+1}{H}\overset{+5}{N}\overset{-6}{O_3}$

(8) In ions, the algebraic sum of oxidation number equals to the charge on ion e.g.

$\left[\overset{+6}{S}\ \overset{-8}{O_4}\right]^{2-}$, $\left[\overset{+5}{P}\ \overset{-8}{O_4}\right]^{3-}$, $\left[\overset{+6}{Cr}\ \overset{-8}{O_4}\right]^{2-}$, $\left[\overset{+7}{Mn}\ \overset{-8}{O_4}\right]^{1-}$.

(9) In any substance, more electronegative atom has the negative oxidation state e.g. $\overset{+2}{O}\overset{-2}{F_2}$, $\overset{+1}{H}\overset{-1}{Cl}$, $\overset{+2}{H_2}\overset{-2}{O}$

Examples:

K<u>Mn</u>O$_4$

$+1 + Mn - 2(4) = 0$

$+1 + Mn - 8 = 0$

$Mn = +8 - 1 = +7$

$Mn = +7$

K$_2$<u>Mn</u>O$_4$

$2(+1) + Mn - 2(4) = 0$

$+2 + Mn - 8 = 0$

$Mn = +8 - 2 = +6$

$Mn = +6$

(3) H<u>N</u>O$_3$

$+1 + N - 2(3) = 0$

$+1 + N - 6 = 0$

$N = +6 - 1 = +5$

$N = +5$

Na$_2$<u>C</u>O$_3$

$2(+1) + C - 2(3) = 0$

$+2 + C - 6 = 6$

$C = +6 - 2 = +4$

$C = +4$

H<u>P</u>O$_3$

$+1 + P - 2(3) = 0$

$+1 + P - 6 = 0$

$P = 6 - 1 = +5$

$P = +5$

Na$_3$<u>P</u>O$_3$

$Na_2S_2O_3 = 0$

$+2 + 2s - 6 = 0$

$2s = 6 - 2 = 4$

$s = \frac{4}{2} = 2$

$Na_2S_4O_6 = 0$

$+2 + 4s - 12 = 0$

$4s = 12 - 2 = 10$

$s = \frac{10}{4} = 2.5$

$C_6H_{12}O_6 = 0$

$6C + 12 - 12 = 0$

$6C = 0$

$C = 0$

$C_{12}H_{22}O_{11} = 0$

$12C + 22 - 2 = 0$

$12C = 0$

$C = 0$

$3(+1) + P - 2(3) = 0$

$+3 + P - 6 = 0$

$P = +6 - 3 = +3$

$P = +3$

$Ca(\underline{Cl}O_3)_2$

$+2 + 2Cl - 2(6) = 0$

$+2 + 2Cl - 12 = 0$

$2Cl = +12 - 2 = +10$

$2Cl = +10$

$Cl = +5$

$Cr_2(\underline{S}O_4)_3$

$2(+3) + 3S - 2(12) = 0$

$+6 + 3S - 24 = 0$

$3S = +24 - 6 = +18$

$3S = +18$

$S = +6$

$\underline{N}H_4^+$

$N + (+1) + 4 = +1$

$N + 4 = +1$

$$\left[\overset{-3}{N}\ \overset{+4}{H_4}\right]^{+1}$$

$N = -4 + 1 = -3$

$N = -3$

$\underline{S}O_4^{2-}$

$SO_4 = -2$

$S - 2(4) = -2$

$$\left[\overset{+6}{S}\ \overset{-8}{O_4}\right]^{-2}$$

$S - 8 = -2$

$S = +8 - 2 = +6$

$S = +6$

$\underline{Mn}O_4^{1-}$

$MnO_4 = -1$

$Mn - 2(4) = -1$ $\left[\overset{+7}{Mn}\,\overset{-8}{O_4}\right]^{-1}$

$Mn = +8 - 1 = +7$

$Mn = +7$

Write down the oxidation – state of chromium in the following compounds.

$CrCl_3$, K_2CrO_4, $K_2Cr_2O_7$, CrO_3, Cr_2O_3, $Cr_2O_7^{2-}$

$CrCl_3$

$Cr - 1(3) = 0$

$Cr - 3 = 0$

$Cr = +3$

K_2CrO_4

$+1(2) + Cr - 2(4) = 0$

$+2 + Cr - 8 = 0$

$Cr = +8 - 2 = +6$

$Cr = +6$

$K_2Cr_2O_7$

$(+1)2 + Cr_2 - 2(7) = 0$

$+2 + Cr_2 - 14 = 0$

$2Cr = +14 - 2 = +12$

$2Cr = +12$

$Cr = +6$

CrO_3

$Cr - 2(3) = 0$

$Cr - 6 = 0$

$Cr = +6$

Cr_2O_3

$2Cr - 2(3) = 0$

$2Cr - 6 = 0$

$2Cr = +6$

$Cr = +3$

$Cr_2O_7^{2-}$

$Cr_2O_7 = -2$

$2Cr - 2(7) = -2$

$2Cr - 14 = -2$

$2Cr = +14 - 2$

$2Cr = +12$

$Cr = +6$

Balancing of Redox Equations by Oxidation Number Method:

Carry out the following steps for balancing of redox equations by oxidation number method.

1. Write down the skeleton equation of the redox reaction under consideration.
2. Identify the elements, which undergo a change in their oxidation number during the reaction.
3. Record the oxidation number above the symbols of the elements, which have undergone a change in the oxidation number.
4. Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation (it shows number of electrons gained or lost).
5. Equate the increase or decrease in the oxidation number (i.e. electrons gained or lost) by multiplying with a suitable digit.
6. Balancing the rest of the equation by inspection method.

Example 1:

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

Solution:

(1) Write down the oxidation number each element.

$$\overset{+2}{K_2}\overset{+12}{Cr_2}\overset{-14}{O_7} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+1}{K}\overset{-1}{Cl} + \overset{+3}{Cr}\overset{-3}{Cl_3} + \overset{0}{Cl_2} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the element whose oxidation have changed. Consider the change per atom. Change of chlorine remains same in KCl and $CrCl_3$ i.e. from – 1 to – 1 so write HCl twice.

$$K_2\overset{+6}{Cr_2}O_7 + H\overset{-1}{Cl} \longrightarrow KCl + \overset{+3}{Cr}Cl_3 + \overset{0}{Cl_2} + H_2O$$

(3) Draw an arrow between those elements whose oxidation numbers have changed. Also balance the same atom on both side, if they are not balance. Then determine the total change in oxidation number by the atom present in the formulas of elements reduced or oxidized.

2 (+ 3) e = + 6 (Reduction)

$$HCl + K_2\overset{+6}{Cr_2}O_7 + H\overset{-1}{Cl} \longrightarrow KCl + \overset{+3}{Cr}Cl_3 + \overset{0}{Cl_2} + H_2O$$

2 (1) e = – 2 (Oxidation)

(4) Multiply – 2 and + 6 to get the common number, so that gain of electrons become equal to loss of electrons.

2 (+ 3) x 1 = 6

$$\mathrm{HCl + K_2\overset{+6}{Cr_2}O_7 + 2H\overset{-1}{Cl} \longrightarrow KCl + 2\overset{+3}{Cr}Cl_3 + \overset{0}{Cl_2} + H_2O}$$

2 (1) x 3 = 6

(5) Use these multiplier as coefficients with respective substance.

$$\mathrm{HCl + 6HCl + K_2Cr_2O_7 \longrightarrow KCl + 2CrCl_2 + 3Cl_2 + H_2O}$$

(6) Balance rest of the species by general inspection.

$$\mathrm{8HCl + 6HCl + K_2Cr_2O_7 \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O}$$

or $$\mathrm{14HCl + K_2Cr_2O_7 \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O}$$

Example 2:

$$\mathrm{Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O}$$

(1) Write the oxidation number of each element.

$$\mathrm{\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-6}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+10}{N}\ \overset{-12}{O}{}_3)_2 + \overset{+4}{N}\overset{-4}{O_2} + \overset{+2}{H_2}\overset{-2}{O}}$$

(2) Identify the elements, whose oxidation number have changed. Consider the change per atom. Also write HNO_3 twice because nitrogen remain same as well as changes.

$$\mathrm{HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O}$$

(3) Mention the change by an arrow, also balance same atoms on both sides, if they are not equal. Determine the total change in oxidation number by the atom present in formulas reduced or oxidized.

– 2e (Oxidation)

$$\mathrm{HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O}$$

+ 1e (Reduction)

(4) Multiply – 2 and + 1 by a number to get a common number so that gain of electrons become equal to lose of electrons.

– 2e x 1

$$\mathrm{HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O}$$

+ 1e x 2

(5) Use these multipliers as coefficients with respective substances.

$$HNO_3 + Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

(6) Balance rest of species by general inspection.

$$2HNO_3 + Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

or $$4HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Example 3:

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$$

(1) Write the oxidation number of each element.

$$\overset{0}{Zn} + \overset{+1}{H}\overset{+5}{N}\overset{-6}{O_3} \longrightarrow \overset{+2}{Zn}(\overset{+10}{N}\overset{-12}{O}_3)_2 + \overset{+2}{N}\overset{-2}{O} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the element whose oxidation number have changed. Consider the change per atom. Also write HNO_3 twice because nitrogen remain same as well as changes.

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

(3) Mention the change by an arrow. Also balance same atoms on both sides, if they are not equal.

– 2e (Oxidation)

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

+ 3e (Reduction)

(4) Multiply – 2 by 3 and + 3 by 2 to get a common number because gain of electrons equal to lose of electrons.

– 2e x 3

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

+ 3e x 2

(5) Use these multipliers as coefficients with respective substances.

$$HNO_3 + 3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + H_2O$$

(6) Balance rest of species by general inspection.

$$6HNO_3 + 3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

or $$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

Example 4:

$$Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$$

(1) Write the oxidation number of each element.

$$\overset{0}{Br_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{-1}{Br} + \overset{+1}{Na}\overset{+5}{Br}\overset{-6}{O_3} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the element whose oxidation number have changed. Consider the change per atom. Split Br_2 to $2Br$ because it is oxidized as well as reduced.

$$\overset{0}{Br} + \overset{0}{Br} + NaOH \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$$

(3) Mention the change by an arrow. Also balance the same atoms on both sides.

– 5e (Oxidation)

$$\overset{0}{Br} + \overset{0}{Br} + NaOH \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$$

+1e (Reduction)

(4) Multiply – 1 by 5 to get a common number because gain of electrons equal to lose of electrons.

$-5e \times 1 = -5e$

$$\overset{0}{Br} + \overset{0}{Br} + NaOH \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$$

$-1e \times 5 = 5e$

(5) Use these multipliers as coefficients with respective species.

$$5Br + Br + NaOH \longrightarrow 5NaBr + NaBrO_3 + H_2O$$

(6) Balance rest of species by general inspection also combine Br atoms to Br_2.

$$3Br_2 + 6NaOH \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$$

Example 5:

$MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(1) Write the oxidation number of each element.

$\overset{+4\,-4}{MnO_2} + \overset{+1-1}{HCl} \longrightarrow \overset{+2\,-2}{MnCl_2} + \overset{0}{Cl_2} + \overset{+2\,-2}{H_2O}$

(2) Identify the element whose oxidation number have changed. Consider the change per atom. Also write HCl twice because Cl^{-1} change to Cl^{-1} and Cl_2^0.

$HCl + \overset{+4}{MnO_2} + \overset{-1}{HCl} \longrightarrow \overset{+2}{MnCl_2} + \overset{0}{Cl_2} + H_2O$

(3) Mention the change in oxidation numbers with arrow. Also balance same atoms on both sides. Multiply HCl with 2.

+ 2e (Reduction)

$HCl + \overset{+4}{MnO_2} + \overset{-1}{2HCl} \longrightarrow \overset{+2}{MnCl_2} + \overset{0}{Cl_2} + H_2O$

2 (– 1e) (Oxidation)

(4) Gain of electrons equal to lose of electrons.

$HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(5) Balance rest of species by general inspection.

$2HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

or $4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Example 6:

$FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4) + H_2O$

(1) Write the oxidation number each element.

$\overset{+2}{Fe}\overset{+6}{S}\overset{-8}{O_4} + \overset{+2}{K_2}\overset{+12}{Cr_2}\overset{-14}{O_7} + \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} \longrightarrow \overset{+2}{K_2}\overset{+6}{S}\overset{-8}{O_4} + \overset{+6}{Cr_2}(\overset{+18}{S}\overset{-24}{O_4})_3 + \overset{+6}{Fe_2}(\overset{+18}{S}\overset{-24}{O_4})_3 + \overset{+2}{H_2}\overset{-2}{O_2}$

(2) Identify the elements, whose oxidation number have changed. Consider the change per atom.

$\overset{+2}{FeSO_4} + \overset{+6}{K_2Cr_2O_7} + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+3}{Cr_2(SO_4)_3} + \overset{+3}{Fe_2(SO_4)_3} + H_2O$

(3) Mention the change by an arrow. Also balance the same atoms on both sides. Multiply (3e) by 2 on both sides because two atoms are present on both sides.

2 (3e) (Reduction)

$\overset{+2}{2FeSO_4} + \overset{+6}{K_2Cr_2O_7} + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+3}{Cr_2(SO_4)_3} + \overset{+3}{Fe_2(SO_4)_3} + H_2O$

– 1e (2) (Oxidation)

(4) Multiply 2 by 3 to get a common number because gain of electrons equal to lose of electrons number.

2 (3e) x 1 = + 6

$$2\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + \overset{+3}{Fe_2}(SO_4)_3 + H_2O$$

– 1e (2) x 3 = – 6

(5) Use these multipliers as coefficients with respective species.

$$6FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

(6) Balance rest of species by general inspection.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

Example 7:

$$HNO_3 + HI \longrightarrow NO + H_2O + I_2$$

(1) Write the oxidation number each element.

$$\overset{+1}{H}\overset{+5}{N}\overset{-6}{O_3} + \overset{+1}{H}\overset{-1}{I} \longrightarrow \overset{+2}{N}\overset{-2}{O} + \overset{+2}{H_2}\overset{-2}{O} + \overset{0}{I_2}$$

(2) Identify the elements, whose oxidation number have changed. Consider the change per atom.

$$H\overset{+5}{N}O_3 + H\overset{-1}{I} \longrightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2O$$

(3) Mention the change by an arrow. Also balance the iodine on both sides.

+ 3e (Reduction)

$$H\overset{+5}{N}O_3 + 2H\overset{-1}{I} \longrightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2O$$

– 1e (2) (Oxidation)

(4) Multiply + 3 to 2 and 2 to 3 to get the common number because gain of electrons equal to lose of electrons.

+ 3e x 2 = + 6

$$H\overset{+5}{N}O_3 + 2H\overset{-1}{I} \longrightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2O$$

– 2 x 3 = – 6

(5) Use these multipliers as coefficients with respective species.

$$2HNO_3 + 6HI \longrightarrow 2NO + 3I_2 + H_2O$$

(6) Balance rest of species by general inspection.

$$2HNO_3 + 6HI \longrightarrow 2NO + 3I_2 + 4H_2O$$

Example 8:

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$$

(1) Write the oxidation number of each element.

$$\overset{0}{Cu} + \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} \longrightarrow \overset{+2}{Cu}\overset{+6}{S}\overset{-8}{O_4} + \overset{+4}{S}\overset{-4}{O_2} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the elements, whose oxidation number have changed. Consider the change per atom. Also write H_2SO_4 twice because it changes from S^{+6} to S^{+6} as well as S^{+4}.

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$$

(3) Mention the change by an arrow. Also balance same atoms on both sides, if they are not equal. Determine the total change in oxidation number by the atom present in formulas reduced or oxidized.

– 2e (Oxidation)

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$$

+ 1e (Reduction)

(4) Multiply – 2 and + 1 by a number to get a common number so that gain of electrons become equal to lose of electrons.

– 2e x 1

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$$

+ 1e x 2

(5) Change of electrons is same, no multiplier will be used.

$$H_2SO_4 + Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$$

(6) Balance rest of species by general inspection.

$$2H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Example 9:

$$HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

(1) Write the oxidation number of each element.

$$\overset{+1}{H}\overset{-1}{I} + \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} \longrightarrow \overset{0}{I_2} + \overset{+4}{S}\overset{-4}{O_2} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the elements, whose oxidation state have changed. Consider the change per atom.

$$H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

(3) Mention the change by an arrow. Also balance the same atom on both side.

– 1e (2) (Oxidation)

$$2H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

+ 2e (Reduction)

(4) Multiply – 2 and + 1 by a number to get a common number so that gain of electrons become equal to lose of electrons.

– 2e x 1

$$2H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

+ 1e x 2

(5) Change of electrons is same, no multiplier will be used.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

(6) Use these multipliers as coefficients with respective substances.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

Example 10:

$$NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$$

(1) Write the oxidation number of each element.

$$\overset{+1}{Na}\overset{-1}{Cl} + \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} + \overset{+4}{Mn}\overset{-4}{O_2} \longrightarrow \overset{+2}{Na_2}\overset{+6}{S}\overset{-8}{O_4} + \overset{+2}{Mn}\overset{+6}{S}\overset{-8}{O_4} + \overset{0}{Cl_2} + \overset{+2}{H_2}\overset{-2}{O}$$

(2) Identify the elements, whose oxidation state have changed. Consider the change per atom.

$$Na\overset{-1}{Cl} + H_2SO_4 + \overset{+4}{Mn}O_2 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{0}{Cl_2} + H_2O$$

(3) Mention the change by an arrow. Also balance the chlorine atoms.

– 1e (2) (Oxidation)

$$\overset{-1}{2NaCl} + H_2SO_4 + \overset{+4}{MnO_2} \longrightarrow Na_2SO_4 + \overset{+2}{MnSO_4} + \overset{0}{Cl_2} + H_2O$$

+ 2e (Reduction)

(4) Change of electrons is same, are multiplier will be used.

$$2NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$$

(5) Balance rest of species by general inspection.

$$2NaCl + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$$

BALANCING OF EQUATIONS BY ION – ELECTRON METHOD

The balancing of redox equations by the loss and gain of electrons usually involves quite a few ions which do not undergo change in valence and which are not really necessary for the process of balancing. The ion – electron method eliminates all the unnecessary ions and retains only those, which are essential. Following are the general rules for balancing the redox equations by ion – electron method.

(i) Write a skeleton equation that shows only those substances that are actually involved in the reaction.

(ii) Split the equation into two half reactions, one showing oxidation and the other reduction.

(iii) The element should not be written as a free atom or ion unless it really exists as such. It should be written as a real molecular or ionic species.

(iv) Balance each partial equation as to the number of atoms of each element. In neutral or acidic solution, H_2O or H^+ ions may be added for balancing oxygen and hydrogen atoms. Oxygen atom are balanced first. If the solution is alkaline, OH^- may be used for each excess oxygen on one side of the equation.

(v) Balance each half reaction as to the number of charges by adding electrons to either the left or the right side of the equation.

(vi) Multiply each half reaction by a number chosen so that the total number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent.

(vii) Add the two half reactions. Count the number of atoms of each element on each side of the equation and also check the net charge on each side, which should be equal on both sides.

Balance of redox equations by ion – electrons method making use of the above rules is illustrated below.

Example 1:

$Cl^- + MnO_4^- \longrightarrow Cl_2 + Mn^{+2}$

Split the equation into two halves (oxidation half reaction).

$Cl^- \longrightarrow Cl_2$

Reduction half reaction.

$MnO_4^- \longrightarrow Mn^{+2}$

Balancing of oxidation half.

Cl: $2Cl^- \longrightarrow Cl_2$

e^-: $2Cl^- \longrightarrow Cl_2 + 2e^-$ (1)

Balancing of reduction half reaction:

$MnO_4^{-1} \longrightarrow Mn^{+2}$

H_2O: $MnO_4^{-1} \longrightarrow Mn^{+2} + 4H_2O$

H^+: $MnO_4^{-1} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$

e^-: $MnO_4^{-1} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$

Multiply Equation (1) by 5 and Equation (2) by 2 than add both equations.

$$\begin{array}{l} 10Cl^- \longrightarrow 5Cl_2 + 10e^- \\ 2MnO_4^{-1} + 16H^+ + 10e^- \longrightarrow 2Mn^{+2} + 8H_2O \\ \hline 10Cl^- + 2MnO_4^{-1} + 16H^+ \longrightarrow 2Mn^{+2} + 8H_2O + 5Cl_2 \end{array}$$

Example 2:

$Fe^{3+} + Sn^{2+} \longrightarrow Fe^{2+} + Sn^{4+}$

Oxidation half.

$Sn^{2+} \longrightarrow Sn^{4+}$

Reduction half.

$Fe^{3+} \longrightarrow Fe^{2+}$

Balancing of oxidation half.

e^-: $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$ (1)

Balancing of reduction half.

e^-: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (2)

Multiply Equation (2) by 2 than add both equation.

$$\begin{array}{l} 2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+} \\ Sn^{2+} \longrightarrow Sn^{4+} + 2e^- \\ \hline Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+} \end{array}$$

Example 3:

$MnO_4^{-1} + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$

Oxidation half.

$C_2O_4^{2-} \longrightarrow CO_2$

Reduction half.

$MnO_4^{-1} \longrightarrow Mn^{2+}$

Balancing of oxidation half reaction.

C: $C_2O_4^{2-} \longrightarrow 2CO_2$

e^-: $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ (1)

Balancing of reduction half reaction:

$MnO_4^{1-} \longrightarrow Mn^{2+}$

H_2O: $MnO_4^{1-} \longrightarrow Mn^{2+} + 4H_2O$

H^+: $MnO_4^{1-} + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

e^-: $MnO_4^{1-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (2)

Multiply Equation (1) by 5 and Equation (2) by 2 than add both equations.

$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$

$2MnO_4^{1-} + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$

$5C_2O_4^{2-} + 2MnO_4^{1-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Example 4:

$Cr_2O_7^{2-} + Cl^- \longrightarrow Cl_2 + Cr^{+3}$

Oxidation half reaction.

$Cl^- \longrightarrow Cl_2$

Reduction half reaction.

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Balancing of oxidation half reaction:

$Cl^- \longrightarrow Cl_2$

Cl^-: $2Cl^- \longrightarrow Cl_2$

e^-: $2Cl^- \longrightarrow Cl_2 + 2e^-$ (1)

Balancing of reduction half reaction:

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Cr: $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

H_2O: $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

e^-: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (2)

Multiply Equation (1) by 3 than add in Equation (2).

$6Cl^- \longrightarrow 3Cl_2 + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \longrightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$

Example 5:

$Cu + NO_3^- \longrightarrow Cu^{2+} + NO_2$

Oxidation half reaction.

$Cu \longrightarrow Cu^{2+}$

Reduction half reaction.

$NO_3^- \longrightarrow NO_2$

Balancing of oxidation half reaction.

$Cu \longrightarrow Cu^{2+}$

e^-: $Cu \longrightarrow Cu^{2+} + 2e^-$ (1)

Balancing of reduction half reaction:

$NO_3^- \longrightarrow NO_2$

H_2O: $NO_3^- \longrightarrow NO_2 + H_2O$

H^+: $NO_3^- + 2H^+ \longrightarrow NO_2 + H_2O$

e^-: $NO_3^- + 2H^+ + 1e^- \longrightarrow NO_2 + H_2O$ (2)

Multiply reaction (2) by 2 and than add both equations.

$Cu \longrightarrow Cu^{2+} + 2e^-$

$2NO_3^- + 4H^+ + 2e^- \longrightarrow 2NO_2 + 2H_2O$

$Cu + 2NO_3^- + 4H^+ \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$

Example 6:

$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$

Oxidation half reaction.

$Fe^{2+} \longrightarrow Fe^{3+}$

Reduction half reaction.

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Balancing of oxidation half.

e^-: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ (1)

Balancing of reduction half reaction:

Cr: $Cr_2O_7^{2-} \longrightarrow 2Cr^{+3}$

H_2O: $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

H^+: $Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

e^-: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (2)

Multiply Equation (1) by 6 and than add both equations.

$$\begin{array}{l} 6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^- \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\ \hline 6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

Example 7:

$S_2O_3^{2-} + OCl^- \longrightarrow Cl^- + S_4O_6^{-2}$

Oxidation half reaction.

$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$

Reduction half reaction.

$OCl^- \longrightarrow Cl^-$

Balancing of oxidation half.

$S_2O_3^{2-} \longrightarrow S_4O_6^{-2}$

S: $2S_2O_3^{2-} \longrightarrow S_4O_6^{-2}$

e^-: $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ (1)

Balancing of reduction half reaction:

$OCl^{-} \longrightarrow Cl^{-}$

H_2O: $OCl^{-} \longrightarrow Cl^{-} + H_2O$

H^{+}: $OCl^{-} + 2H^{+} \longrightarrow Cl^{-} + H_2O$

e^{-}: $OCl^{-} + 2H^{+} + 2e^{-} \longrightarrow Cl^{-} + H_2O$ (2)

Electrons on both sides are equal so add Equation (1) and Equation (2).

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^{-}$

$OCl^{-} + 2H^{+} + 2e^{-} \longrightarrow Cl^{-} + H_2O$

$2S_2O_3^{2-} + OCl^{-} + 2H^{+} \longrightarrow Cl^{-} + S_4O_6^{2-} + H_2O$

Example 8:

$IO_3^{-} + AsO_3^{3-} \longrightarrow I^{-} + AsO_4^{3-}$

Oxidation half.

$AsO_3^{3-} \longrightarrow AsO_4^{3-}$

Reduction half.

$IO_3^{-} \longrightarrow I^{-}$

Balancing of oxidation half reaction:

$AsO_3^{3-} \longrightarrow AsO_4^{3-}$

H_2O: $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-}$

H^{+}: $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^{+}$

e^{-}: $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^{+} + 2e^{-}$ (1)

Balancing of reduction half reaction:

$IO_3^{-} \longrightarrow I^{-}$

H_2O: $IO_3^{-} \longrightarrow I^{-} + 3H_2O$

H^{+}: $IO_3^{-} + 6H^{+} \longrightarrow I^{-} + 3H_2O$

e^{-}: $IO_3^{-} + 6H^{+} + 6e^{-} \longrightarrow I^{-} + 3H_2O$ (2)

Multiply Equation (1) by 3 and than add both the equations.

$3AsO_3^{3-} + 3H_2O \longrightarrow 3AsO_4^{3-} + 6H^{+} + 6e^{-}$

$IO_3^{-} + 6H^{+} + 6e^{-} \longrightarrow I^{-} + 3H_2O$

$3AsO_3^{3-} + IO_3^{-} \longrightarrow I^{-} + 3AsO_4^{3-}$

Example 9:

$$Cr^{3+} + BiO_3^{1-} \longrightarrow Cr_2O_7^{2-} + Bi^{3+}$$

Oxidation half.

$$Cr^{3+} \longrightarrow Cr_2O_7^{2-}$$

Reduction half.

$$BiO_3^{1-} \longrightarrow Bi^{3+}$$

Balancing of oxidation half reaction:

Cr: $2Cr^{3+} \longrightarrow Cr_2O_7^{2-}$

H_2O: $2C_r^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2}$

H^+: $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+$

e^-: $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$ (1)

Balancing of reduction half reaction:

$BiO_3^{1-} \longrightarrow Bi^{3+}$

H_2O: $BiO_3^{1-} \longrightarrow Bi^{3+} + 3H_2O$

H^+: $BiO_3^{1-} + 6H^+ \longrightarrow Bi^{3+} + 3H_2O$

e^-: $BiO_3^{1-} + 6H^+ + 2e^- \longrightarrow Bi^{3+} + 3H_2O$ (2)

Multiply Equation (2) by 3 and than add both equations.

$$2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$$

$$3BiO_3^{1-} + 18H^+ + 6e^- \longrightarrow 3Bi^{3+} + 9H_2O$$

$$2Cr^{3+} + 3BiO_3^{1-} + 4H^+ \longrightarrow 2H_2O + 3Bi^{3+} + Cr_2O_7^{2-}$$

Example 10:

$$Cr_2O_7^{2-} + H_3AsO_3 \longrightarrow H_3AsO_4 + Cr^{3+}$$

Oxidation half.

$$H_3AsO_3 \longrightarrow H_3AsO_4$$

Reduction half.

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Balancing of oxidation half reaction:

$H_3AsO_3 \longrightarrow H_3AsO_4$

H_2O: $H_3AsO_3 + H_2O \longrightarrow H_3AsO_4$

H^+: $H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+$

e^-: $H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2e^-$ (1)

Balancing of reduction half reaction:

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Cr: $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

H_2O: $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

H^+: $Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

e^-: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (2)

Multiply Equation (1) by 3 and than add both equations.

$$\begin{array}{l} 3H_3AsO_3 + 3H_2O \longrightarrow 3H_3AsO_4 + 6H^+ + 6e^- \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\ \hline 3H_3AsO_3 + Cr_2O_7^{2-} + 8H^+ \longrightarrow 4H_2O + 2Cr^{3+} + 3H_3AsO_4 \end{array}$$

Basic Medium:

Example 11:

Balancing according to basic medium.

$CN^- + MnO_4^- \longrightarrow CNO^- + MnO_2$

Oxidation half.

$CN^- \longrightarrow CNO^-$

Reduction half.

$MnO_4^- \longrightarrow MnO_2$

Balancing of oxidation half reaction:

$CN^- \longrightarrow CNO^-$

H_2O: $CN^- + H_2O \longrightarrow CNO^-$

H^+: $CN^- + H_2O \longrightarrow CNO^- + 2H^+$

e^-: $CN^- + H_2O \longrightarrow CNO^- + 2H^+ + 2e^-$

Change the medium of reaction. For the basic medium add $2OH^-$ ions on both sides in above equation.

Add OH^-: $CN^- + H_2O + 2OH^- \longrightarrow CNO^- + 2H^+ + 2OH^- + 2e^-$

$CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e^-$ (1)

Balancing of reduction half reaction

$MnO_4^- \xrightarrow{\qquad} MnO_2$

H_2O: $MnO_4^- \xrightarrow{\qquad} MnO_2 + H_2O$

H^+: $MnO_4^- + 4H^+ \xrightarrow{\qquad} MnO_2 + 2H_2O$

e^-: $MnO_4^- + 4H^+ + 3e^- \xrightarrow{\qquad} MnO_2 + 2H_2O$

Change the medium of reaction. For this purpose and $4OH^-$ ions on both sides in above equation.

OH^-: $MnO_4^- + 4H^+ + 4OH^- + 3e^- \xrightarrow{\qquad} MnO_2 + 2H_2O + 4OH^-$

$MnO_4^- + 2H_2O + 3e^- \xrightarrow{\qquad} MnO_2 + 4OH^-$ (2)

Multiply Equation (1) by 3 and Equation (2) by 2 than add both equation.

$3CN^- + 6OH^- \xrightarrow{\qquad} 3CNO^- + 3H_2O + 6e^-$

$2MnO_4^- + 4H_2O + 6e^- \xrightarrow{\qquad} 2MnO_2 + 8OH^-$

$3CN^- + 2MnO_4^- + H_2O \xrightarrow{\qquad} 2MnO_2 + 3CNO^- + 2OH^-$

Example 12:

Balancing according to basic medium.

$MnO_4^- + C_2O_4^{2-} + H_2O \xrightarrow{\qquad} MnO_2 + CO_2 + OH^-$

Split up equation into oxidation half and reduction half.

Reduction half reaction.

$MnO_4^- \xrightarrow{\qquad} MnO_2$

Oxidation half.

$C_2O_4^{2-} \xrightarrow{\qquad} CO_2$

Balancing of oxidation half reaction:

$MnO_4^- \xrightarrow{\qquad} MnO_2$

H_2O: $MnO_4^- \xrightarrow{\qquad} MnO_2 + 2H_2O$

H^+: $MnO_4^- + 4H^+ \xrightarrow{\qquad} MnO_2 + 2H_2O$

e^-: $MnO_4^- + 4H^+ + 3e^- \xrightarrow{\qquad} MnO_2 + 2H_2O$

For the basic medium add $4OH^-$ ions on both sides.

$MnO_4^- + 4H^+ + 4OH^- + 3e^- \xrightarrow{\qquad} MnO_2 + 2H_2O + 4OH^-$

$MnO_4^- + 4H_2O + 3e^- \xrightarrow{\qquad} MnO_2 + 2H_2O + 4OH^-$

$MnO_4^- + 2H_2O + 3e^- \xrightarrow{\qquad} MnO_2 + 4OH^-$ (1)

Balancing of oxidation half reaction:

$$C_2O_4^{2-} \longrightarrow CO_2$$

C: $$C_2O_4^{2-} \longrightarrow 2CO_2$$

e⁻: $$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \qquad (2)$$

Multiply Equation (1) with 2 and Equation (2) by 3 so that gain of electrons becomes equal to loss of electrons and then add both the equations.

$$2MnO_4^- + 4H_2O + 6e^- \longrightarrow 2MnO_2 + 8OH^-$$

$$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$$

$$2MnO_4^- + 4H_2O + 3C_2O_4^{2-} \longrightarrow 2MnO_2 + 8OH^- + 6CO_2$$

Electrochemical Cells:

"The cell in which a chemical reaction utilizes electrical energy or produces electrical energy is called **electrochemical cell**."

(1) Electrolytic Cell:

(2) Voltaic or Galvanic Cell:

(1) Electrolytic Cell:

"An electrochemical cell in which electric current is used to drive a non–spontaneous redox reaction is called **electrolytic cell**." For example:

(i) Electrolysis of molten NaCl (Down's cell).

(ii) Electrolysis of aqueous NaCl (Nelson's cell).

Electrolysis:

"When a non–spontaneous redox reaction takes place at the expense of electrical energy, the process is called **electrolysis**."

$$NaCl_{(l)} \xrightarrow{\text{Electrolysis}} Na + \frac{1}{2}Cl_2$$

$$2NaCl_{(l)} + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2 + Cl_2$$

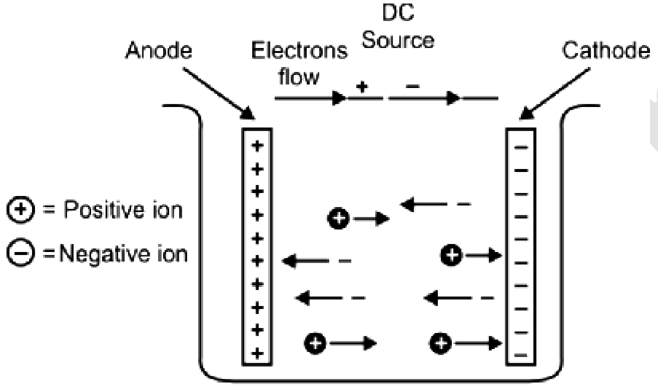
(2) Galvanic Cell:

"An electrochemical cell in which electric current is produced as a result of spontaneous redox reaction is called **galvanic cell or voltaic cell**."

For example, Zn – Cu cell or Daniel cell, nickel – cadmium cell (NICAD). Dry cell, silver oxide batteries, alkaline batteries, lead storage batteries etc.

AN ELECTROLYTIC CELL (WORKING)

Consider the electrolytic cell shown in Figure. When a direct current (D.C) source is connected to the electrodes of the cell containing positive and negative ions of the electrolyte, each electrode acquires an electric charge. Thus, when an electric potential is applied, **the positive ions migrate towards the negative electrode**, called **cathode** and the negative ions move towards the positive electrode, called the **anode**. This movement of ionic charges through the liquid brought by the application of electricity is called **electrolytic conduction** and the apparatus used is known as Electrolytic Cell.



Electrolytic cell

When electrolytic conduction occurs, electrochemical reactions takes place as the ions in the liquid come in contact with the electrodes. At the **anode** the negative ions give up electrons and are, therefore, oxidized. At the **cathode** the positive ions pick up electrons and are reduced. Thus during electrolytic conduction, **oxidation takes place at the anode and reduction takes place at the cathode**. The liquid will continue to conduct electricity only as long as oxidation–reduction reactions, occurring at the electrodes continue.

The electrochemical reactions that occur at the electrodes during electrolytic conduction constitute the phenomenon of electrolysis.

Anode:

"The surface of the cell at which oxidation half reaction takes place. In electrolytic cell positive electrode is called **anode**."

Cathode:

"The surface of the cell at which reduction half reaction takes place. In electrolytic cell negative electrode is called **cathode**."

Products of Some Selective Electrolytic Cell:

(1) Electrolysis of Molten $PbBr_2$:

$$PbBr_{2(l)} \longrightarrow Pb^{2+}_{(l)} + 2Br^{-}_{(l)}$$

At cathode: $Pb^{2+}_{(l)} + 2e^{-} \longrightarrow Pb$

At anode: $2Br^{-} \longrightarrow Br_2 + 2e^{-}$

$$PbBr_{2(l)} \longrightarrow Pb_{(s)} + Br_{2(g)}$$

(2) Electrolysis of Fused NaCl:

$$NaCl_{(l)} \longrightarrow Na^{+}_{(l)} + Cl^{-}_{(l)}$$

At cathode: $2Na^{+}_{(l)} + 2e^{-} \longrightarrow 2Na_{(s)}$

At anode: $2Cl^{-}_{(l)} \longrightarrow Cl_{2(g)} + 2e^{-}$

$$2NaCl_{(l)} \longrightarrow 2Na_{(s)} + Cl_{2(g)}$$

Products of Electrolysis using inert electrodes of platinum or graphite		
Electrolyte	**Cathode**	**Anode**
$PbBr_{2\ (molten)}$	Pb(s)	Br_2(g)
NaCl (molten)	Na(s)	Cl_2(g)
NaCl (aq)	H_2 (g)	Cl_2 (g)
$CuCl_2$ (aq)	Cu(s)	Cl_2 (g)
$CuSO_4$ (aq)	Cu (s)	O_2 (g)
KNO_3 (aq)	H_2 (g)	O_2 (g)
NaOH(aq)	H_2 (g)	O_2 (g)
H_2SO_4 (aq)	H_2 (g)	O_2 (g)
H_2SO_4 (aq)	H_2 (g)	O_2 (g)
NH_4NO_3 (aq)	H_2 (g)	O_2 (g)

(3) Electrolysis of Aqueous NaCl:

$$NaCl_{(l)} \longrightarrow Na^{+}_{(l)} + Cl^{-}_{(l)}$$

At cathode: $2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-}$

At anode: $2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

$$2Cl^{-} + 2H_2O \longrightarrow 2OH^{-} + H_2 + Cl_2$$

(4) Electrolysis of Aqueous $CuCl_2$:

$$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^{-}$$

At cathode: $Cu^{2+} + 2e^{-} \longrightarrow Cu$

At anode: $2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

$$CuCl_2 \longrightarrow Cu + Cl_2$$

(5) Electrolysis of Aqueous $CuSO_4$ (graphite electrode):

$$CuSO_4 \longrightarrow Cu^{2+} + 2SO_4$$

At cathode: $Cu^{2+} + 2e^{-} \longrightarrow Cu$

At anode: $2OH^{-} \longrightarrow H_2O + \frac{1}{2} O_2 + 2e^{-}$

$$Cu^{2+} + 2OH^{-} \longrightarrow H_2O + \frac{1}{2} O_2 + Cu$$

(6) Electrolysis of Aqueous $CuSO_4$ (copper electrode):

$$CuSO_4 \longrightarrow Cu^{2+} + 2SO_4$$

At cathode: $Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$

At anode: $Cu_{(s)} \longrightarrow Cu^{2+} + 2e^{-}$

$$Cu^{2+}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+} + Cu_{(s)}$$

(7) Electrolysis of Aqueous KNO_3:

$$KNO_3 \longrightarrow K^+ + NO_3^-$$

At cathode: $4H^+ + 4e^- \longrightarrow 2H_2$

At anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

$$4H^+ + 4OH^- \longrightarrow 2H_2O + O_2 + 2H_2$$

or $2H_2O \longrightarrow O_2 + 2H_2$

H^+ has greater reduction potential than K^+, so it is reduced, OH^- has high oxidation potential than NO_3^-.

(8) Electrolysis of Aqueous NaOH and H_2SO_4 have same products and same chemical reaction as in case of KNO_3.

(9) Electrolysis of Aqueous $AgNO_3$ in the presence of HNO_3

At cathode: $Ag^+_{(aq)} + 1e^- \longrightarrow Ag_{(g)}$

At anode: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + 1e^-$

1. Electrolysis of Fused Salts:

When a fused salt is electrolyzed, the metal ions arrive at the cathode which being negatively charged supplies electrons to them and thus discharge the cations. The anions move towards the anode, give up their electrons and are thus discharged. In the case of lead chloride the equations for electrode processes are given as under:

$Pb^{2+}_{(l)} + 2e^- \longrightarrow Pb_{(s)}$ (Reduction)

$Cl^-_{(l)} \longrightarrow Cl_{(g)} + e^-$ (Oxidation)

The electrode process is followed by the formation of Cl_2 molecule.

$$Cl_{(g)} + Cl_{(g)} \longrightarrow Cl_{2(g)}$$

Electrons flow through the external circuit from anode to cathode. The electric current is conducted through the cell by the ions and through the external circuit by the electrons.

2. Electrolysis of Aqueous Solution of Salts:

The electrolysis of aqueous solution is somewhat more complex because of the ability of water to be oxidized as well as reduced and the products of electrolysis are not precisely predictable. Some metal cations are not discharged from their aqueous solutions. While electrolyzing aqueous sodium nitrate solution, sodium ions present at cathode are not discharged. A small concentration of hydroxonium and hydroxyl ions arises from the dissociation of water:

$$2H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

Hydroxonium ions accept electrons from the cathode to form hydrogen atoms:

$H_3O^+_{(aq)} + e^- \longrightarrow H_{(g)} + H_2O$ (Reduction)

Subsequently, hydrogen atoms combine rapidly to form hydrogen molecules.

$$H_{(g)} + H_{(g)} \longrightarrow H_{2(g)}$$

Although the concentration of hydroxonium ions is only 10^{-7} mole dm^{-3} in water, when these are discharged more ions are formed by further dissociation of water molecules. This give a continuous supply of hydroxonium ions to be discharged. Sodium ions remains in solution, while hydrogen is evolved at the cathode. Thus reduction of the solute cations depends on the relative ease of the two competing reactions.

At the anode both nitrate and hydroxide ions are present. Hydroxide ions are easier to discharge than nitrate ions. Nitrate ions remains in solution while the electrode reaction is:

$$OH^-_{(aq)} \longrightarrow OH_{(aq)} + e^-$$

Followed by

$$4OH^- \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$$

The expected order of the discharge of ions may also depend upon their concentrations.

Electrolysis Processes of Industrial Importance:

1. Electrolysis cell is used for **preparation of sodium metal** and Cl_2. It is also called **Down's cell**.

   In this cell, molten sodium chloride is electrolyzed between iron cathode and graphite anode. Chlorine is obtained as a by – product.

$$NaCl_{(s)} \longrightarrow Na^+ + Cl^-$$

At cathode:

$$Na^+_{(l)} + e^- \longrightarrow Na_{(s)}$$

At anode:

$$Cl^-_{(l)} \longrightarrow Cl_{(g)} + e^-$$

$$Cl_{(g)} + Cl_{(g)} \longrightarrow Cl_{2(g)}$$

Net Cell Reaction:

$$2NaCl \longrightarrow 2Na + Cl_2$$

2. **Caustic Soda:** is obtained on industrial scale by the electrolysis of concentrated aqueous solution of sodium chloride (brine) using titanium anode and mercury or steel cathode (Nelson's Cell).

At anode:

$$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$$

At cathode:

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

By combining the electrode reactions and including Na^+ ions (which are actually spectator ions) the overall reaction is

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Cl_{2(g)} + H_{2(g)} + 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

3. **Magnesium and calcium** metals are extracted by the electrolysis of their fused chlorides.
4. Aluminum is extracted by electrolyzing fused bauxite ($Al_2O_3 . 2H_2O$) in the presence of fused cryolite (Na_3AlF_6) (Hall-Beroult's Process).
5. **Anodized aluminum** 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 aluminum oxide layer resists attack by corrosive agents. The freshly anodized aluminum is hydrated and can absorb dyes.
6. Electrolytic cell can also be used for the **purification of copper** where impure copper is made the anode and a thin sheet of pure copper is made the cathode. Copper sulphate solution is used as an electrolyte.
7. Copper, silver, nickel or chromium **plating** is done by various types of electrolytic cells.

VOLTAIC CELL OR GALVANIC CELL

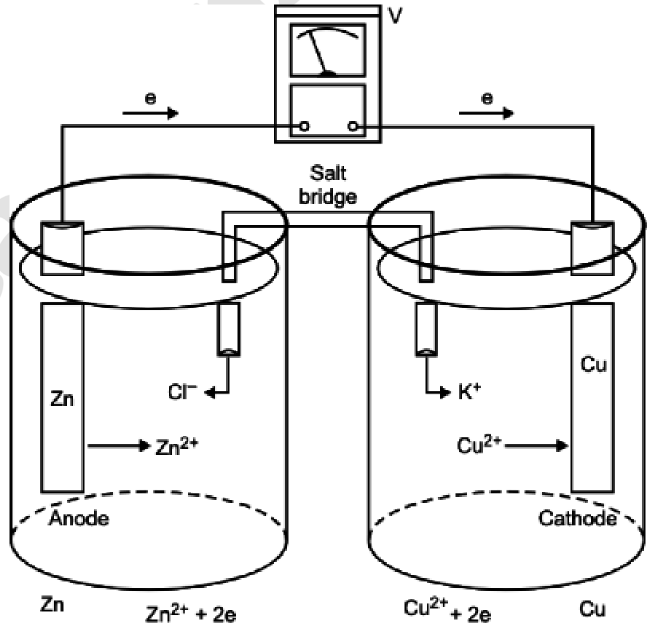
"An electrochemical cell in which electricity is produced as a result of spontaneous redox reaction in called **galvanic cell or voltaic cell**."

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

(a) Construction of the Cell:

A voltaic or a galvanic cell consists of two half–cells that are electrically connected. Each half–cell is a portion of the total cell in which a half reaction takes place. The left half–cell consists of a strip of zinc metal dipped in IM solution of zinc sulphate giving the following equilibrium:

$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$



A Galvanic Cell

The right half–cell is a copper metal strip that dips into IM copper sulphate solution and the equilibrium here is represented as follows.

$$Cu_{(s)} \xrightarrow{\hspace{2cm}} Cu^{+2}_{(aq)} + 2e^{-}$$

A **salt bridge** connects these half–cells electrically. If the solutions were to mix, direct chemical reactions would take place, destroying the half–cells. The salt bridge contains an aqueous solution of **potassium chloride in a gel**. Since zinc tends to lose electrons more readily than copper, Zn electrode takes on a negative charge relative to the copper electrode. If the external circuit is closed by connecting the two electrodes as shown in the figure, electrons flow from the zinc through the external circuit to copper electrode.

(b) Cell Reaction:

The reactions, which occur at each electrodes, are called **half–cell reactions**.

At anode:

$$Zn_{(s)} \xrightarrow{\hspace{2cm}} Zn^{2+}_{(aq)} + 2e^{-}$$

At cathode:

$$Cu^{2+}_{(aq)} + 2e^{-} \xrightarrow{\hspace{2cm}} Cu^{o}_{(s)}$$

Net Cell Reaction:

$$Zn + Cu^{2+} \xrightarrow{\hspace{2cm}} Cu + Zn^{2+}$$

Representation of Cell Reaction:

Oxidation || Reduction or $M/M^{+} \parallel M^{+}/M$

Where M is metal, M^{+} is metal ion and || is salt bridge. Daniel cell is represented as

$$Zn_{(s)}/Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)}/Cu_{(s)}$$

(c) Sign of the Electrodes in Galvanic Cell:

In galvanic cell anode is negative and cathode is positive. In case of electrolytic cells cathode is negative and anode is positive.

(d) FUNCTION OF SALT BRIDGE

Salt bridge or porous partition makes the **solution electrically neutral**. Zinc ions are produced in the zinc compartment and number of Zn^{2+} ions increase from the sulphate ions. Salt bridge is filled with KCl or KNO_3 in gel. Cl^{-} ions in the salt bridge move toward zinc compartment to neutralize the excess Zn^{2+}. Similarly in copper compartment, number of Cu^{2+} ions are decreasing but SO_4^{2} ions are constant. The solution of copper compartment becomes negative. K^{+} ions of the salt bridge move toward copper and neutralize it.

If salt bridge or porous partition will not be used, net charge accumulating in the beakers would immediately stop the flow of electrons through external wire. As a result, the oxidation – reduction reaction will stop.

(e) Electromotive Force or EMF of Cell or Cell Potential:

The electric current obtained from galvanic cell is a result of electrons being pushed or forced from the negative electrode, through an external wire, to positive electrode. The force with which these electrons move through the wire is called **electromotive force or EMF**. It is measured in volts. The EMF produced by the cell is also called **cell potential or E_0 cell**.

E_0 cell is calculated as:

$$E_{0cell} = E_{0cathode} - E_{0anode}$$

$$= 0.34 - (-0.07)$$

$$E_{0cell} = 1.1 \text{ volt.}$$

(f) Reversibility in the Voltaic Cell:

In a voltaic cell, the electric current in the external circuit can be used to light a bulb, drive a motor and so on. On the other hand, if the external circuit is replaced by a source of electricity that opposes the voltaic cell, the electrode reactions can by reversed. Now the external source pushes the electrons in the opposite direction and supplies energy to the cell so that the reverse non–spontaneous reaction occurs. Such a cell is called **reversible cell or secondary cell**.

For the zinc copper cell the half–cell reactions are reversed to give

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

and the overall reaction becomes.

$$Zn^{2+}_{(aq)} + Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$$

Now, oxidation occurs at the copper electrode and reduction takes place at the zinc electrode and the cell operates as an electrolytic cell in which energy from an external source drives a non–spontaneous reaction.

Whether a cell operates as a voltaic or an electrolytic the electrode at which reduction occurs is called the **cathode** while the electrode at which oxidation takes place is called the **anode**.

SINGLE ELECTRODE POTENTIAL

"The difference of potential of cell, consisting of a particular electrode and the standard hydrogen electrode which have zero potential, is called **electrode potential**."

If concentration of solutes are one molar at 25°C (298 K) and one atmospheric pressure potential measured is called **standard electrode potential**. It is abbreviated as E_0 where "0" knot shows the standard conditions (298 K and 1 atmosphere).

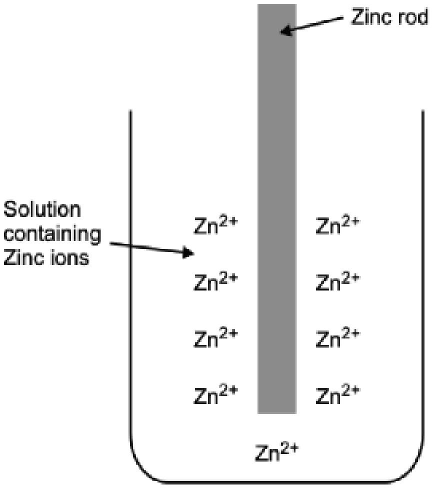
Construction of Single Electrode:

A metal strip is dipped in the one molar solution of its own ion. for example in zinc electrode, zinc strip is dipped in Zn^{2+} or $ZnSO_4$ solution which provides Zn^{2+} ions.

When an electrode is dipped in own ions in solution, a electrode potential is set up. **An equilibrium is set up** between the metal atoms and metal ions in solution.

$$M_{(s)} \rightleftharpoons M^{+}_{(aq)} + e^{-}$$

It is believed that when a metal is placed in solution, some of its atoms tend to give electrons to the piece of metal and pass into the solution as positively charged ions. At the same time, the metallic ions already present in solution tend to take up electrons from the piece of metal and deposit themselves as neutral atoms. Whichever **tendency is greater** in a given case determines whether the metal becomes **negatively or positively** charged, compared with the solution.



Equilibrium between zinc and its ions in solution

When equilibrium is attained, the two opposing processes continue at the same rate and there is no further change in the potential difference. A rod of zinc, for example, will bear an accumulation of negative charges owing to the net ionization of some of its atoms and this will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in Figure. The equilibrium can, therefore, be represented as:

$$Zn_{(s)} \rightleftharpoons Zn^{+}_{(aq)} + 2e^{-}$$

MEASUREMENT OF ELECTRODE POTENTIAL

It is impossible to measure the electrode potential of a single electrode. However we can measure the difference of reduction potential for any two half reactions. If cell potential E_0 cell and the E_0 for one of the half reaction are known, the E_0 for other reaction can be calculated. Half reaction which is chosen for this purpose is reduction potential of hydrogen. Its value is taken zero. It is an arbitrary value.

$$E_{0cell} = E_{0(SHE)} + E_{0(unknown\ electrode)}$$

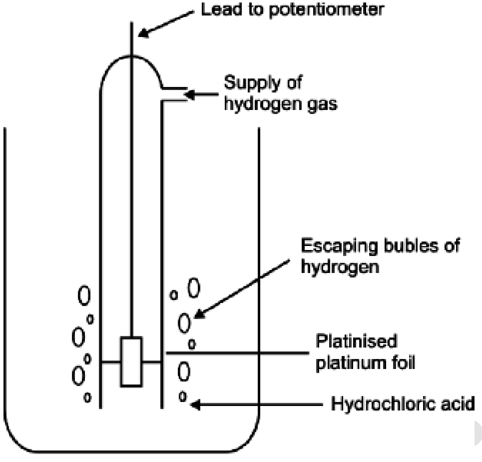
STANDARD HYDROGEN ELECTRODE (SHE)

A standard hydrogen electrode which is used as a standard is shown in figure.

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**. Pure hydrogen gas at one atmosphere pressure is continually bubbled into $1MHCl$ solution. The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The potential of this electrode is arbitrary taken as zero.

$2H^{2+}_{(aq)} + 2e^{-} \longrightarrow H_{2(g)}$ 0.0 volt (Reduction half reaction)

$H_{2(g)} \longrightarrow 2H^{2+}_{(aq)} + 2e^{-}$ 0.0 volt (Oxidation half reaction)

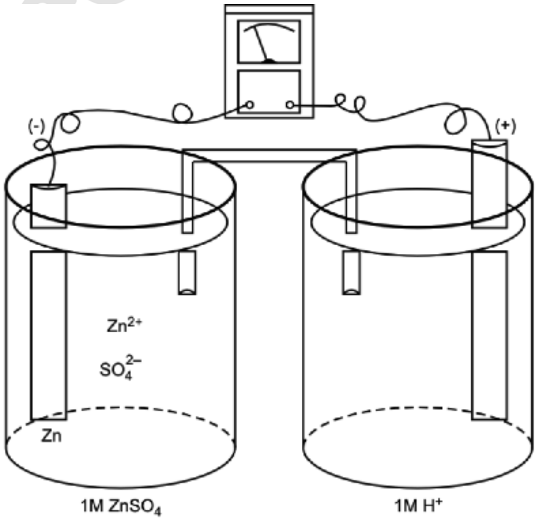


Standard Hydrogen Electric

For example, measurement of two electrode potentials copper and zinc are given below.

MEASUREMENT OF ZINC ELECTRODE POTENTIAL

In any measurement of electrode potential, the concerned electrode is joined with the standard hydrogen electrode and a galvanic cell is established. The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride may be used to provide a highly conducting path between the two electrolytic solutions. The potential difference is measured by a voltmeter, which gives the potential of the electrode, as the potential of SHE is zero. An oxidation or reduction may take place at SHE depending upon the nature of the electrode, which is coupled with it.



A galvanic cell that can be used to determine the standard reduction potential of Zn^{2+}

To measure the electrode potential of zinc, a galvanic cell is established between zinc electrodes, dipped in 1M solutions of Zn^{2+} ions and standard hydrogen electrode at 25°C as shown in Figure. 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 gas. In other words, the half reaction

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$$

has greater tendency to occur than

$$H_{2(g)} \longrightarrow 2H^+ + 2e^-$$

by 0.76 volts. The standard electrode potential of zinc is, therefore 0.76 volts. The electrode reactions will be shown as follows.

At anode:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

At cathode:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

$$E_{0cell} = E_{0cathode} - E_{0anode}$$

$$= 0.0 - 0.76$$

$$E_{0cell} = -0.76 \text{ volt.}$$

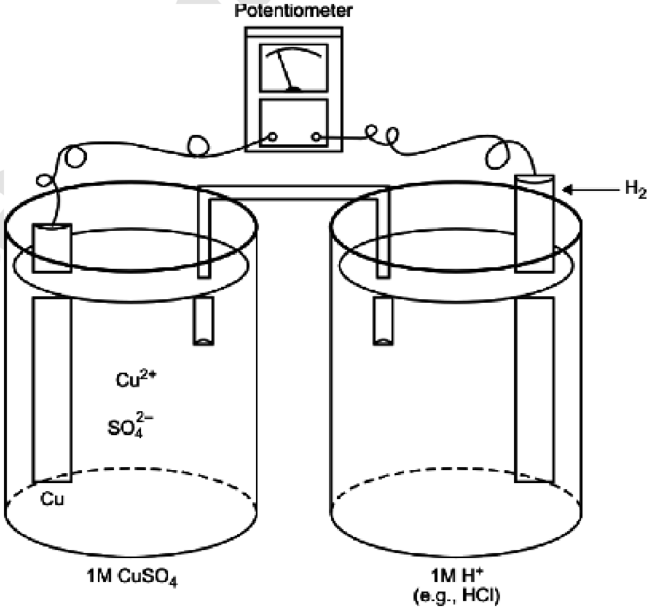
Cell representative:

Oxidation // Reduction

$Zn_{(s)}/Zn^{2+}$ // $H^+_{(aq)}/H_2/Pt.$

Measurement of Copper Electrode Potential:

The electrode potential of copper can also be measured using the same type of galvanic cell in which copper is an electrode dipped in 1M solution of its ions Figure.



The hydrogen electrode used in galvanic cell

Under standard conditions, the voltmeter reads 0.34 volts and the deflections is in such as direction as to indicate that hydrogen has a greater tendency to give off electrons than copper has. In other words, the half reaction.

$$H_{2(g)} \xrightarrow{\qquad} 2H^{+} + 2e^{-}$$

has a greater tendency to occur than

$$Cu_{(s)} \xrightarrow{\qquad} Cu^{2+} + 2e^{-}$$

by 0.34 volts. So the standard electrode potential of Cu is 0.34 and the reactions taking place at the two electrons will be shown as follows.

$$E_{0cell} = E_{0cathode} - E_{0anode}$$

$$= 0.34 - 0.0$$

$$E_{0cell} = 0.34 \text{ volts}$$

Cell representation:

Oxidation // Reduction

$H_{2(g)}/Pt^{+},\ H^{+}_{(aq)}\ //\ Cu^{2+}_{(aq)},\ Cu_{(s)}$.

Standard Cell Potential or Standard Electrode Potential:

"The difference of potential between two electrodes when concentration of ions is 1.00M, temperature is 25^{O}C and pressure of gases is one atmosphere is called **standard cell potential**".

$$E_{0cell} = E_{0cathode} - E_{0anode}$$

ELECTROCHEMICAL SERIES

"When elements are arranged in the order of their standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series."

Such a series of elements is shown in Table. The electrode potentials have been given in the reduction mode as recommended by the International Union of Pure and Applied Chemistry (IUPAC). In some textbooks, half reactions are written in the oxidation mode and the corresponding potentials are oxidation potentials. The magnitude of the potential is not affected by the change in mode but the sings are reversed. Therefore, before using standard electrode potential data, it is necessary to ascertain which mode is being used. An important point to remember in using reduction potential values is that they relate only to standard conditions i.e. 1M solution of ions, 25^{O}C and one atmospheric pressure. Changes in temperature concentration. Pressure will affect the values of reduction potential.

Standard Reduction Potentials (E_0) of Elements at 298 K		
Element	**Electrode**	**Standard Reduction Potential (E_0)**
Li	$Li^+ + e^- \longrightarrow Li$	–3.045
K	$K^+ + e^- \longrightarrow K$	–2.925
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
Na	$Na^+ + e^- \longrightarrow Na$	–2.714
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.37
Al	$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
Cd	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.403
Nl	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
Pb	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.126
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.0000
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
Cu	$Cu^{2+} + e^- \longrightarrow Cu$	0.521
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	0.535
Fe	$Fe^{3+} + 3e^- \longrightarrow Fe$	0.771
Ag	$Ag^+ + e^- \longrightarrow Ag$	0.7994
Hg	$Hg^{2+} + 2e^- \longrightarrow Hg$	0.885
Br_2	$Br_2 + 2e^- \longrightarrow 2Br^-$	1.08
Cl_2	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.360
Au	$Au^{3+} + 3e^- \longrightarrow Au$	1.50
F_2	$F_2 + 2e^- \longrightarrow 2F^-$	2.87

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. For 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.

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $E_0 = +0.34$ volt.

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ $E_0 = -0.76$ volt.

Since zinc is being oxidized so the reverse reaction will be considered.

$Cu^{+2} + Zn \longrightarrow Cu + Zn^{+2}$ $E_{0cell} = +1.1$ volt.

The overall reaction will thus be

$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$ $E_{0cell} = +1.1$ volt.

The overall positive value of the reaction potential suggests that the process is energetically feasible. If the sum of E_0 value of the two half cell reaction is negative then there reaction will not be feasible.

$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ $E_{0cell} = -0.34$ volt.

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ $E_0 = -0.76$ volt.

$Cu_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Cu^{2+} + Zn_{(s)}$ $E_0 = -1.1$ volt.

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. Similarly the electrode occupying the lower position in the series will act, as a cathode and reduction will take place on it. Let us find out a cell potential of $Cu - Zn$ cell.

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation half reaction)

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Reduction half oxidation)

$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$ (Net cell reaction)

The cell voltage or EMF of the cell is given by

$E_{0cell} = E_{0x} + E_{0red}$

$= 0.76 + 0.34$

$E_{0cell} = 1.10$ volt.

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 or Reduced:

The value of the reduction potential of a metal or a non–metal tells us the tendency to lose electrons and act as a reducing 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 hence to act as an oxidizing agent. For example, ions like Au^{3+}, Pt^{+2}, Hg^{2+} Ag^{+}, Cu^{2+} and the non–metal 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.

The series tell us that strong oxidizing agents have a large positive value of standard reduction potentials while strong reduction agents have a large negative value.

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**. For example, metals like Li, Na, K and Rb are highly reactive. Coinage metals, Cu, Ag and Au are the least reactive because they have positive reduction potentials. Similarly, metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas, while the 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 from metal ions and so weaker is its tendency to displace H_2. For example, metals like Au, Pt and Cu which have sufficiently high positive values of reduction potentials, do not liberate hydrogen from acids. While 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.

$Mg + 2HCl \xrightarrow{\qquad\quad} MgCl_2 + H_2$

$Au + HCl \xrightarrow{\qquad\quad}$ no reaction.

6. Displacement of one Metal by another from its Solution:

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. For example, Fe can displace Cu from $CuSO_4$, Zn does not displace Mg from solution of $MgSO_4$.

$CuSO_4 + Fe \xrightarrow{\qquad\quad} FeSO_4 + Cu$

$MgSO_4 + Zn \xrightarrow{\qquad\quad}$ no reaction.

Fe displace copper because it is above in electrochemical series.

MODERN BATTERIES AND FUEL CELLS

1. Primary Cell:

"The voltaic or galvanic cell which cannot be recharged is called **primary cell**."

For example, alkaline battery.

2. Secondary Cell:

"The voltaic or galvanic cell which can be charged is called **secondary cell**."

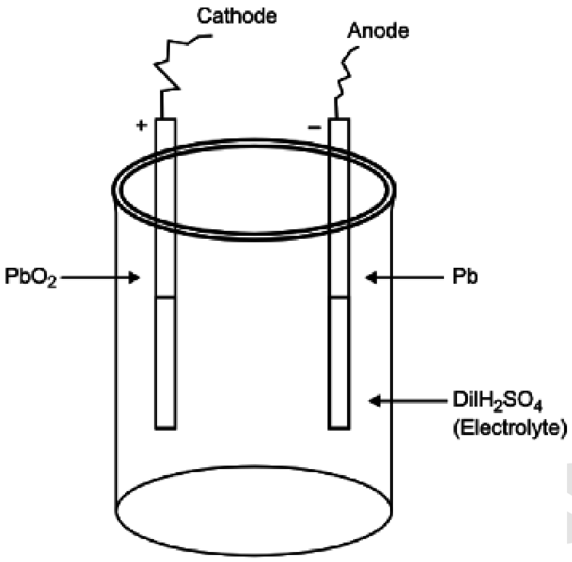
For example, lead storage battery.

LEADS STORAGE BATTERY OR LEAD ACCUMULATOR (RECHARGEABLE)

"The combination of two or more cells is called **battery**."

Automobile battery is lead storage battery. Usually it has six cells. The voltage of **each cell is 2V** and total voltage is **12V**.

In this battery anodes are made up of **lead metal** while cathodes are made up of **lead oxide PbO_2**. The electrolytic solution, in which these electrodes are immersed is 30% sulphuric acid solution having density 1.25 g/cm^3. When two electrodes are connected through an external circuit, electric current is produced.



Single cell of battery

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 $PbSO_4$.

$$\begin{array}{l} Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^- \qquad \text{(Anode)} \\ Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} \\ \hline Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^- \end{array}$$

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 and PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water as follows:

$$\begin{array}{l} PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)} \\ Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \\ \hline PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O \end{array}$$

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.

Net Cell Reaction:

At anode:

$$Pb_{(s)} + SO_4^{2-} \longrightarrow PbSO_{4(s)} + 2e^-$$

At cathode:

$$\underline{PbO_{2(s)} + 4H^{+}_{(aq)} + SO_4^{2-} + 2e^{-} \longrightarrow PbSO_{4(s)} + H_2O_{(l)}}$$

$$PbO_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

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. These reactions are summarized as follows:

At cathode:

$$PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$\underline{Pb^{2+}_{(aq)} + 2e^{-} \longrightarrow Pb_{(s)}}$$

$$PbSO_{4(s)} + 2e^{-} \longrightarrow Pb_{(s)} + SO^{2-}_{4(aq)}$$

At anode:

$$PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$\underline{Pb^{2+}_{(aq)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + 2e^{-}}$$

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + SO_4^{2-} + 2e^{-}$$

The overall reaction is:

$$2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO^{2-}_{4(aq)}$$

During the process of discharging, the concentration of the acid falls decreasing its density to 1.15 g cm^{-3}. After recharging, the acid is concentrated again bringing its density to its initial value of 1.25 g cm^{-3}. At the same time the voltage of the cell, which has dropped during discharging, return to around 2 volts.

ALKALINE BATTERY (NON-RECHARGEABLE)

It is a dry alkaline cell, which uses zinc and manganese dioxide as reactants. Zinc rod serves as the anode and manganese dioxide function as the cathode. The electrolyte, however, contains potassium hydroxide (non-rechargeable) (alkaline). The battery is enclosed in a steel container. The zinc anode is also slightly porous giving it a larger surface area. This allows the cell to deliver more current than the common dry cell. It has also longer life.

The reaction in the alkaline battery are shown as follows:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

$$\underline{Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Zn(OH)_{2(s)}}$$

$$Zn_{(s)} + 2OH^{-}_{(aq)} \longrightarrow Zn(OH)_{2(s)} + 2e^{-} \qquad \text{(at anode)}$$

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^{-} \longrightarrow Mn_2O_{3(s)} + 2OH^{-}_{(aq)} \quad \text{(at cathode)}$$

Net Cell Reactant:

$$Zn_{(s)} + 2MnO_{2(s)} + 2H_2O_{(l)} \longrightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$$

The voltage of this cell is 1.5 volt.

Silver Oxide Battery (Non-rechargeable / Rechargeable):

These tiny and rather expensive batteries have become popular as power sources in electronic watches, auto exposure cameras and electronic calculators. The cathode is of silver oxide, Ag_2O and the anode is of zinc metal. The following reactions occur in a basic electrolyte.

At anode:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$$

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$$

At cathode:

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$$

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow 2Ag_{(s)} + Zn(OH)_{2(s)}$$

Net Cell Reaction:

The voltage of this cell is 1.5 volt.

Nickel Cadmium Cell (Re-chargeable):

A strong cell that has acquired wide spread use in recent years in the NICAD or Nickel Cadmium battery. The anode is composed of cadmium, which undergoes oxidation in an alkaline electrolyte.

$$Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^- \qquad \text{(at anode)}$$

$$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^- \qquad \text{(at cathode)}$$

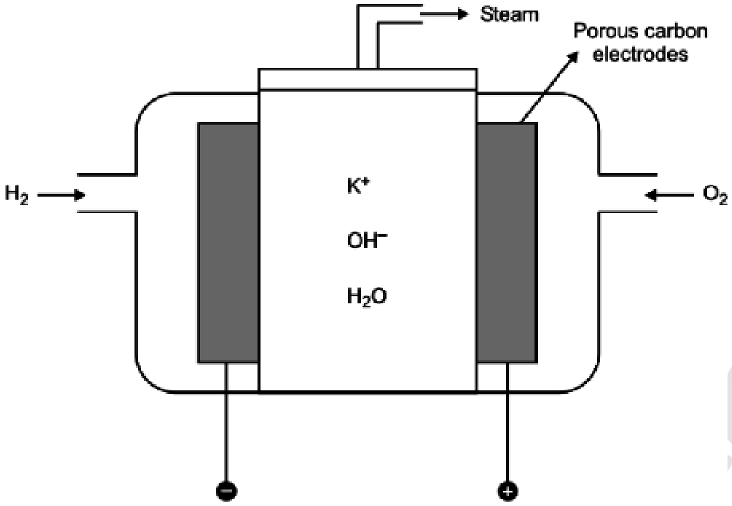
The net cell reaction during the discharge is therefore:

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

The voltage of cell is 1.4 volt.

FUEL CELLS (RECHARGEABLE)

Fuel cells are other means by which chemical energy may be converted into electrical energy. When gaseous fuels, such as hydrogen and oxygen are allowed to undergo a reaction, electrical energy can be obtained. This type of a cell finds importance in space vehicles. The cell is illustrated in Figure. The electrodes are hollow tubes made of porous compressed carbon impregnated with platinum, which acts as a catalyst.



Hydrogen-oxygen fuel cell

The electrolyte is KOH. At the electrodes, hydrogen is oxidized to water and oxygen is reduced to hydroxide ions.

$[H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-]\ 2$ (at anode)

$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$ (at cathode)

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ (overall reaction)

Such a cell runs continuously as long as reactants are supplied. The voltage of cell is 0.9 volt.

This fuel cell is operated at a high temperature so that the water formed as product of the cell reaction evaporates and may be condensed and used as **drinking water for an astronaut**. A number of these cells are usually connected together so that several kilowatts of power can be generated.

The fuel cell produce electricity and pure water during space flights. Fuel cells are light, portable and source of electricity. Many fuel cells do not produce pollutants. Reactions of some other fuel cells are given below:

(i) $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$

(ii) $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$

(iii) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Note: Fuel cell is refueled instead of re-charged.

EXERCISE

Q.1 Multiple choice questions. For each question there are four possible answer a, b, c and d. chose the one your consider correct.

(i) The cathodic reaction in the electrolysis of dil. H_2SO_4 with Pt electrodes is:
- (a) Reduction
- (b) Oxidation
- (c) Both oxidation and reduction
- (d) Neither oxidation or reduction

(ii) Which of the following statements is not correct about galvanic cell?
- (a) Anode is negatively charged
- (b) Reduction occurs at anode
- (c) Cathode is positively charge
- (d) Reduction occurs at cathode.

(iii) Stronger the oxidizing agent, greater is the:
- (a) Oxidation potential
- (b) Reduction potential
- (c) Redox potential
- (d) E.M.F of cell.

(iv) If the salt bridge is not used between two half cells, then the voltage.
- (a) Decrease rapidly
- (b) Decrease slowly
- (c) Does not change
- (d) Drops to Zero

(v) If a strip of Cu metal is placed in a solution of $FeSO_4$:
- (a) Cu will be precipitated out
- (b) Fe is precipitated out
- (c) Cu and Fe both dissolve
- (d) No reaction take place

ANSWERS

Answers		Reasons
(i)	(a)	When electrolysis of dil. H_2SO_4 is done with Pt-electrodes, H^+ ions are reduced to H_2 at cathode. $2H^+ + 2e^- \longrightarrow H_2$
(ii)	(b)	Reduction always takes place at cathode and oxidation at anode. In galvanic cell, anode is negatively charged because loss of electrons takes place here whereas cathode is positively charged because electrons enter into the cell through it and reduction takes place here.
(iii)	(b)	Reduction potential is the tendency of an element to gain electrons and to act as oxidizing agent. Greater the reduction potential. Stronger the oxidizing agent.
(iv)	(d)	In the absence of salt bridge, there is net charge accumulation in the two half cells. As a result of that, the two half cell reactions stops and cell voltage drops to zero.
(v)	(d)	Cu being below Fe in electrochemical series, cannot displace it from $FeSO_4$. And hence, no. reaction occurs.

Q.2 Fill in the blanks:

(i) The oxidation number of O-atom is ———— in OF_2 and is ———— in H_2O_2

(ii) Conductivity of metallic conductors is due to the flow of ———— while that of electrolytes is due to flow of ————.

(iii) Reaction taking place at the ———— is termed as oxidation and at the ———— is called as reduction.

(iv) ———— is set up when a metal is dipped in its own ions.

(v) Cu metal ———— the Cu-cathode when electrolysis is performed for $CuSO_4$ solution with Cu-cathodes.

(vi) The reduction potential of Zn is ———— volts and its oxidation potential is ———— volts.

(vii) In a fuel cell, ———— react together in the presence of ————.

ANSWERS

(i)	+2, –1	(ii)	Electrons, ions	(iii)	Anode, cathode
(iv)	Electrode potential	(v)	Deposited at	(vi)	–0.76, +0.76
(vii)	Hydrogen and oxygen, KOH				

Q.3 Mark the following statement true or false:

(i) In electrolytic conduction, electrons flow through the electrolyte.

(ii) In the process of electrolysis, the electrons in the external circuit flow from cathode to anode.

(iii) Sugar is a non-electrolyte in solid form and when dissolved in water will allow the passage of an electric current.

(iv) A metal will only allow the passage of an electric current when it is in cold state.

(v) The electrolytic products of aqueous copper (II) chloride solution are copper and chlorine.

(vi) Zinc can displace iron from its solution.

(vii) S.H.E acts as cathode when connected with Cu-electrode.

(viii) A voltaic cell produces electrical energy at the expense of chemical energy.

(ix) Lead storage battery is not a reversible cell.

(x) Cr changes its oxidation number when $K_2Cr_2O_7$ is reacted with HCl.

ANSWERS

Answers		Reasons
(i)	False	In electrolytic conduction, ions flow through the electrolyte.
(ii)	False	In the process of electrolysis, the electrons in the external circuit flow from anode to cathode.
(iii)	False	Sugar is non-electrolyte in solid form and when dissolved in water will not allow the current to pass through it.
(iv)	False	Metal will allow the passage of electric current when it is in cold or hot state.
(v)	True	In case of aqueous solution of $CuCl_2$, Cu^{2+} having greater reduction potential, in comparison to H^+ is discharge at cathode to form copper. Whereas at anode, Cl^- ions are discharged in preference with OH^- and Cl_2 gas is formed.
(vi)	True	Since zinc lies above iron in the electrochemical series. Therefore, it can displace iron from its solution.
(vii)	False	S.H.E acts as anode when connected with Cu-electrode. (Because copper has 0.34 volt more tendency to accept electrons than hydrogen and hence copper act as cathode).
(viii)	True	In voltaic cell, spontaneous redox reaction proceeds to produce electrical energy.
(ix)	False	Lead storage battery is a reversible cell.
(x)	True	When $K_2Cr_2O_7$ is reacted with HCl, Cr changes its oxidation state from +6 to +3.

Q.4 (a) Explain the term oxidation number with examples.

(b) Describe the rules used for the calculation of oxidation number of an element in molecules and ions giving examples.

(c) Calculate the oxidation number of chromium in the following compounds:

(i) $CrCl_3$ **(ii)** $Cr_2(SO_4)_3$ **(iii)** K_2CrO_4

(iv) $K_2Cr_2O_7$ **(v)** CrO_3 **(vi)** Cr_2O_3

(vii) $Cr_2O_7^{-2}$

(d) Calculate the oxidation number of elements underlined in the following compounds.

(i) $Ca(\underline{Cl}O_3)_2$ **(ii)** $Na_3\underline{P}O_4$ **(iii)** $Cr_2(\underline{S}O_4)_3$

(iv) $K_2\underline{Mn}O_4$ **(v)** $Na_2\underline{C}O_3$ **(vi)** $H\underline{N}O_3$

(vii) $H\underline{P}O_3$

Ans. For answer of part "a" and "b", see text book.

(c) (i) $CrCl_3$:

$$\begin{aligned}\text{Oxidation no. of Cr} + (\text{Oxidation no. of Cl})3 &= 0\\ Cr + 3(-1) &= 0\\ Cr &= +3\end{aligned}$$

(ii) $Cr_2(SO_4)_3$:

$$\begin{aligned}
2(\text{O.N of Cr}) + 3(\text{O.N of S}) + 12(\text{O.N of O}) &= 0\\
2Cr + 3(+6) + 12(-2) &= 0\\
2Cr + 18 + (-24) &= 0\\
2Cr + 18 - 24 &= 0\\
2Cr &= 6\\
Cr &= \frac{6}{2} = +3
\end{aligned}$$

(iii) K_2CrO_4:

$$\begin{aligned}
2(\text{O.N of K}) + \text{O.N of Cr} + 4(\text{O.N of O}) &= 0\\
2(+1) + Cr + 4(-2) &= 0\\
2 + Cr - 8 &= 0\\
Cr &= +6
\end{aligned}$$

(iv) $K_2Cr_2O_7$:

$$\begin{aligned}
2(\text{O.N of K}) + 2(\text{O.N of Cr}) + 7(\text{O.N of O}) &= 0\\
2(+1) + 2Cr + 7(-2) &= 0\\
+2 + 2Cr - 14 &= 0\\
2Cr &= 12\\
Cr &= \frac{12}{2} = +6
\end{aligned}$$

(v) CrO_3:

$$\begin{aligned}
\text{O.N of Cr} + 3(\text{O.N of O}) &= 0\\
Cr + 3(-2) &= 0\\
Cr - 6 &= 0\\
Cr &= +6
\end{aligned}$$

(vi) Cr_2O_3:

$$\begin{aligned}
2(\text{O.N of Cr}) + 3(\text{O.N of O}) &= 0\\
2Cr + 3(-2) &= 0\\
2Cr - 6 &= 0\\
2Cr &= +6\\
Cr &= \frac{6}{2} = +3
\end{aligned}$$

(vii) $Cr_2O_7^{2-}$:

$$\begin{aligned}
2(\text{O.N of Cr}) + 7(-2) &= -2\\
2Cr - 14 &= -2\\
2Cr &= 14 - 2\\
Cr &= \frac{12}{2} = +6
\end{aligned}$$

(d) (i) $Ca(ClO_3)_2$:

$$\begin{aligned} \text{O.N of Ca} + (\text{O.N of Cl})_2 + 6(\text{O.N of O}) &= 0 \\ +2 + 2Cl + 6(-2) &= 0 \\ +2 + 2Cl - 12 &= 0 \\ 2Cl &= 10 \\ Cl &= \frac{10}{2} = +5 \end{aligned}$$

(ii) $Na_3\underline{P}O_4$:

$$\begin{aligned} 3(\text{O.N of Na}) + \text{O.N of P} + 4(\text{O.N of O}) &= 0 \\ 3(+1) + P + 4(-2) &= 0 \\ 3 + P - 8 &= 0 \\ P &= +5 \end{aligned}$$

(iii) $Cr_2(\underline{S}O_4)_3$:

$$\begin{aligned} 2(\text{O.N of Cr}) + 3(\text{O.N of S}) + 12(\text{O.N of O}) &= 0 \\ 2(+3) + 3S + 12(-2) &= 0 \\ 6 + 3S - 24 &= 0 \\ 3S &= 18 \\ S &= \frac{18}{3} = +6 \end{aligned}$$

(iv) $K_2\underline{Mn}O_4$:

$$\begin{aligned} 2(\text{O.N of K}) + \text{O.N of Mn} + 4(\text{O.N of O}) &= 0 \\ 2(+1) + Mn + 4(-2) &= 0 \\ 2 + Mn - 8 &= 0 \\ Mn &= +6 \end{aligned}$$

(v) $Na_2\underline{C}O_3$:

$$\begin{aligned} 2(\text{O.N of Na}) + \text{O.N of C} + 3(\text{O.N of O}) &= 0 \\ 2(+1) + C + 3(-2) &= 0 \\ C &= +4 \end{aligned}$$

(vi) $H\underline{N}O_3$:

$$\begin{aligned} (\text{O.N of H}) + \text{O.N of N} + 3(\text{O.N of O}) &= 0 \\ +1 + N + 3(-2) &= 0 \\ 1 + N - 6 &= 0 \\ N &= +5 \end{aligned}$$

Q.5 (a) Describe the general rules for balancing a redox equation by oxidation number, method.

(b) Balance the following equations by oxidation number method.

- **(i)** $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$
- **(ii)** $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$
- **(iii)** $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$
- **(iv)** $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$
- **(v)** $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + H_2O$
- **(vi)** $HNO_2 + HI \longrightarrow NO + H_2O + I_2$
- **(vii)** $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$
- **(viii)** $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O + CI$
- **(ix)** $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$

Ans.

(a) Descriptive question, consult text book.

(b) (i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

Steps Involved:

1. Write the oxidation number of each element.

$$Cu^{\circ} + \overset{+1}{H}\,\overset{+5}{N}O_3^{-6} \longrightarrow \overset{+2}{Cu}(\overset{+10}{N}O_3^{-12})_2 + \overset{+4}{N}O_2^{-4} + \overset{+2}{H_2}\overset{-2}{O}$$

2. Identify the elements whose oxidation number have changed.

$$HNO_3 + H\overset{+5}{N}O_3 + Cu^{\circ} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

3. Mention the changed by arrow, also balance same atom on both sides, if they are not equal. Determine change in oxidation and reduction process by loss and gain of electron.

−2e oxidation

$$HNO_3 + Cu^{\circ} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

+1e reduction

4. Equate the number of electrons by multiply −2e with 1 and +1e with 2. So that gain and loss of electrons become equal.

$-2e \times 1 = -2e$

$$HNO_3 + Cu^{\circ} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

$+1e \times 2 = +2e$

5. Use the multiplier as co-efficient with respective substance.

$$\mathrm{HNO_3 + Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O}$$

6. Balance rest of equation by inspection method.

$$\mathrm{2HNO_3 + Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O}$$

* Balanced Equation:

$$\mathrm{Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O}$$

(ii) $\mathrm{Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O}$

* Steps Involved:

1. $$\mathrm{Zn^\circ + \overset{+1}{H}\,\overset{+5}{N}O_3^{-6} \longrightarrow \overset{+2}{Zn}(\,\overset{+10}{N}\;\overset{-12}{O}{}_3)_2 + \overset{+2}{N}\,\overset{-2}{O} + \overset{+2}{H_2}\overset{-2}{O}}$$

2. $$\mathrm{HNO_3 + Zn^\circ + \overset{+5}{H N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O}$$

3. −2e oxidation

$$\mathrm{HNO_3 + Zn^\circ + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O}$$

+3e reduction

4. −2e (3) = −6e

$$\mathrm{HNO_3 + Zn^\circ + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O}$$

+3e (2) = +6e

5. $$\mathrm{HNO_3 + 3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + H_2O}$$

6. $$\mathrm{6HNO_3 + 3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O}$$

* Balance Equation:

$$\mathrm{3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O}$$

(iii) $\mathrm{Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O}$

* Steps Involved:

1. $$\mathrm{Br_2^0 + \overset{+1}{Na}\overset{-1}{OH} \longrightarrow \overset{+1}{Na}\ \overset{-1}{Br} + \overset{+1}{Na}\ \overset{+5}{Br}O_3^{-6} + \overset{+2}{H_2}\overset{-2}{O}}$$

2. $$\mathrm{Br^\circ + Br^\circ + NaOH \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O}$$

3. +1e reduction

$$\mathrm{Br^\circ + Br^\circ + Na\overset{+5}{O}H \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O}$$

−5e oxidation

+1e (5) = +5e

4. $Br^{o} + Br^{o} + \overset{+5}{NaOH} \longrightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$

−5e (1) = −5e

5. $5Br + Br + NaOH \longrightarrow 5NaBr + NaBrO_3 + H_2O$

* Balanced Equation:

$3Br_2 + 6NaOH \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$

(iv) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

* Steps Involved:

1. $\overset{+4}{Mn}O_2^{-4} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}\overset{-2}{Cl_2} + \overset{+2}{H_2}\overset{-2}{O} + \overset{o}{Cl_2}$

2. $HCl + \overset{+4}{MnO_2} + \overset{-1}{HCl} \longrightarrow \overset{+2}{MnCl_2} + Cl_2^{o} + H_2O$

+2ē reduction

3. $HCl + \overset{+4}{MnO_2} + \overset{-1}{HCl} \longrightarrow \overset{+2}{MnCl_2} + \overset{o}{Cl_2} + H_2O$

−1e oxidation

+2e

4. $HCl + \overset{+4}{MnO_2} + \overset{-1}{HCl} \longrightarrow \overset{+2}{MnCl_2} + \overset{o}{Cl_2} + H_2O$

−1e (2) = −2e

5. $HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

6. $2HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

* Balanced Equation:

$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(v) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

* Steps Involved:

1. $\overset{+2}{Fe}\overset{+6}{S}\overset{-8}{O_4} + \overset{+2}{K_2}\overset{+12}{Cr_2}\overset{-14}{O_7} + \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} \longrightarrow \overset{+6}{Fe_2}(\overset{+18}{S}\overset{-24}{O_4})_3 + \overset{+6}{Cr_2}(\overset{+18}{S}\overset{-24}{O_4})_3 + \overset{+2}{K_2}\overset{+6}{S}\overset{-8}{O_4} + \overset{+2}{H_2}\overset{-2}{O}$

2. $\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$

$-1e$ oxidation

3. $\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$

$2x\ (+3\bar{e}) = 6e$ reduction

$-1e\ (6) = -6e$

4. $\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$

$+6\bar{e}$

* Balanced Equation:

5. $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$

(vi) $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

* Steps Involved:

1. $\overset{+1}{H}\ \overset{+5}{N}\ \overset{-6}{O_3} + \overset{+1}{H}\ \overset{-1}{I} \longrightarrow \overset{+2}{N}\ \overset{-2}{O} + \overset{+2}{H_2}\overset{-2}{O} + \overset{o}{I_2}$

2. $H\overset{+5}{N}O_3 + HI^{-} \longrightarrow \overset{+2}{N}O + H_2O + I_2^{o}$

$+3e$ reduction

3. $H\overset{+5}{N}O_3 + HI^{-1} \longrightarrow \overset{+2}{N}O + H_2O + I_2^{o}$

$2 \times -1e = -2e$ oxidation

$+3e(2) = +6e$

4. $H\overset{+5}{N}O_3 + 2HI^{-1} \longrightarrow \overset{+2}{N}O + I_2^{o} + H_2O$

$-2e(3) = -6e$

* Balanced Equation:

$2HNO_3 + 6HI \longrightarrow 2NO + 3I_2 + 4H_2O$

(vii) $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

* Steps Involved:

1. $Cu^{\circ} + \overset{+2}{H_2}\overset{+6}{S}\ \overset{-8}{O_4} \longrightarrow \overset{+2}{Cu}\overset{+6}{S}\ \overset{-8}{O_4} + \overset{+4}{S}\ \overset{-4}{O_2} + \overset{+2}{H_2}\overset{-2}{O}$

2. $Cu^{\circ} + H_2SO_4 + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$

$-2e$ oxidation

3. $Cu^{o} + H_2SO_4 + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$

$+2e$ reduction

4. $Cu + H_2SO_4 + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

* Balanced Equation:

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(viii) $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

* Steps Involved:

1. $\overset{+1}{H}\ \overset{-1}{I} + \overset{+2}{H_2}\overset{+6}{S}\ \overset{-8}{O_4} \longrightarrow \overset{o}{I_2} + \overset{+4}{S}\ \overset{-4}{O_2} + \overset{+2}{H_2}\overset{-2}{O}$

2. $HI^{-} + H_2\ \overset{+6}{S}\ O_4 \longrightarrow \overset{o}{I_2} + \overset{+4}{S}\ O_4 + H_2O$

$-1e(\times 2) = -2e$ oxidation

3. $HI^{-1} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{o}{I_2} + \overset{+4}{S}O_2 + H_2O$

$+2e$ reduction

4. $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

* Balance Equation:

$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(ix) $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$

* Steps Inolved:

1. $\overset{+1}{Na}\ \overset{-1}{Cl} + \overset{+2}{H_2}\ \overset{+6}{S}\ \overset{-8}{O_4} + \overset{+4}{Mn}\ \overset{-4}{O_2} \longrightarrow \overset{+2}{Na_2}\ \overset{+6}{S}\ \overset{-8}{O_4} + \overset{+2}{Mn}\ \overset{+6}{S}\ \overset{-8}{O_4} + \overset{+2}{H_2}\ \overset{-2}{O} + \overset{o}{Cl_2}$

2. $NaCl^{-1} + H_2SO_4 + \overset{+4}{Mn}O_2 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{o}{Cl_2}$

$-1\bar{e}$ oxidation

3. $NaCl^{-1} + H_2SO_4 + \overset{+4}{Mn}O_2 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + Cl^{o}$

$+2\bar{e}$ reduction

$$\overbrace{NaCl^{-1} + H_2SO_4 + \underbrace{\overset{+4}{Mn}O_2 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}}_{+2\overline{e}}SO_4 + Cl^{o}}^{-1\overline{e}\,(2) = -2e} + H_2O$$

4.

5. $2NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$

* Balanced Equation:

$2NaCl + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$

Q.6 (a) Describe the general rules of balancing a redox equation by ion-electron method.

(b) Balance the following ionic equations by ion-electron method.

(i) $Fe^{+3} + Sn^{+2} \rightarrow Fe^{+2} + Sn^{+4}$

(ii) $MnO_4^{-1}(aq) + C_2O_4^{-2} \rightarrow Mn^{+2}(aq) + CO_2\,(g)$

(iii) $Cr_2O_7^{-2} + C1^{-} \rightarrow Cr^{+3} + Cl_2$

(iv) $Cu + NO_3^{-1} \rightarrow Cu^{+2} + NO_2$

(v) $Cr_2O_7^{-2} + Fe^{+2} \rightarrow Cr^{+3} + Fe^{+3}$ (acidic media)

(vi) $S_2O_3^{-2} + OC1^{-1} \rightarrow C1^{-} + S_4O_6^{-2}$ (acidic media)

(vii) $IO_3^{-1} + AsO_3^{-3} \rightarrow I + AsO_4^{-3}$ (acidic media)

(viii) $Cr^{+3} + BiO_3^{-1} \rightarrow Cr_2O_7^{-2} + Bi^{+3}$ (acidic media)

(ix) $H_2AsO_3 + Cr_2O_7^{-2} \rightarrow H_3AsO_4 + Cr^{+3}$ (acidic media)

(x) $CN^{-} + MnO_4^{-1} \rightarrow C\overline{N}O + MnO_2\,(s)$ (basic media)

Ans.

(a) Descriptive question consult text book for details.

(i) $Fe^{+3} + Sn^{+2} \longrightarrow Fe^{+2} + Sn^{+4}$ (acidic media)

* Steps Involved:

1. Split the equation into two halves.

$Sn^{+2} \longrightarrow Sn^{+4}$ (oxidation half)

$Fe^{+3} \longrightarrow Fe^{+2}$ (reduction half)

2. Balance the atoms and changes on both the sides of half reactions separately.

$Sn^{+2} \longrightarrow Sn^{+4}$

$Sn^{+2} \longrightarrow Sn^{+4} + 2\overline{e}$ …… (i)

$Fe^{+3} \longrightarrow Fe^{+2}$

$1\overline{e} + Fe^{+3} \longrightarrow Fe^{+2}$ …… (ii)

3. Multiply eq. (ii) by 2 and add it into eq. (i):

$2Fe^{+3} + 2\overline{e} \longrightarrow 2Fe^{+2}$

$Sn^{+2} \longrightarrow Sn^{+4} + 2\overline{e}$

* Balanced Equation: $\boxed{2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}}$

(ii) $MnO_{4(aq)}^{-1} + C_2O_{4(aq)}^{-2} \longrightarrow Mn_{(aq)}^{+2} + CO_{2(g)}$ (acidic media)

1. $MnO_4^{-1} \longrightarrow Mn^{+2}$ (reduction half)

$C_2O_4^{-2} \longrightarrow CO_2$ (oxidation half)

2. $C_2O_4^{-2} \longrightarrow CO_2$

$C_2O_4^{-2} \longrightarrow 2CO_2$

$C_2O_4^{-2} \longrightarrow 2CO_2 + 2\bar{e}$ …… (i)

$MnO_4^{-1} \longrightarrow Mn^{+2}$

$MnO_4^{-1} \longrightarrow Mn^{+2} + 4H_2O$

$8H^+ + MnO_4^{-1} \longrightarrow Mn^{+2} + 4H_2O$

$5\bar{e} + 8H^+ + MnO_4^{-1} \longrightarrow Mn^{+2} + 4H_2O$ …… (ii)

3. Multiply eq. (i) by 5 and eq. (ii) by 2 and then add:

$5C_2O_4^{-2} \longrightarrow 10CO_2 + 10\bar{e}$

$10\bar{e} + 16H^+ + 2MnO_4^{-1} \longrightarrow 2Mn^{+2} + 8H_2O$

* Balanced Equation: $5C_2O_4^{-2} + 16H^+ + 2MnO_4^{-1} \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$

(iii) $Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ (acidic media)

1. $Cl^- \longrightarrow Cl_2$ (oxidation half)

$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$ (reduction half)

2. $Cl^- \longrightarrow Cl_2$

$2Cl^- \longrightarrow Cl_2$

$2Cl^- \longrightarrow Cl_2 + 2\bar{e}$ …… (i)

$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$6\bar{e} + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ …… (ii)

3. Multiply eq. (i) by 3 and add it into eq. (ii):

$6Cl^- \longrightarrow 3Cl_2 + 6e^-$

$6\overline{e} + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

---

* Balance Equation: $6Cl^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$

(iv) $Cu + NO_3^{-1} \longrightarrow Cu^{+2} + 2NO_2$ (acidic media)

1. $Cu \longrightarrow Cu^{+2}$ (oxidation half)

$NO_3^{-1} \longrightarrow NO_2$ (reduction half)

2. $Cu \longrightarrow Cu^{+2} + 2\overline{e}$ …… (i)

$NO_3^{-1} \longrightarrow NO_2$

$NO_3^{-1} \longrightarrow NO_2 + H_2O$

$2H^+ + NO_3^{-1} \longrightarrow NO_2 + H_2O$

$1\overline{e} + 2H^+ + NO_3^{-1} \longrightarrow NO_2 + H_2O$ …… (ii)

3. Multiply eq. (ii) by 2 and add it into (i):

$2\overline{e} + 4H^+ + 2NO_3^{-1} \longrightarrow 2NO_2 + 2H_2O$

$Cu \longrightarrow Cu^{+2} + 2\overline{e}$

---

* Balance Equation: $4H^+ + 2NO_3^{-1} + Cu \longrightarrow 2NO_2 + 2H_2O + Cu^{+2}$

(v) $Cr_2O_7^{-2} + Fe^{+2} \longrightarrow Cr^{+3} + Fe^{+3}$ (acidic medium)

1. $Cr_2O_7^{-2} \longrightarrow Cr^{+3}$ (reduction half)

$Fe^{+2} \longrightarrow Fe^{+3}$ (oxidation half)

2. $Fe^{+2} \longrightarrow Fe^{+3}$

$Fe^{+2} \longrightarrow Fe^{+3} + 1\overline{e}$ …… (i)

$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$6\overline{e} + 14H+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ …… (ii)

3. Multiply eq. (i) by 6 and add it into eq. (ii):

$6Fe^{+2} \longrightarrow 6Fe^{+3} + 6\overline{e}$

$6\overline{e} + 14H^{+} + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

* Balance Equation: $6Fe^{+2} + 14H^{+} + Cr_2O_7^{-2} \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O$

(vi) $S_2O_3^{-2} + OCl^{-} \longrightarrow S_4O_6^{-2} + Cl^{-}$ (acidic medium)

1. $S_2O_3^{-2} \longrightarrow S_4O_6^{-2}$ (oxidation half)

$OCl^{-} \longrightarrow Cl^{-}$ (reduction half)

2. $S_2O_3^{-2} \longrightarrow S_4O_6^{-2}$

$2S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2\overline{e}$ …… (i)

$OCl^{-} \longrightarrow Cl^{-}$

$OCl^{-} \longrightarrow Cl^{-} + H_2O$

$2H^{+} + OCl^{-} \longrightarrow Cl^{-} + H_2O$

$2\overline{e} + 2H^{+} + OCl^{-} \longrightarrow Cl^{-} + H_2O$ …… (ii)

3. Add eq. (i) into (ii):

$2S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2\overline{e}$

$2\overline{e} + 2H^{+} + OCl^{-} \longrightarrow Cl^{-} + H_2O$

* Balance Equation: $2S_2O_3^{-2} + 2H^{+} + OCl^{-} \longrightarrow S_4O_6^{-2} + Cl^{-} + H_2O$

(vii) $IO_3^{-1} + AsO_3^{-3} \longrightarrow I^{-} + AsO_4^{-3}$ (acidic media)

1. $AsO_3^{-3} \longrightarrow AsO_4^{-3}$ (oxidation half)

$H_2O + AsO_3^{-3} \longrightarrow AsO_4^{-3}$

$H_2O + AsO_3^{-3} \longrightarrow AsO_4^{-3} + 2H^{+}$

$H_2O + AsO_3^{-3} \longrightarrow AsO_4^{-3} + 2H^{+} + 2\overline{e}$ …… (i)

2. $IO_3^{-1} \longrightarrow I^{-1}$

$IO_3^{-1} \longrightarrow I^- + 3H_2O$

$6H^+ + IO_3^{-1} \longrightarrow I^- + 3H_2O$

$6e^- + 6H^+ + IO_3^{-1} \longrightarrow I^- + 3H_2O$ …… (ii)

3. Multiply eq. (i) by 3 and add if into eq. (ii):

$3H_2O + 3AsO_3^{-3} \longrightarrow 3AsO_4^{-3} + 6H^+ + 6\overline{e}$

$6\overline{e} + 6H^+ + IO_3^{-1} \longrightarrow I^- + 3H_2O$

* Balance Equation: $3AsO_3^{-3} + IO_3^{-1} \longrightarrow AsO_4^{-3} + I^-$

(viii) $Cr^{+3} + BiO_3^{-1} \longrightarrow Cr_2O_7^{-2} + 3Bi^{+3}$ (acidic media)

1. $BiO_3^{-1} \longrightarrow Bi^{+3}$ (reduction half)

$Cr^{+3} \longrightarrow Cr_2O_7^{-2}$ (oxidation half)

2. $Cr^{+3} \longrightarrow Cr_2O_7^{-2}$

$2Cr^{+3} \longrightarrow Cr_2O_7^{-2}$

$7H_2O + 2Cr^{+3} \longrightarrow Cr_2O_7^{-2} + 14H^+$

$7H_2O + 2Cr^{+3} \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6\overline{e}$ …… (i)

$BiO_3^{-1} \longrightarrow Bi^{+3}$

$BiO_3^{-1} \longrightarrow Bi^{+3} + 3H_2O$

$6H^+ + BiO_3^{-1} \longrightarrow Bi^{+3} + 3H_2O$

$2\overline{e} + 6H^+ + BiO_3^{-1} \longrightarrow Bi^{+3} + 3H_2O$ …… (ii)

3. Multiply eq. (ii) by 3 and it into eq. (i):

$6\overline{e} + 18H^+ + 3BiO_3^{-1} \longrightarrow 3Bi^{+3} + 9H_2O$

$7H_2O + 2Cr^{+3} \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6\overline{e}$

* Balance Equation: $4H^+ + 3BiO^{-1} + 2Cr^{+3} \longrightarrow 3Bi^{+3} + 2H_2O + Cr_2O_7^{-2}$

(ix) $H_3AsO_3 + Cr_2O_7^{-2} \longrightarrow H_3AsO_4 + 2Cr^{+3}$ (acidic media)

1. $H_3AsO_3 \longrightarrow H_3AsO_4$ (oxidation half)
$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$ (reduction half)

2. $H_3AsO_3 \longrightarrow H_3AsO_4$
$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4$
$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4 + 2H^+$
$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4 + 2H^+ + 2\overline{e}$ …… (i)
$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$
$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$
$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$
$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ …… (ii)
$6\overline{e} + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

3. Multiply eq. (i) by 3 and add it into (ii):
$3H_2O + 3H_3AsO_3 \longrightarrow 3H_3AsO_4 + 6H^+ + 6\overline{e}$
$6\overline{e} + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

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* Balance Equation: $3H_3AsO_3 + 8H^+ + Cr_2O_7^{-2} \longrightarrow 3H_3AsO_4 + 2Cr^{+3} + 4H_2O$

(x) $CN^- + MnO_4^{-1} \longrightarrow CNO^{-1} + MnO_2$ (basic media)

1. $CN^- \longrightarrow CNO^{-1}$ (oxidation half)
$MnO_4^{-1} \longrightarrow MnO_2$ (reduction half)

2. $CN^- \longrightarrow CNO^{-1}$
$H_2O + CN^- \longrightarrow CNO^{-1}$
$H_2O + CN^- \longrightarrow CNO^- + 2H^+$

Since this is an equation of basic medium, add $\overline{O}H$ ions on both sides of equation equal to the no. of H^+ ions.

$2\overline{O}H + H_2O + CN^- \longrightarrow CNO^{-1} + 2H^+ + 2\overline{O}H$

$2\overline{O}H + H_2O + CN^- \longrightarrow CNO^{-1} + 2H_2O$

$2\overline{O}H + CN^- \longrightarrow CNO^- + H_2O$

$2\overline{O}H + CN^- \longrightarrow CNO^- + H_2O + 2\overline{e}$ …… (i)
$MnO_4^{-1} \longrightarrow MnO_2$
$MnO_4^{-1} \longrightarrow MnO_2 + 2H_2O$
$4H^+ + MnO_4^{-1} \longrightarrow MnO_2 + 2H_2O$

Since this is an equation of basic medium. Hence, we add $\bar{O}H$ ions equal to the no. of H^+ ions on both sides of equation.

$$4\bar{O}H + 4H^+ + MnO_4^{-1} \longrightarrow MnO_2 + 2H_2O + 4\bar{O}H$$

$$4H_2O + MnO_4^{-1} \longrightarrow MnO_2 + 2H_2O + 4\bar{O}H$$

$$2H_2O + MnO_4^{-1} \longrightarrow MnO_2 + 4\bar{O}H$$

$$3\bar{e} + 2H_2O + MnO_4^{-1} \longrightarrow MnO_2 + 4\bar{O}H \qquad \text{...... (ii)}$$

3. Multiply eq. (i) by 3 and eq. (ii) by 2 and add them.

$$6\bar{O}H + 3CN^- \longrightarrow 3CNO^- + 3H_2O + 6\bar{e}$$

$$6\bar{e} + 4H_2O + 2MnO_4^{-1} \longrightarrow 2MnO_2 + 8\bar{O}H$$

* Balance Equation: $3CN^- + H_2O + 2MnO_4^{-1} \longrightarrow 3CNO^- + 2MnO_2 + 2\bar{O}H$

Q.7 Describe the electrolysis of molten sodium chloride, and a concentrated solution of sodium chloride.

Ans. Electrolysis of Molten NaCl: Solid NaCl when heated, it melts and ionizes as following:

$$NaCl_{(s)} \longrightarrow Na^+_{(l)} + Cl^-_{(l)}$$

At Cathode:

$$2Na^+_{(l)} + 2\bar{e} \longrightarrow 2Na_{(s)}$$

At Anode:

$$2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2\bar{e}$$

Overall Reaction:

$$2Na^+_{(l)} + 2Cl^-_{(l)} \longrightarrow 2Na^o_{(s)} + Cl_{2(g)}$$

"Electrolysis of Aqueous" Solution of NaCl:

$$NaCl_{(s)} \xrightleftharpoons{H_2O} \overset{+}{Na}_{(aq)} + \overset{-}{Cl}_{(aq)}$$

At Cathode:

$$2H_2O + 2\bar{e} \longrightarrow H_{2(g)} + 2\bar{O}H_{(aq)}$$

At Anode:

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2\bar{e}$$

Over Reaction:

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O \longrightarrow H_{2(g)} + Cl_{2(g)} + Na^+_{(aq)} + \bar{O}H_{(aq)}$$

Q.8 What is the difference between single electrode potential and standard electrode potential? How can it be measured? Give its importance.

Ans.

Single Electrode Potential	Standard Electrode Potential
The potential set up, when an electrode is in contact with one molar solution of its ions is called as single electrode potential.	The potential set up, when electrode is in contact with one molar solution of its own ions at 298K is called as standard electrode potential.

For measurement and importance consult text book.

Q.9 Outline the important applications of electrolysis. Write the electrochemical reactions involved there in. Discuss the electrolysis of $CuSO_4$ using Cu-electrodes and $AgNO_3$ solution using Ag electrode.

Ans. For applications of electrolysis consult text book.

Electrolysis of $CuSO_4$ using Cu-electrode:

$$CuSO_{4(s)} \overset{H_2O}{\rightleftharpoons} Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

At Cathode:

$$Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu^{o}_{(s)} \qquad \text{(deposited at cathode)}$$

At Anode:

$$Cu^{o}_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\bar{e} \qquad \text{(from anode)}$$

In this electrolysis $CuSO_4$ ionizes to produce Cu^{2+} ions and SO_4^{2-}. Cu^{2+} ion pick up electrons and are deposited at cathode. From anode, copper atoms loose electrons and form Cu^{2+} ions in the solution. In other words Cu from Cu-anode dissolves into the solution and is deposited at Cu-cathode.

Electrolysis of $AgNO_3$ using Ag-electrode:

$$AgNO_{3(s)} \overset{H_2O}{\rightleftharpoons} Ag^{+}_{(aq)} + NO^{1-}_{3(aq)}$$

At Cathode:

$$Ag^{+}_{(aq)} + 1\bar{e} \longrightarrow Ag^{o}_{(s)} \qquad \text{(deposited at cathode)}$$

At Anode:

$$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + 1\bar{e} \qquad \text{(from anode)}$$

In this type of electrolysis, $AgNO_3$ ionizes to give Ag^+ ions and NO_3^{1-} ions. Ag^+ ion pick up electrons and are deposited at cathode. From anode, $Ag_{(s)}$ atoms loose electrons to form Ag^+ ions in the solution.

In other words, Ag from Ag-anode dissolves into the solution and is deposited at Ag-cathode.

Q.10 Describe the construction and working of standard hydrogen electrode.

Ans. Descriptive question consult text book for details.

Q.11 Is the reaction Fe^{+3} + Ag → Fe^{+2} Ag^{+} spontaneous? If not, write spontaneous reaction involving theses species.

Ans.

$$Fe^{3+} + Ag^{\circ} \longrightarrow Fe^{2+} + Ag^{+}$$

Reduction potential of Fe = +0.771 volt

Reduction potential of Ag = +0.799 volt

Since, Ag is oxidized in this reaction, its oxidation potential will be –0.799 volt.

$$E^{o}_{cell} = E^{o}_{oxi} + E^{o}_{red}$$

$$E^{o}_{cell} = -0.799 + 0.771$$

$$E^{o}_{cell} = -0.028 \text{ volt}$$

Thus, the reaction is not spontaneous because, E° for the cell is negative. The reverse of above reaction is spontaneous and feasible. i.e.,

$$Fe^{2+} + Ag^{+} \longrightarrow Fe^{3+} + Ag^{\circ}$$

$$E^{o}_{cell} = E^{o}_{oxi} + E^{o}_{red}$$

$$E^{o}_{cell} = -0.771 + 0.799$$

$$E^{o}_{cell} = +0.028 \text{ volt}$$

Q.12 Explain the difference between:

(a) Ionization and electrolysis.

(b) Electrolytic cell and voltaic cell.

(c) Conduction through metals and molten electrolytes.

Ans.

(a) Difference between ionization and electrolysis:

Ionization	Electrolysis
(i) Splitting up of ionic compound into ions in molten state or in aqueous form is called ionization.	(i) Decomposition of a substance in solution or molten state by passing electricity is called electrolysis.
(ii) In this case, electrodes, electricity and electrolytic cell is not required.	(ii) For electrolysis electrodes, electricity and electrolytic cell is required.
(iii) During ionization, ions are produced.	(iii) During electrolysis, ions are oxidized or reduced to neutral atoms or molecules.
(iv) Example: $NaCl_{(s)} \xrightarrow{H_2O} Na^{+}_{(aq)} + Cl^{-}_{(aq)}$	(iv) Example: $2NaCl_{(l)} \xrightarrow[H_2O]{\text{Electrolysis}} 2Na_{(s)} + Cl_{2(g)}$

(b) Difference between electrolytic cell and voltaic cell:

Electrolytic Cell	Voltaic Cell
(i) A cell in which electrical energy is converted into chemical energy is called electrolytic cell.	(i) A cell in which chemical energy is converted into electrical energy is called voltaic cell.
(ii) In this cell current is used.	(ii) In this cell current is produced.
(iii) Non-spontaneous redox reaction take place here.	(iii) Spontaneous redox reaction take place in it.
(iv) Example: Down's cell, Nelson's cell.	(iv) Example: Daniel cell, Fuel cell.

(c) Difference between conduction through metals and molten electrolytes:

Conduction Through Metals	Conduction Through Molten Electrolytes
(i) In metals, conduction takes place due to free electrons, so it is called as electronic conduction.	(i) In molten electrolytes, conduction takes place due to free ions, so it is called as electrolytic conduction.
(ii) In this case, conduction takes place through external circuit.	(ii) In this case, conduction takes place through liquid medium.
(iii) There is no change of properties of conductors.	(iii) There is decomposition of electrolytes as a result of chemical reaction during conduction.
(iv) There is increase of resistance with the rise of temperature.	(iv) There is decrease of resistance with rise of temperature.
(v) Examples: All metals.	(v) Examples: Molten salts.

Q.13 Describe a galvanic cell explaining the function of electrodes and the salt bridge.

Ans. Descriptive question consult text book.

Q.14 Write comprehensive notes on:

- **(a) Spontanity of oxidation reduction reactions.**
- **(b) Electrolytic conduction.**
- **(c) Alkaline, sliver oxide and nickel-cadmium batteries , fuel cell.**
- **(d) Lead accumulator, its desirable and undesirable features.**

Ans. Descriptive question consult text book.

Q.15 Will the reaction be spontaneous for the following set of half reactions. What will be the value of E° Cell?

(i) $\mathbf{Cr^{3+}_{(aq)} + 3\bar{e} \rightarrow Cr_{(s)}}$

(ii) $\mathbf{MnO_{2(s)} + 4H^+ + 2\bar{e} \rightarrow Mn^{2+}{}_{(aq)} + 2H_2O_{(l)}}$

Standard reduction potential for reaction.

(i) –0.74 v and for the reaction (ii)= + 1.28V

Ans. Yes this reaction is spontaneous, when $Cr_{(s)}$ with low reduction potential act as anode and MnO_2 with high reduction potential act as cathode:

(i) $(Cr_{(s)} \longrightarrow Cr^{3+}_{(aq)} + 3\bar{e}) \times 2$ $\quad E^o_{oxi} = +0.74$ v

(ii) $(MnO_{2(s)} + 4H^+ + 2\bar{e} \longrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}) \times 3$ $\quad E^o_{red} = +1.28$ v

$$E^o_{cell} = E^o_{oxi} + E^o_{red}$$

$$= +0.74 + 1.28$$

$$E^o_{cell} = 2.02 \text{ volt}$$

Q.16 Explain the following with reason:

(a) A porous plate or a salt bridge is not required in lead storage cell.

(b) The standard oxidation potential of Zn is 0.76 V and its reduction potential is –0.76V.

(c) Na and K can displace hydrogen from acids but Pt, Pd and Cu cannot.

(d) The equilibrium is set up between metal atoms of electrode and ions of metal in a cell.

(e) A salt bridge maintains the electrical neutrality in the cell.

(f) Lead accumulator is a chargeable battery.

(g) Impure Cu can be purified by electrolytic process.

(h) SHE acts as anode when connected with Cu electrode but as cathode with Zn electrode.

Ans.

(a) A porous plate or salt bridge is used in those cells where two different electrolytes are used and are required to kept separate. In case of lead storage cell, only dil. H_2SO_4 is used as an electrolyte. Hence, no separation is required by porous plate or salt bridge.

(b) The tendency of an element measured when coupled with SHE is shown with the positive sign, and reverse tendency is shown with negative sign.

Zinc when coupled with SHE, have 0.76 v more tendency to show oxidation than hydrogen. Hence, its oxidation potential is 0.76 v and is shown with positive sign (+0.76 v). Therefore, its reduction potential will be shown with negative sign (–0.76 v) because it has 0.76 v less tendency to show reduction than hydrogen.

(c) Na and K have very low value of reduction potential and lie very much above hydrogen in the electrochemical series. Hence, can displace hydrogen from acids.

Pt, Pd and Cu have very high value of reduction potentials and lie below hydrogen in electrochemical series. Therefore, these metals cannot displace hydrogen from acids.

(d) When metal is dipped into the solution of it own ions, metal atoms loose electrons, form positive ions and enter into the solution. Already present ions in the solution, pick up electrons and are deposited on electrode.

This process continuous and a stage reaches when rate of both the process becomes equal. This stage is called equilibrium stage.

(e) A salt bridge is a U-tube containing saturated solutions of strong electrolytes. e.g., KCl, KNO_3. It connects the two electrolytic solution. When electrochemical reaction takes place in the cell it allows the passage of negative ions from cathode compartment (where they are in excess) to anode compartment (where cations in excess). As a result of that both compartments become neutral.

(f) The lead accumulator is a secondary cell. It is charged by passing direct current through it. To recharge it, anode and cathode of external source are connected to its anode and cathode of lead accumulator respectively. The redox reactions at the respective electrodes are reversed during recharging again. The density of H_2SO_4 is also regained during this process.

(g) During purification of Cu, impure Cu is made anode and thin sheet of pure Cu is made cathode and $CuSO_4$ solution is taken as electrolyte.

Cu-atoms at anode loose electrons, come into the solution as Cu^{2+} ion. They migrate to cathode where they gain electrons and are deposited at cathode. In this way Cu atoms are migrated from anode to cathode. Impurities are left at the bottom of anode and pure Cu is obtained as thick cathode.

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\overline{e} \qquad \text{(anode)}$$

$$Cu_{(aq)} + 2\overline{e} \longrightarrow Cu^{o}_{(s)} \qquad \text{(cathode)}$$

(h) SHE has electrode potential equal to zero. When it is coupled with Zn, Zn has low reduction potential and has 0.76 v more tendency than hydrogen to show oxidation and act as anode. Hydrogen act as cathode.

When Cu is coupled with hydrogen, Cu has high reduction potential and has 0.34 v more tendency than hydrogen to show reduction and acts as cathode. Then hydrogen acts as anode.

DO YOU KNOW?

1. The conversion of electrical energy into chemical energy in the electrolytic cell and the conversion of chemical energy into the electrical energy in the galvanic or voltaic cell is called electrochemistry.

2. The substance in which electricity can pass is called conductor.

3. The flow of charge in an electronic conductor is due to the flow of electrons.

4. The flow of charge in the electrolytic conductor is due to the movement of ions.

5. Oxidation state of O in OF_2 is +2.

6. Oxidation state of O in peroxides (Na_2O_2, H_2O_2) is −1.

7. Oxidation state of O in super oxides (KO_2) is $-\frac{1}{2}$.

8. Oxidation is due to loss of electrons.

9. Reduction is due to the gain of electrons.

10. Oxidation takes place at the anode.

11. Reduction takes place at the cathode.

12. An electrochemical cell in which electric current is used to drive a non-spontaneous redox reaction is called electrolytic cell. For example: Down's cell, Nelson's cell.

13. An electrochemical cell in which electric current is produced as a result of spontaneous redox reaction is called galvanic cell or voltaic cell. For example: Lead storage battery dry cell, Daniel cell (Zn – Cu cell).

14. Lead storage battery has usually six cell, the voltage of each cell is 2 and the total voltage is 12 V.

15. 30% H_2SO_4 having density of 1.25 g cm^{-3} is used as electrolyte in the lead storage battery.

16. The electrolyte in fuel cell is KOH.

17. In the NICAD battery, anode is composed of cadmium.

18. In the silver oxide battery, cathode is Ag_2O and anode is made of zinc.

19. The voltage of alkaline battery is 1.5.

20. The oxidation and reduction potential of SHE is arbitrarily taken as zero.

21. In electrolytic cell, cathode is negatively charged and anode is positively charged.

22. In Galvanic cell, cathode is positively charged and anode is negatively charged.

Chapter 11

REACTION KINETICS

CHEMICAL KINETICS

“The study of rate of a chemical reaction, factors affecting the reaction rates and mechanism of the reaction is called **chemical kinetics or reaction kinetics**.”

Mechanism:

“The path of reaction of steps involved in chemical reaction is called **mechanism**.”

Mechanism describes how a chemical reaction occurs. It is a series of steps that defines the order in which bonds are broken and new bonds are formed until the final products are obtained.

On the basis of rate there are three types of reaction, i.e. **rapid, moderate and slow**.

For example, a white precipitate of silver chlorides is formed immediately on addition of silver nitrate solution to sodium chloride solution. Some reactions proceed at a moderate rate e.g. hydrolysis of an ester. Still other reactions take a much longer time e.g. rusting of iron, the chemical weathering of stone work of buildings by acidic gases in the atmosphere and the fermentation of sugars.

Importance of Reaction Kinetics:

The rates of reactions and their control are often important in industry as they might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction and it is important to discover the conditions under which the reaction will proceed most economically.

Rate Determining Step:

“If a reaction consists of several steps, one step will be slowest than all other steps. The slowest step is rate determining step. Other step will not affect the rate.

RATE OF REACTION

“The change in concentration of reactants or products per unit time is called **velocity or rate of chemical reaction**.”

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken for change}} = \frac{\Delta C}{\Delta t}$$

The **unit** of rate of reaction is:

$$\text{Rate of reaction} = \frac{\text{mol dm}^{-3}}{\text{second}} = \text{mole dm}^{-3}\ \text{sec}^{-1}$$

For gas phase reactions, the pressure units are used instead of molar concentration.

The concentration of reactant decreases with passage of time and concentration of product increases with time.

Consider a reaction is which reactant A changes to product B.

$$A \longrightarrow B$$

With the passage of time, concentration of reactant decreases.

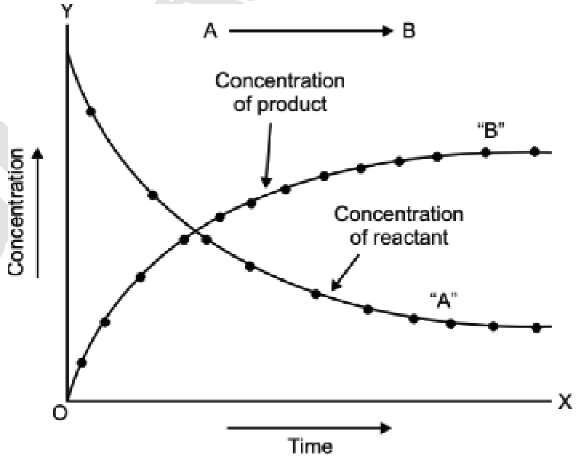
$$\text{Rate} = \frac{-\Delta A}{\Delta t} = \frac{\text{Change in Concentration}}{\text{Time}}$$

Minus sign indicates to the decrease in concentration. On the other hand concentration of product increases. It can be represented as:

$$\text{Rate} = \frac{\Delta B}{\Delta t} = \frac{\text{Change in Concentration}}{\text{Time}}$$

If we plot a graph between the concentration of reactants and products and time following shape is obtained.

The slope of the graph for the reactant or the product is the **steepest at the beginning** showing rapid decrease in the concentration of the reactant and the consequently a rapid increase in the concentration of the product. As the reaction proceed the slope becomes less steep indicating that the reaction is **slowing down with time**. Where the graph becomes a horizontal straight line, the reaction stops.



Change in the concentration of reactants and products with time for the reaction A → B

(Change in the concentration of reactants and products with time for the reaction $A \longrightarrow B$)".

It shows from the above graph that the change in concentration of the reactant A or the product B is much more at the start of reaction and then it deceases gradually. So the reaction rate decreases with time. **It never remains uniform** during different time periods. It decreases continuously till the reaction ceases.

TYPE OF RATES

(i) Average rate (ii) Instantaneous rate

(i) Average Rate:

"The rate of reaction between two specific times is called **average rate**."

(ii) Instantaneous Rate:

"The rate at any one instant during a specific interval of time is called **instantaneous rate**."

The average rate and instantaneous rate are equal for only one instant in any time interval. At first, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate becomes lower than the average rate. As the time interval becomes smaller, the average rate becomes closer to the instantaneous rate. **The average rate will be equal to the instantaneous rate when the time interval approaches zero**. Thus the rate of reaction is defined as the instantaneous change in the concentration of a reactant or a product at a given moment of time.

$$\text{Rate of reaction} = \frac{dx}{dt}$$

Where "dx" is a very small change in the concentration of a product in a very small time interval "dt".

The rate of a general reaction, $A \longrightarrow B$ can be expressed in terms of rate of disappearance of the reactant A of the rate of appearance of the product B. Mathematically,

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

Where d [A] and d [B] are the changes in the concentrations of A and B respectively. The negative sign in the term indicates a decrease in the concentration of the reactant. Since the concentration of product increase with time, the sign in the product should be positive.

SPECIFIC RATE CONSTANT

The relationship between the rate of a chemical reaction and the active masses (expressed as concentrations) of the reacting substances is summarized in the law of mass action. It states that the rate of reaction is proportional to the active mass of the reactant or the product of active masses if more than one reactants are in a chemical reaction (for dilute solutions, active mass is considered as equal to concentration). By applying the law of mass action to a general reaction.

$$aA + bB \xrightarrow{\qquad} cC + dD$$

$$\text{Rate of reaction} = k\,[A]^a\,[B]^b$$

This expression is called **rate equation**. The brackets [ ] represent the concentrations and the proportionality constant k is called **rate constant or velocity constant for the reactions**.

Let $[A] = 1 \text{ mole dm}^{-3}$ and $[B] = 1 \text{ mol dm}^{-3}$

Rate of reaction = $k \times 1^a \times 1^b = k$.

Hence the specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity. Under the given conditions, k remains, constant but it changes with temperature. The unit of rate constant is **"mole dm^{-3} sec^{-1}"**.

ORDER OF REACTION

"The sum of exponents of the concentrations of the reacting species in the observed rate law is called **order of reaction**."

or "The number of reacting molecules whose concentrations alter as a result of chemical change."

Order of a reaction cannot be predicted from a balance equation but must be determined form **rate law** which is obtained **experimentally**.

$$aA + bB \longrightarrow cC + dD$$

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.

We can write the rate equations or rate law as:

Rate of reaction = $k [A]^a [B]^b$

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 order of b with respect to B. The overall order of reaction is (a + b).

The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation. The chemical reactions are classified as zero, first, second and third order reactions. The order of reactions provides valuable information about the mechanism of a reaction.

ZERO ORDER REACTIONS

"The reactions in which rate of reaction does not depends upon the concentration of any reactant."

A ……… Product

Rate = $k [A]^o$

Rate = k

(1) All photochemical reactions are of zero order. For example, rate does not depends upon the concentration of CO_2 or H_2O in photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} C_6H_{12}O_6 + 6O_2$$

(2) Decomposition of NH_3.

$$2NH_3 \xrightarrow{W} N_2 + 3H_2$$

(3) Decomposition of PH_3.

(4) Thermal decomposition of HI.

$$2HI \xrightarrow{\text{Gold surface}} H_2 + I_2$$

FIRST ORDER REACTION

"The reactions in which rate of reaction depends upon the concentration of only one substance are called **first order reaction**."

For Examples:

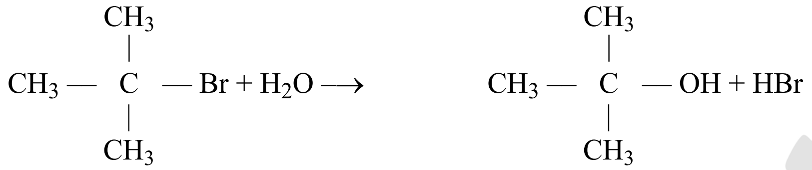
(1) Decomposition of nitrogen pent-oxide involves the following equation.

$$2N_2O_{5(g)} \xrightarrow{\qquad} 2N_2O_{4(g)} + O_{2(g)}$$

The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = K[N_2O_5]$$

(2) Hydrolysis of tertiary butyl bromide.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br + H_2O \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + HBr$$

The rate equation determined experimentally for this reaction is

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such type of reactions have been named as **pseudo first order reactions**.

(3) Hydrolysis of sugar.

$$\underset{}{C_{12}H_{22}O_{11} + H_2O} \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(4) $2H_2O_2 \xrightarrow{\qquad} 2H_2O + O_2$

SECOND ORDER REACTIONS

For Example:

(1) The rate equation for this reaction is which shows that it is second order reaction.

$$NO_{(g)} + O_{3(g)} \xrightarrow{\qquad} NO_{2(g)} + O_{2(g)}$$

$$\text{Rate} = k[NO][O_3]$$

(2) Decomposition of HI in gas phase.

$$2HI \xrightarrow{\qquad} H_2 + I_2$$

(3) Decomposition of Acetaldehyde:

$$2CH_3CHO \xrightarrow{\qquad} 2CH_4 + 2CO$$

Third Order Reaction:

"The reactions in which rate of reaction depends upon the concentration of three molecules."

For Example:

(1) Consider the following reaction.

$$2FeCl_{3(aq)} + 6KI_{(aq)} \xrightarrow{\qquad} 2Fel_{2(aq)} + 6KCI_{(aq)} + I_2$$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[FeCl_3][KI]^2$$

This rate equation suggests that the reaction is, in fact, taking place in more than one steps. The possible steps of the reaction are shown below.

$$FeCl_3 + 2KI_{(aq)} \xrightarrow{\text{Slow}} FeI_{2(aq)} + 2KCI_{(aq)} + Cl^-_{(aq)}$$

$$2KI_{(aq)} + 2Cl^-_{(aq)} \xrightarrow{\text{Fast}} 2KCI_{(aq)} + I_{2(s)}$$

(2) Reaction between $SnCl_2$ and $FeCl_3$.

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

Fractional Orders:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Consider the formation of carbon tetrachloride from chloroform.

$$CHCI_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

$$\text{Rate} = k\,[CHCl_3]\,[Cl_2]^{1/2}$$

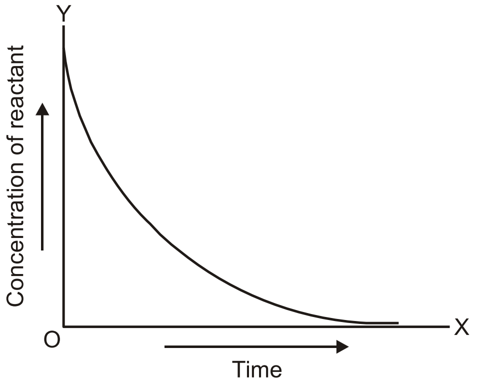
The sum of exponents will be 1 + ½ = 1.5, so the order of this reaction is 1.5.

HALF LIFE PERIOD

"Half life period of a reaction is the time required to convert 50% of the reactants into products."

For example, the half life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

It means that if we decompose 0.10 mole dm^{-3} of N_2O_5 at 45°C, then after 24 minutes 0.05 mole dm^{-3} of N_2O_5 will be left behind. Similarly after 48 minutes 0.025 mole dm^{-3} of N_2O_5 will remain un–reacted and after 72 minutes (3 half times) 0.0125 mole dm^{-3} of N_2O_5 will remain un–reacted.



Decomposition of N_2O_5 is a first order reaction and the above experiment proves that the **half–life period of this reaction is independent of the initial concentration** of N_2O_5. This is true for all first order reactions. The disintegration of radioactive $^{235}_{92}U$ has a half–life of 7.1 x 10^8 years or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of $^{235}_{92}U$ 0.25 kg disintegrates in the next 710 million year. So the half–life period for the disintegration of radioactive substance is independent of the amount of that substance.

It is true for the half–life period of first order reactions. It is not true for the reactions having higher orders. In the case of 2nd order reaction, the half–life period is inversely proportional to the initial concentration of the reactant and for a 3rd order reaction, it is inversely proportional to the square of initial concentration of reactants.

Briefly we can say that;

First order reaction equation:

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

At half change:

$$x = 0.5a$$

$$t_{1/2} = \frac{2.303}{k}\log\frac{a}{a-0.5a}$$

$$[t_{1/2}] \infty \frac{1}{a^{o}} \;, \quad \text{Since } [t_{1/2}]_1 = \frac{0.693}{k}$$

$$[t_{1/2}] \infty \frac{1}{a^{1}} \;, \quad \text{Since } [t_{1/2}]_2 = \frac{1}{ka}$$

$$[t_{1/2}] \infty \frac{1}{a^{2}} \;, \quad \text{Since } [t_{1/2}]_3 = \frac{1.5}{ka^{2}}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{0.5a}$$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{0.693}{k}$$

Where $[t_{1/2}]_1$, $[t_{1/2}]_2$ and $[t_{1/2}]_3$ are the half–life periods for 1st, and 2nd and 3rd order reactions respectively and 'a' is the initial concentration of reactants.

In general for the reaction of nth order:

$$[t_{1/2}]_n \propto \frac{1}{a^{n-1}}$$

"The half–life period of any order reaction is, thus, inversely proportional to the initial concentration raised to the power one less than the order of that reaction."

So if one knows the initial concentration and half–life period of a reaction, then order of that reaction can be determined.

Example 1:

Calculate the half–life period of the following reaction when the initial concentrations is 0.05 M.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

$k = 0.079 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $508^{o}C$.

Rate $= k [HI]^2$

So $$[t_{1/2}] = \frac{1}{k \times a^{2-1}}$$

$$= \frac{1}{(0.079 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(0.050 \text{ mol dm}^{-3})}$$

$[t_{1/2}] = 253$ seconds.

RATE DETERMINING STEP

If a reaction occurs in several steps, one of the step is the **slowest**. The rate of this step determines to overall rate of reaction. This slowest step is called the **rate determining or rate limiting step**. The number of molecules (reacting species) taking part in the rate determining steps appear in the rate equation of the reaction. Let us consider the following reaction.

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The rate equation of the reaction is found to be

Rate $= k [NO_2]^2$

This equation shows that the rate of reaction is independent of the concentration of carbon monoxide. In other words, the equation tells us that reaction involves more than one steps and two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} NO_{3(g)} + NO_{(g)} \qquad \text{(Rate determining step)}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{\text{Fast}} NO_{2(g)} + CO_{2(g)}$$

The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the **reaction intermediate**. The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products. This is a species with normal bonds and may be stable enough to be isolated under special conditions. This reaction is a clear example of the fact that a balanced chemical equation may be give any information about the way the reaction actually take place.

DETERMINATION OF THE RATE OF A CHEMICAL REACTION

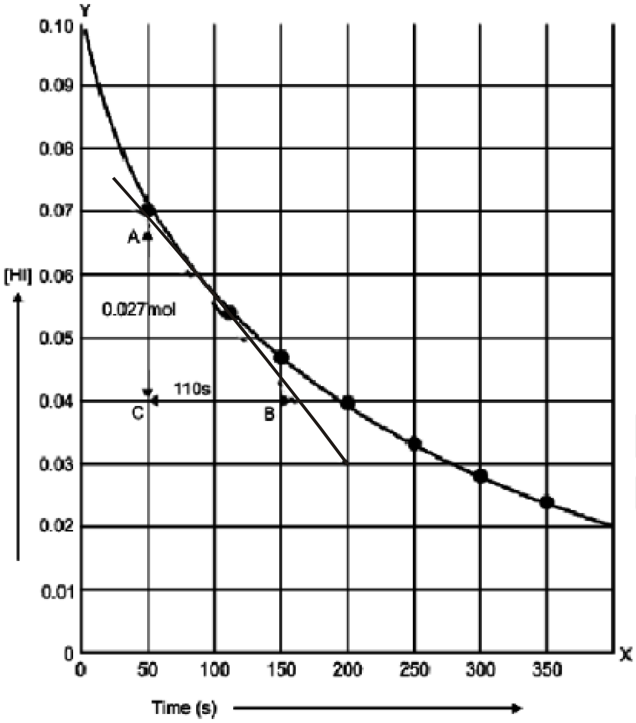
Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals as the reaction progresses. When the reaction goes on, the concentrations of reactants decrease and those of products increase the rate of a reaction, therefore, is expressed in terms of the rates at which the concentrations change.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t} = \frac{\text{moles dm}^{-3}}{\text{sec}}$$

$$= \text{moles dm}^{-3}\ \text{s}^{-1}$$

Suppose the concentration of a reactant of any chemical reaction changes by 0.01 mole dm^{-3} in one second, then rate of reaction is 0.01 mole dm^{-3} s^{-1}.

Rate of a chemical reaction always decreases with the passage of time during the progress of reaction. To determine the rate of reaction for a given length of time, a graph is plotted between time on x–axis and concentration or reactant on y–axis whereby a curve is obtained.



The change in the HI concentration with time for the reaction $2HI_{(g)}$ $H_{2(g)}$ + $I_{2(g)}$ at 508°C.

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 508°C. Table tell us that the change in concentration of HI for first 50 seconds is 0.0284 mole dm^{-3} but between 300 to 350 sec, the decrease is 0.0031 moles dm^{-3}. The steepness of the concentration time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Concentration of HI (mole dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.387	200
0.0336	250
0.0296	300
0.0265	450

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e. after 100 seconds. A right angle triangle ABC is completed with a tangent as hypotenuse. Figure shows that in 48 sec, the change in concentrations is 0.037 mole dm^{-3}, and hence the

$$\text{Slope or Rate} = \frac{0.027 \text{ moles dm}^{-3}}{110 \text{ sec}}$$

$$= 2.5 \times 10^{-4} \text{ moles dm}^{-3} \text{ s}^{-1}$$

This value of rate means that in a period of one sec in dm^{-3} solution, the concentration of HI disappears by 2.5×10^{-4} moles, changing into the products.

The change in concentrations of reactants or products can be determined by both physical and chemical method depending upon the type of reactants or products involved.

(A) PHYSICAL METHODS

Some of the methods used for this purpose are the following:

1. Spectroscopy:

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiations. The rate of reaction can be measured by measuring the amount of radiations absorbed.

2. Electrical Conductivity Method:

The rate of 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 or the ions formed during the reaction. The conductivity will be proportional to the rate of **change in the concentration** of the reacting ions or the ions formed.

3. Dilatometric Method:

This method is useful for those reactions, which involve small **volume changes** in solutions. The volume change is directly proportional to the extent of reactions.

4. Refractrometric Method:

This method is applicable to reactions in solutions where there are changes in refractive indices of the substances taking part in the chemical reaction.

5. Optical Rotation Method:

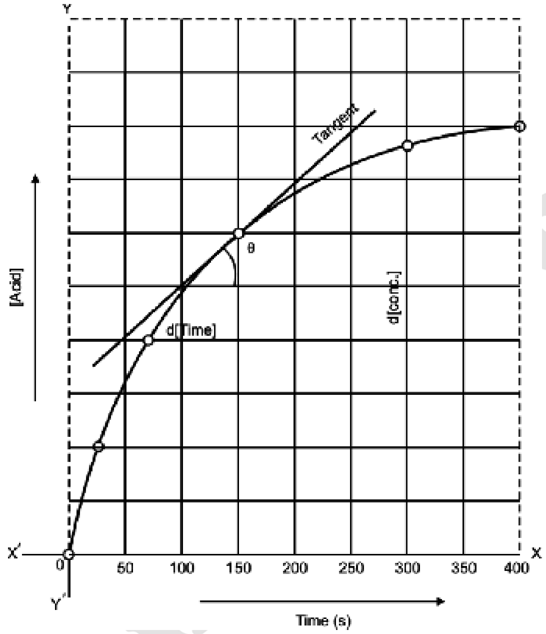
In this method, the angle through which **plane polarized light** is rotated by the reacting mixture is measured by a polarimeter. The extent of rotation determines the concentration of optically active substance. If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate reaction.

(B) CHEMICAL METHODS

This is particularly suitable for reaction in solution such as the acid hydrolysis an ester (ethyl acetate).

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \xrightarrow{H^+} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

In case of **hydrolysis of an ester**, the solution of ester and the acid acting as a catalyst are allowed to react. 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. The dilution and chilling stops the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator. The analysis is repeated at various time intervals. The different concentrations of acetic acid are plotted against the time whereby a 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.



$$\tan\theta = \frac{d\,[\text{acid}]}{d\,[\text{time}]} = \frac{dx}{dt}$$

$$\frac{dx}{dt} = \text{Rate of reaction}$$

If we plot a graph for decreasing concentration of $CH_3COOC_2H_5$, then falling curve is obtained.

This reaction is psuedo first order reaction because rate of reaction does not depend upon concentration of water. Actually water is in large excess as compared to ester and does not affect the rate.

COLLISION THEORY AND ENERGY OF ACTIVATION

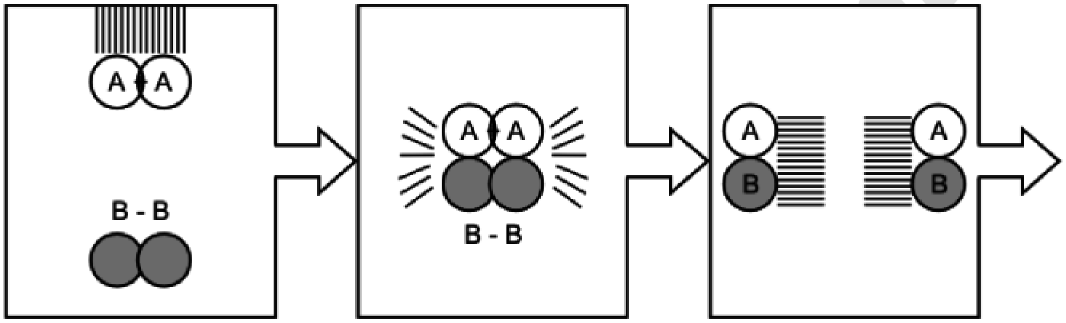
For a chemical reaction to take place, the particles (atoms, ions or molecules) of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective they give rise to the products otherwise the colliding particles just bounce back. The **effective collisions** can take place only when the colliding particles will possess certain amount of energy and they approach each other with the **proper orientation**. The idea of proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other.

"The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collision is called **activation energy**."

If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time.

Most of the reactions, are however, slow showing that all the collisions are not equally effective.

Let us study a reaction between molecules A and B to form a new molecule AB. If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed. The phenomenon is shown in Figure.



Covalent bonds between atoms of A and between atoms of B

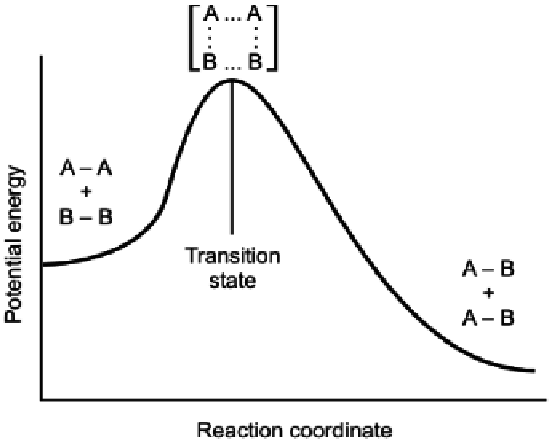
A-A and B-B bonds partially broken, A-B bonds partially formed (activated complex)

A-A, B-B bonds broken A-B bonds formed in AB molecules

$$\begin{array}{ccccc} A — A & & A\cdots\cdots A & & A \qquad A \\ + & \rightarrow & \vdots \qquad\quad \vdots & \rightarrow & \vdots \;\; + \;\; \vdots \\ B — B & & B\cdots\cdots B & & B \qquad B \\ \text{Reactant} & & \text{Activated complex} & & \text{Products} \end{array}$$

Activated complex is an unstable combination of all the atoms involved in the reaction for products immediately. It has a transient existence, that is why it is also called a **transitions state**.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective then the molecules flying apart are chemically different otherwise the same molecules just bounce back. When the molecules slow down just before the collision, their kinetic energy decrease and this results in the corresponding increase in their potential energy. The process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules.



Transition state theory and the potential energy diagram for a reaction

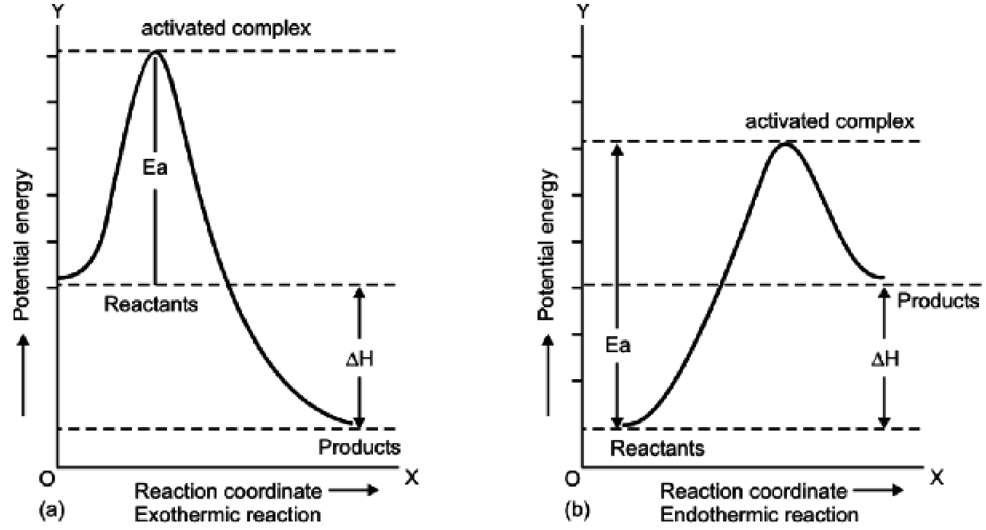
The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a **potential energy hill** between reactants and the products. Only the colliding molecules with proper activation energy, will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a, they will be unable to reach the top of the hill and fall back chemically unchanged.

ACTIVATION ENERGY FOR EXOTHERMIC AND ENDOTHERMIC REACTIONS

The potential energy diagram can also be used to study the heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and the products. For **exothermic reactions**, the products are at a **lower energy level than the reactants** and the decrease in potential energy appears as increase in kinetic energy of the products.

For **endothermic reactions**, the products are at **higher energy level than the reactants** and for such reactions a continuous source of energy is needed to complete the reaction.

The energy of activation of forward and backward reactions are different for all the reactions. For exothermic reactions, the energy of activation of forward reaction is less than that of backward reaction, while reverse is true for endothermic reactions.



A graph between path of reaction and the potential energy of the reaction

Energy of activation of a reaction provided a valuable information about the way a reaction takes place and thus helps to understand the reaction.

FINDING THE ORDER OF REACTION

The order of a reaction is the sum of exponents of the concentration terms in the rate expression of that reaction. It can be determined by the following methods.

1. Method of hit and trial
2. Graphical method
3. Differential method
4. Half–life method
5. Method of large excess

1. Half – Life Method:

As mentioned earlier, 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.

Therefore, $(t_{1/2})_n \propto \frac{1}{a^{n-1}}$

Let us perform a reaction twice by taking two different initial concentrations ‘a_1’ and ‘a_2’ and their half–life periods are found to be t_1 and t_2 respectively.

$(t_1)_n \propto \frac{1}{a_1^{n-1}}$ and $t_2 \propto \frac{1}{a_2^{n-1}}$

Dividing the two relations.

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides:

$$\log\frac{t_1}{t_2} = \log\left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log\frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$

Rearranging

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

So if we know the two initial concentrations and two half–life values we can calculate the order of reactions (n).

Example 2:

In the thermal decomposition of N_2O at 76^oC the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290 mm Hg and 212 seconds at the initial pressure of 360 mm Hg. Find the order of this reaction.

Solution:

$a_1 = 290$ mm Hg $\quad t_1 = 255$ seconds

$a_2 = 360$ mm Hg $\quad t_2 = 212$ seconds

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

$$n = 1 + \frac{\log\left[\frac{255}{212}\right]}{\log\left[\frac{360}{290}\right]}$$

$$n = 1 + \frac{0.0802}{0.0940}$$

$$n = 1 + 0.85 = 1.85 = 2$$

Hence the reaction is of second order.

Method of Large Excess:

In this method, one of the reactants is taken in a small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance controls the rate, which is taken in small amount and the order is noted with respect to that.

In this way, the reaction is repeated by taking rest of the substances in small amount and overall order is calculated. The method will be further elaborated in factor of concentration.

FACTORS AFFECTING RATE OF REACTION

All the factors which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows.

1. Nature of Reactants:

The rate of reaction depends upon the nature of reacting substances and the chemical reactivity of the substances is controlled by the **electronic arrangements** in their outer most orbital. The elements of I – A group have one electron in their outermost s–orbital, and they react with water more swiftly than those of II – A group elements having two electrons in their outermost orbital. Similarly, 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:

The frequency with which the molecules collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate while a decrease in the concentrations will have a reverse effect.

For Examples;

1. Combustion that occurs slowly in air (21% oxygen) will occur more rapidly in pure oxygen.
2. Similarly, lime stone reacts with different concentrations of hydrochloric acid at different rates.
3. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. therefore, a mixture of H_2 or CI_2 is increased form 0.5 to 1.0 atmosphere in the presence of excess of the other component.

The effect of change in concentration on the rate of a chemical reaction can be understand from the following gaseous reactions.

$$2NO_{(g)} + 2H_2 \xrightarrow{\qquad} 2H_2O_{(g)} + N_{2(g)}$$

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. the following table has been obtained experimentally.

Experiment number	NO (mole dm^{-3})	H_2 (mole dm^{-3})	Initial rate atmosphere (min^{-1})
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.025
6	0.003	0.009	0.056

Table shows the results of six experiments. In the first three experiments the concentrations 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.

$$\text{Rate} \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant by doubling the concentration of NO, the rate is increases four times and by tripling the concentration of NO, the rate is increased nine times. So, the rate is proportional to square of concentration of NO.

$$\text{Rate} \propto [NO]^2$$

So the overall equation of reaction.

$$\text{Rate} \propto [H_2]^1 \ [NO]^2$$

Hence the reaction is a **third order one**. This final equation is the rate law for this reaction. It should be kept in mind that rate law cannot be predicted from the balanced chemical equation. This set of experiments helps us to determine the order of reaction as well. The possible mechanism of the reaction is as follows.

$$2NO_{(g)} + H_{2(g)} \xrightarrow{\text{Slow}} N_{2(g)} + H_2O_{2(g)} \qquad \text{(rate determining step)}$$

$$2H_2O_{2(g)} + H_{2(g)} \xrightarrow{\text{Fast}} 2H_2O_{(g)}$$

3. Surface Area:

The increased surfaced area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance e.g. Al foil reacts with NaOH moderately when warmed but powdered Al reacts rapidly with cold NaOh and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

$CaCO_3$ in the powder form reacts with dilute HCl more efficiently than its big pieces.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

4. Light:

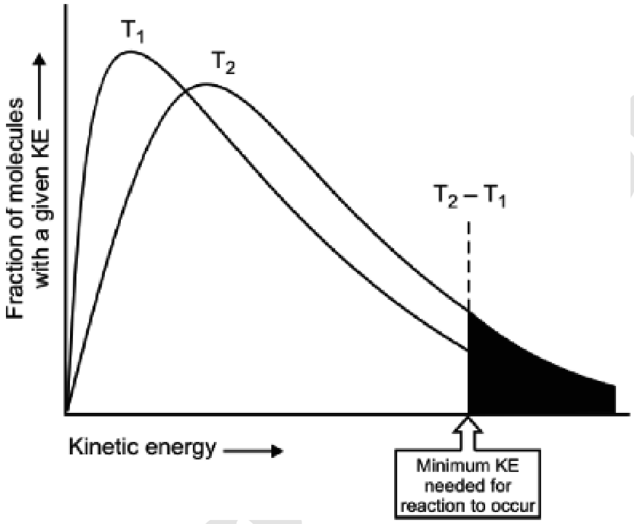
Light consists of photons having definite amounts of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced. The reaction of CH_4 and Cl_2 required light.

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in day–light but explosive in sun–light. Similarly light is vital in photosynthesis. Photography is the commercial example in which reaction involving silver halides is influenced by light.

5. Effect of Temperature:

The collision theory of reaction rates convinces us that the rate of a reaction is proportional to the number of collisions among the reactant molecules. **Anything that can increase the frequency of collisions should increase the rate**. We also know that every collision does not lead to a reaction. For a collision to be effective the molecules must to posses 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.



Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the **shaded areas** under the curves are proportional to the total fraction of the **molecules that posses the minimum 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 refraction or molecules is indicated as shaded in Figure.

As the **temperature increases**, the number of molecules is this fraction also increases. So, the **number of effective collisions increases**, when the temperature of the reacting gases is raised by 10 K, the fraction of molecules with energy more than E_a, roughly doubles and so the reaction rate also doubles.

ARRHENIUS EQUATION AND EFFECT OF TEMPERATURE

Arrhenius equation explains the effect of temperature on the rate of a reaction. The rate constant ‘k’ for many simple reactions is found to vary with temperature. According to Arrhenius.

$$K = Ae^{-Ea/RT}$$

So ‘k’ is exponentially related to activation energy E_a and temperature. T.R is general gas constant and e is the base of logarithm. The equation shows that the **increase in temperature, increases the rate constant** and the reactions of high activation energy have low ‘k’ values. The factor ‘A’ is called **Arrhenius constant** and it depends upon the collision frequency of reacting substances. This equation helps us to determine the energy of activation of the reaction as well. For this purpose, we take natural log (ln) on Arrhenius equation.

$$\ln k = \ln A + \ln e^{-Ea/RT}$$

$$\ln k = \ln A + \frac{-E_a}{RT} \ln e$$

Since $\ln e = 1$

Therefore,

$$\ln k = \frac{-E_a}{RT} + \ln A$$

$$\ln = 2.303 \log$$

$$2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A.$$

Dividing the whole equation by 2.303.

$$\log k = \frac{-E_a}{2.303\, RT} + \log A$$

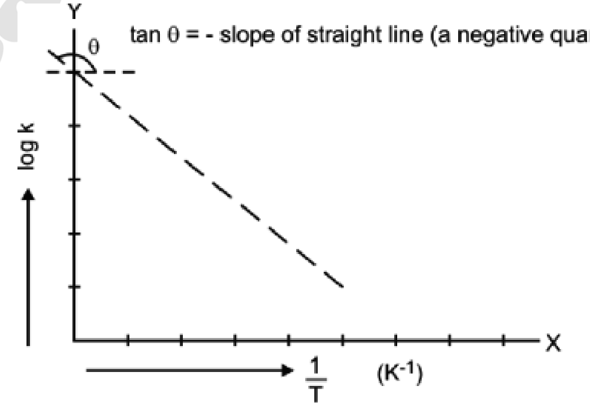
$$\log k = \frac{-E_a}{2.303\, R} \cdot \frac{1}{T} + \log A$$

↓ ↓ ↓ ↓ (y = mx + c is general equation of straight)

y = m x c

This is the equation of straight line. Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like E_a, R and A are constants for a given reactions.

When a graph is plotted between $\frac{1}{T}$ on x–axis and log k on y–axis, a straight line is obtained with a negative slope. The slope of the straight line is measured by taking tangent of that angle θ which this straight line makes with the x–axis. Thus the slope is equal to $\frac{-E_a}{2.303\, R}$. This equation is helpful to calculate activation energy of reaction.



Arrhenuis plot to calculate the energy of activation

$$\text{Slope} = \frac{-E_a}{2.303\ R}$$

Therefore,

$$E_a = -\text{Slope} \times 2.303\ R$$

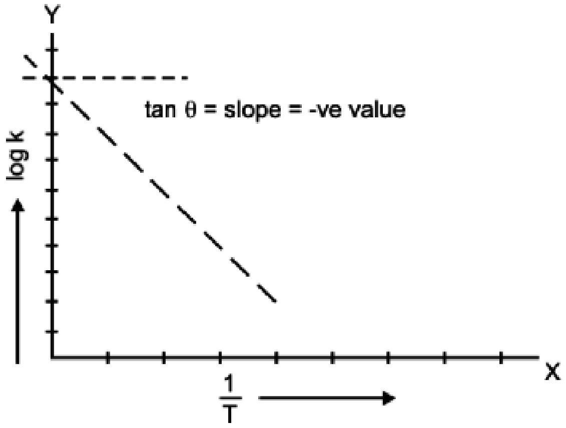
The straight lines of different reactions will have different slopes and different E_a values. The unit of slope of Kelvin (K).

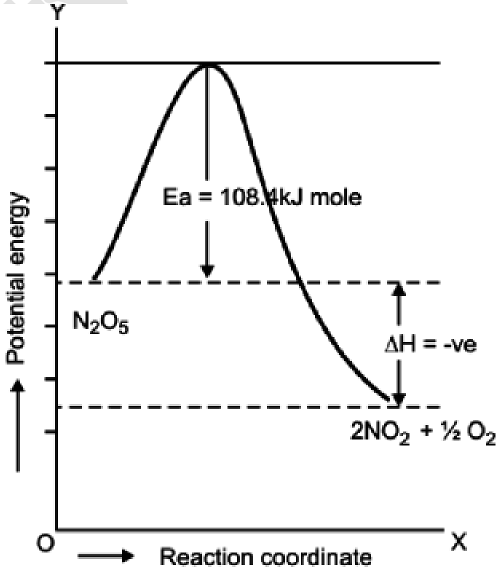
$$\text{Slope} = \frac{-E_a}{2.303\ R}$$

$$\text{Slope} = \frac{\text{J mol}^{-1}}{2.303\ \text{J K}^{-1}\ \text{mol}^{-1}} = \text{K}$$

Example 3:

(i) A plot of Arrhenius equation for the thermal decompositions of N_2O_5 is shown in the following Figure. The slope is found to be – 5400 K. Calculate the energy of activation of this reaction.





Solution:

$$\begin{aligned} E_a &= -\text{Slope} \times 2.303\ R \\ &= -(-5400\ \text{K}) \times 2.303 \times 8.3143\ \text{J K}^{-1}\ \text{mol}^{-1} \\ &= 103410\ \text{J mol}^{-1} \\ E_a &= 103.410\ \text{kJ mol}^{-1} \end{aligned}$$

(ii) Hence the decomposition of N_2O_5 needs 103.4 kJ mol^{-1} of the energy more than the average energy barrier.

The intercept of the straight line is log A and by taking the anti–log of intercept the value of Arrhenius constant A can be determined. Value of A is 4.3×10^{13} for thermal decomposition of N_2O_5. It units are the same as of k, so the Arrhenius rate equation for N_2O_5 is

$$K = 4.3 \times 10^{13} e^{\frac{-E_a}{2.303\ RT}}$$

(iii) With the help of this equation, it is possible to predict the rate of decomposition of N_2O_5 at any temperature.

CATALYST

"The substance which alters the rate of a chemical reaction is called **catalyst**."

A catalyst is often present in very small amount.

There are two types of catalyst.

(i) Positive catalyst (ii) Negative catalyst

(i) POSITIVE CATALYST

"The substance which increase the rate of reaction is called **positive catalyst**."

For example, the reaction between H_2 and O_2 in very slow at ordinary condition of temperature but proceed more rapidly in the presume of platinum catalyst.

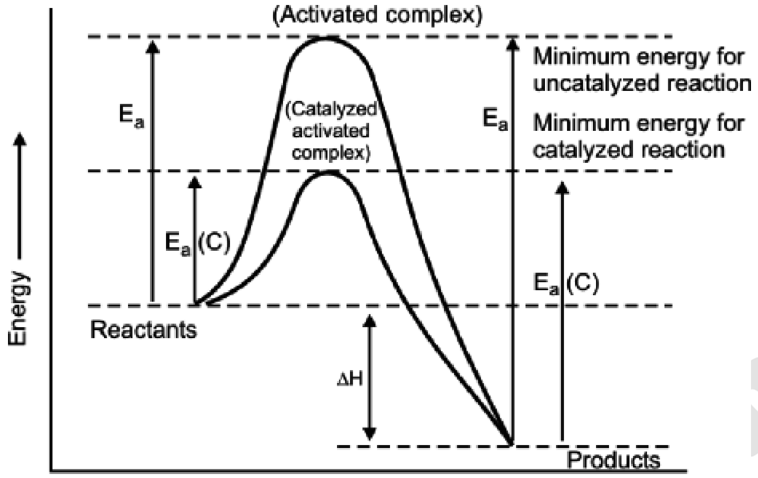
$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2. HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

By using a catalyst, the number of effective collision increases and rate of reaction increases. A catalyst changes the reaction mechanism, by providing a different, low energy mechanism for the formation of product. ΔH or enthalpy change will remain same for each path. A path of catalyzed and un–catalyzed reaction is shown in the Figure.



Catalyzed and uncatalyzed reactions.

(ii) NEGATIVE CATALYST

When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre–ignition.

AUTO CATALYSIS

"In some reactions, a product formed act as catalyst and this phenomena is called **auto catalysis**."

For Examples;

(i) In hydrolysis of ethyl acetate, acetic acid acts as catalyst for further reaction,

$$CH_3COOC_2H_5 + H_2O \overset{H_3O^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

(ii) When copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally becomes very fast. This is due to the **formation of nitrous acid** (HNO_2) during the reaction, which accelerates the process.

(iii) The reaction of oxalic acid and acidified $KMnO_4$ is slow at the beginning, but after sometime Mn^{2+} are produced in the reaction, which speed up the reaction.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \xrightarrow{Mn^{2+}} K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

PROMOTER OR ACTIVATOR

"Such a substance which promotes the activity of a catalyst is called **a promoter or an activator**. It is also called "**catalyst for a catalyst**".

For Examples:

(a) Hydrogenation of vegetable oils is accelerated by nickel. The catalytic activity of nickel can be increased by using copper and tellurium.

(b) In Haber's process for the manufacture of ammonia, iron is used as a catalyst. If small amounts of some higher melting oxides like aluminum oxide, chromium oxide or rate earth oxides are added, they increase the efficiency of iron.

Catalysis:

"The reactions which take place in the presence of catalyst are called **catalysis**."

There are two types of catalysis.

(i) Homogeneous catalyst (ii) Heterogeneous catalyst

(i) Homogeneous Catalyst:

"In the process, the catalysts and reactants have same phase and the reacting system is homogeneous throughout."

For Examples:

(i) The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphur acid, needs NO as a catalyst. Both the reactants and the catalyst are gases.

$$2SO_{2(g)} + O_{2(g)} \overset{NO_{(g)}}{\rightleftharpoons} 2SO_{3(g)}$$

(ii) Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \overset{H_3O^+}{\rightleftharpoons} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

(ii) Heterogeneous Catalysis:

"If the catalyst and reactants have different phases, it is called **heterogeneous catalysis**."

Mostly the catalyst is in the solid phase, while reactants are in the gaseous or liquid phase.

For Examples:

(i) Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_{3(g)} + 5O_{2(g)} \overset{Pt}{\rightleftharpoons} 4NO_{(g)} + 6H_2O_{(g)}$$

(ii) Hydrogenation of unsaturated organic compounds are catalyzed by finely divided Ni.

$$CH_2 = CH_{2(g)} + H_{2(g)} \overset{Ni}{\rightleftharpoons} CH_3 - CH_{3(g)}$$

(iii) $CO_{(g)} + 2H_{2(g)} \xrightarrow{ZnO - Cr_2O_{3(s)}} CH_3OH_{(l)}$

CHARACTERISTIC OF CATALYST

There are many types of catalyst with varying chemical compositions, but the following features are common to most of them.

1. A catalyst **remains unchanged** in mass and chemical compositions at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition of $KCIO_3$ 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. Sometimes we need a **traces amount** of a metal catalyst to affect very large amount of reactants. For example, 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. Dry HCl and NH_3 do not combine but in the presence of trace of moisture, they give dense white fumes of NH_4CI. Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.
3. A catalyst is **more effective** when it is present in a **finely divided** form. For 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. Fine catalyst has greater surface area.
4. 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. A catalyst cannot start a reaction, which is **not thermodynamically** feasible. The mechanism of a catalyzed reaction is different from that of an un–catalyzed reactions.
6. A catalyst is **specific in its action**. When a particular catalyst works for one reaction it may not necessarily work for any other reaction. If different catalysts are used for the same reactant than the products may change.

For Examples;

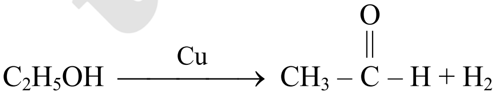
(i) Formic acid is decomposed by Al_2O_3 to water and CO while Cu causes its decomposition to H_2 and CO_2.

$$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$

(ii)

$$C_2H_5OH \xrightarrow{Al_2O_3} CH_2 = CH_2 + H_2O$$



$$C_2H_5OH \xrightarrow{Cu} CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - H + H_2$$

7. **Temperature affects the role of catalyst**. Some catalysts are physically altered by a change in temperature and hence their catalytic power will be decreased. For example, colloidal catalysts like platinum may be coagulated with rise in temperature.
8. "**Deactivation of catalyst by small amount of impurities is called poisoning of a catalyst**." Catalytic poisoning happens due to presence of trace amounts of foreign substances which render them ineffective. Such substances are called **poisons**. The poisoning of a catalyst may be temporary or permanent. In permanent poisoning, the poison reacts chemically with the catalyst. The compounds of sulphur and arsenic behave as poisons to many metallic catalysts.

For Examples:

(a) The presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst in the Haber's process for the manufacture of NH_3.

(b) The manufacture of H_2SO_4 in the contact process needs platinum as a catalyst. The traces of arsenic present as impurities in the reacting gases makes platinum ineffective. That's why arsenic purifier is employed in the contact process.

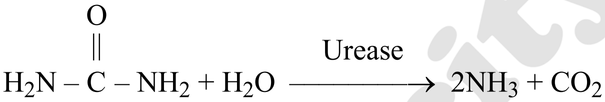
ENZYME CATALYSIS

Enzyme are complex proteins which catalyzed the chemical reactions in living systems. They are often called **biological catalysts or biocatalysts**. The reaction in which enzymes are used as catalyst are called **enzyme catalysis**.

Many enzymes have been identified and obtained in the pure crystalline state. However, first enzyme was prepared in the laboratory in 1969.

For Examples:

(a) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soybean.



$$H_2N - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

(b) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called **invertase**, present in the yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(c) Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

MODE OF ENZYME ACTION

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 molecule enters the cavities, form complex, reacts and the product get out of the cavity immediately.

In 1913, Lenore Michaels and his student M.L. Manton, studied the mechanism of enzyme catalysis.

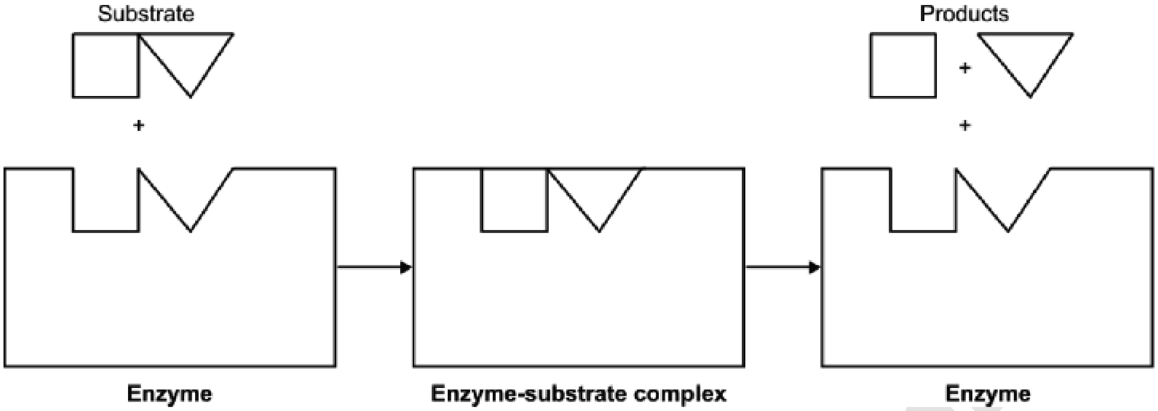
$$E + S \rightleftharpoons ES$$

$$ES \longrightarrow P + E$$

Where E = Enzyme, S = Substrate

ES = Activated complex (Reactant)

P = Product



CHARACTERISTICS OF ENZYMES CATALYSIS

The role of enzymes as catalysts is like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity.

For Examples:

(a) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.

(b) Enzyme catalysis is highly specific, for example, urea's catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.

(c) Enzyme catalytic reactions have the maximum rates at an optimum temperature.

(d) The pH of the medium also control the rates of the enzyme catalyzed reactions 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.

(e) The catalytic activity of enzymes is greatly enhanced by the presence of a co–enzyme or activator.

Co–enzyme:

"A substance needed by enzyme in order to function is called **co–enzyme**."

EXERCISE

Q.1 Multiple choice questions:

(i) In zero order reaction, the rate is independent of:

(a) temperature of reaction (b) concentration of reactants

(c) concentration of products (d) none of these

(ii) If the rate equation of a reaction 2A + B → products is, rate = $k[A]^2[B]$, and A is present in large excess, then order of reaction is:

(a) 1 (b) 2

(c) 3 (d) none of these

(iii) The rate of reaction:

(a) increases as the reaction proceeds

(b) decreases as the reaction proceeds

(c) remains the same as the reaction proceeds

(d) may decrease or increase as the reaction proceeds

(iv) With increase of 10°C temperature the rate of reaction doubles. This increase in rate of reaction is due to:

(a) decrease in activation energy of reaction.

(b) decrease in the number of collisions between reactant molecules.

(c) increase in activation energy of reactants.

(d) increase in number of effective collisions.

(v) The unit of the rate constant is the same as that of the rate of reaction in:

(a) first order reaction (b) second order reaction

(c) zero order reaction (d) third order reaction

ANSWERS

Answers		**Reasons**
(i)	(b)	The reaction whose rate is independent of concentration of reactants is said to have zero order.
(ii)	(a)	The substance which is taken in large excess and does not affect the rate of reaction and the order with respect to that reactant is zero. The order with respect to "A" is zero and that with respect to "B" is one. Hence overall order is also one.
(iii)	(b)	As the reaction proceeds, concentration of reactants decreases and rate of reaction also decreases.
(iv)	(d)	The rate of reaction depends upon no of effective collisions between reactant molecules. For every 10°C rise of temperature no of effective collisions are almost doubled and so the rate of reaction.
(v)	(c)	For zero order reaction, rate of reaction is independent of concentration of reactants. Hence, Rate $= K[\text{Reactants}]^\circ$ $= K \times 1$ Rate $= K$ For zero order reaction, units of rate and rate constant of reaction are same.

Q.2 Fill in the blanks:

(i) The rate of an endothermic reaction ―――――― with the increase in temperature.

(ii) All radioactive disintegration nuclear reactions are of ―――――― order.

(iii) For a fast reaction the rate constant is relatively ―――――― and half-life is ――――――.

(iv) The second order reaction becomes ―――――― if one of the reactants is in large excess.

(v) Arrhenius equation can be used to find out ―――――― of a reaction.

ANSWERS

Answers		Explanation
(i)	Increases	In endothermic reactions, heat is absorbed during the reaction. Hence rise of temperature will increase the rate of reaction.
(ii)	First order	
(iii)	Greater, short	
(iv)	First order	
(v)	Activation energy	

Q.3 Indicate true or false as the case may be:

(i) The half-life of a first order reaction increases with temperature.
(ii) The reactions having zero activation energies are instantaneous.
(iii) A catalyst makes a reaction more exothermic.
(iv) There is difference between rate law and the law of mass action.
(v) The order of reaction is strictly determined by the stoichiometry of the balanced equation.

ANSWERS

Answers	**Correct Statement**
(i) False	The half-life of a first order reaction decreases with temperature.
(ii) True	Activation energy is the energy barrier between reactants and products. If its value is zero, then reactants can instantly be converted into products.
(iii) False	A catalyst makes the reaction faster.
(iv) True	
(v) False	The order of reaction is not strictly determined by the stoichiometry of balance equation.

Q.4 What is chemical kinetics? How do you compare chemical kinetics with chemical equilibrium and thermodynamics?

Ans. **Chemical Kinetics:** The study of rates of chemical reactions and factors affecting the rate is called as "chemical kinetics".

Difference between chemical kinetics and chemical equilibrium:

Chemical Kinetics	Chemical Equilibrium
(i) The study of rates and mechanism of reaction is called chemical kinetics.	(i) A state of reversible reaction at which forward and backward rates become equal is called chemical equilibrium.
(ii) Rate study is possible for both reversible and irreversible reactions.	(ii) Chemical equilibrium is the characteristics of reversible reactions only.
(iii) It is related to rate of reactions and factors affecting it.	(iii) It is related to state of equilibrium and factors affecting it.

Q.5 The rate of a chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with a negative sign. Explain it with reference to the following hypothetical reaction.

$$aA + bB \longrightarrow cC + dD$$

Ans. The rate of reaction can be written with respect to reactants or products concentration. The rate of reaction with respect to concentration of reactants is written with negative sign because concentration of reactants decrease with the passage of time.

$$\text{Rate} = \frac{-d[A]}{dt} \quad \text{or} \quad \frac{-d[B]}{dt}$$

The rate of reaction with respect to concentration of products is written with positive sign because concentration of products increases as the time passes.

$$\text{Rate} = \frac{+d[C]}{dt} \quad \text{or} \quad \frac{+d[D]}{dt}$$

Q.6 What are instantaneous and average rates? Is it true that the instantaneous rate of a reaction at the beginning of the reaction is greater than average rate and becomes far less than the average rate near the completion of reaction?

Ans. The rate measured at any moment of reaction during the progress is called instantaneous rate, whereas rate of reaction between two time intervals is called average rate.

Instantaneous rate is very fast at the start. It slows down with decreasing concentration of reactants and very slow at the end, but average rate has an intermediate value (neither very slow nor very fast) because it is obtained by dividing the whole change in concentration with time.

It clearly shows that instantaneous rate is faster than average rate at start but slower than average rate at the end.

Q.7 Differentiate between:

(i) Rate and rate constant of a reaction.

(ii) Homogeneous and heterogeneous catalyses.

(iii) Fast step and the rate determining step.

(iv) Enthalpy change of reaction and energy of activation of reaction.

Ans. (i)

Rate of Reaction	Rate Constant of Reaction
(i) It is the change in concentration of reactant or product per unit time. $\text{Rate} = \frac{dx}{dt}$	(i) It is the proportionality constant and is the ratio of rate and concentration of reactants $K = \frac{\text{Rate}}{[A]^a [B]^b}$
(ii) Its units are moles.dm^{-3}.s^{-1}.	(ii) Its units are variable depending upon order of reaction.
(iii) It is a variable parameter.	(iii) It is always constant under given conditions.

(ii)

Homogeneous Catalysis	**Hetrogeneous Catalysis**
(i) A catalysed reaction in which catalyst and reaction mixture are in same phase is called homogeneous catalysis.	(i) A catalysed reaction in which catalyst and reaction mixture are in different phases is called hetrogeneous catalysis.
(ii) Example: $2SO_{2(g)} + O_{2(g)} \overset{NO_{(g)}}{\rightleftharpoons} 2SO_{3(g)}$	(ii) Example: $CH_2 = CH_{2(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}}$ $CH_3 - CH_{3(g)}$
(iii) In this case, catalyst is distributed uniformly throughout the system.	(iii) In this case, catalyst is not uniformly distributed throughout the system.

(iii)

Fast Step	**Rate Determinine Step**
(i) A step in a multi-step reaction that has high speed and do not affect the overall rate of reaction is called fast step.	(i) A step in a multi-step reaction that is slowest one and controls the overall rate of reaction is called rate determining step.
(ii) The reactants in fast step are not involved in rate equation.	(ii) Reactants in rate determining step are involved in rate equation.
(iii) Example: $NO_2 + NO_2 \xrightarrow{\text{Slow}} NO_3 + NO$ $NO_3 + CO \xrightarrow{\text{Fast}} NO_2 + CO_2$ Second step is fast step.	(iii) Example: $NO_2 + NO_2 \xrightarrow{\text{Slow (RDS)}} NO_3 + NO$ $NO_3 + CO \xrightarrow{\text{Fast}} NO_2 + CO_2$ First slow step is rate determining step.

(iv)

Enthalpy Change of Reaction	**Energy of Activation of Reaction**
(i) Heat change accompanied by chemical reaction is called enthalpy change.	(i) The minimum amount of energy in addition to average K.E, sufficient to convert reactants into products is called activation energy.
(ii) It is denoted by ΔH.	(ii) It is denoted by E_a.
(iii) It is the difference of enthalpies of reactants and products.	(iii) It is the energy barrier between reactants and products.
(iv) It may be negative or positive.	(iv) It is always positive.

Q.8 Justify the following statements:

(i) Rate of chemical reaction is an ever changing parameter under the given conditions.

(ii) The reaction rate decreases every moment but rate constant 'k' of the reaction is a constant quantity, under the given conditions.

(iii) 50% of a hypothetical first order reaction completes in one hour. The remaining 50% needs more than one hour to complete.

(iv) The radioactive decay is always a first order reaction.

(v) The unit of rate constant of a second order reaction is $dm^3\ mol^{-1}\ .\ s^{-1}$, but the unit of rate of reaction is $mol\ .\ dm^{-1}\ .\ s^{-1}$.

(vi) The sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction.

(vii) The order of a reaction is obtained from the rate expression of a reaction and the rate expression is obtained from the experiment.

Ans.

(i) The rate of a reaction is directly proportional to concentration of reactants. As the concentration of reactants is maximum at start, the rate is fast. As the time passes, the concentration of reactants decreases and rate of reaction also slows down.

During the progress of reaction, the rate of reaction slows down every moment with the decreasing concentration of reactants. Hence, it is ever changing parameter.

(ii) The rate of reaction decreases every moment with decreasing concentration of reactants. For understanding of rate constant, consider the following hypothetical reaction.

$$A + B \longrightarrow C + D$$

$$\text{Rate} = K[A][B]$$

or

$$K = \frac{\text{Rate}}{[A][B]}$$

From above equation, it is clear that rate constant "K" is the ratio of rate of reaction and concentration of reactants. As the concentration of reactants decreases, rate of reaction also decreases but the ratio remains constant.

Hence, rate constant "K" always a constant quantity.

(iii) 50% of hypothetical reaction is completed in one hour and 50% left behind.

From this 50% reaction, 25% will be completed in one hour and 25% will be left behind. Among this 12.5% will need one more hour to be completed.

37.5% of remaining 50% reaction took 2 hours and 12.5% will still left behind. Hence this remaining 50% requires more than one hour to complete.

$$(100\% \xrightarrow{\text{1 hour}} 50\% \xrightarrow{\text{1 hour}} 25\% \xrightarrow{\text{1 hour}} 12.5\% \ldots)$$

(iv) During radioactive decay, nuclei of only one type are broken up and no other specie is involved. The rate of this decay depends upon concentration of nuclei of only one type. Hence, it follows first order kinetics.

(v) Equation for rate of reaction is:

$$\text{Rate} = \frac{\text{DC}}{\text{Dt}} = \frac{\text{Change in conc.}}{\text{Change in time}}$$

$$= \frac{\text{moles.dm}^{-3}}{\text{s}^{1}}$$

$$\text{Rate} = \text{moles.dm}^{-3}.\text{s}^{-1}$$

Second order reaction:

$$A + B \longrightarrow C + D$$

$$\text{Rate} = K\,[\,A\,]\,[\,B\,]$$

$$K = \frac{\text{Rate}}{[\,A\,]\,[\,B\,]}$$

$$= \frac{\text{moles.dm}^{-3}.\text{s}^{-1}}{\text{moles.dm}^{-3} \times \text{moles.dm}^{-3}}$$

$$K = \text{dm}^{3}.\text{mol}^{-1}.\text{s}^{-1}$$

(vi) For many reactions, the order is not equal to the sum of co-efficient of balanced because reaction proceeds in more than one steps and order and rate expression is derived from slowest step (rate determining step).

Consider the reaction:

$$2NO + 2H_2 \longrightarrow 2H_2O + N_2$$

The sum of coefficients is four and order is three. This order is experimentally determined from mechanism of reaction.

Mechanism:

$$2NO + H_2 \xrightarrow{\text{Slow}} H_2O_2 + N_2 \qquad \text{(rate determining step)}$$

$$H_2O_2 + H_2 \xrightarrow{\text{Fast}} 2H_2O$$

$$\text{Rate} = K\,[H_2]^1\,[NO]^2$$

(vii) Many reactions that consists of more than one steps. There is always one step which is slowest one and controls the overall rate and order of reaction. This slow step is called rate determining step and is experimentally determined. And rate expression is written on the basis of this step.

Experimentally determined mechanism of reaction is:

$$NO_2 + NO_2 \xrightarrow{\text{Slow}} NO_3 + NO$$

$$NO_3 + CO \xrightarrow{\text{Fast}} NO_2 + CO_2$$

and rate expression is:

$$\text{Rate} = K\,[NO_2]^2$$

Q.9 Explain that half-life method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.

Ans. Descriptive question consult text book for details.

Q.10 A curve is obtained when a graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points give us the instantaneous rates of reaction. Explain with suitable examples.

Ans. Descriptive question consult text book for details.

Q.11 The rate determining step of a reaction is found out from the mechanism of that reaction. Explain with few examples.

Ans. Detailed question for answer see text book.

Q.12 Discuss the factors which influence the rates of chemical reactions.

Ans. Descriptive question see text book.

Q.13 Explain the following facts about the reaction.

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

(i) The changing concentrations of reactants, change the rates of this reaction.

(ii) Individual orders with respect to NO and H_2 can be measured.

(iii) The overall order can be evaluated by keeping the concentration of one of the substances constant.

Ans.

(i) The effect of changing concentration or rates of this reaction can be studied from following experimental data.

	[NO]	[H_2]	Rates
1.	0.006	0.001	0.025
2.	0.006	0.002	0.050
3.	0.006	0.003	0.075
4.	0.001	0.009	0.0063
5.	0.002	0.009	0.025
6.	0.003	0.009	0.056

The data shows that rate of reaction is changed when concentration of one reactant is changed by keeping the other's constant.

(ii) Above data shows that when rate is studied by changing the concentration of H_2 and by keeping the concentration of NO constant. It comes out to be that rate of reaction is directly proportional to the concentration of H_2.

$$\text{Rate} = K [H_2]^1$$

And individual order with respect to hydrogen is one.

Similarly, rate of reaction is directly proportional to the square of concentration of NO. It is clear from data, when concentration of NO is increased to two times, rate increases four times.

$$\text{Rate} = K [NO_2]^2$$

And individual order with respect to NO is 2 and reaction is of 2nd order.

(iii) When concentration of NO is kept constant, the rate of reaction comes out to be directly proportional to concentration of H_2 and order is 1.

$$\text{Rate} = K\,[H_2]^1$$

When concentration of H_2 is kept constant, the rate of reaction comes out to be directly proportional to square of concentration of NO and order is 2.

$$\text{Rate} = [NO]^2$$

Hence, overall rate expression is:

$$\text{Rate} = K\,[H_2]^1\,[NO]^2$$

So, overall order is 3 and reaction is of third order.

Q.14 The collision frequency and the orientation of molecules are necessary conditions for determing the proper rate of reaction. Justify the statement.

Ans. Descriptive question consult text book.

Q.15 How does Arrhenius equation help us to calculate the energy of activation of reaction?

Ans. Detailed question see text book for answer.

Q.16 Define the following terms and give examples:

(i) Homogeneous catalysis **(ii) Heterogeneous catalysis**
(iii) Activation of a catalyst **(iv) Auto-catalysis**
(v) Catalytic poisoning **(vi) Enzyme catalysis**

Ans. For definitions consult text book.

Q.17 Briefly describe the following with examples:

(i) Change of physical state of a catalyst at the end of reaction.
(ii) A very small amount of a catalyst may prove sufficient to carry out a reaction.
(iii) A finely divided catalyst may prove more effective.
(iv) Equilibrium constant of a reversible reaction is not changed in the presence of a catalyst.
(v) A catalyst is specific in its action.

Ans.

(i) A catalyst remains chemically unchanged but changes physically at the end of reaction.

Example:

(i) Granular catalyst (MnO_2) for the decomposition of $KClO_3$ is converted into powder form.

(ii) Shining surface of Pt is made dull, when it is used as catalyst for hydrogenation of vegetable oil.

(ii) Since, catalyst itself is not used up, it can catalyse a reaction between large amount of reactants.

Example:

(i) 1 g of Pt can catalyse a reaction between 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to form water.

(ii) Thousands of dm^3 of H_2O_2 can decompose in the presence of 1 g of colloidal platinum.

(iii) When catalyst is finely divided, it has greater surface area and is more effective.

Example:

(i) Colloidal platinum has far more catalytic activity than lump of Pt.

(ii) For hydrogenation of vegetable oils, finely divided Nickel is used.

(iv) When catalyst is added at the equilibrium position of a reversible reaction, it equally speed up the rate of forward and backward reaction. Hence, equilibrium is not disturbed and equilibrium constant remains constant.

Example:

$$2SO_2 + O_2 \xrightleftharpoons{V_2O_5} 2SO_3$$

(v) When a particular catalyst works for one reaction, it may not necessarily work for any other reaction. If different catalysts are used for same reactants then the product may change.

Example:

(i) $HCOOH \xrightarrow{Al_2O_3} H_2O + CO$

(ii) $HCOOH \xrightarrow{Cu} H_2 + CO_2$

Q.18 What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis.

Ans. Detailed question consult text book.

Q.19 In the reaction of NO and H_2, it was observed that equimolecular mixture of gases at 340.5 mm of Hg, was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction.

Ans. Initial pressure of NO and H_2 are the initial concentrations of reactants and denoted by "a" and "a_2". The half life period are t_1 and t_2.

a_1 = 340.5 mm Hg

Half-life period t_1 = 102 seconds

a_2 = 288 mm Hg

Half-life period t_2 = 140 seconds

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Putting the values:

$$n = 1 + \frac{\log\left[\frac{102}{140}\right]}{\log\left[\frac{288}{340.5}\right]}$$

$$n = 1 + \frac{\log(0.728)}{\log(0.845)}$$

$$n = 1 + \frac{-0.1378}{-0.0731}$$

$$n = 1 + 1.88 = 2.88$$

The value of n is very close to three, so, the reaction is third order.

Q.20 A study of chemical kinetics of a reaction

$$\mathbf{A + B \longrightarrow Products}$$

gave the following data at 25°C. Calculate the rate law.

[A]	[B]	Rate
1.00	0.15	4.2×10^{-6}
2.00	0.15	8.4×10^{-6}
1.00	0.2	5.6×10^{-6}

Ans. The rate of this chemical reaction is directly proportional to A and B concentrations with certain exponents. We have to determine those exponents.

In first two experiments it is clear that when the concentration of A is doubled, the rate is doubled. Hence, rate of reaction with respect to A is with exponent as unity.

So, $\text{Rate} \propto [\,A\,]^1$

Reaction is first order with respect to A.

Compare experiment 1 and 3. When the concentration of B is increased from 0.15 to 0.2, the rate increases for 4.2×10^{-6} to 5.6×10^{-6}. The increase is proportional to the first power of B;

$$\text{Rate} \propto [\,B\,]^1$$

In order words, the reaction is first order with respect to B.

The overall rate law is:

$$\text{Rate} \propto [\,A\,][\,B\,]$$

$$\text{Rate} = K[\,A\,][\,B\,]$$

So, the reaction is of second order.

Q.21 Some reactions taking place around room temperature have activation energies around 50 KJ mol^{-1}:

(i) What is the value of the factor $e^{-\frac{Ea}{KT}}$ at 25°C?

(ii) Calculate this factor at 35°C and 45°C and note the increase in this factor for every 10°C rise in temperature.

(iii) Prove that for every 10°C rise in of temperature, the factor doubles and so rate constant also doubles.

Ans.

(i) To calculate the exponential factor at 25°C, we put E_a and T in Arrhenius factor.

(i) E_a = 50 KJ mol^{-1} = 50000 J mol^{-1}

T = 25°C = 298 K

R = 8.3143 JK^{-1} mol^{-1}

$e^{-\frac{Ea}{RT}}$ = ?

Putting the values:

$$= e^{-\frac{50000}{8.3143 \times 298}}$$

$$= e^{-\frac{50000}{2477.6}}$$

$$= e^{-20.188} = 1.72 \times 10^{-9}$$

(ii) Exponential factor at 35°C:

E_a = 50000 J mol^{-1}

R = 8.3143 K^{-1}J mol^{-1}

Putting values:

$$e^{-\frac{Ea}{RT}} = e^{-\frac{50000 \text{ J mol}^{-1}}{8.3143 \times 308}}$$

$$= e^{-19.52} = 3.31 \times 10^{-9}$$

(iii) Exponential factor at 45°C:

E_a = 50000 J mol^{-1}

R = 8.3143 K^{-1} mol^{-1}

T = 45°C = 318 K

$$= e^{-\frac{50000}{8.314 \times 318}}$$

$$= e^{-18.91} = 6.12 \times 10^{-9}$$

The results indicate that:

Exponential factor at 25°C = 1.72×10^{-9}

Exponential factor at 35°C = 3.31×10^{-9}

Exponential factor at 45°C = 6.12×10^{-9}

(iii) $$\text{Rate} = Ae^{-\frac{Ea}{RT}}$$

Since the factor A is almost constant for a particular reaction, hence, when the exponential factor doubles, then rate is doubled. For every 10°C increase of temperature, the rate has almost doubled.

Q.22 H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures (K) have been collected:

(i) Plot a graph between $\frac{1}{T}$ on x-axis and log k on the y-axis.

(ii) Measure the slope of this straight line and calculate the energy for activation of this reaction.

Temp. (K)	Rate constant ($cm^3\ mol^{-1}\ s^{-1}$) (k)
500	6.814×10^{-1}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

Ans.

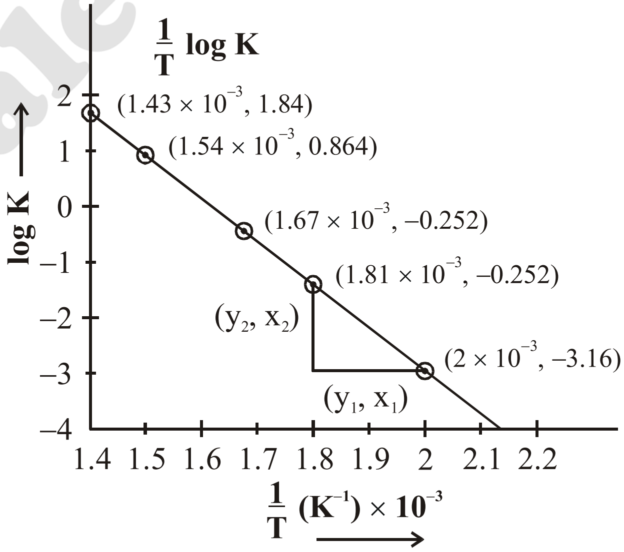
(i)

	$\frac{1}{T}$ (K^{-1}) units	log K
1.	2×10^{-3}	−3.16
2.	1.8×10^{-3}	−1.578
3.	1.67×10^{-3}	−0.252
4.	1.54×10^{-3}	0.864
5.	1.43×10^{-3}	1.824

GRAPH:

Scale: On x-axis 1 big square = 0.2×10^{-3}

On y-axis 1 big square = 2



(ii) Slope:

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

$$= \frac{-1.578 - (-3.16)}{1.81 \times 10^{-3} - 2 \times 10^{-3}}$$

$$= \frac{1.582}{-0.19 \times 10^{-3}}$$

$$\boxed{\text{Slope} = -8326.32}$$

$$\boxed{\text{Ea} = -\text{Slope} \times 2.303\ R}$$

$$= -(-8326.32) \times 2.303 \times 8.314$$

$$= 159425.15 \text{ J/mol}$$

$$= 159.42515 \text{ kJ/mol}$$

$$\sim 160 \text{ kJ/mol}$$

KNOW?

1. Units of rate of reaction = moles dm^{-3} sec^{-1}.
2. The rate of reaction between two specific times is called average rate.
3. The rate of any one instant in a specific interval of time is called instantaneous rate.
4. The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction.
5. Total number of molecules taking part in a chemical reaction is called molecularity.
6. The sum of exponents of the concentrations of the reacting species in the observed rate law is called order of a reaction.
7. The reaction in which rate of reaction does not depend upon the concentration of any reactant is called zero order reaction.
8. All photochemical reactions are of the zero order.
9. The reaction in which rate of reaction depends upon the concentration of only one substance is called first order reaction. For example: decomposition of N_2O_5.
10. The reaction in which rate of reaction depends upon the concentration of two molecules of the reacting substances is called second order reaction. For example:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

11. The reaction in which rate of reaction depends upon the concentration of three molecules of the reacting substances is called third order reaction. For example:

$$FeCl_3 + 3KI \longrightarrow FeI_2 + 3KCl + \frac{1}{2} I_2$$

12. The time required to convert 50% of the reactants into the products is called "half-life period".

13. In the first order reaction, half-life period of the reaction is independent of the initial concentration.

14. The minimum amount of energy in addition to average kinetic energy which the molecules must possess for effective collision is called activation energy.

15. The increased surface area increases the rate of reaction.

16. Increase in temperature also increase the rate of reaction.

17. The substance which alters the rate of chemical reaction is called catalyst.

18. The catalyst which increases the rate of chemical reaction is called positive catalyst. For example:

$$2H_2 + O_2 \xrightarrow{\text{Pt}} 2H_2O$$

19. The substance which decreases the rate of chemical reaction is called negative catalyst. For example: Tetra ethyl lead is negative catalyst in the combustion of petrol.

20. In some reaction, one of the products formed acts as a catalyst. It is called auto-catalysis. For example: In the hydrolysis of ethyl acetate, acetic acid produced acts as catalyst.

21. The substance which promotes the activity of a catalyst is called promoter or activator. It is also called "catalyst for a catalyst". For example: In the hydrogenation of vegetable oils, Ni is used as catalyst. The catalytic activity of N, is increased by adding copper or tellurium.

22. The process in which the catalyst and reactants have same phase is called homogeneous catalysis. For example: In the lead chamber process for the manufacture of H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[NO_{2(s)}]{NO_{(g)}} 2SO_3$$

23. The process in which catalyst and the reactants have different phases is called hetrogenoeus catalysis. For example: In the oxidation of NH_3 to form NO in the ostwald's process pt is used as catalyst.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{\text{Pt}} 4NO_{(g)} + 6H_2O_{(g)}$$

24. Units of rate of reaction $=$ mol dm^{-3} sec^{-1}

$$\begin{bmatrix}\text{Units of K for zero-order reaction and}\\ \text{Units of K and reaction of reaction are same}\end{bmatrix} \longrightarrow \text{mol dm}^{-3}\text{ sec}^{-1}$$

Units of K for the first order reaction $=$ s^{-1}

Units of K for the second order reaction $=$ dm^3 mol^{-1} s^{-1}

Units of K for the third order reaction $=$ dm^6 mol^{-2} sec^{-1}