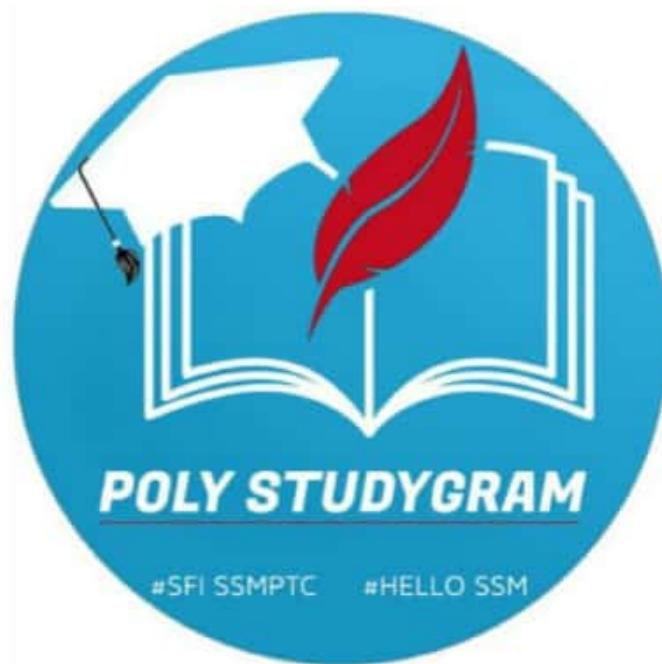


CHEMISTRY

1st sem



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MODULE I

ATOMIC STRUCTURE I, NANO CHEMISTRY AND CATALYSIS

ATOMIC STRUCTURE I

Chemistry plays very important role in our daily life. It has helped us to meet all our requirements for a better life such as food, good health, comforts etc. Without the knowledge of Chemistry, our life would have been very dull and dreary.

Chemistry is defined as a branch of science which deals with the study of composition, structure and properties of matter as well as its changes under different conditions. Antoine Lavoisier is known as father of modern Chemistry.

Matter is defined as anything that have mass, occupies space and the presence of which can be felt by any one or more of our five senses namely sight, touch, smell, hearing and taste.

Classification of Matter

Matter is generally classified into two types

(A) Physical Classification

(B) Chemical Classification

(A) Physical Classification:-

Based on physical state under ordinary conditions of temperature and pressure, matter is classified into three types:-

(1) Solids (2) Liquids (3) Gases

(B) Chemical Classification:-

Matter is broadly classified into two types

(1) Homogeneous (2) Heterogeneous.

A material is said to be homogeneous if it has uniform composition and identical properties throughout, that is, it consists of only one phase.

A material is said to be heterogeneous if it consists of more than one phase.

A more scientific way of chemical classification of matter is as follows.

A material containing only one substance is called a pure substance, whereas materials containing more than one substance are not pure and are called mixtures.

Pure substance are further classified into (a) Elements and (b) Compounds. An Element is defined as a pure substance that contains only one type of atoms and is classified into :-

(i) Metals :- example : Silver (Ag), Gold (Au), Copper (Cu) etc.

(ii) Non Metals:- example : Oxygen (O_2), Nitrogen (N_2), Fluorine (F_2) etc.

(iii) Semi Metals (Metalloids):- example : Silicon (Si), Germanium (Ge), Antimony (Sb) etc.

A compound is a pure substance containing two or more elements combined together in a fixed proportion by weight and which can be decomposed into its constituent elements by chemical methods.

All compounds may be divided into the following two categories:-

(1) Organic Compounds :	They are compounds containing carbon and a few other elements like hydrogen, oxygen, nitrogen etc. These were originally obtained from plants and animals: example: Methane (CH_4), Benzene (C_6H_6) etc.
(2) Inorganic Compounds:	They contain any two or more elements. They are Obtained from minerals and rocks: example : Water (H_2O), Ammonia (NH_3) etc.

A material containing two or more elements or compounds in any proportion is called a mixture.

Mixtures are also of two types :

(a) Homogeneous mixture : example: pure air, salt dissolved in water, brass etc.

- (b) Heterogeneous mixture: example: Impure air, mixture of Iron and Sulphur, Milk, smoke etc.

Atom and Molecule

Although we have seen classification of matter into Elements, Compounds and Mixtures, a number of following type of questions still remain unanswered, such as different elements differ in their properties, elements combines to form compounds etc.

To answer these questions, it is essential to look into structure of matter, that is, what are the building block of matter. The concept that matter was made up of small particles was put forward by Greek philosopher Democritus and these ultimate particles were called 'atomos' which means indivisible. The continued sub divisions of matter would ultimately yield atoms which would not be further divisible. These ideas about atoms were only speculations which remained dominant for a very long time.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British School teacher in 1808 and his theory is known as **Dalton's atomic theory**.

According to this theory, an atom is the smallest particle of an element which can take part in a chemical reaction. It may or may not be capable of independent existence.

An idea about another important fundamental particle of matter, namely molecule, was proposed by an Italian Scientist, Amedeo Avagadro. According to him, a molecule is the smallest particle of an element or compound which is always capable of independent existence.

Sl. No.	Atom	Molecule
1.	Atom is the smallest particle of an element	Molecule is the smallest particle of element or compound
2.	It may or may not exist in the free state	It can always exist in the free state
3.	It is indivisible by chemical means	It can be split by chemical means
4.	It can directly take part in chemical reaction	Molecule split into atoms during a chemical reaction and these atoms then take part in reactions
5.	It may or may not exhibit the properties of element	It can exhibit properties of element or compound.

The Dalton's atomic theory continued to hold good for a number of years. However, the researches done by various eminent scientists like J.J.Thomson, Goldstein, Rutherford, Chadwick, Bohr and others have established that atom was not the smallest indivisible particle but had a complex structure of its own and is made up of still smaller particles like electrons, protons, neutrons etc.

At present, about 35 different subatomic particles are known, but the three particles namely electron, proton and neutron are regarded as the fundamental particles.

Fundamental Particles - Their Charge And Mass

The charge and mass of the fundamental particles are given below:-

Name	Symbol	Absolute Charge (C)	Relative Charge	Mass (kg)	Mass (u)	Approximate Mass (u)
Electron	e	-1.6022x10 ⁻¹⁹	-1	9.10939x10 ⁻³¹	0.00054	0
Proton	p	+1.6022x10 ⁻¹⁹	+1	1.67262x10 ⁻²⁷	1.00727	1
Neutron	n	0	0	1.67493x10 ⁻²⁷	1.00867	1

One u = one a.m.u = 1/12th the mass of one

Carbon - 12 atom = 1.66056x10⁻²⁷ kg

(u=unified mass ; a.m.u=atomic mass unit)

An electron is defined as a fundamental particle which carries one unit negative charge and has mass nearly equal to 1/1837th that of hydrogen atom.

It is represented as $_{-1}e^0$

Electron was discovered by **J.J.Thomson** and name was assigned by **Johnstone stoney**. The charge of electron was determined by **R.A. Millikan** with the help of **oil drop experiment**. The ratio of charge/mass (e/m) of electron was determined by **J.J.Thomson** and the value was found to be **1.7588x10¹¹ Ckg⁻¹**.

A proton is defined as a fundamental particles which carries one unit positive charge and has a mass nearly equal to that of hydrogen atom. It is represented as $_{+1}p^1$ or $_{+1}H^1$.

Proton was discovered by **Goldstein** and name was given by **Rutherford**. The ratio of Charge/mass (e/m) of proton is **9.58 x 10⁷ Ckg⁻¹**.

A neutron is defined as a fundamental particles which carries no charge and has a mass nearly equal to that of hydrogen atom or proton. It is represented as $_{0}n^1$. Neutron was discovered by **James Chadwick**.

Atomic Number(Z) and Mass Number (A)

Atomic number of an element is defined as number of protons present in the nucleus of one atom or total number of electrons present in neutral atom.

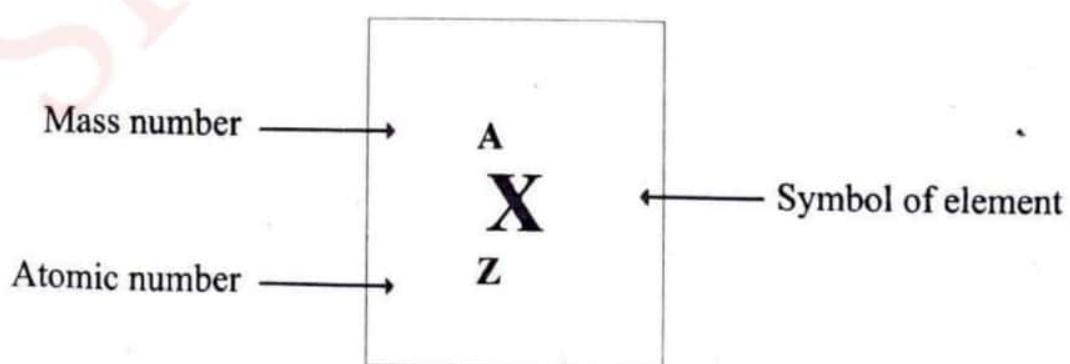
Atomic number (Z) = Total number of protons
in the nucleus of atom.
= Total number of electrons
in a neutral atom.

Since Protons and neutrons are together present in the nucleus of atom, they are collectively known as **nucleons**.

Mass number of an element is defined as total number of protons and neutrons present in the nucleus of atom or the total number of nucleons.

Mass number (A) = No of protons (Z) + No.
of neutrons (n)
= Z + n

The atomic number (Z) and mass number (A) of an element, X are usually represented along with the Symbol of the element as



Number of electrons	=	number of protons	=	Atomic number (z)
Number of protons	+	number of neutrons	=	Mass number (A)
No. of neutrons	=	Mass number (A)	-	Atomic number (z)

Eg:

- 1) $^{23}_{11}\text{Na}$: Element = Na = Sodium
 Atomic number (Z) = 11
 Mass number (A) = 23
 No. of protons = No. of electrons = 11
 No. of neutrons = A-Z = 23-11 = 12
- 2) $^{35}_{17}\text{Cl}$ Element = Cl = chlorine
 Atomic number (Z) = 17
 No of electrons = No. of protons = 17
 No. of neutrons = A-Z = 35-17 = 18

NANOCHEMISTRY

Nanochemistry is a new branch of **nanoscience** related with the production and the reactions of particles at the molecular level. **Nano Chemistry** presents a unique approach to building devices with a molecular scale precision.

Studies of nano chemical systems includes many areas like study of interaction of individual atoms, control of chemical reactions at atomic level and to build larger molecular assemblies like polymers.

As nano chemistry offers a method of building objects and devices atom by atom, the advantages of nano devices is used in scientific exploration, medicines, electronics and a host of other fields. Nano chemistry is an integral part of the multidisciplinary technology at the nano scale which is known as **nanotechnology**.

Nano Scale

The prefix “nano” (Greek for “dwarf”) means one billionth. One nano meter (nm) is one billionth or 10^{-9} , of a meter. How small is a nano can be shown by an example : Population of India is one billion and assume that each one has a height of 1 nm. If the entire population stands one over the other, the total length will be 1 meter.

Nano chemistry is the study of materials of the size 1 to 100 nm range. $1\text{ nm} = 10^{-9}\text{ m} = \text{one billionth of a meter}$.

Limit of eye's ability to see $\approx 10,000\text{ nm}$

Diameter of hair $\approx 750000\text{ nm}$

Nano sized materials

- | | |
|--------------------|--------------------------|
| 1. DNA width | $\approx 2\text{ nm}$ |
| 2. H-atom | $\approx 0.1\text{ nm}$ |
| 3. Bucky ball | $\approx 1\text{ nm}$ |
| 4. Carbon nanotube | $\approx 1.3\text{ nm}$ |
| 5. E.Coli bacteria | $\approx 2000\text{ nm}$ |

Applications of nano materials

1. Nano materials or nano crystals provide large surface area. Hence they act as better catalysts.
2. Tumours can be detected and located with incredible accuracy.

3. Nano shells (100 nm diameter) can float through the body attaching only to cancer cells. When excited by a laser beam, they give off heat and thereby destroy tumour.
4. New borns will have their DNA mapped quickly.
5. Nano technology will enable the delivery of right amount of medicines to the exact spot of the body.
6. Nano technology can create biocompatible joint replacements and artery stents that will last the life of the patients. Hence these need not be replaced every few years.

Carbon nanotube (CNT)

A carbon nanotube is a structure which seems to be formed by rolling a sheet of graphite into the shape of a cylindrical tube. Some of these tubes are closed at the ends and some are open.

Varieties of carbon nanotubes

There are two varieties of carbon nanotubes.

- (a) SWCNT – Single Walled Carbon nanotube
- (b) MWCNT – Multi Walled Carbon nanotube.

SWCNT is just a single cylinder whereas MWCNT consists of multiple concentric nanotube cylinders. Based on the orientations of lattices, nanotubes are of three different types. Arm chair, Zigzag and Chiral.

Synthesis of Carbon nanotubes

Different methods are available for synthesis of carbon nanotubes.

(1) High pressure carbon monoxide deposition (HiPCO)

In this method, Carbon monoxide gas and small clusters of Iron atoms are heated in a chamber under pressure. Carbon monoxide molecules settle on iron clusters and breaks into Carbon and Oxygen atoms. Iron acts as catalyst for breaking. One Carbon atom binds with other Carbon atom to start the formation of nanotube lattices. Oxygen atoms combine with carbon monoxide to give Carbondioxide.

(2) Chemical vapour deposition (CVD)

In this method, a hydrocarbon like methane, acetylene etc is led into a heated chamber containing a substrate coated with Iron catalyst. Due to high temperature in the chamber, C – H bonds breaks and C atoms are formed. They bind together forming nanotubes.

(3) Plasma Process (Plasma enhanced CVD)

In this methane gas which is the source of Carbon is passed through a plasma torch. The C-H bond of methane breaks and carbon atoms formed combine to form nanotubes.

(4) Arc – discharge method.

An electric arc is created between two graphite electrodes, one positive and the other negative, by passing a current of 50 amperes in an atmospheres of Helium.. At this high temperature of electric arc, Carbon from negative electrode, (cathode) vapourises and deposit in the form of Carbon nanotubes. This method is an expensive method and yields less than 30% CNT. It was initially used to produce fullerenes .

5) Laser ablation method:

A laser, which is a source of pumping high energies in a short amount of time, is used to vapourise graphite (Carbon). The vapourised Carbon is then condensed on a cooled surface when carbon nanotubes are formed. This method is more expensive relative to Arc discharge method and chemical vapor deposition method, but has a higher yield and is better controlled.

Properties of Carbon nanotubes

1. Carbon nanotubes are very very strong.
2. Their tensile strength is 100 times greater than that of steel of the same diameter.
3. Young's modulus (a measure of force required to bend a material) is about 5 times higher than for steel.
4. They have high thermal conductivity – more than 10 times that of silver.
5. They conduct electricity better than metals.
6. Electron travelling through a carbon nanotube behaves like a wave travelling through a smooth channel. This movement of electron within a nanotube is called 'ballistic transport'.
7. They are light weight, density about one fourth of steel.
8. They are sticky due to Van der Waal's forces of attraction.

Applications of nanotubes

1. They are strengtheners of composite materials.
2. They act as molecular size test tubes or capsules for drug delivery.
3. Depending on their size, they act as electrical conductors or semiconductors.

4. They are used as tips for analysis of DNA and proteins by atomic force microscopy (AFM).
5. They are used as heat conductors, without no energy loss.
6. They are used as replacement for copper in integrated circuits due to its high current – carrying capacity and stable thermal and structural properties.
7. Single walled nanotubes are used in photovoltaic industry.

CATALYSIS

Potassium chlorate (KClO_3), when heated strongly decomposes slowly giving dioxygen. The decomposition occurs slowly even in a high temperature range of 653 - 873 K.



However, when a little of manganese dioxide (MnO_2) is added, the decomposition takes places at a much faster rate at a lower temperature range, of 473—633 K. The added MnO_2 remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the presence of a foreign substance. The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius. In 1835, he suggested the term 'Catalyst' for such substances.

A substance which can change the speed of a chemical reaction without being used up in the reaction and recovered unchanged chemically and quantitatively at the end of the reaction is known as **Catalyst** and the phenomenon is known as **Catalysis**.

A catalyst accelerates the rate of a chemical reaction by providing an alternate easier path way for the reaction which requires lower energy.

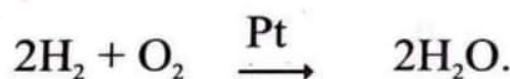
A small amount of the catalyst can catalyse a large amount of reactants. A catalyst cannot initiate a chemical reaction. A catalyst does not change equilibrium concentrations of reactants and products as well as equilibrium constant of a reaction. Since a catalyst catalyses the forward and backward reactions to the same extent, the equilibrium state remains same, but it attains faster.

Two important features of a solid catalyst are:

1. Activity 2. Selectivity

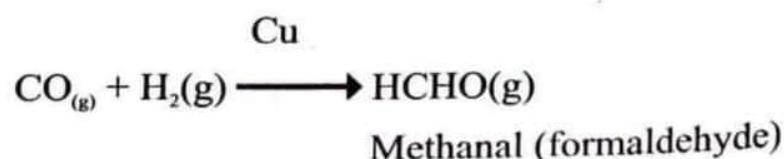
(1) Activity: By activity of the catalyst, we mean its capacity to increase the speed of the chemical reaction.

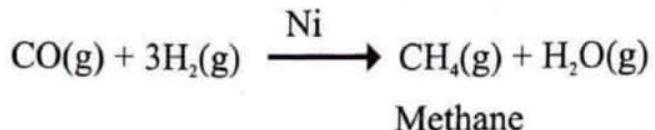
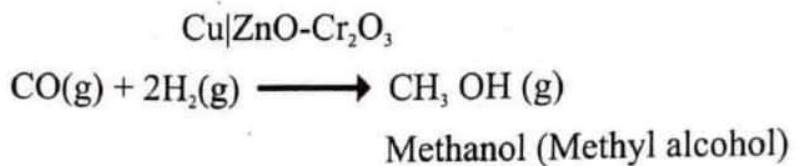
For example, combination of H₂ and O₂ in the presence of Platinum as catalyst to form water occurs with explosive violence where as in the absence of Platinum, H₂ and O₂ do not combine.



(2) Selectivity: By selectivity of a catalyst means its ability to direct the reaction to form particular products excluding others.

For example : Carbon monoxide (CO) and dihydrogen (H₂) react to form different products in presence of different catalysts as follows.



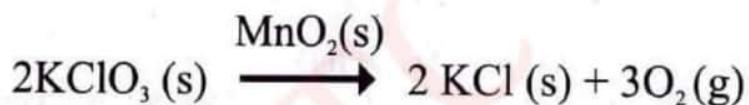


IMPORTANT TERMS

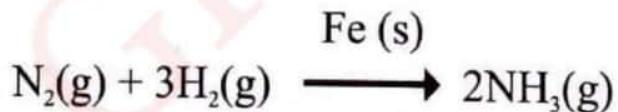
Positive Catalyst : When a catalyst increases the rate of a reaction, it is called **positive catalyst**.

Examples:

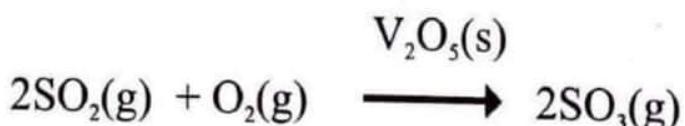
- a) Decomposition of Potassium Chlorate (KClO_3) using Manganese dioxide (MnO_2) catalyst.



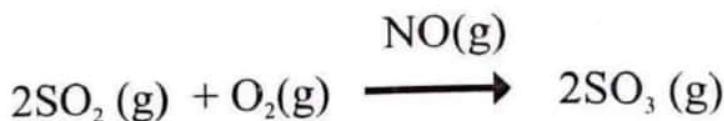
- b) Manufacture of Ammonia by Haber's Process using Iron as catalyst.



- c) Oxidation of Sulphur dioxide (SO_2) to Sulphur trioxide (SO_3) using V_2O_5 (Vanadium Pentoxide) (or) Platinum (Pt) catalyst in Contact process for manufacture of Sulphuric acid (H_2SO_4)



- d) Oxidation of SO_2 to SO_3 using Nitric Oxide (NO) as catalyst in Lead Chamber Process for manufacture of H_2SO_4 .

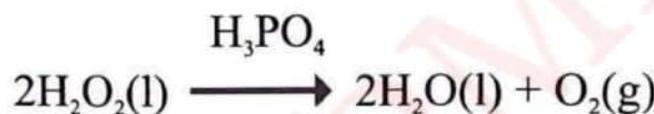


2) Negative Catalyst : (Inhibitor / Retarder)

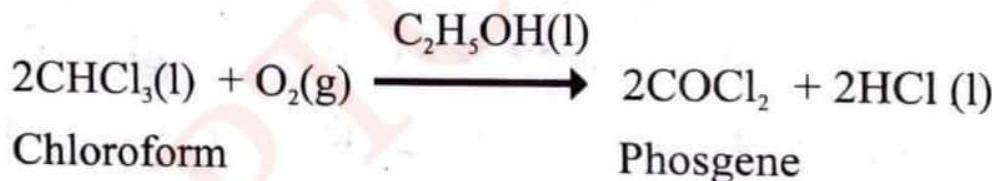
When a catalyst decreases the rate of a reaction, it is called **negative catalyst**.

Examples:

- a) Decomposition of Hydrogen Peroxide (H_2O_2) is retarded in presence of phosphoric acid (H_3PO_4) or glycerine.



- b) Oxidation of chloroform is retarded in presence of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)

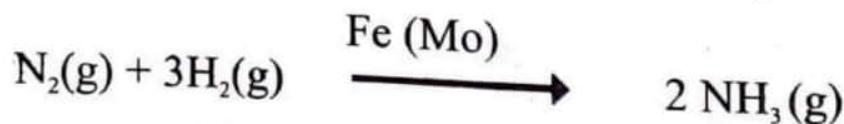


3) Promoter:

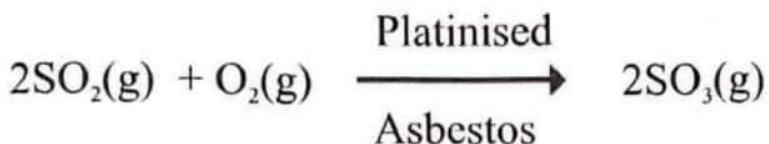
A substance which can enhance the activity of a catalyst is called **promoter**. Thus promoter act as a catalyst for a catalyst.

Examples:

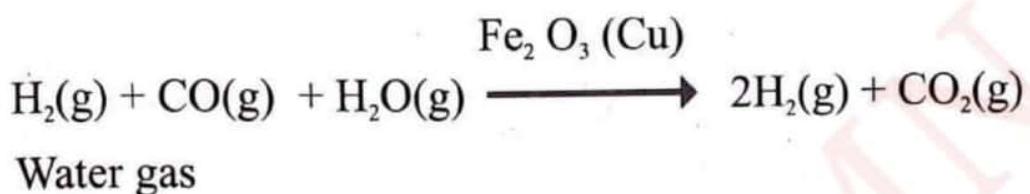
- a) In the manufacture of Ammonia by Haber's Process, molybdenum act as promoter for Iron catalyst.



- b) Asbestos act as a promoter for platinum catalyst in contact process for manufacture of H_2SO_4



- c) In Bosch's Process for manufacture of H_2 from water gas, metallic copper promotes the activity of Fe_2O_3 catalyst.

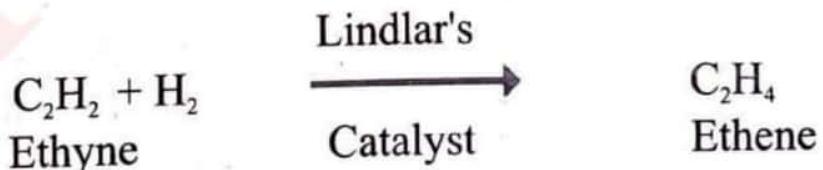


4) Poison:

A substance which can decrease the activity of a catalyst is called **catalytic poison**.

Example:-

- a) Arsenious oxide (As_2O_3) acts as a poison to Platinised asbestos used as a catalyst in the manufacture of H_2SO_4 by Contact process.
 - b) In the presence of Lindlar's Catalyst ($\text{Pd} + \text{BaSO}_4$ poisoned by Sulphur), ethyne reacts with H_2 to give ethene.



- c) Hydrogen Sulphide (H_2S) act as poison to Iron catalyst in the Haber's process for manufacture of Ammonia.

TYPES OF CATALYSIS

Catalysis can be broadly divided into two groups

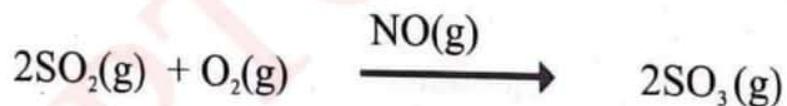
- 1) Homogeneous Catalysis
- 2) Heterogeneous Catalysis

1. Homogeneous Catalysis

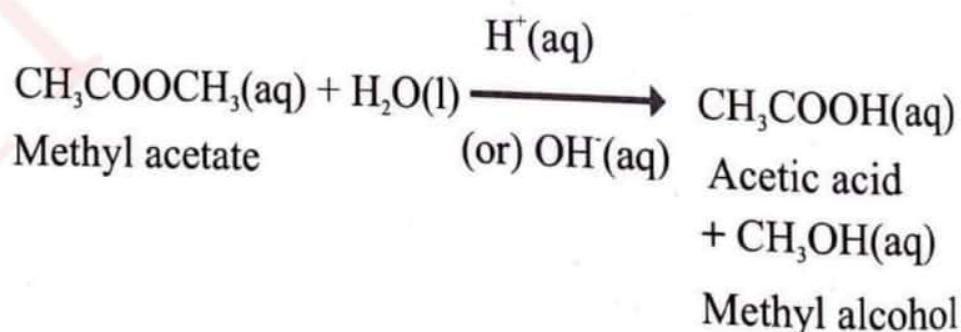
When the reactants and the catalyst are in the same phase (i.e. liquid or gas), the process is known as **homogeneous catalysis**.

Examples:

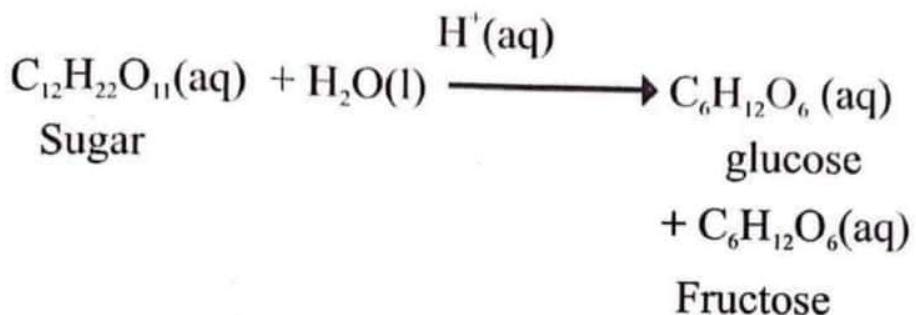
- a) Oxidation of SO_2 into SO_3 with O_2 in the presence of oxides of Nitrogen as the catalyst in the Lead Chamber process.



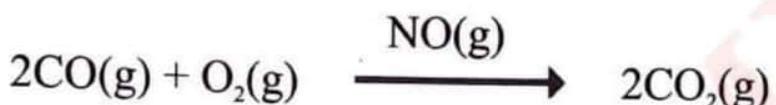
- b) Hydrolysis of methyl acetate in the presence of H^+ ions from an acid or OH^- ions from a base



- c) Hydrolysis of sugar in the presence of H^+ ion from H_2SO_4 .



- d) Oxidation of Carbon monoxide (CO) into Carbon dioxide (CO₂) in presence of Nitric Oxide (NO)

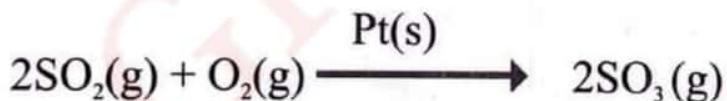


2) Heterogeneous Catalysis

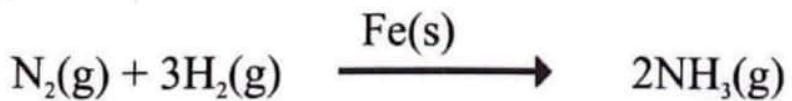
The catalytic process in which the reactants and catalyst are in different phases is known as **heterogeneous catalysis**.

Example:

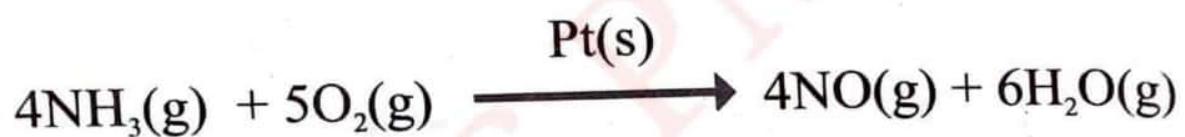
- a) Oxidation of SO₂ into SO₃ in the presence of Pt



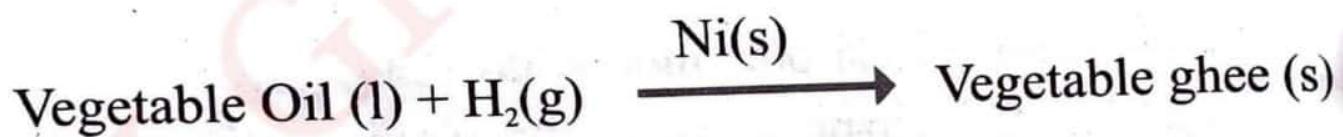
- b) Combination between dinitrogen (N₂) and dihydrogen (H₂) to form Ammonia (NH₃) is presence of Iron in Haber's process



- c) Oxidation of ammonia into Nitric Oxide (NO) in presence of Platinum in Ostwald's process for manufacture of Nitric acid (HNO₃)



d) Hydrogenation (Addition of hydrogen) of vegetable oils in presence of Nickel as catalyst .



MODULE II

FUNDAMENTALS OF ANALYTICAL CHEMISTRY

Acids and bases are two important classes of inorganic compounds. They differ widely in their properties. An acid is defined as a substance whose aqueous solution tastes sour, turns blue litmus red and neutralizes bases.

Examples :-

Hydrochloric acid, HCl ; Nitric acid, HNO₃, Carbonic acid, H₂CO₃,

Sulphuric acid, H₂SO₄, Acetic acid, CH₃COOH.

Characteristics of Acids

- i) Turns blue litmus red
- ii) Has sour taste
- iii) Liberates hydrogen gas when treated with active metals like zinc or magnesium .
- iv) Liberates carbon dioxide gas when treated with carbonates.

- v) Conduct electricity in solution
- vi) Loses the above properties when neutralised by a base

A base is defined as a substance whose aqueous solutions tastes bitter, turns red litmus blue and neutralises acids.

Examples:

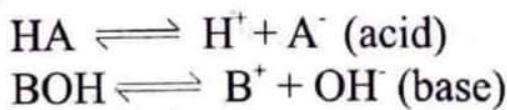
Sodium hydroxide, NaOH ; Ammonium hydroxide, NH₄OH; Calcium hydroxide, Ca(OH)₂.

THEORIES OF ACIDS AND BASES

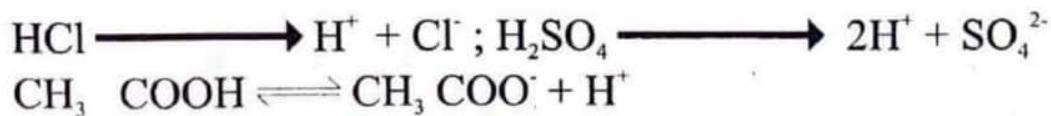
Throughout the history of chemistry various acid-base concepts have been proposed. The different concepts put forth from time to time are the following.

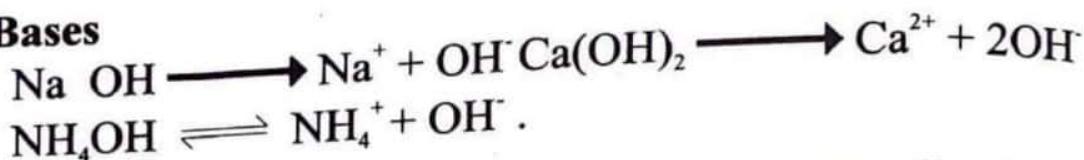
(1) Arrhenius concept

According to Arrhenius concept, all substances which contain hydrogen and give H⁺ ions when dissolved in water are called **acids** while those which contains hydroxyl groups and which when dissolved in water give OH⁻ ions are called **bases**.

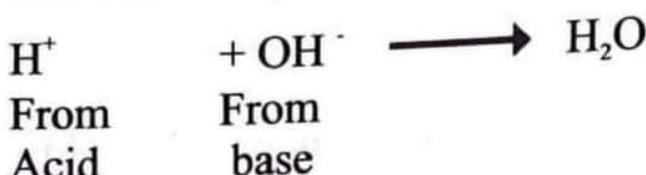


Examples : Acids



Bases

According to Arrhenius concept, neutralization in aqueous solution involves combinations of H^+ ions from acids and OH^- ions from bases to form water (H_2O)

**(2) Bronsted - Lowry concept**

According to this concept an acid is a substance that can donate proton (i.e. H^+ ion) and a base is a substance that can accept a proton. In other words an acid is a proton donor (**protogenic**) and a base is a proton acceptor (**protophilic**).



In this HCl behaves as an acid because it donates a proton to the water molecule. Water on the other hand is a base because it accepts the proton given by the acid. Similarly consider the dissolution of ammonia in water.

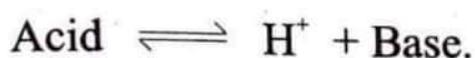


In this water act as an acid as it donates H^+ to NH_3 to form NH_4^+ . Ammonia molecule NH_3 act as a base because it accepts the proton given by water.

Water can act as a base in presence of an acid or it can act as an acid in presence of a base. Such substances which can act both as an acid as well as base are called **amphiprotic** or **amphoteric substances**. Eg. Water, ammonia, Hydrogen sulphate ion (HSO_4^-) Hydrogen carbonate ion (HCO_3^-)

Concept of conjugate acid - base pair.

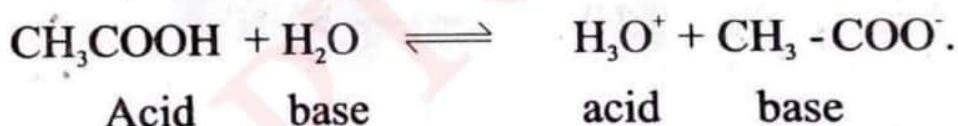
When an acid loses a proton (H^+), the remaining part of it has a tendency to regain a proton. Therefore this remaining part is a base.



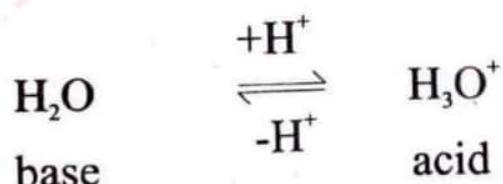
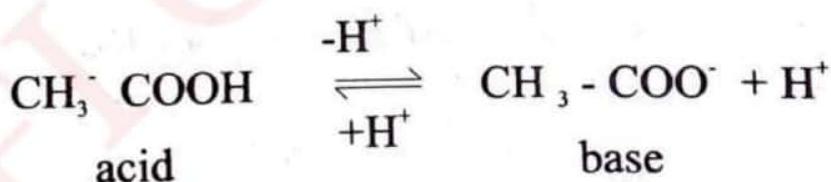
Acid base

A pair of acid and base which are formed from one another by gain or loss of a proton is known as **conjugate acid-base pair**.

The acid and base which differ by only one proton are known to form a conjugate pair of acid and base. Thus every acid has a conjugate base and every base has a conjugate acid. HCl and Cl^- is a conjugate acid-base pair. The conjugate base of HCl is Cl^- and conjugate acid of Cl^- is HCl .



This involves two conjugate pairs.



Thus CH_3-COOH and CH_3COO^- as well as H_3O^+ and H_2O are conjugate acid-base pair.

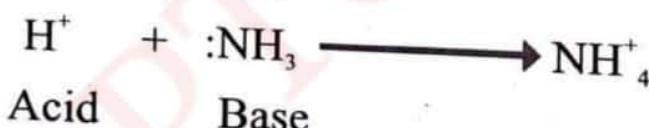
Examples : acid₁ + base₂ \rightleftharpoons Acid₂ + Base₁



(3) Lewis Concept

According to this concept an **acid** is a substance which is capable of **accepting an electron pair** and **base** is a substance which is capable of **donating an electron pair**.

Example.:



According to this concept the following species can act as Lewis acids.

- (a) Molecules with the central atom having incomplete octet.



- (b) Simple cations : H⁺, Ag⁺ etc.

Similarly following species can act as Lewis bases.

- (a) Species having at least one lone pair of electrons
NH₃, R-OH, R-NH₂, R-O-R etc.

- (b) Negatively charged species.
CN⁻, Cl⁻, OH⁻ etc.

Basicity of an acid: It is the number of replaceable or ionisable hydrogen atom in a molecule of the acid.

Example :

Monobasic acids: HCl, HNO₃, CH₃-COOH etc.

Dibasic acids : H₂SO₄, H₂CO₃ (Carbonic acid), H₂C₂O₄ (Oxalic acid) etc.

Tribasic acids : H₃PO₄. (Phosphoric acid) etc.

Acidity of a base: It is the number of replaceable OH groups present in one molecule of the base.

Monoacidic base - NaOH, KOH etc.

Diacidic base - Ca(OH)₂, Mg(OH)₂ etc.

Triacidic base - Fe(OH)₃, Al(OH)₃ etc.

Equivalent weight of an Acid: It is defined as the weight of the acid which contains 1.008 parts by weight of replaceable hydrogen.

Mathematically,

$$\text{Equivalent weight of the acid} = \frac{\text{Molecular weight}}{\text{Basicity}}$$

Acid	Molecular weight	Basicity	Equivalent weight
HCl	36.5	1	36.5
H NO ₃	63	1	63
H ₂ SO ₄	98	2	49
H ₂ C ₂ O ₄	90	2	45
H ₂ C ₂ O ₄ 2H ₂ O	126	2	63

Equivalent weight of a base: It is the weight of the base which exactly neutralizes one equivalent weight of an acid.

Mathematically,

$$\text{Equivalent weight of a base} = \frac{\text{Molecular weight}}{\text{Acidity}}$$

Base	Molecular weight	Acidity	Equivalent
Na OH	40	1	40
K OH	56	1	56
NH ₄ OH	35	1	35
Ca (OH) ₂	74	2	37

(Atomic weights of common elements:-

H-1 Al-27 C-12 N-14 O=16
 S=32 K-39 Ca-40 Cl=35.5 Ba-137
 Fe-56 Ag-108 Mg-24 Na=23 P=31 Cu=63.5)

Self-Ionisation of Water - Ionic Product of Water

Since water is an amphoteric substance, water undergoes ionisation to a very small extent producing H⁺ and OH⁻ ions. There is an equilibrium between these ions and the unionised water molecules.



The product of the concentrations of the H⁺ and OH⁻ ions in water is called **ionic product of water, K_w**.

Mathematically,

$$K_w = [\text{H}^+] [\text{OH}^-]$$

In pure water [H⁺] = 10⁻⁷ moles per litre at 25°C

and $[\text{OH}^-] = 10^{-7}$ moles per litre at 25°C

$$K_w = [\text{H}^+] [\text{OH}^-] = 10^{-7} \times 10^{-7} \text{ moles}^2 \text{ per litre}^2$$

$$\text{i.e., } K_w = 10^{-14} \text{ moles}^2 \text{ per litre}^2 \text{ that is } [\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

Thus ionic product of water is 10^{-14} moles 2 / litre 2 at 25°C

From ionic product of water, $[\text{H}^+]$ and $[\text{OH}^-]$ can be found out as

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} \quad \text{and} \quad [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]}$$

Ionic product of water depends only on temperature. Since ionisation of water increases with increase of temperature, ionic product also increases with increase of temperature.

Nature of solution and hydrogen ion concentration.

In neutral solution $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ moles / litre

In acidic solution $[\text{H}^+] > [\text{OH}^-]$

In basic solution $[\text{H}^+] < [\text{OH}^-]$

In other words;

if $[\text{H}^+] = 10^{-7}$ the solution is neutral.

if $[\text{H}^+] > 10^{-7}$ the solution is acidic

if $[\text{H}^+] < 10^{-7}$ the solution is basic

pH value, scale of acidity

pH scale is a method of expressing hydrogen ion concentration. It is defined as negative logarithm to the base ten of hydrogen ion concentration in moles per litre.

Mathematically,

$$\text{pH} = -\log_{10} [\text{H}^+]$$

In pure water, $[\text{H}^+]$ is 10^{-7} moles per litre at 25°C

$$\text{pH of water} = -\log [\text{H}^+] = -\log 10^{-7}$$

$$= -\{-7\log 10\} = 7$$

$$\{\log a^b = b \log a\}$$

Acidic solution will have a $\text{pH} < 7$. Basic solution will have a $\text{pH} > 7$. Neutral solution will have a $\text{pH} = 7$

Applications and Importance of pH value

1. To find out acidic, basic or neutral nature of a medium.

2. Selection of pH can reduce the rate of corrosion.
Solutions with low pH value (acidic medium) increases the rate of corrosion. Similarly, when the pH is very high and temperature is also high results in caustic embrittlement which is a type of boiler corrosion.

3. In the production of potable water, coagulation of impurities by the addition of alum takes place satisfactorily in the slightly acidic pH range.

4. Effluent Treatment: Effluents from chemical factories are either acidic or alkaline, i.e., they have low pH or high pH than 7. They must be properly neutralised before discharging them into rivers.

5. Electroplating: pH is one the factor which affects the character and appearance of the deposit caused by electroplating.

6. In Agriculture: pH value of the soil is very important in agriculture. If the soil is too acidic (low pH), lime is added to increase the pH. If the soil is alkaline (high pH), gypsum is added to neutralise the alkali.

7. **Digestive System:** Different digestive enzymes are most effective at particular pH range. If the pH value vary considerably, enzyme activity will be affected and digestion of food will not be proper.
8. **Vomiting:** pH of human gastric juice is between 1 and 3. Increase of pH generally causes vomiting.
9. **Textile industry:** Acidity in water when used for bleaching cotton will do harm to the textiles. Hence pH should be controlled.
10. **Sugar Industry:** Sugar cane juice from which sugar is produced, should have pH close to 7. If it is acidic or alkaline, decomposition will take place and unwanted products will be formed.
11. In food preservation, pH is to be known.
12. pH of human blood = 7.36 to 7.42, a change in pH by 0.2 units results in death and hence the pH is important to maintain our life.
13. From pH value, hydrogen ion concentration can be calculated using the relation $[H^+] = 10^{-pH}$.

p^{OH} Scale

p^{OH} of a solution is defined as the negative logarithm to the base ten of hydroxyl ion concentration in moles/litre. It is mathematically defined as

$$p^{OH} = -\log_{10} [OH^-]$$

Relation between p^H and p^{OH}

p^H and p^{OH} values are related by the expression

$$\begin{aligned} p^H + p^{OH} &= p^{Kw} = 14 \\ \therefore p^H &= 14 - p^{OH} \\ p^{OH} &= 14 - p^H \end{aligned}$$

$$\begin{aligned} p^{Kw} &= -\log_{10} K_w \\ &= -\log_{10} (1 \times 10^{-14}) = 14 \end{aligned}$$

Problem 1

Calculate the pH value of the following solutions with hydrogen ion concentrations (a) 10^{-11} (b) 0.0001 (c) 0.0123 moles/litre.

Solution:

$$(a) [H^+] = 10^{-11}$$

$$\begin{aligned} p^H &= -\log [H^+] &= -\log 10^{-11} \\ &= -[-11 \times 1] &= \underline{\underline{11}} \end{aligned}$$

$$(b) [H^+] = 0.0001 = 10^{-4}$$

$$\begin{aligned} p^H &= -\log [H^+] &= -\log 10^{-4} \\ &= -[-4] &= \underline{\underline{4}} \end{aligned}$$

$$(c) [H^+] = 0.0123 = 1.23 \times 10^{-2}$$

$$\begin{aligned} p^H &= -\log [H^+] &= -\log [1.23 \times 10^{-2}] \\ &= -[\log 1.23 + \log 10^{-2}] \\ &= -[0.0899 + \log 10^{-2}] \\ &= -[0.0899 - 2] &= -[-1.9101] \\ &= \underline{\underline{1.91}} \end{aligned}$$

Problem 2

Calculate the pH of the following solutions.

- (a) 0.1 M HCl (b) 0.005 M H_2SO_4 (c) $\frac{M}{1000} HNO_3$

Solution

(a) 0.1 M HCl will ionise and will give 0.1 moles of H^+ ions per litre $\therefore [H^+] = 10^{-1}$

$$p^H = -\log [H^+] = -\log 10^{-1} = \underline{\underline{1}}$$

(b) 0.005 M H_2SO_4 will ionise giving 0.01 moles (0.005×2) of H^+ ions per litre.

$$p^{\text{H}} = -\log 0.01 = -\log 10^{-2} = 2$$

(c) $\frac{1}{1000}$ M HNO_3
 $[\text{H}^+] = 10^{-3}$ and $\text{pH} = -\log 10^{-3} = 3$

Problem 3 ✓

Calculate the pH of 0.002M H_2SO_4

Solution

H_2SO_4 is a dibasic acid. Hence, one mole of it will give two moles of H^+ ions on ionisation.



$$[\text{H}] \text{ of } 0.002 \text{ M } \text{H}_2\text{SO}_4 = 2 \times 0.002 \text{ moles per litre}$$

$$= 0.004 \text{ moles/litre} = 4 \times 10^{-3} \text{ moles/litre}$$

$$p^{\text{H}} = -\log [\text{H}^+] = -[\log 4 \times 10^{-3}]$$

$$= -[\log 4 + \log 10^{-3}] = -[0.6021 - 3] = [-2.39]$$

$$= 2.39$$

Problem 4

Concentration of hydrogen ion in a cup of black coffee is 1×10^{-5} M/L. Find the pH of the coffee. Is the coffee, acidic or alkaline..?

Solution

$$[\text{H}^+] = 1 \times 10^{-5} \text{ moles/litre}$$

$$p^{\text{H}} = -\log 10^{-5} = 5$$
$$= -[-5 \log 10] = 5$$

Since pH is less than 7, it is acidic.

Problem 5

A solution is prepared by dissolving 0.4g. of NaOH in 500ml. of the solution. What is the pH of the solution?

Solution

$$\text{Molarity of the solution} = \frac{\text{Weight of solute per litre}}{\text{Molecular weight}}$$

$$= \frac{0.4 \times 1000}{40 \times 500} = 0.02\text{M}$$

$[\text{OH}]$ in 0.02 M NaOH solution is $0.02 = 2 \times 10^{-2}$ moles/litre

$$[\text{H}^+] [\text{OH}] = 10^{-14}$$

$$[\text{H}^+] = \frac{10^{-14}}{2 \times 10^{-2}} = \frac{1}{2} \times 10^{-12} = 0.5 \times 10^{-12} = 5 \times 10^{-13}$$

$$\begin{aligned} \text{p}^{\text{H}} &= -\log [\text{H}^+] = -[\log 5 \times 10^{-13}] \\ &= -[0.6990 - 13 \log 10] = -[0.6990 - 13] \\ &= -[-12.301] = \underline{\underline{12.3}} \end{aligned}$$

Problem 6

Calculate the pH of (a) $\text{M}/_{100}$ HCl (b) $\text{M}/_{100}$ NaOH solutions.

Solution

(a) $\text{M}/_{100}$ HCl is 0.01 M HCl; $[\text{H}^+] = 10^{-2} \text{ Mol L}^{-1}$, $\text{p}^{\text{H}} = -\log 10^{-2} = \underline{\underline{2}}$

(b) $\text{M}/_{100}$ NaOH is 0.01 M NaOH, $[\text{OH}^-] = 10^{-2}$

$$[\text{H}^+] = \frac{10^{-14}}{10^{-2}} = 10^{-12}, \text{p}^{\text{H}} = -\log 10^{-12} = \underline{\underline{12}}$$

Problem 7

Find the p^H of 0.002 M acetic acid solution, if it is only 2.3% ionized at the given dilution.

Solution

Since 0.002M acetic is only 2.3% ionized, the hydrogen ion concentrations will be

$$\frac{0.002 \times 2.3}{100} = \frac{2 \times 10^{-3} \times 2.3 \times 10^{-2}}{100} = 4.6 \times 10^{-5} \text{ M}$$

$$\begin{aligned} p^H &= -\log(4.6 \times 10^{-5}) \\ &= -\{\log 4.6 + \log 10^{-5}\} \\ &= -\{0.6628 + (-5)\} \\ &= -\{-4.3372\} \\ &= \underline{\underline{4.3372}} \end{aligned}$$

Problem 8

Calculate the pH and pOH values of the following solutions assuming complete ionization

(a) 0.365g l^{-1} HCl solution

(b) 0.001M Ba(OH) $_2$ solution

Solution

(a) Molar mass of HCl = 36.5

$$\text{Molar concentration} = \frac{\text{Weight in g per litre}}{\text{Molar mass}} = \frac{0.365}{36.5}$$

$$[\text{H}^+] = 1 \times 10^{-2} = 1 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(1 \times 10^{-2}) = -(2 \log 10) = \underline{\underline{2}}$$

$$\begin{aligned}\text{Since pH} + \text{pOH} &= 14; \text{pOH} = 14 - \text{pH} \\ &= 14 - 2 \\ &= \underline{\underline{12}}\end{aligned}$$

(b) One mole of $\text{Ba}(\text{OH})_2$ on complete dissociation gives 2 moles of OH^- ions.



$$\text{Molarity of Ba(OH)}_2 = 0.001 \text{ M} = 10^{-3} \text{ M}$$

$$\begin{aligned}[\text{OH}^-] &= 2 \times 10^{-3} \text{ M} \\ \text{pOH} &= -\log 2 \times 10^{-3} = -\{\log 2 + \log 10^{-3}\} \\ &= -\{0.3010 + (-3)\} = -\{-2.6990\} \\ &= \underline{\underline{2.699}}\end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.699 = \underline{\underline{11.3010}}$$

Problem 9

The hydrogen ion concentration of a solution is 0.001M. What will be the hydroxyl ion concentration?

Solution

We know that $[\text{H}^+] [\text{OH}^-] = 10^{-14}$

$$\text{Is } [0.001] [\text{OH}^-] = 10^{-14}$$

$$[\text{OH}^-] = \frac{10^{-14}}{0.001} = \frac{10^{-14}}{10^{-3}} = \underline{\underline{10^{-11} \text{ M}}}$$

Problem 10

A solution of nitric acid of molarity 10^{-2} is diluted 100 times. Calculate the pH of the diluted acid.

Solution

Molarity of nitric acid before dilution = 10^{-2} M

This means that acid contains 10^{-2} moles in 1 litre.

When diluted 100 times, volume of solution of the acid becomes 100 litre.

Number of moles of acid per litre

$$\text{after dilution} = \frac{10^{-2}}{100} = \frac{10^{-2}}{10^2} = 10^{-4}$$

$$p^H = -\log 10^{-4} = -[\log 10^{-4}] = -[-4] = \underline{\underline{4}}$$

Problem 11

Calculate the pH of a solution obtained by diluting 25 ml of 0.01M HCl to 500 ml, assuming complete ionisation.

Solution

If M_1 and V_1 be the molarity and volume of solutions before dilution and M_2 and V_2 after the dilution.

Using Dilution formula (refer page 55)

$$M_1 V_1 = M_2 V_2$$

$$0.01 \times 25 = M_2 \times 500$$

$$M_2 = \frac{0.01 \times 25}{500} = \frac{10^{-2}}{2 \times 10} = 5 \times 10^{-4} \text{ M}$$

$$[\text{H}^+] = 5 \times 10^{-4} \text{ mol/L}$$

$$\text{p}^{\text{H}} = -\log(5 \times 10^{-4}) = -(\log 5 + \log 10^{-4})$$

$$= -[0.6990 - 4] = \underline{\underline{3.30}}$$

Problem 12

Equal volumes of two solutions one having pH = 4 and the other having p^H = 10 are mixed. Calculate the p^H value of the mixture of the two solution.

Solution

When p^H = 4; [H⁺] = 10⁻⁴. Similarly when p^H = 10, [H⁺] = 10⁻¹⁰. In the second solution since [H⁺] is 10⁻¹⁰, the [OH] will be 10⁻⁴. In the first solution [H⁺] = 10⁻⁴ moles/litre and in the second [OH] = 10⁻⁴ moles/litre.

These two will neutralize each other and the resulting solution will have a pH of 7

Problem 13

Equal volumes of two solutions with pH = 3 and pH = 5 are mixed. Calculate the pH of the mixture.

Solution

When pH = 3, [H⁺] = 10⁻³ and when pH = 5, [H⁺] = 10⁻⁵. On mixing equal volumes of the two solutions the volume gets doubled and concentrations gets halved.

$$[\text{H}^+] \text{ in the mixtures} = \frac{10^{-3} + 10^{-5}}{2} = \frac{10^{-3}\{1+10^{-2}\}}{2} = \frac{10^{-3} \times (1.01)}{2}$$

$$= 0.5 \times 10^{-3} \times 1.01 = 5.05 \times 10^{-4}$$

$$\text{p}^{\text{H}} = -\log 5.05 \times 10^{-4} = -[0.7033-4]$$

$$= -[-3.296]$$

$$= \underline{\underline{3.296}}$$

Important points to be remembered

- (i) as pH decreases acidic nature increases
 - (ii) as solution becomes more acidic its $[H_3O^+]$ increases but p^H decreases
 - (iii) as solution become more basic, its $[OH^-]$ increases $[H_3O^+]$ decrease, p^{OH} decreases but pH increases.
 - (iv) p^H scale runs from 0 to 14.
- If the p^H of solution is 7, it is a neutral solution.

If p^H is between 0 and 7 it is acidic, if it is between 7 and 14 it is basic. Thus the nature of the solution can be known by knowing the p^H value the solution.

p^H of a solution can be determined using a universal indicator paper. Depending on the pH of the test sample, indicator paper undergoes a suitable colour change.

Buffer Solution

It is observed that solutions and even pure water can not retain constant pH for long period. Contact with air may result in absorption of CO_2 and result in decrease of pH. A buffer has reserved acidity or alkalinity and can resist a change of pH on addition of small amounts of acid or alkali or on dilution.

A **Buffer Solution** is defined as a solution that resists change in pH when a small amount of acid or base is added or when the solution is diluted.

Classification of Buffers

Buffers are classified into two classes. **Acidic Buffers and Basic Buffers.**

(I) **An Acidic Buffer** is obtained by mixing a weak acid and its salt with a strong base. It contains a weak acid and its conjugate base. Its pH is below 7.

Example:

- (i) Acetic acid and Sodium acetate.
- (ii) Boric acid and Borax
- (iii) Carbonic acid and Sodium Carbonate.

(II) **A basic buffer** is produced by mixing a weak base and its salt with a strong acid. It contains a weak base and its conjugate acid. Its pH is above 7.

Example:

- (i) Ammonium hydroxide and Ammonium Chloride
- (ii) Glycine and Glycine Hydrochloride,

Buffer Capacity (Buffer Index)

Buffer Capacity is defined as the number of moles of acid or base added to one litre of buffer solution as to change the pH by unity.

**No of moles of acid or
base added to one litre of buffer**

$$\text{Buffer Capacity } \Phi = \frac{\text{No of moles of acid or base added to one litre of buffer}}{\text{Change in pH}}$$

Buffer Capacity is a positive number. Higher the value of Buffer Capacity or Index, higher is the resistance of the

solution to pH change. Human blood has a pH of 7.4. This is maintained constant by the buffer action of carbonic acid /sodium carbonate ($\text{H}_2\text{CO}_3\text{CO}_3^{2-}$) system.

Methods of Expressing Concentration of Solution

Concentration of a solution is the amount of solute dissolved in a known amount of the solvent or solution. The concentration of solution can be expressed in various common ways as discussed below.

(1) Molarity (M)

Molarity of a solution is defined as the number of moles of the solute dissolved in one litre of solution.

A Molar solution contains one gram molecular weight of solute in one litre of the solution

Mathematically,

$$M = \frac{\text{No of moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Weight of solute in grams per litre of solution}}{\text{Molecular weight of solute}}$$

$$\text{Molarity, } M = \frac{W \times 1000}{m \times V (\text{ml})}$$

where W = Weight of solute in g

m = Molar mass of the solute

V = Volume in ml of the solution

(2) Normality (N)

Normality of a solution is defined as the number of gram equivalents of the solute present in one litre of solution.

A Normal solution contains one gram equivalent weight of solute in one litre of the solution

Mathematically,

$$N = \frac{\text{No of gram equivalents of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Weight of solute in grams per litre of solution}}{\text{Equivalent weight of solute}}$$

$$\text{Normality, } N = \frac{W \times 1000}{E \times V (\text{ml})}$$

where W = Weight of solute

E = Equivalent weight of the solute

V = Volume in ml of the solution

(3) Parts per million (ppm)

When the solute present is in minute quantities, the concentration is expressed in ppm. It is defined as the number of parts by mass of the solute per million parts by mass of solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Relation between Molarity and Normality

$$\frac{\text{Molarity}}{\text{Normality}} = \frac{\text{Equivalent mass}}{\text{Molar mass}}$$

For an acid, $\frac{\text{molarity}}{\text{normality}} = \frac{1}{\text{basicity}}$

$$\frac{\text{molarity}}{\text{normality}} = \frac{1}{\text{acidity}}$$

∴ For an acid, $N = M \times \text{Basicity}$ and

For a base, $N = M \times \text{Acidity}$

Dilution Formulae

a) $N_1 V_1 = N_2 V_2$ where N_1 = initial normality of acid / base.

V_1 = initial volume of acid / base.

N_2 = final normality of acid / base.

V_2 = final volume of acid / base.

b) $M_1 V_1 = M_2 V_2$ where M_1 = initial molarity of acid / base.

V_1 = initial volume of acid / base.

M_2 = final molarity of acid / base.

V_2 = final volume of acid / base.

Problem 1

Calculate the molarity of the Sodium Carbonate (Na_2CO_3) solution if 1.075g of Sodium Carbonate is present in 250ml of its solution (Na-23 ; C-12 ; O-16).

Solution

$$\text{Molarity, } M = \frac{W \times 1000}{m \times V \text{ in ml}}$$

$$W = 1.075 \text{ g}; m = (2 \times 23) + 12 + (3 \times 16) = 106$$

$$V = 250 \text{ ml}$$

$$M = \frac{1.075 \times 1000}{106 \times 250} = \underline{\underline{0.04M}}$$

Problem 2

A solution is prepared by dissolving 2.88g of potassium hydroxide (KOH) in water to give 500ml of the solution. Calculate the molarity of the solution (K-39).

Solution

$$\text{Molarity, } M = \frac{W \times 1000}{m \times V \text{ in ml}}$$

$$W = 2.88 \text{ g}; m = 39 + 16 + 1 = 56; V = 500 \text{ ml}$$

$$M = \frac{2.88 \times 1000}{56 \times 500} = \underline{\underline{0.0103M}}$$

Problem 3

Calculate the weight of oxalic acid $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (dibasic acid) required to prepare 250ml of 0.15M solution.

Solution

$$\text{Molarity, } M = \frac{W \times 1000}{m \times V \text{ in ml}}$$

Since weight is required, rearrange as

$$M \times m \times V$$

$$W = \frac{M \times m \times V}{1000}$$

$$M = 0.15M ; m = 2 + 24 + 64 + 36 = 126 ; V = 250 \text{ ml}$$

Substituting ,

$$W = \frac{0.15 \times 126 \times 250}{1000} = 4.725 \text{ g}$$

Problem 4

A 0.1M solution of an acid contains 2.25g in 250ml of its solution. What is the molar mass of the acid ?

Solution

$$\text{Molarity, } M = \frac{W \times 1000}{m \times V \text{ (ml)}}$$

Since molar mass, m is required, rearrange as

$$m = \frac{w \times 1000}{M \times V \text{ (ml)}} = \frac{2.25 \times 1000}{0.1 \times 250} = 90$$

Problem 5

Calculate the weight of K_2CO_3 required to prepare 250ml of 0.05N solution (Eq.wt of K_2CO_3 is 138).

Solution

Normality,

$$N = \frac{W \times 1000}{E \times V \text{ in ml}}$$

Since weight is required, rearrange as

$$W = \frac{N \times E \times V}{1000} = \frac{0.05 \times 138 \times 250}{1000} = 1.725\text{g}$$

Problem 6

Calculate the normality of KMnO_4 solution ; 100ml of which contains 1.58g (Eq. wt of KMnO_4 is 31.6).

Solution

$$\text{Normality, } N = \frac{W \times 1000}{E \times V \text{ in ml}} = \frac{1.58 \times 1000}{31.6 \times 100} = 0.5\text{N}$$

Problem 7

What is the normality of 1M, H_3PO_4 ?

Solution

$$N = M \times \text{Basicity} = 1 \times 3 = 3N$$

(Basicity of Phosphoric acid , H_3PO_4 = 3)

Problem 8

What is the normality of 10 % (weight/volume) acetic acid solution ? (Equivalent mass of acetic acid is 60).

Solution

10%(wt/vol) solution means 10g in 100ml

$$\text{Normality, } N = \frac{W \times 1000}{E \times V \text{ in ml}} = \frac{10 \times 1000}{60 \times 100} = 1.7\text{ N}$$

VOLUMETRIC ANALYSIS

Volumetric analysis is a mode of quantitative analysis that depends on methods involving accurate measurement of volumes of liquids. This method of quantitative analysis is quick and accurate.

This is a method of estimation. It involves the determination of the volume of standard solution required to react quantitatively with a known volume of the solution to be estimated.

Standard Solution: A solution of known strength or concentration is called a standard solution.

In Volumetric analysis two solutions are made to react in a conical flask called **titration flask**. One of the two solutions is taken in the burette (**titrant**) and the other in the titration flask (**titrate**). The solution from the burette is slowly added to the flask with constant shaking of the flask. The process of finding the volume of one solution required to react completely with a known volume of the other solution is known as **titration**. The exact point at which the reaction is completed during titration is called the **equivalent point**. In order to recognize the equivalent point, certain substances called **indicators** are added which exhibit a marked colour change at the completion of the reaction. The point at which, the indicator shows a colour change is called the **end point**. In ideal titration equivalent point and end point coincide. This difference if any should be minimized by selecting the proper indicator.

When an acid solution is gradually added from a burette into the flask containing an alkali solution, a point is

reached when all the alkali is completely neutralized. This point representing the end of neutralization of alkali by acid is the **end point** of the reaction which is indicated by a colour change of an indicator. The important nature of an indicator is that it exhibits one colour in alkaline solution, another in acidic solution and yet another colour in neutral solution. The choice of indicator depends upon the nature of acid and alkali to be titrated.

An **acid-base indicator** is a weak organic acid or base which can change its colour with variation in the pH value of the solution to which it is added. The change from acid colour to basic colour occurs over a range of pH called **Colour-Change Interval or pH Range of Indicator**. For example **Phenolphthalein** changes colour from colourless to pink in the pH range of 8.3 to 10. For **Methyl orange** the pH range is 3.1 to 4.5 in which it changes its colour from orange red to golden yellow.

Indicator	pH Range	Colour	
		Acid Medium	Basic Medium
Phenolphthalein	8.3 - 10	Colourless	Pink
Methyl Orange	3.1 - 4.5	Pink	Yellow
Litmus	4.5 - 8.3	Red	Blue

Choice of indicators in acid- base titrations

a. Titration of Strong Acid against Strong Base

eg: HCl/HNO₃/H₂SO₄ vs NaOH/KOH

The change of pH value at the end point in this type of titration is roughly from 4 to 10. Hence indicator which changes its colour between $p^H = 4$ and 10, can be used.

eg:-Methyl orange or Phenolphthalein.

b. Titration of Weak Acid against Strong Base

eg: Oxalic acid /Acetic acid vs NaOH/KOH

In this titration, pH changes from 6.5 to 10 at the end point. Hence Phenolphthalein having p^H range of 8.3 to 10 is used as indicator. (Methyl orange can not be used).

c:-Titration of Strong Acid against a Weak Base

eg: HCl/HNO₃ vs Na₂CO₃/K₂CO₃,

In this type of titration p^H changes from 3.5 to 7.5 at the end point. A suitable indicator is Methyl orange which has p^H range of 3.1 to 4.5 (Phenolphthalein cannot be used).

d. Titration of a Weak Acid against a Weak Base

eg: Acetic acid /Oxalic acid vs Na₂CO₃/K₂CO₃,

There is no sharp change in p^H value at the end point when a weak base is added to a weak acid. Hence none of the indicators can give correct result and so such titrations are not done using acid-base indicators.

Principle of Volumetric Analysis

The titration is based on the basic principle that at the end point, the product of normality and volume of solution added from the burette (**titrant**) is equal to the product of normality and volume of solution taken in the titration flask (**titrate**) that is

$$N_1 V_1 = N_2 V_2$$

Where N_1 = normality of titrant

V_1 = volume of titrant

N_2 = normality of titrate

V_2 = volume of titrate

This equation is known as **Law of Normality or Normality Equation.**

For acid-base titrations, the **Normality Equation** is

$$N_a V_a = N_b V_b$$

Where N_a = normality of acid

V_a = volume of acid

N_b = normality of base

V_b = volume of base

Problem 1

Calculate the normality and molarity of following solutions.

- A solution of 3.16 g of Na_2CO_3 in 500 ml.
- NaOH solution containing 15 g of NaOH per 250 ml.
- 250 ml of a solution which contains 0.63 g oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)
- Nitric acid which contains 3.15 g per 100 ml

Solution

$$\text{a. Normality} = \frac{\text{weight in g / litre}}{\text{equivalent weight}} = \frac{3.16 \times 1000}{53 \times 500} = 0.119 \text{ N}$$

$$\text{Molarity} = \frac{\text{weight in g / litre}}{\text{molecular weight}} = \frac{3.16 \times 1000}{106 \times 500} = 0.0595 \text{ M}$$

$$(\text{equivalent weight of } \text{Na}_2\text{CO}_3 = \frac{\text{molecular weight}}{2})$$

$$\text{b. Normality} = \frac{15 \times 1000}{40 \times 250} = 1.5 \text{ N}$$

$$\text{Molarity} = \frac{15 \times 1000}{40 \times 250} = 1.5 \text{ M} \quad (\text{Equivalent mass} = \text{Molecular Mass})$$

$$\text{c. Normality} = \frac{0.63 \times 1000}{63 \times 250} = 0.04 \text{ N}$$

$$\text{Molarity} = \frac{0.63 \times 1000}{126 \times 250} = 0.2 \text{ M} \quad (\text{Equivalent mass} = \frac{\text{Molecular Mass}}{2})$$

$$\text{d. Normality} = \frac{3.15 \times 1000}{63 \times 100} = 0.5 \text{ N}$$

$$\text{Molarity} = \frac{3.15 \times 1000}{63 \times 100} = 0.5 \text{ M} \quad (\text{Equivalent mass} = \frac{\text{Molecular Mass}}{2})$$

Problem 2

500 ml of a decinormal solution is diluted by adding 300 ml of water. What is the normality of resulting solution?

Solution

Using dilution formula,

$$\begin{array}{lcl} N_1 V_1 & = & N_2 V_2 \\ \text{Initial} & & \text{final} \end{array} \quad N_1 = \frac{1}{10} = 0.1$$

$$0.1 \times 500 = N_2 \times 800 \quad V_1 = 500 \text{ ml}$$

$$\text{ie. } N_2 = \frac{0.1 \times 500}{800} = \mathbf{0.0625 \text{ N}} \quad V_2 = (500 + 300)$$

$$= 800 \text{ ml}$$

$$N_2 = ?$$

Problem 3

500 ml of a seminormal solution is diluted by adding 3500 ml of water. What is the normality of the resulting solution?

Solution

Using dilution formula,

$$\begin{array}{rcl} N_1 V_1 & = & N_2 V_2 \\ \text{initial} & & \text{final} \end{array} \quad N_1 = \frac{1}{2} = 0.5$$

$$0.5 \times 500 = N_2 \times 4000 \quad V_1 = 500 \text{ ml} \quad V_2 = 500 + 3500 \\ = \mathbf{4000 \text{ ml}}$$

$$\text{ie. } N_2 = \frac{0.5 \times 500}{4000} = \mathbf{0.0625 \text{ N}} \quad N_2 = ?$$

Problem 4

Calculate the normality of hydrochloric acid which contains 2.281 g of the acid in 200 ml. Find out the volume of this solution required to neutralise exactly 50 ml of 0.12 N Sodium hydroxide solution.

Solution

$$\text{Normality} = \frac{\text{weight in g. per litre}}{\text{Equivalent weight}} = \frac{2.281 \times 1000}{36.5 \times 200} \\ = \mathbf{0.3125 \text{ N}}$$

Using law of normality,

$$\begin{array}{rcl} N_a V_a & = & N_b V_b \\ \text{HCl} & & \text{NaOH} \\ & & \end{array} \quad \begin{array}{l} N_a = 0.3125 \\ V_a = ? \\ \hline \end{array} \quad \begin{array}{l} N_b = 0.12 \\ V_b = 50 \text{ ml} \\ \hline \end{array}$$

$$0.3125 \times V_a = 0.12 \times 50$$

$$\text{ie } V_a = 0.12 \times 50$$

$$\frac{\text{---}}{0.3125} = \frac{\text{---}}{\text{---}} = 19.2 \text{ ml}$$

Problem 5

20 ml of potassium hydroxide solution containing 5.6 g of KOH per litre of the solution is titrated against sulphuric acid solution. The volume of acid required is 18.8 ml. Calculate the normality and strength of the acid solution.

Solution

$$\text{Normality of KOH solution} = \frac{5.6}{56} = 0.1 \text{ N}$$

Using law of normality,

$$N_b V_b = N_a V_a$$



$$0.1 \times 20 = N_a \times 18.8$$

$$N_a = \frac{0.1 \times 20}{18.8} = 0.106 \text{ N}$$

Strength of the

$$\begin{aligned} \text{solution} &= \text{weight in gram of H}_2\text{SO}_4/\text{litre} \\ &= \text{Normality} \times \text{equivalent weight} \\ &= 0.106 \times 98 \end{aligned}$$

$$\frac{2}{\text{---}} = 5.19 \text{ g / litre.}$$

Problem 6

20 ml of sodium hydroxide solution was neutralised by 25 ml of an acid of normality 0.11. Find the normality of the base.

Solution

Using law of normality,

$$\begin{array}{rcl} V_b N_b & = & V_a N_a \\ \text{alkali} & & \text{acid} \end{array}$$

$$20 \times N_b = 25 \times 0.11$$

$$N_b = \frac{25 \times 0.11}{20} = 0.1375$$

Normality of base = **0.1375 N**

Problem 7

250 ml of 0.5 normal H_2SO_4 and 100 ml of water are mixed together. Find out the normality of resulting solution.

Solution

Volume of solution after mixing = $250 + 100 = 350$ ml

Using dilution formula,

$$\begin{array}{rcl} V_1 N_1 & = & V_2 N_2 \\ \text{before} & & \text{after} \\ \text{mixing} & & \text{mixing} \end{array}$$

$$250 \times 0.5 = 350 \times N_2$$

$$N_2 = \frac{250 \times 0.5}{350} = 0.357 \text{ N}$$

Normality of the mixture = **0.357 N**

Problem 8

A solution is prepared by dissolving 9.125 g of Sodium Hydroxide in water to give 200 ml of solution. Calculate molarity of Sodium hydroxide solution

Solution

$$\text{Weight of NaOH in grams per litre} = \frac{9.125 \times 1000}{200}$$

$$\text{Molecular weight of NaOH} = 23 + 16 + 1 = 40$$

$$\text{Molarity} = \frac{\text{Weight in grams per litre}}{\text{molecular weight}} = \frac{9.125 \times 1000}{200 \times 40} = \underline{\underline{1.141 \text{ M}}}$$

Problem 9

How many moles and how many grams of Sodium Chloride are present in 250 ml of 0.25 M NaCl solution?

Solution

Number of moles present
in 1000 ml solution of molarity 0.25 = 0.25 moles

$$\text{Number of moles present} = \frac{0.25}{1000} \times 250 = \underline{\underline{0.0625 \text{ moles}}}$$

$$\text{Molar mass of NaCl} = 23 + 35.5 = 58.5$$

Mass of 0.0625 mols = Number of moles x Molar mass
of NaCl

$$= 0.0625 \times 58.5 = \underline{\underline{3.656 \text{ g}}}$$

MODULE III

WATER AND ITS TREATMENT

Water is the most common and readily available of all chemical compounds. It is essential for all forms of life and is a crucial compound for the survival of plant and animal kingdom.

Oceans cover nearly 78% of the earth's surface and hold 97% of available water. Only less than 2.7% of total surface water is fresh. In nature it occurs in three states - Solid (ice), Liquid (water), and Gas (water vapour).

Water contains soluble as well as insoluble impurities. It has to be purified before it can be utilized for domestic or industrial purpose.

Physical properties of water :

- i. Pure water is a colourless, odourless and tasteless liquid.
- ii. It gives a bluish tinge in thick layers.
- iii. It freezes at 0°C and boils at 100°C .

- iv. Its density is 1.0 g cm^{-3} .
- v. Water molecule is polar.
- vi. Ionic and polar compounds dissolve in water.
- vii. Water associates through hydrogen bonding and exists as $(\text{H}_2\text{O})_n$.
- viii. Water molecule has an angular or V shape and H-O-H bond angle is 104.5° .
- ix. Pure water is a poor conductor of electricity.
- x. Organic and non polar compounds are insoluble in water.

Soft Water and Hard Water

Based upon the behavior towards soap, the natural water has been classified as soft water and hard water.

Water which produces lather readily with soap solution is called **Soft water**.

Water which does not produce lather readily with soap solution is said to be **Hard water**.

Hardness of water is due to the dissolved impurities such as Bicarbonates, Chlorides or Sulphates of Calcium and Magnesium. These salts are not present in soft water.

Why Hard Water do not form lather with soap?

Ordinary soaps are Sodium salts of fatty acids, like Stearic Acid ($\text{C}_{17}\text{H}_{35}\text{COONa}$). When treated with hard water, Soap reacts with the dissolved impurities like Calcium and Magnesium ions present in the hard water and forms their insoluble salts. Hence hard water do not form lather with soap. Lather is formed only after all the dissolved impurities are completely precipitated and removed.

DISTINCTION BETWEEN SOFTWATER & HARD WATER

SOFT WATER	HARD WATER
1. Water that gives ready lather with soap is called Soft Water.	1. Water that does not give ready lather with soap is called Hard Water.
2. Does not form insoluble scum with soap.	2. Form insoluble scum with soap.
3. Does not contain dissolved impurities like calcium and magnesium salts.	3. Contain dissolved Bicarbonates, Chlorides, and Sulphates of Ca and Mg.
4. Advantages Softwater is suitable for <ul style="list-style-type: none"> a) Cooking purposes b) Bathing c) Laundry purposes d) dyeing textiles e) Boilers etc. 	4. Advantages <ul style="list-style-type: none"> a) It contains Ca and Mg ions required for health b) It does not dissolve out lead from lead pipes used in water supply system.

5) Disadvantages

- a) It dissolves the lead of lead pipes leading to lead poisoning.
- b) Does not contain dissolved salts of metals like Ca,Mg, etc. which are trace elements required for healthy life.

5) Disadvantages

- a) Pulses do not cook well in it
- b) Causes wastage of soap in laundry.
- c) Causes wastage of fuel in boiler
- d) Not suitable in dyeing & printing textiles, photography, sugar industry etc.

Types of hardness :-

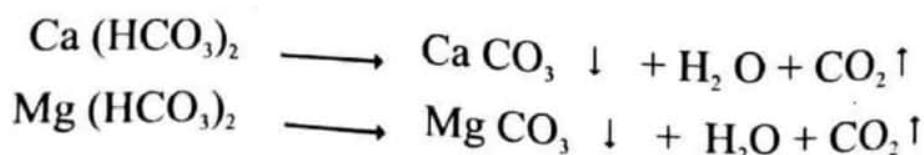
There are two types of hardness

(a) Temporary hardness and (b) Permanent Hardness.

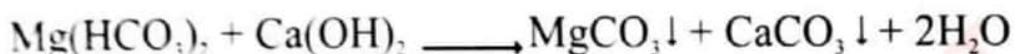
Temporary Hardness is caused by the presence of dissolved Bicarbonates of Calcium and Magnesium

Methods of Removal of Temporary Hardness

(1) **By Boiling:** When boiled, the dissolved bicarbonates decompose and become insoluble Carbonate and CO₂ gas. The precipitated Carbonates are removed by filtration.



(2) **Clarke's Process:** This is also a method for the removal of temporary hardness. Required quantity of slaked lime ($\text{Ca}(\text{OH})_2$) is added to water when Calcium and Magnesium ions are precipitated as insoluble Carbonates.



Precipitated insoluble Carbonates are removed by filtration to get soft water.

Permanent Hardness

Permanent hardness is caused by the presence of chlorides and sulphates of Calcium and Magnesium in water.

This can be removed by **Ion exchange method** in which synthetic resins called **Cation exchanger and Anion exchanger** are used. Hard water is first passed through a tank with a bed of cation exchanger (E-H) capable of removing all positive ions (cations) by exchange with H^+ ions.



This water coming out of cation exchanger is then passed through a second tank containing an anion exchanger (E-OH) and all anions are removed.



H^+ and OH^- formed combine to give water



Thus all the dissolved cations and anions are removed from hard water by this method.

Note:

1. Regeneration of ion exchanger. The cation exchanger is regenerated by using an acid, and the anion exchanger is regenerated by using an alkali solution.
2. Ion exchange process can be used even when water is highly acidic or alkaline.
3. The equipment and the ion exchange resins are highly expensive.

Disadvantages of Hard water.

Some of the disadvantages of hard water when used for various purposes are explained below.

1. **In domestic use:-** (a) Calcium and Magnesium ions in hard water will react with soap when used for washing and a precipitate of Calcium and Magnesium soap will be formed. This causes wastage of soap. (b) The precipitate of Calcium and Magnesium soap will cause spots and streaks on the clothes. (c) When used for bathing, cleaning quality of soap is reduced. (d) When used for cooking, there will be wastage of fuel, unpleasant taste for tea, coffee etc. (e) Use of hard water for drinking may lead to the formation of Calcium Oxalate crystals in urinary track and stones in kidney.
2. **In Industrial use :-** (a) In textile industry when hard water is used for dyeing, there will be malformation of colour due to the salts present in it. (b) When soap is used for washing textiles with hard water, wastage of soap and

undesirable precipitates are formed. (c) Hard water when used in paper industry reduces the quality of paper.

3. In Steam generating boilers :-

a. **Formation of boiler scales:** Hard water on boiling deposits a hard crust or scale on the inner walls of the boiler and the steam pipes. This scale is hard and heat insulating and it leads to wastage of fuel.

b. **Danger of explosion :-** Sometimes the boiler scales crack and the water suddenly comes in contact with overheated iron plates of the boiler. As a result, large amounts of steam are formed. Suddenly, high pressure is developed and the boiler explodes.

c. **Corrosion :-** Magnesium chloride present in hard water gets hydrolysed generating free hydrochloric acid.



The acid corrodes the metal with which the boiler is made and shortens its life.

POTABLE WATER

Water from most of the natural sources is not fit for drinking because it is impure. Potable water is safe to drink but need not be pure water like distilled water.

Characteristics of potable water

- i) It should be clear and odourless
- ii) It should be pleasant to taste
- iii) It should be free from disease producing micro organism like bacteria and germs which are pathogenic.

- iv) It should be free from objectionable dissolved gases like H_2S , CO_2 , NH_3 and minerals like nitrites and nitrates.
- v) It should be free from suspended impurities.
- vi) Its pH should be around 8.
- vii) Total dissolved solids should be less than 500 ppm.
- viii) It should be reasonably soft.

Treatment processes to make potable water.

Generally purification of water involves the following steps.

(i) Screening

(ii) Sedimentation

(iii) Coagulation

(iv) Filtration and

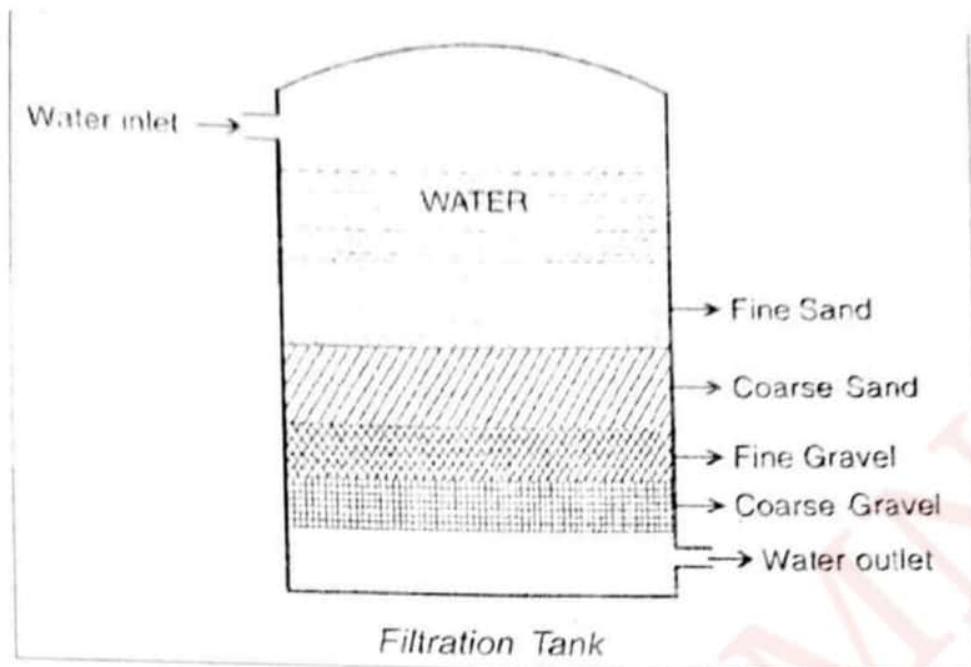
(v) Sterilization

i) Screening: The raw water is passed through bar screens or mesh screens to remove coarse soils, gravel or slit.

ii) Sedimentation: In this process, water is allowed to stand undisturbed in big tanks for 6 to 12 hours. During this most of the suspended particles settle down under force of gravity.

iii) Coagulation: Finely divided suspended particles can be made to settle down by adding certain chemicals called coagulants. Common coagulants used are alum, ferrous sulphate, ferric chloride, sodium aluminate etc.

iv) Filtration: By filtration process, insoluble colloidal and bacterial impurities are removed from water by means of filters.



a) Operation of gravity sand filter

It consists of a rectangular tank made of concrete. Filtering medium is a thick top layer of fine sand placed over coarse sand layer and graded gravel. It is provided with an inlet for water and clear filtered water collects in the underdrain channel from where it is drawn out.

During filtration, the sand pores get clogged at the top layer and filtration become slow. Then this top fine sand layer is removed, washed and dried and can be used again.

b) Operation of pressure filter

Filter media for pressure filter is essentially same as that of gravity filter. Filtering material is kept in a closed cylinder and water is forced into the filter under pressure. This method can be used for hot water and the pressure filter requires less space.

v) Sterilization

Water even after sedimentation, coagulation and filtration operations may contain a small percentage of

pathogenic bacteria. The process of destroying the disease producing bacteria and micro organisms from the water and making it safe for drinking is called **sterilization or disinfection**. Chemicals used for sterilization are called sterilizers or disinfectants.

a) Sterilization by chlorine (Chlorination)

Chlorination is the most widely used process for sterilization throughout the world. Chlorine gas or chlorine water can be used.

The advantages of this process are:

- i) It is effective and economical.
- ii) It leaves no salt impurities with treated water.
- iii) Chlorine is available in pure form.
- iv) It requires little space for storage.

However, disadvantages are:

- i) Excess chlorine if present causes unpleasant odour and taste and irritation in the mucous membrane.
- ii) The quantity of free chlorine in treated water should not exceed 0.1 to 0.2 ppm. If it exceeds, dechlorination by activated charcoal or by passing SO_2 gas should be adopted.

Break-point chlorination or free residual chlorination

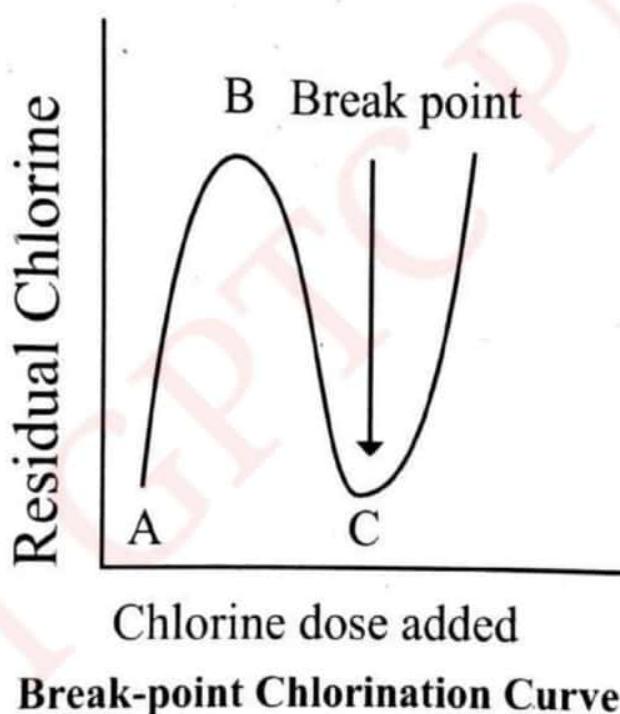
This is a controlled chlorination process in which enough chlorine is added to oxidize

- a) Organic matter
- b) Reducing substances and
- c) Free ammonia in raw water and leaving little free chlorine to destroy pathogenic bacteria.

Thus break point chlorination of water is chlorination of water to the extent that living organisms and organic impurities are destroyed.

Over chlorination beyond break-point produces unpleasant taste and smell of chlorine in water.

When chlorine is added to water, it is consumed by oxidisable bacteria and other organic matter. Unused chlorine left behind is residual chlorine. A graph connecting residual chlorine and chlorine dose added called break-point chlorination curve is given below.



The amount of residual chlorine increases with increasing dose of chlorine giving a straight line AB. At a particular chlorine dose a decrease in residual chlorine is noted. C is the break point. This behavior is due to the fact that some organic compounds which defy oxidation at lower

chlorine concentration, get oxidized when break point dose is reached. Also these compounds are responsible for bad taste and odour. With their oxidation, bad taste and odour get eliminated.

Advantages of break-point chlorinations

- a) It destroys all the disease producing bacteria.
- b) Removes colour and taste from water.
- c) Oxidizes organic compounds and ammonia and other reducing compounds.
- d) Prevents the growth of any weeds in water.

b) Sterilization by bleaching power

Water can be disinfected by mixing about 1Kg. of bleaching power (CaOCl_2) to 1000 kilolitre of water and allow to remain undisturbed for several hours. HOCl (Hypochlorous acid) and nascent oxygen produced are powerful germicides.



Calculated amount of bleaching power should be used for treatment of water. Excess if added will give bad taste and disagreeable odour.

One disadvantage of this process is Calcium ions get introduced in water which makes it hard.

c) Sterilization by Ozone

Ozone gas (O_3) when passed through water, nascent oxygen is generated. It is very effective and kills all the germs and bacteria.

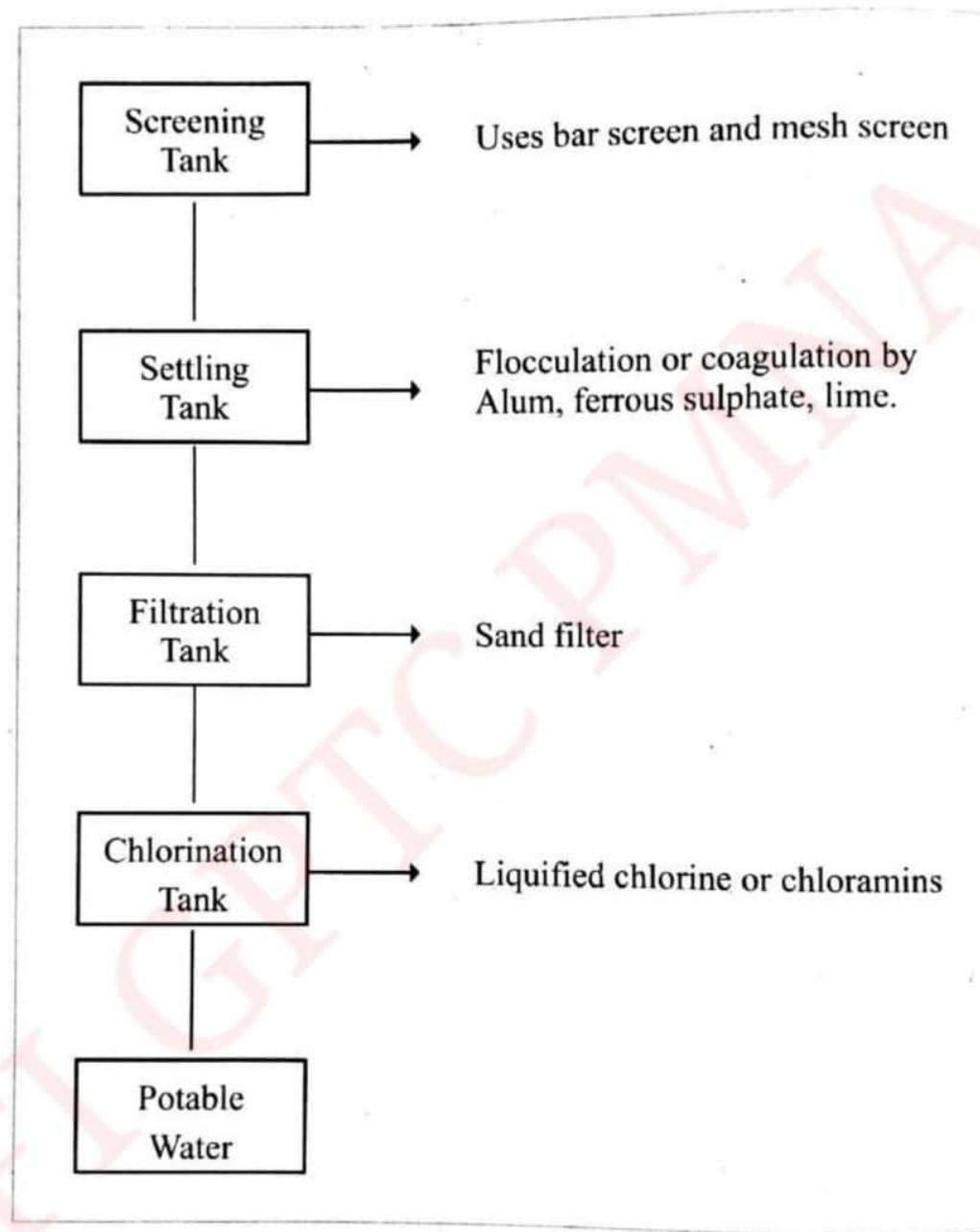


Ozone acts as a sterilizing agent, bleaching, decolorizing and deodourising agent. Its excess is not harmful and it produces a very palatable form of water.

d) **Sterilization by Ultra violet radiation**

U.V. radiation coming from electric mercury lamp can disinfect water effectively. U.V. rays kills all pathogenic bacteria. Addition of a little eosin helps the process of disinfection. This method can be adopted when chemical methods are objectionable. However, this is more expensive than chemical methods.

Stages for the production of potable water for municipal supply.



Desalination of salt water

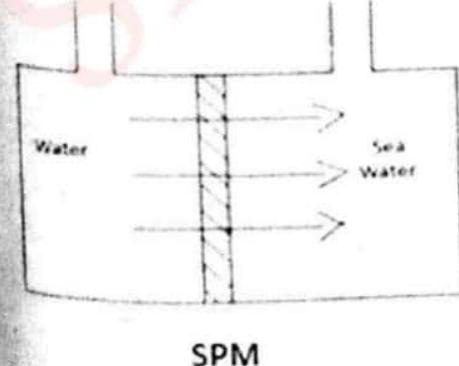
Water containing high concentrations of dissolved salts like sodium chloride with salty taste is called **Saline Water**. Sea water which contains 3.5% by mass(3500ppm) dissolved salts is unfit for domestic and industrial use. The

process of removing salts present in water is called **desalination**. One of the method used for desalination is **reverse osmosis (r.o.)**.

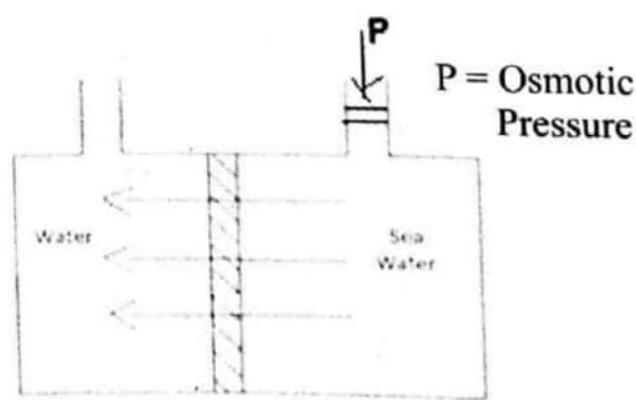
Reverse Osmosis:

Reverse osmosis is the technique used for the purification of the salty water to get drinking water. Osmosis is the flow of solvent from a dilute solution to a concentrated solution through a semi permeable membrane. The minimum excess pressure that has to be applied on the concentrated solution side to prevent osmosis is called **osmotic pressure**.

The principle of reverse osmosis is that when a hydrostatic pressure greater than osmotic pressure is applied on the concentrated solution, the solvent is forced to move from concentrated solution to dilute solution across the membrane. In other words, pure water is separated from salty water rather than removing the impurity salts from the water. **Reverse osmosis** is also called **Super filtration** or **Hyper filtration**. Principles of Osmosis and Reverse Osmosis are represented below :



OSMOSIS



REVERSE OSMOSIS

A pressure of 15-40 kgcm⁻² is applied on the impure water side to force out pure water alone through the membrane. Membranes used are made of cellulose acetate or polymethacrylate or polymide.

Advantages of Reverse Osmosis:

1. It can remove ionic, non ionic, colloidal and high molecular weight organic impurities.
2. It removes colloidal silica which is not removed by demineralization.
3. Capital cost required is less.
4. Only maintenance cost is for the replacement of membranes.
5. Since the membrane can be replaced within few minutes, the water supply is almost continuous.

QUESTIONS

Part A

Answer in one or two sentences (Each question carries 2 marks)

1. Give any two physical properties of water
2. Define Soft water
3. Define Hard Water
4. Name the salts that causes temporary hardness
5. Name the salts that causes permanent hardness
6. Name two methods use to remove temporary hardness
7. Name the compound used in Clarke's process used to remove hardness of water and give its chemical formula
8. Name the method used to remove permanent hardness

9. Mention any two characteristics of potable water.
10. Define the term Sterilization of water
11. Mention any two methods used for sterilization of water
12. Define the term 'breakpoint chlorination' of water.
13. Define desalination of sea water.
14. Define reverse Osmosis.

Part B
(Each question carries 6 marks)

15. Distinguish between
 - (a) Soft water and Hard Water (3 marks)
 - (b) Temporary hardness and Permanent hardness (3 marks)
16. Explain any three disadvantages of hard water
17. How can temporary hardness of water be removed by (a) Boiling (b) Clarke's Process (3+3=6 marks)
18. How can permanent hardness of water be removed using ion exchange method
19. List any six characteristics of potable water
20. Explain the various steps involved in the treatment process of making potable water.
21. (a) Give the block diagram for production of potable water used in Municipal supply of drinking water. (3 marks)
(b) Give different chemical changes involved in the sterilization of water by bleaching powder. (3 marks)

Part C
(Each question carries 15 marks)

22. (a) Give any five physical properties of water (5 marks)
- (b) Distinguish between soft water and hard water. (2 marks)
- (c) Give the causes of temporary hardness and permanent hardness of water (3 marks)
- (d) How can temporary hardness be removed by the following
(i) Boiling (ii) Clarke's Process (6 marks)
23. (a) How can permanent hardness be removed by ion exchange method (4 marks)
- (b) List any four characteristics of potable water (4 marks)
- (c) Explain with the help of block diagram, the different steps involved in the purification of water by Municipal supply (4 marks)
- (d) Define terms (a) Reverse Osmosis
(b) Desalination of water (2marks)
- (e) Give any two advantages of desalination of water (1 mark)

MODULE IV

METALS AND ALLOYS

The known elements may be classified into three groups:- Metals, non-metals and metalloids. Out of these, metals are found in combination with one or more other elements in the crust of the earth. The most abundant metal on the earth crust is Aluminium. Metals are generally lustrous, malleable, ductile and good conductors of heat and electricity. Metals find application in the construction of buildings, bridges, ships, air crafts, automobiles, rails, railway carriages, agricultural implements etc.

Physical Properties of Metals

1. **Malleability**:- It is the property of a metal which allows it to be beaten into thin sheets. Gold is the most malleable metal.
2. **Ductility**:- It is the property of a metal which allows it to be drawn into wires. Gold is the most ductile of all the metals.

3. **Thermal conductivity:-** It is the ability of a metal to conduct heat. Silver has the highest thermal conductivity of all the metals.
4. **Electrical conductivity:-** It is the ability of a metal to allow the passage of electricity through it. Silver is the best electric conductor.
5. **Weldability:-** It is the ability of a metal to be welded together by the application of heat or pressure or both.
6. **Machinability:-** It is the property due to which a metal can be easily cut into desired shapes using cutting tools.
7. **Melting point:-** In general, metals possess high melting point. Exceptions are tin, lead, gallium etc.
8. **Toughness:-** It is the property of a metal which enables it to withstand bending without fracture.
9. **Hardness:-** It is the property of a metal which enables it to resist abrasion or scratching by other materials.
10. **Specific gravity:-** It is the ratio of density of the metal and density of water. Metals possess high specific gravity or density.

Industrial Metals

Since the metals possess the above unique physical properties, they are widely used for industrial purposes. The commonly used industrial metals are cast iron, pig iron, wrought iron and steel. Pig iron is the impure form of iron obtained from iron ore.

PROPERTY	CAST IRON / PIG IRON	WROUGHT IRON	STEEL
1. Composition	2-5% Carbon	Less than 0.2% Carbon	0.2 to 2% Carbon
2. Structure	Crystalline	Fibrous	Granular
3. Melting point	Lowest, 1200°C	Highest, 1500°C	Between 1300-1400°C
4. Hardness	Hard	Soft	Medium hardness
5. Malleability	Brittle	Malleable	By heat treatment and alloying, it can be made brittle and malleable
6. Weldability	Can not be welded	Can be welded	Can be welded with difficulty
7. Tempering	Can not be tempered	Can not be tempered	Can be tempered
8. Magnetisation	Can not be permanently magnetized	Easily magnetized but not permanent	Can be permanently magnetized

Effect of Impurities in steel

In Carbon Steel, the element Carbon is not considered as impurity. Other elements like Silicon, Sulphur, Manganese, Phosphorus, Oxygen and Nitrogen are considered as impurities when present in steel. These impurities when present in Steel change the physical properties of the Steel as given below.

- i) **Silicon:-** Upto 0.2% Silicon if present increases the strength of the steel without decreasing its ductility. Thus Silicon has a beneficial effect on steel.
- ii) **Sulphur:-** Sulphur may be present as Ferrous Sulphide (FeS) or Manganese Sulphide (MnS). The presence of these sulphides is desirable for machining operations. Presence of FeS is undesirable as it surround the metallic grains and melts during hot working of steel. This makes steel red short, that is brittle at red heat. Up to 0.3% Sulphur is helpful in cutting thread on screws.
- iii) **Manganese:-** Manganese is an undesirable impurity. If present above 1%, it makes steel harder and brittle.
- iv) **Phosphorus:-** Phosphorus is highly undesirable impurity as it makes steel cold short that is brittle at room temperature and shock resistance becomes poor. Upto 0.1% , Phosphorus is tolerable as it adds strength and hardness to steel.
- vi) **Oxygen:-** Oxygen is present as Ferrous Oxide (FeO). It may cause fracture of Steel under load.
- vii) **Nitrogen:-** Nitrogen is present as nitride in Steel and it makes Steel hard and undesirable for working operations.

Heat Treatment of Steel

Heat treatment of Steel is the process of heating and then cooling the Steel under controlled conditions to develop certain required physical properties without changing the chemical composition. This process removes trapped gases and changes its grain structure. By heating the steel to different temperatures and allowing to cool in different ways, hardness and elasticity of Steel can be varied. Annealing quenching, tempering and nitriding are different ways of heat treatment of Steel.

Annealing :- It is process of heating the metal to a certain high temperature in a furnace and cooling it slowly in a planned manner. Annealing makes Steel

- (i) soft and ductile .
- (ii) improves machinability.
- (iii) increases shock resistance
- (iv) relieves internal strains and
- (v) reduces hardness but increases toughness.

Quenching or Hardening:- This is a process of heating Steel beyond redness (1123 K) and suddenly cooling it by plunging in water or oil. Quenching makes Steel hard. Faster the rate of cooling, harder will be the steel. Quenching increases

- (i) resistance to wear
- (ii) strength
- (iii) ability to cut other metals
- (iv) brittleness

Tempering:- Quenched Steel is heated to a temperature of about 550 K. It is then kept at that temperature for sometime

and cooled slowly. This is called **tempering** of the steel. Tempered Steel is quite hard but less brittle. It is used for making razor blades, axes, knives, swords etc.

Nitriding :- In this process Steel is heated to about 820 K in an atmosphere of ammonia gas. After heating for long periods (2 to 60 hours), it is slowly cooled. Nitriding provides a hard coating of Nitrides of metals like Al, Cr, Mo, V etc. on the surface of Steel. This process makes Steel

- (i) very hard
- (ii) resistant to wear
- (iii) resistant to atmospheric corrosion. The hardness is not lost even when heated to high temperatures.

ALLOYS

An alloy is a homogeneous solid mixture of two or more elements, one of which is essentially a metal. In other words, an alloy may consist of two or more metals or a metal and a non metal like Carbon. Alloys containing liquid Mercury (a metal) as one of the constituents are called amalgams.

Example: Sodium amalgam is an alloy of Sodium and Mercury. Some commonly used alloys are (i) Brass (Cu and Zn)(ii) Bronze (Cu and Sn) and (iii) Stainless steel (Fe, Ni, Cr, C).

The properties of alloys are significantly different from those of the constituent elements.

Purposes of making alloys

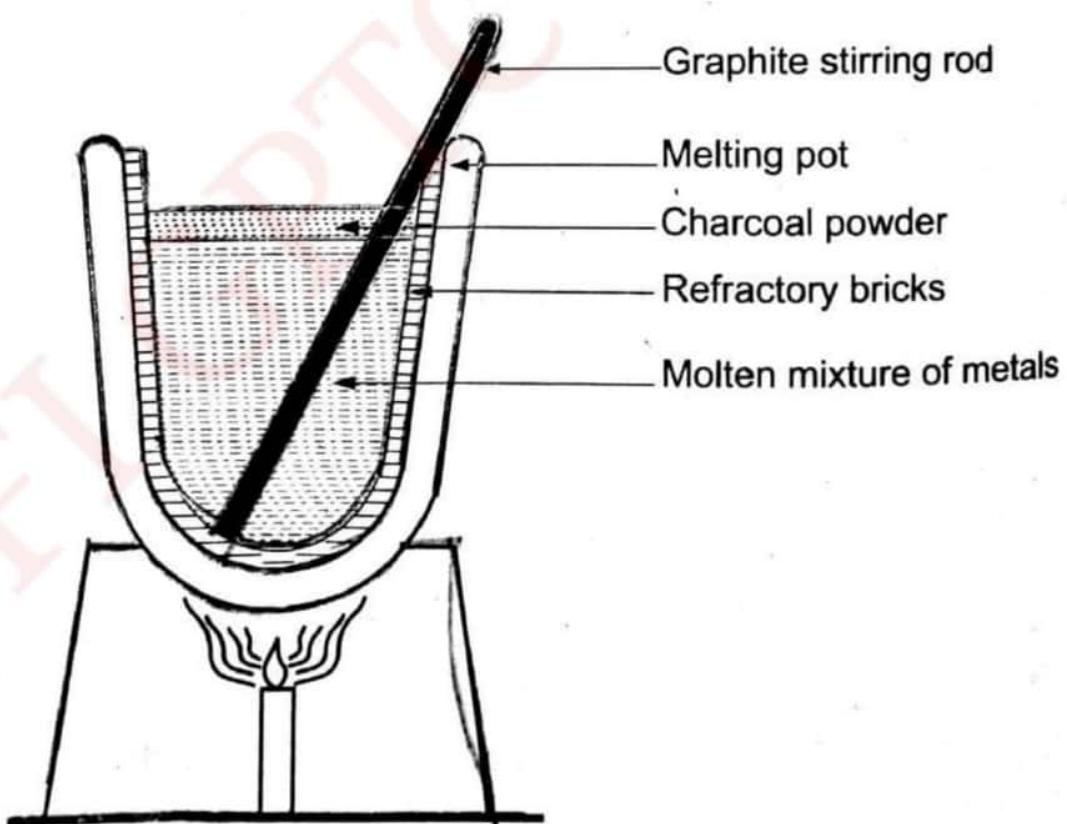
1. **To increase the resistance to corrosion:-** Pure iron is corroded even in moist air. But stainless steel which is a alloy of Fe with Cr, Ni and C is not corroded.
2. **To increase the hardness of the metal:-** Pure iron is very soft. When it is alloyed with 1% carbon steel is produced which is very hard.
3. **To lower the melting point of the metal and to make it easily fusible:-** Solder is an alloy of tin and lead and it melts at 180°C which is lower than the melting points of the component metals. Wood metal (an alloy of Bi, Sn, Pb & Cd) melts even in boiling water.
4. **To modify the chemical activity of the metal:-** Iron reacts with chemicals like acids. But stainless steel which is an alloy of Fe with Cr and Ni resists the attack by chemicals.
5. **To modify colour:-** Brass, an alloy of copper (red) and zinc (silver white) has an attractive yellow colour .
6. **To provide better castability:-** The material used for casting printing types should expand on solidification, fill the mould and make good impressions. Type metal which is an alloy of Pb, Sn and Sb (Lead, Tin and Antimony) has the above properties and is used for casting printing types.

Preparation of alloys by Fusion method

The oldest method of making alloys is by Fusion. In fusion method, the components of the alloy are fused together in a refractory brick-lined crucible or melting pot. The component with higher melting point is first melted in

the crucible and then the component with lower melting point is added. The melt is thoroughly stirred with a graphite rod. To prevent oxidation of the melt at the surface by atmospheric air, a layer of powdered Carbon is spread on the surface. The molten mass after mixing well is allowed to cool slowly when solid alloy is obtained.

Production of brass by Fusion method can be considered as an example:- Components of Brass are Copper (1089°C) and Zinc (420°C). Pure Copper metal is first melted in the melting pot and then required amount of Zinc is added. The surface of the melt is covered with a layer of powdered charcoal to avoid atmospheric oxidation. The molten mass is thoroughly stirred, pourd into moulds and allowed to cool slowly to get brass.



Fusion method of alloy making

Composition and Uses of alloys - Brass, Bronze, Duralumin and Solder.

1. **Brass** Cu=60 – 90% Used for making utensils, parts of machinery, wires etc.
Zn=40 – 10%
2. **Bronze** Cu=80 – 95% Used for making Statues, coins, cooking utensils etc.
Sn=20 – 5%
3. **Duralumin** Al = 95% Used for making aeroplanes, automobile parts, pressure cookers etc.
Cu=4%
Mn=0.5%
Mg=0.5%
4. **Solder** Pb=50% Used for Soldering
Sn=50%

POWDER METALLURGY

Powder Metallurgy may be defined as a technology of producing metallic articles by compacting metal powder in a die with little or no melting followed by sintering. When compacting and sintering are done simultaneously, the process is called **pressure sintering** (compacting is the conversion of metal powder to briquetts of desired size and shape. Sintering brings the particles closer and bonds them together into coherent bodies).

Powder Metallurgy consists of mainly five steps namely:

- i) **Atomization and Reduction**
- ii) **Chemical Mixing or Blending**
- iii) **Compacting**
- iv) **Pre sintering and**
- v) **Sintering**

Metal Chips are cleaned to remove impurities and subjected to fragmentation using high energy ball mills and the following steps are adopted.

(IA) Atomization : The cleaned and milled material is first melted in a furnace and fed into a tun dish. (a device to provide uniformly flowing melt stream). The molten metal flowing out through the nozzle is subjected to a stream of compressed inert gas (nitrogen, helium or Argon) or water when melt disintegrates into droplets and then into fine powder. The inert gas atmosphere is provided to avoid oxidation. The important parameters that decides the size of the powder particles are :

- i) Water pressure and its velocity
- ii) Viscosity, density and surface tension of the melt and the ratio of the flow rate of melt and that of water.

This method is used for metals like Zn, Pb, Sn Al etc.

(IB) Reduction: Metal oxides can be reduced by Hydrogen, Carbon or Carbon monoxide or another metal to get spongy metal.



(II) Chemical Mixing or Blending or Powder Conditioning.

Some additives are added for lubrication, plasticizing and binding of the metal powder. Plasticizers

and lubricants reduces the friction between inter-particles and particles and die walls and helps in smooth movement of the powder particles.

III) Compacting

It is the process of converting loose metal powder into well defined mass of particular size and shape. Required amount of blended powder is taken in the cavity of a die and compressed with a top die. The compact mass obtained is called **green compact**.

IV) Pre Sintering

The binder in the **green compact** has to be removed before sintering. This has to be done without disruption to the particles and without causing any contamination to the compact. Two techniques are available to remove the lubricants and binders, namely thermal debinding and solvent debinding. In thermal debinding, evaporation or decomposition of the binder takes place. Solvent debinding is carried out by dipping the compact in a solvent which dissolves the binder. Presintering enhances the strength of the compact.

V) Sintering

During this process, the metal particles sinter, that is they bind together into coherent bodies. For this the compacted, pre sintered pieces are heated in a furnace to a temperature below the melting point of the metal, usually in an atmosphere of hydrogen gas. Temperature and duration of sintering depends on

- i) Compressive load
- ii) Nature of the metal and
- iii) The strength required for the finished product.

In activated sintering, some additives called dopants are added for rapid sintering. For example: 0.1% Ni lowers the sintering temperature of W.

Uses of Powder Metallurgy: Products produced by Powder Metallurgy are used in

- 1) Surgical implants such as Ti - Ta (Titanium – Tantalum) composites
- 2) Filaments of electric bulbs
- 3) Parts of gas turbines and cutting tools (carbides of W, Ti etc)
- 4) Refractory metal composites.(Mo,W,Pt etc with ceramic Oxides and Carbides)
- 5) Magnetic materials Like Alnico (Alloy of Fe, Ni, Al and Co)
- 6) Electric clocks and Sewing Machines
- 7) Diamond – Impregnated cutting tools
- 8) Bearings for automobiles, clutches, brakes etc.

Advantages of Powder Metallurgy

- 1) Rate of production is high.
- 2) Dimensional accuracy and good surface finish is obtained. So product hardly requires machining etc.
- 3) Cleaner and quieter operation.
- 4) Life of component parts is longer.
- 5) Products with relatively much uniform structures (free from defects like voids etc) are produced.
- 6) Quite complex shapes can be produced
- 7) No material is wasted (ie process makes use of 100% raw materials)
- 8) Parts with wide variations in composition can be produced

- 9) Highly skilled labour is not required
- 10) Complex shapes obtained possess excellent reproducibility.
- 11) Porous parts can be produced
- 12) Impossible parts like super – hard cutting tools can be produced.

Limitations of Powder Metallurgy

1. **Toxicity:** The metal powders are hazardous. The toxic effect of such powder on humans depends on their size, route of its entry into the body and biochemical characteristics.
2. **Pyrophoricity:** Metal powders may become self igniting at ambient temperatures. This property is known as **pyrophoricity**.
3. **Explosivity:** Metal powders are highly explosive. Flames and electric sparks are major sources of ignition for metallic dust clouds. In case of fire, only dry powder extinguishers should be used.

QUESTIONS

Part A

**Answer the question in one or two sentences
(Each question carries 2 Marks)**

1. Name the metals with highest malleability and conductivity.
2. Name the most impure and pure forms of Iron.
3. Give the composition of Steel.
4. Give the composition of Cast Iron.
5. Give the composition of Wrought Iron.

6. Name the commercial form of Iron having highest malleability and highest purity. Give its composition.
7. Define tempering.
8. Define quenching.
9. Define Nitriding.
10. Define Alloys.
11. Give the composition of Brass
12. Give the composition of Bronze.
13. Give the composition of Duralumin.
14. Give the composition of Solder.
15. Define Powder Metallurgy.
16. Define Compacting.
17. Define Sintering.
18. Mention any two uses of Powder Metallurgy.
19. Mention any two advantages of Powder Metallurgy.
20. Mention any two limitations of Power Metallurgy

Part B

(Each question carries 6 marks)

21. (a) Give any three physical properties of metals (3 marks)
(b) Give composition of Cast Iron Wrought Iron and Steel (3 marks)
22. Name any three impurities of Steel and give their effects on its properties.
23. Define the terms (a) Tempering
(b) Quenching
(c) Nitriding
24. (a) Define alloys (2 marks)

- (b) Explain preparation of alloys by Fusion method with the help of a diagram. (4 marks)
25. Give the composition of the following alloys
(a) Brass (b) Bronze (c) Duralumin (d) Solder
26. (a) Define Powder Metallurgy (2 marks)
(b) Give any two uses and two advantages of Powder Metallurgy (4 marks)

Part C

(Each question carries 15 marks)

27. (a) Explain composition of Cast Iron, Steel and Wrought iron with any two properties of each. (6 marks)
(b) Name any three impurities of Steel and give their effects on the properties of Steel (3 marks)
(c) Explain the following methods of heat treatment of Steel
(i) Tempering (ii) Quenching (6 marks)
(iii) Nitriding (1 mark)
28. (a) Define alloys
(b) Give any three purposes of making alloys (3 marks)
(c) Explain preparation of alloys by Fusion method with the help of a diagram. (5 marks)
- (a) Give composition of following alloys
(a) Brass (b) Bronze (c) Duralumin (6 marks)
(d) Solder (1 mark)
29. (a) Define Powder Metallurgy
(b) Explain Powder Metallurgy with different steps involved (8 marks)
(c) Mention any two uses, two advantages and two limitations of Powder Metallurgy (6 marks)