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SCHOOL OF SCIENCE AND HUMANITIES
DEPARTMENT OF CHEMISTRY

UNIT – 1 – Water Technology – SCY1213

WATER QUALITY PARAMETERS

Water is essential for the survival of all living organisms. About 80% of the earth's surface is covered by water. The main sources of water are: (i) rain (ii) river water and lake water (iii) sea water. Among the above sources of water, rain water is the purest form of water whereas sea water is the most impure form. For drinking and industrial purposes we need water free from undesirable impurities. So, first we must understand the nature and types of impurities present in water so that the water can be treated suitably to remove the undesirable impurities.

1. PHYSICAL CHARACTERISTICS

COLOUR: Surface waters (lakes, rivers and canals) will usually be brownish yellow in colour. It is due to: (i) organic substances such as tannin, humic acid (ii) inorganic compounds such as dissolved iron and manganese salts.

The recommended maximum concentration of colour in drinking water should be less than 5 units.

TURBIDITY: Turbidity in water is due to the presence of fine suspended impurities (clay, sand, decomposed vegetable and animal matters) that interferes with the passage of light through the water.

The recommended concentration of turbidity in drinking water must be less than 5 nephlometric turbidity units.

TASTE AND ODOUR: Chemical substances such as iron, free chlorine and phenols impart unpleasant tastes to water. Objectionable odors in water are caused by decaying vegetation and inorganic substances such as mercaptanes, sulphides.

TOTAL DISSOLVED SOLIDS (TDS): Total dissolved solids (TDS) in water includes soluble salts of chlorides, nitrates, sulphates, phosphates of *Na, K, Ca, Mg, Fe, Mn*, etc., and suspended solids.

The recommended concentration of total dissolved solids in drinking water should not exceed 500 ppm.

2. CHEMICAL CHARACTERISTICS

HARDNESS: Hardness of water is due to the presence of dissolved salts like chlorides, sulphates and bicarbonates of calcium and magnesium.

The recommended concentration of total hardness in drinking water must be less than 125ppm.

ACIDITY: Acidity in water is mainly due to CO_2 gas which may enter surface waters by absorption from the atmosphere. Humic, fulvic and other organic acids produced by decomposing vegetation also make the water acidic.

ALKALINITY: Alkalinity in water is due to the presence of bicarbonates, carbonates and hydroxides of *Ca*, *Mg*, *Na* and *K*.

DISSOLVED OXYGEN: Surface water of good quality must be saturated with sufficient amount of dissolved oxygen.

The optimum dissolved oxygen in natural water must be 4-6 ppm, which is essential for supporting aquatic life.

pH: Most natural waters are generally alkaline due to presence of sufficient quantity of carbonates. It is a measure of the intensity of acidity or alkalinity of water.

3. BIOLOGICAL CHARACTERISTICS

PATHOGENIC MICROORGANISMS: Drinking water should be free from pathogenic micro organisms. Coliform bacteria (*typically Escherichia coli*) are used as indicator organisms whose presence suggests that the water is contaminated.

Drinking water should not contain more than one coliform per 100ml.

SPECIFICATIONS FOR DRINKING WATER

Potable water (or) Drinking water: Water, which is safe for drinking, is called potable water. It should satisfy the following essential requirements.

- ⇒ Water should be crystal clear (colourless) and odourless.
- ⇒ Water should be free from pathogenic microorganisms.
- ⇒ Water should also be free from harmful dissolved gases like H_2S and minerals like Pb, Cr, As etc.
- ⇒ Its turbidity should be less than 25 ppm.
- ⇒ It must be reasonably hard and total hardness of water should be less than 150 ppm as $CaCO_3$ equivalent.
- ⇒ pH of the water must be between 7.0 and 8.5.
- ⇒ Total dissolved solid (TDS) content should be less than 500 ppm.

CONTAMINATION OF WATER BY ARSENIC, LEAD, FLUORIDE, MERCURY AND THEIR REMOVAL

1. ARSENIC

Maximum Contaminant Level (MCL): 10 μg/L

Sources Arsenic Contaminant: Erosion of natural deposits; Effluents from glass, paint and semiconductors industries etc.

Potential Health Effects for Long Term Exposure above the MCL:

Arsenicosis: People who drink water containing arsenic for a longer period lead to arsenic poisoning known as arsenicosis. Inorganic trivalent arsenite [As(III)] and pentavalenet arsenate [As(V)] have been classified as Group I carcinogens. They cause lung and bladder cancer and skin changes in people ingesting arsenic in drinking water at concentration of 50μg/lit or even lower.

Blackfoot disease: A disease caused by long term exposure to arsenic, which damages blood vessels in the lower limbs and leads to progressive gangrene. It was observed in Taiwan and China.

Possible Antidote: Dimercaprol; d-Penicillamine; Succimer.

2. FLUORIDE

Maximum Contaminant Level (MCL): 2 mg/L

Sources of Fluoride Contaminant: Erosion of natural deposits rich with NaF and fluorosilicates; As water additive, which promotes strong teeth; Effluents from fertilizer and aluminum factories.

Potential Health Effects for Long Term Exposure above the MCL:

Fluorosis: People who drink water containing fluoride in excess of MCL over many years could get bone disease (pain and bone fracture); Children get increased chance of developing pits in the tooth enamel (mottled teeth).

Possible Antidote: No Treatment.

3. LEAD

Maximum Contaminant Level (MCL): Zero mg/L

Sources of Lead Contaminant: Erosion of natural deposits; Effluents from storage battery industries; Corrosion of household plumbing systems.

Potential Health Effects for Long Term Exposure above the MCL:

Inorganic lead disrupts the synthesis of hemoglobin and it causes anemia. Lead replaces calcium in bones. TEL selectively attacks central nervous system of man and causes severe mental disorder.

Possible Antidotes: Calcium-EDTA chelate; 2,3-Dimercapto propanol; d-Penicillamine.

4. MERCURY

Maximum Contaminant Level (MCL): 0.002 mg/L

Sources of Mercury Contaminant: Erosion of natural deposits; Effluents from chlor-alkali industries (for the manufacture of Cl_2 and NaOH using mercury electrodes), electrical and electronic industries (in the manufacture of Hg-vapour lamps and Hg-batteries). Organo-mercurials used as fungicide for seed dressing.

Potential Health Effects for Long Term Exposure above the MCL:

Mercury is a teratogen, capable of inducing abortions and embryo toxic effects. Hg^{2+} ions are fairly toxic because of their affinity with sulphur containing amino acids and to hemoglobin.

Minamata disease: A disease caused by Methyl mercury which dissolve directly in fats, cell membranes and brain tissues of the central nervous system. Those people who ate fish and shellfish contaminated with methyl mercury (caught in Minamata Bay, China) get affected their central nervous system (brain damage) and about 40 people were died.

Possible Antidotes: Sodium formaldehyde sulfoxide; Dimercaprol; d-Penicillamine; Isotonic NaCl solution.

Mechanism of removal of water contaminants:

Electrocoagulation (EC) is an electrolytic process by which metallic hydroxide flocks are created within aqueous solution by electro-dissolution of soluble anodes.

Examples of soluble anodes used are: aluminium and iron.

The aluminum and iron hydroxide flocks normally act as adsorbents. These flocks trap the water contaminants like fluoride, arsenic and heavy metals like lead and mercury and eliminate them from the solution.

During EC, the following main reactions take place at the electrodes. At anode, oxidation of Al or Fe takes place.

$Al \rightarrow Al^{3+} + 3e^-$

$Fe \rightarrow Fe^{2+} + 2e^-$

At cathode, reduction of water takes place.

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Under alkaline pH,

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\downarrow$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$

(i) Removal of fluoride:

$Al(OH)_3\downarrow + F^- \rightarrow [Al(OH)_2. F] + OH^-$

(ii) Removal of arsenate:

$Al(OH)_3\downarrow + AsO_4^{4-} \rightarrow [Al(OH).AsO_4] + 2OH^-$

(iii)Removal of lead:

$Fe(OH)_2\downarrow + Pb \rightarrow [Fe^{2+}\text{–}Pb] + 2OH^-$

(iv)Removal of mercury:

$Fe(OH)_2\downarrow + Hg \rightarrow [Fe^{2+}\text{–}Hg] + 2OH^-$

HARDNESS: TYPES, EXPRESSION, UNITS

- **HARD WATER:** Water which does not lather with soap solution but forms an insoluble white precipitate is called hard water.

- **SOFT WATER:** Water which lathers easily with soap solution is called soft water.

- **TEST TO DETECT HARDNESS:** When a hard water sample is treated with soap, it does not produce lather but forms a white precipitate of calcium and magnesium soaps.

$$\underset{\text{Soap (Sodium stearate)}}{2\,C_{17}H_{35}COONa} + \underset{\substack{\text{Soluble hardness}\\ \text{causing salt}}}{CaCl_2} \longrightarrow \underset{\substack{\text{Insoluble white precipitate}\\ \text{of calcium stearate}}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2\,NaCl$$

- **DISADVANTAGES OF USING HARD WATER FOR DOMESTIC PURPOSES**

⇒ Hard water when used for drinking affects our digestive system and also leads the formation of stones (calcium oxalate crystals) in kidneys.

⇒ Hard water when used for washing does not lather with soap and thereby causing wastage of soap.

- **HARDNESS OF WATER**

⇒ Hardness is the characteristic property of water, which prevents the lathering of soap.

⇒ The various hardness causing constituents are: $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $MgCl_2$, $CaCl_2$, $MgSO_4$ and $CaSO_4$.

TYPES OF HARDNESS OF WATER

Depends upon the types of dissolved calcium and magnesium salts present in water, hardness of water are classified into two types.

1. TEMPORARY HARDNESS (or) CARBONATE HARDNESS (or) ALKALINE HARDNESS

Temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium. It can be merely removed by boiling the water. Boiling removes bicarbonates of calcium and magnesium into their respective insoluble carbonates and hydroxides.

$$Ca(HCO_3)_2 \xrightarrow{Boiling} CaCO_3\downarrow + H_2O + CO_2\uparrow$$
$$Mg(HCO_3)_2 \xrightarrow{Boiling} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

2. PERMANENT HARDNESS (or) NON-CARBONATE HARDNESS (or) NON - ALKALINE HARDNESS

Permanent hardness of water is due to the presence of chlorides and sulphates of calcium and magnesium. It cannot be removed by boiling. However, permanent hardness can also be removed by ion exchange process of water softening.

EXPRESSION OF HARDNESS OF WATER (or) $CaCO_3$ STANDARD

The amount of hardness causing substances is expressed in terms of an equivalent amount of $CaCO_3$. The choice of $CaCO_3$ is because: *(i) its molecular weight is 100 (equivalent weight = 50) and (ii) it is the most insoluble salt that can easily be precipitated in water treatment.*

$$CaCO_3\ equivalent = x \times \frac{Molecular\ weight\ of\ CaCO_3}{Molecular\ weight\ of\ hardenss\ causing\ substance} \qquad \ldots(1)$$

Where, x is the amount of hardness causing substance.

Equation (1) can also be written as:

$$CaCO_3\ equivalent = x \times \frac{Equivalent\ weight\ of\ CaCO_3}{Equivalent\ weight\ of\ hardenss\ causing\ substance} \qquad \ldots(2)$$

UNITS OF HARDNESS OF WATER

The various units of hardness are (i) ppm (ii) mg/litre (iii) Clarke's degree and (iv) Degree of French.

1. PARTS PER MILLION (ppm)

It is defined as "the number of parts of $CaCO_3$ equivalent hardness present per 10^6 parts of water".

1ppm = 1 part of $CaCO_3$ *equivalent hardness in* 10^6 *parts of water*

2. MILLIGRAMS PER LITRE (mg/litre)

It is defined as "the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water".

1mg/litre = 1mg of $CaCO_3$ *equivalent hardness in 1 litre of water*

3. CLARKE'S DEGREE (°Cl)

It is defined as "the number of parts of $CaCO_3$ equivalent hardness present in 70,000 or 1 gallon parts of water".

4. DEGREE OF FRENCH (°Fr)

It is defined as "the number of parts of $CaCO_3$ equivalent hardness present in 10^5 parts of water".

- **Relationship between ppm and mg/litre**

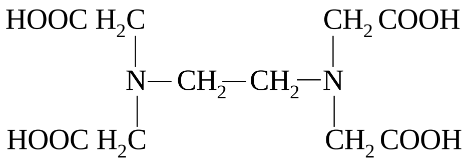
1 litre of water weighs 1kg (or) 1000gm (or) 10^6mg.

By definition,

- 1mg/litre $=$ 1mg of $CaCO_3$ equivalent hardness in 1 litre of water
- 1mg/litre $=$ 1mg of $CaCO_3$ equivalent hardness in 10^6 mg of water
- 1mg/litre $=$ 1ppm [∵ 1 litre = 10^6 mg]

ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD

Principle:



$$\begin{array}{ccccc} HOOC\,H_2C & & & & CH_2\,COOH \\ & \diagdown & & \diagup & \\ & N - CH_2 - CH_2 - N & & & \\ & \diagup & & \diagdown & \\ HOOC\,H_2C & & & & CH_2\,COOH \end{array}$$

Structure of EDTA

$$M^{2+} + EBT \xrightarrow{pH = 9-10} \underset{\substack{\text{Unstable, wine red} \\ \text{colour complex} \\ \text{(Indicator–Metal ion complex)}}}{[M-EBT]}$$

where, $M^{2+} = Ca^{2+}$ *and* Mg^{2+}

$$\underset{\substack{\text{Free,} \\ \text{uncomplexed} \\ \text{metal ion}}}{M^{2+}} + EDTA \xrightarrow{pH = 9-10} \underset{\text{Colourless, stable complex}}{[M-EDTA]}$$

$$\underset{\substack{\text{Unstable,} \\ \text{wine red colour} \\ \text{complex}}}{[M-EBT]} + EDTA \xrightarrow{pH = 9-10} \underset{\substack{\text{Stable} \\ \text{complex}}}{[M-EDTA]} + \underset{\substack{\text{Steel} \\ \text{blue}}}{EBT}$$

Preparation of Standard hard water

(i) Standard hard water: Dissolve 1gm of dry, pure $CaCO_3$ in minimum quantity of dil.HCl and evaporate it to dryness. Dissolve the residue in 1000ml distilled water.

1ml of standard hard water contains = 1mg of $CaCO_3$ equivalent hardness

Procedure

Description	1. Standardization of EDTA	2. Estimation of Total hardness	3. Estimation of Permanent hardness

Burette solution	EDTA	EDTA	EDTA
Pipette solution	20ml of Standard hard water + 5ml of buffer	20ml of Sample hard water + 5ml of buffer	20ml of boiled water sample + 5ml of buffer
Indicator	A pinch of EBT	A pinch of EBT	A pinch of EBT
Endpoint	Colour change from wine red to steel blue	Colour change from wine red to steel blue	Colour change from wine red to steel blue
Observation	Let the volume of EDTA consumed be V_1 ml	Let the volume of EDTA consumed be V_2 ml	Let the volume of EDTA consumed be V_3 ml

Calculations

(i) Standardization of EDTA using standard hard water:

1ml of standard hard water contains = 1mg of $CaCO_3$ equivalent hardness
50ml of standard hard water contains = 50mg of $CaCO_3$ equivalent hardness … (1)
50ml of standard hard water consumes = V_1 ml of EDTA … (2)
From (1) and (2), we have
V_1 ml of EDTA ≡ 50mg of $CaCO_3$ equivalent hardness
(or) 1ml of EDTA ≡ $\frac{50}{V_1}$ mg of $CaCO_3$ equivalent hardness … (3)

(ii) Estimation of total hardness of water sample using standardized EDTA:

50ml of water sample consumes = V_2 ml of EDTA … (4)

Using (3), the equation (4) can be written in terms of $CaCO_3$ equivalent as:

50ml of water sample contains ≡ $\frac{V_2}{V_1} \times 50$ mg of $CaCO_3$
(or)
1000ml of water sample has hardness ≡ $\frac{V_2}{V_1} \times 50 \times \frac{1000}{50}$

Total hardness of water sample = $1000 \times \frac{V_2}{V_1}$ ppm

(iii)Estimation of permanent hardness of water sample using standardized EDTA:

50ml of boiled water sample consumes = V_3 ml of EDTA … (5)

Using (3), the equation (5) can be written in terms of $CaCO_3$ equivalent as:

50ml of boiled water sample contains $\equiv \frac{V_3}{V_1} \times 50$ mg of $CaCO_3$

(or) $\equiv \frac{V_3}{V_1} \times 50 \times \frac{1000}{50}$

1000ml of boiled water sample has hardness

Permanent hardness of water sample $= 1000 \times \frac{V_3}{V_1}$ ppm

(iv) Determination of temporary hardness of water sample:

Temporary hardness of water sample = Total hardness – Permanent hardness

$= 1000 \times \frac{V_2}{V_1} - 1000 \times \frac{V_3}{V_1}$

Temporary hardness of water sample **=** $\frac{1000}{V_1} \times (V_2 - V_3)$ ppm**.**

PROBLEMS BASED ON HARDNESS

1. **A water sample contains 73 mg of Mg $(HCO_3)_2$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalents?**

Given:

Amount of $Mg(HCO_3)_2$ = 73 mg/litre

We know that,

146 mg/litre of $Mg(HCO_3)_2$ $\equiv$ 100 mg/litre of $CaCO_3$

$\therefore$ 73 mg/litre of $Mg(HCO_3)_2$ $\equiv 73 \times \frac{100}{146}$

Hardness of water sample in terms of $CaCO_3$ equivalent = 50 mg/litre (or) ppm.

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2. **What is the hardness of a solution containing 0.585 g of NaCl and 0.6 g of $MgSO_4$ per litre?**

Given:

Amount of $MgSO_4$ = 0.6 g/litre

NaCl will not make the water hard. Hence, it is ignored in hardness calculation.

We know that,
120 g/litre of $MgSO_4$ ≡ 100 g/litre of $CaCO_3$

$\therefore$ 0.6 g/litre of $MgSO_4$ ≡ $0.6 \times \frac{100}{120}$

Hardness of water sample in terms of $CaCO_3$ equivalent = 0.5 g/litre

= **500 mg/litre (or) ppm.**

3. **If a sample of water contains 36.5 mg of temporary magnesium hardness (TMgH) per litre, calculate the hardness in terms of $CaCO_3$ equivalent.**

Given:
Amount of *TMgH*, $Mg(HCO_3)_2$ = 36.5 mg/litre
We know that,
146 mg/litre of $Mg(HCO_3)_2$ ≡ 100 mg/litre of $CaCO_3$

$\therefore$ 36.5 mg/litre of $Mg(HCO_3)_2$ ≡ $\frac{36.5 \times 100}{146}$

Hardness of water in terms of $CaCO_3$ equivalent = **25 mg/litre (or) ppm.**

4. **Calculate temporary hardness and permanent hardness of a sample of water containing $Mg(HCO_3)_2$ = 73 mg/l; $Ca(HCO_3)_2$ = 162 mg/l; $MgCl_2$ = 95 mg/l; $CaSO_4$ = 136 mg/l.**

Name of the hardness producing salt	**Amount in mg/lit.**	**Molecular weight**	**Equivalents of $CaCO_3$**
$Mg(HCO_3)_2$	73	146	$73 \times \frac{100}{146}$ = 50 mg/lit.
$Ca(HCO_3)_2$	162	162	$162 \times \frac{100}{162}$ = 100 mg/lit.
$MgCl_2$	95	95	$95 \times \frac{100}{95}$ = 100 mg/lit.
$CaSO_4$	136	136	$136 \times \frac{100}{136}$ = 100 mg/lit.

Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$
= 50 + 100
= **150 mg/lit.**

Permanent hardness = $MgCl_2 + CaSO_4$
= 100 + 100
= **200 mg/lit.**

Total hardness = Temporary hardness + Permanent hardness
150 + 200
= **350/lit.**

5. 100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of the same EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm $CaCO_3$ per litre. Calculate hardness of water sample in ppm.

Given (i): *1 litre of standard hard water contains 1gm of $CaCO_3$*
i.e., 1000ml of standard hard water contains 1000mg of $CaCO_3$
(or) 1 ml of standard hard water ≡ 1 mg of $CaCO_3$ ...(1)

Given (ii): *100 ml standard hard water required 22ml of EDTA*
From equation (1),
100 ml of standard hard water ≡ 100 mg of $CaCO_3$
22 ml of EDTA ≡ 100 mg of $CaCO_3$
$\therefore$ 1 ml of EDTA ≡ $\frac{100}{22}$ mg of $CaCO_3$
= 4.5454 mg of $CaCO_3$

100ml of water sample requires = 18ml of EDTA
= 18× 4.5454
(Since 1ml of EDTA ≡ 4.5454mg of $CaCO_3$)
= 81.8172mg of $CaCO_3$
For 1000ml of water sample = $81.8172 \times \frac{1000}{100}$
= 818.17mg/litre

Hardness of water sample = 818.17mg/lit. (or) ppm.

0.5 gm of $CaCO_3$ was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA. Calculate the hardness.

Given (i): *500 ml of standard hard water contains 0.5 gm of $CaCO_3$*
i.e., 500 ml of standard hard water contains 500 mg of $CaCO_3$
(or) 1 ml of standard hard water ≡ 1 mg of $CaCO_3$ ...(1)

Given (ii): *50 ml standard hard water required 48 ml of EDTA*
From equation (1),
50 ml of standard hard water ≡ 50 mg of $CaCO_3$
48 ml of EDTA ≡ 50 mg of $CaCO_3$
$\therefore$ 1 ml of EDTA ≡ $\frac{50}{48}$ mg of $CaCO_3$
= 1.0416 mg of $CaCO_3$

50 ml of hard water sample required = 15 ml of EDTA
≡ 15 × 1.0416
(Since 1ml of EDTA ≡ 1.0416mg of $CaCO_3$)

= 15.624 mg of $CaCO_3$

For 1000 ml of water sample = $15.624 \times \frac{1000}{50}$

= 312.48 mg/litre

Total hardness of water sample = 312.48 mg/lit. (or) ppm.

Given (ii): *50 ml of hard water sample after boiling and filtration required 10 ml of EDTA*

50 ml of hard water sample after boiling and filtration required = 10 ml of EDTA

≡ 10 × 1.0416
(Since 1 ml of EDTA ≡ 1.0416 mg of $CaCO_3$)

= 10.416mg of $CaCO_3$

For 1000 ml of water sample = $10.416 \times \frac{1000}{50}$

= 208.32 mg/litre

Permanent hardness of water sample = 208.32 mg/lit. (or) ppm.

Temporary hardness of water sample = Total hardness – Permanent hardness

= 312.48 – 208.32

= 104.16 mg/lit.

Temporary hardness of water sample = 104.16 mg/lit. (or) ppm.

ESTIMATION OF IRON, CALCIUM AND MAGNESIUM: AAS METHOD

Definition of AAS:

Atomic absorption spectroscopy (AAS) is an analytical technique by which concentration (amount) of different metals at trace levels (1–100ppm) can be measured as a function of absorbance using a suitable hollow cathode lamp.

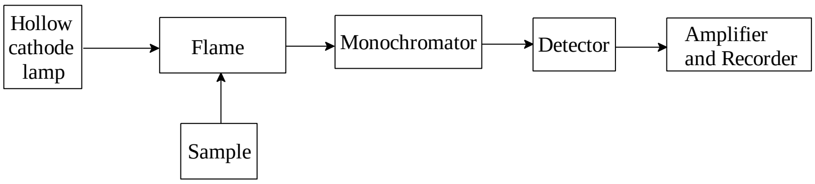


Fig. 1.1: Block diagram of Atomic Absorption Spectrophotometer

Principle and Instrumentation of AAS:

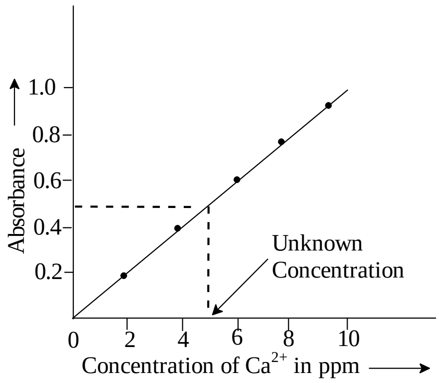
In AAS, a hollow cathode lamp (HCL) is used as light source. It can emit the atomic spectrum of a particular wavelength.

In AAS, a long flame (Air-acetylene gives flame temperature of 2400 K; Nitrous oxide-acetylene gives flame temperature of 2900 K) is used to convert the liquid sample containing metal ions into the corresponding atomized vapour form. When a monochromatic light of a particular wavelength is passed through a long flame, the free atoms absorb photons of characteristic emission of HCL. The amount of absorbance is directly proportional to the concentration of metal ion/element present in solution, and using the Beer-Lambert law ($A = \varepsilon bc$ where 'ε' is the molar absorbtivity, 'b' is the path length of light taken, and 'c' is the concentration) its concentration can be calculated.

Estimation: The atomic absorption spectrophotometer is warmed up for about 10 minutes. Then appropriate HCL is chosen based on the element to be analyzed. By using the ion free water, the meter is adjusted to zero absorbance.

Operating Parameters	**For Ca^{2+} Estimation**	**For Mg^{2+} Estimation**	**For Fe^{2+} Estimation**
Light Source	HCL (Ca)	HCL (Mg)	HCL (Fe)
Wavelength	422.7 nm	285.2 nm	480 nm
Flame Type	Air-acetylene	Air-acetylene	Air-acetylene
Preparation of Stock Solution	Dissolve 1g of dry $CaCO_3$ in dilute HCl and dilute to 1 litre using de-ionized water. 1ml of solution contains 1mg of Ca^{2+} ion.	Dissolve 1g of dry MgO in dilute HCl and dilute to 1 litre using de-ionized water. 1ml of solution contains 1mg of Mg^{2+} ion.	Dissolve 1g of dry FAS in dilute H_2SO_4 and dilute to 1 litre using de-ionized water. 1ml of solution contains 1mg of Fe^{2+} ion.

First, the standard solutions are introduced into the air-acetylene flame one by one. A part of the light from HCL is absorbed by the excited metal atoms. This results in the decrease of light intensity. The decrease of light intensity is measured as absorbance, and it is directly proportional to the concentration of metal ion. The unknown solution (hard water sample) is also introduced into the flame and its absorbance is measured. The absorbance values for standard solutions are used to construct the calibration curves. With the help of calibration curve, the amount of metal ions present in the test solution can be measured.



WATER SOFTENING

ZEOLITE PROCESS OF WATER SOFTENING

Zeolites are hydrated salts of sodium alumino silicates. The chemical structure of sodium zeolite may be written as $Na_2O.\ Al_2O_3.\ xSiO_2.\ yH_2O$ where $x = 2–10$ and $y = 2–6$. Sodium zeolite is simply represented as Na_2Z, where Z is insoluble, stable zeolite framework in which two sodium atoms are loosely bonded. In water technology, zeolites are used to produce soft water.

Process: The zeolite process involves alternate cycles of softening and regeneration.

Softening: When hard water is passed through a bed of active granular zeolite bed, Ca^{2+} and Mg^{2+} ions are removed from water and held by zeolite. The zeolite bed releases an equivalent amount of Na^+ ions to the water. The treated water therefore contains large amount of dissolved solids in the form of sodium salts.

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow CaZ + 2\,NaHCO_3$$
$$Na_2Z + Mg(HCO_3)_2 \longrightarrow MgZ + 2\,NaHCO_3$$
$$Na_2Z + CaCl_2 \longrightarrow CaZ + 2\,NaCl$$
$$Na_2Z + MgCl_2 \longrightarrow MgZ + 2\,NaCl$$
$$Na_2Z + CaSO_4 \longrightarrow CaZ + Na_2SO_4$$
$$Na_2Z + MgSO_4 \longrightarrow MgZ + Na_2SO_4$$

Stationary Solid Phase	**Mobile Liquid Phase**	**Stationary Solid Phase**	**Mobile Liquid Phase**

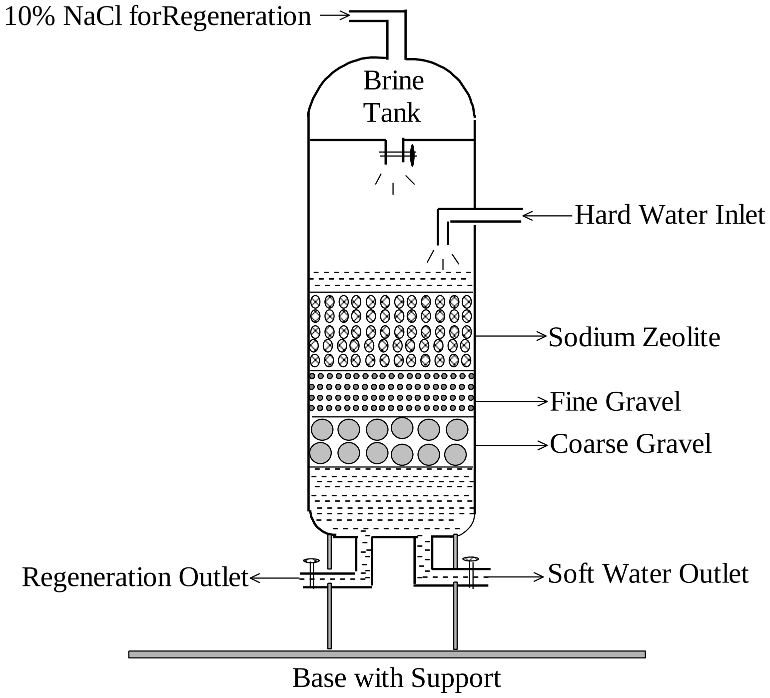


Fig. 1.2: Zeolite Softener

Regeneration: When the zeolite bed is saturated with Ca^{2+} and Mg^{2+}, it can be regenerated and reused. Concentrated brine (10% NaCl) is used for regeneration. The products formed during regeneration are mainly $CaCl_2$ and $MgCl_2$. They are highly water soluble and can be easily rinsed out from the zeolite bed.

$$\begin{array}{lllllll} CaZ & + & 2\,NaCl & \longrightarrow & Na_2Z & + & CaCl_2 \\ MgZ & + & 2\,NaCl & \longrightarrow & Na_2Z & + & MgCl_2 \\ \textbf{Stationary Solid Phase} & & \textbf{Mobile Liquid Phase} & & \textbf{Stationary Solid Phase} & & \textbf{Mobile Liquid Phase} \end{array}$$

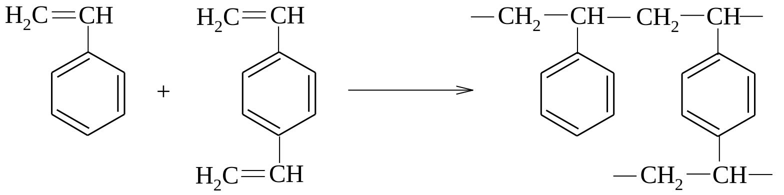
Advantages: Water softened by zeolite process has a residual hardness of about 10 to 15 ppm; Equipment is compact and occupies less space.

Disadvantages: Turbid water cannot be treated because turbid clogs the pores of the zeolite bed and thereby making it inactive; Fe, Mn – containing water cannot be treated because they are irreversibly exchanged; Acidic water cannot be treated because it decomposes the network structure of zeolite.

DEMINERALIZATION PROCESS OF SOFTENING OF WATER

Principle: De-mineralization process is an ion exchange process in which synthetic resins (polymers) are used as ion exchangers. Both cation and anion exchange resins are used in the deionizer. Deionizer is capable of producing ion free water by absorbing both cations as well as anions present in water sample.

Ion Exchangers: Ion exchangers are water insoluble, cross-linked polymers and possess micro porous structure. They are mainly copolymers of styrene and divinyl benzene.



Styrene Divinyl benzene Poly(styrene-co-divinylbenzene)

Cation Exchange Resin: The poly styrene–divinyl benzene can be chemically activated to perform cation exchange resin by treating it with concentrated sulphuric acid (the process is known as sulphonation).

Example: Polystyrene–divinyl benzene containing sulphonic acid and carboxylic acid

Anion Exchange Resin: The poly styrene–divinyl benzene can be chemically activated to perform anion exchange resin by treating it with alkyl (methyl) chloride and ammonia (the process is known as chloromethylation and amination).
Example: Polystyrene–divinyl benzene containing quaternary alkyl amino group

Cation exchange resin may be represented as RH^+ whereas anion exchange resin may be represented as $R'\,OH^-$.

Process: The demineralisation process also involves alternate cycles of softening and regeneration.

Softening: The hard water sample is *first passed through cation exchange column.* The column absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} etc. and releases an equivalent amount of H^{+} ions to water.

$$2RH^{+} + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^{+}$$
$$2RH^{+} + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^{+}$$
$$RH^{+} + Na^{+} \longrightarrow RNa^{+} + H^{+}$$

The cation free water is then passed through the anion exchange column. The column removes all the anions like SO_4^{2-}, $C1^{-}$, CO_3^{2-} etc. and releases an equivalent amount of OH^{-} to water.

$$2R'OH^{-} + SO_4^{2-} \longrightarrow R_2'SO_4^{2-} + 2OH^{-}$$
$$R'OH^{-} + Cl^{-} \longrightarrow R'Cl^{-} + OH^{-}$$
$$R'OH^{-} + HCO_3^{-} \longrightarrow R'\ HCO_3^{-} + OH^{-}$$

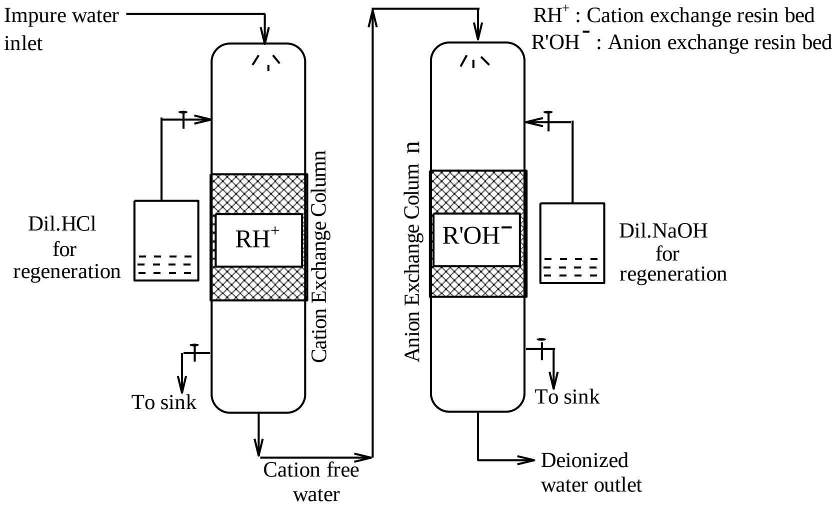


Fig. 1.3: Deionizer

H^{+} and OH^{-} ions released from cation and anion exchange column respectively get combined to produce water molecule.

$$H^{+} + OH^{-} \longrightarrow H_2O$$

In this way water coming out from anion exchange column becomes free from all the cations and anions. This ion free water is called "deionized water" or "de-mineralized water".

Regeneration: When the cation exchange column is exhausted, it can be regenerated by passing a solution of dil. HCl or dil. H_2SO_4.

$$R_2Ca^{2+} + 2H^{+} \longrightarrow 2RH^{+} + Ca^{2+}$$
$$R_2Mg^{2+} + 2H^{+} \longrightarrow 2RH^{+} + Mg^{2+}$$
$$RNa^{+} + H^{+} \longrightarrow RH^{+} + Na^{+}$$

When the anion exchange column is exhausted, it can be regenerated by passing a solution of dil. NaOH.

$$R_2'SO_4^{2-} + 2OH^- \longrightarrow 2R'OH^- + SO_4^{2-}$$
$$R'Cl^- + OH^- \longrightarrow R'OH^- + Cl^-$$
$$R'\,HCO_3^- + OH^- \longrightarrow R'OH^- + HCO_3^-$$

Advantages: The process can be used to soften highly acidic or alkaline waters; It produces water of very low hardness, say 2ppm. So it can be used in high pressure boilers.

Disadvantages: The cost of equipment is relatively high and also more expensive chemicals (resins) are needed; Fe, Mn – containing water and turbid water cannot be treated because Fe and Mn are irreversibly exchanged and turbidity reduces the efficiency of the process.

Table 1.1: Comparison of Zeolite Process and Demineralisation Process of Water Softening

S. No.	Characteristics	Zeolite Process	Demineralization Process
1.	Requirements	Sodium zeolites.	Ion exchange resins.
2.	Exchange of ions	Exchanges only cations.	Both anion exchanger and cation exchanger are available in deionizer.
3.	Nature of water produced	Produces soft water.	Produces De-ionized (ion free) water.
4.	Residual hardness	10–15 ppm.	0–2 ppm.
5.	Nature of raw water	Should be free from turbidity, Fe^{2+} and Mn^{2+} salts, acids.	Should be free from turbidity, Fe^{2+} and Mn^{2+} salts, acids.
6.	Total dissolved solids (TDS)	Treated water contains more of TDS in the form of sodium salts.	TDS is almost nil in treated water.
7.	Regeneration	NaCl is used.	Acids and bases are used.
8.	Operating cost	Less because of NaCl; this is very cheap.	More.
9.	Application	Used for laundry purposes.	Deionised water can be used in boilers

DESALINATION

Desalination: The process of removing of dissolved solids (NaC1) from water is described as desalination or desalting.

REVERSE OSMOSIS (OR) HYPER FILTRATION

Definition: Reverse osmosis (RO) is a membrane process in which water is separated from seawater by filtering through semi permeable membrane at a pressure greater than osmotic pressure.

Process: Osmosis is a natural process in which spontaneous flow of water takes place when two solutions of unequal concentration are separated by a semi permeable membrane (SPM).

The driving force for the movement of water in osmosis is known as “osmotic pressure or hydrostatic pressure”.

Semi permeable membrane is permeable only to water molecules. Examples of SPM are: Cellulose acetate and Polyamide composite, Polymethylacrylate, Polyimide etc.

This osmosis process can be reversed by applying pressure higher than the osmotic pressure of the order 15 – 40 kg/cm^2 on the concentrated solution so that the fresh water is forced to move from concentrated side (brackish water/seawater) to dilute side (fresh water) across the membrane. Such a process of reversing of osmosis is called “reverse osmosis”.

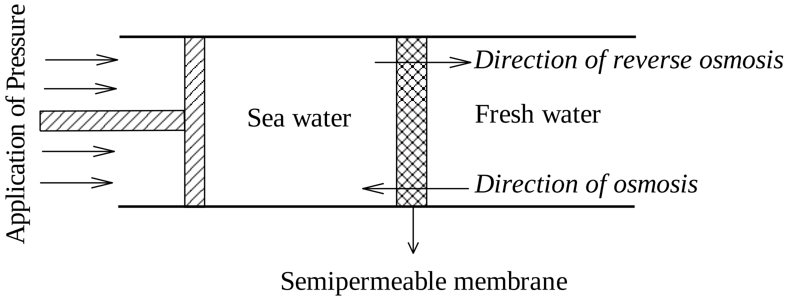


Fig. 1.4: Desalination-Reverse Osmosis

Advantages and Applications of RO:

RO removes bacteria, sugars, salts, proteins, silica and other high molecular constituents; RO is reliable and economical for converting sea water in to fresh water; Life of the membrane is about 2–3 years and can be easily replaced within few minutes. Extremely high quality water required for nuclear power plants can be made from seawater by reverse osmosis process.

Disadvantages:

Periodic cleaning of membrane is required to maintain water transfer efficiency; Sometimes pre-treatment of raw water is required to inhibit bacterial growth and scale formation ($CaCO_3$) at the surface of membrane.

ELECTRODIALYSIS METHOD OF DESALINATION

Desalination: The process of removing of dissolved solids (NaC1) from water is described as desalination or desalting.

Definition and Principle: Electrodialysis is a process in which salt is separated from sea water in the form of ions under the influence of direct current using ion selective membranes. The process follows the mechanism of electrolysis. Ion selective membranes are permeable to only one kind of ions with specific charge.

Cation selective membrane is permeable to cations but not to anions. ***Example:*** Polystyrene based sulphonate. Anion selective membrane is permeable only to anions and impermeable to cations. ***Example:*** Polystyrene based quaternary ammonium ion.

Description and Process*:* An electrodialysis unit consists of a large number of ion selective membranes and a pair of inert electrodes (graphite). An alternate arrangement of ion selective membranes with two inert electrodes forms a number of compartments in electrodialysis unit. One of the inert electrodes called cathode is placed near to cation selective membrane while the other inert electrode called anode is placed near to anion selective membrane. For desalination to occur sea water is fed into the different compartments from the top of the unit at a rate of 5-6 kg/m^2 and simultaneously direct current is passed through the inert electrodes to produce electrolysis in the unit. Electrolysis causes the ions (Na^+ and Cl^-) present in different compartments to move towards oppositely charged electrodes through ion selective membranes.

Na^+ ions present in the 2nd compartment move towards cathode through cation selective membrane and get retained in the 1st compartment. Similarly Cl^- ions in the 2nd compartment move towards anode through anion selective membrane and retained in the 3rd compartment. Hence the movement of ions (Na^+ and Cl^-) in the 2nd compartment produces soft water but it increases the concentration of NaCl in nearby compartments (1st and 3rd compartments). Similar mechanism involves in 3rd, 4th and 5th compartments also. That is the 4th compartment produces soft water and the salt concentration increases in the 3rd and 5th compartments. Therefore the electrodialysis unit produces desalination in the alternate compartments.

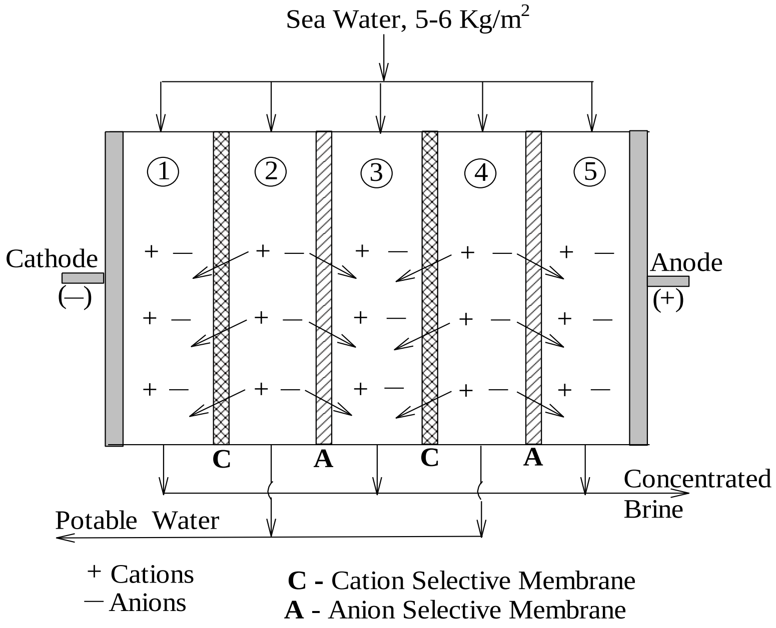


Fig. 1.5: Desalination-Electrodialysis

Merits and Demerits: The capital cost for electrodialysis plant depends upon mainly the dimensions and membranes required for desalination; The operating cost is dominated by the electricity consumption which in turn depends upon the extend of salinity of water to be treated; If electricity is easily available, this method is the best method for converting sea water in to fresh water.

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DEPARTMENT OF CHEMISTRY

UNIT – 2 – Electrochemical Power Sources – SCY1213

ELECTROCHEMISTRY

Electrochemistry is a branch of physical chemistry, which deals with the relationship between chemical energy and electrical energy. The knowledge of electrochemistry is essential for understanding various electrochemical processes such as Batteries and Fuel cells, Corrosion and its prevention, Industrial metal finishing etc. for transfer of electrons as ions inside the cell between the anode and cathode.

BASICS OF ELECTROCHEMICAL CELL

- **Electrochemistry:** It explains the inter-conversion of chemical energy and electrical energy.

- **Metals**: According to modern electrochemistry, metals are made up of their positive metal ions and their valence electrons. They are usually represented as:

$$M^{n+} + ne^{-} \rightleftharpoons M$$

$$Al^{3+} + 3e^{-} \rightleftharpoons Al$$

$$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$$

$$Na^{+} + e^{-} \rightleftharpoons Na$$

- **Electrolytic cell:** A device in which electrical energy is used to bring chemical changes.

- **Electrochemical cell**: A device in which chemical energy is utilized to produce electrical energy.

- **Anode**: It is a negative electrode, which supplies electrons when connected to cathode of electrochemical cell.

- **Cathode**: It is a positive electrode, which receives electrons readily when connected to anode of electrochemical cell.

- **Cell**: It consists of two half cells namely anode half cell and cathode half-cell.

- **Half-cell**: An electrode (metal) immersed in a solution containing its own metal salt.

- **Salt Bridge**: It consists of ammonium nitrate or potassium chloride in agar-agar gel. It provides electrical contact between the two half-cells.

- **Interface**: Space between metal and solution (electrolyte).

- **Helmholtz Electrical Double Layer**: When a metal is placed in solution containing its own metal ions, a layer forms with specific charge close to the metal surface containing opposite charge.

- **Electrode potential**: It is the potential difference of electrical double layer develops at the interface of electrode and electrolyte.

- **Single Electrode Potential (E):** The measure of tendency of a metallic electrode to lose or gain electrons when it is immersed in a solution containing its own metal ion.

- **Standard Electrode Potential (E°):** The measure of tendency of a metallic electrode to lose or gain electrons when it is placed in a solution of its own salt of 1 M concentration at 25°C.

- **Oxidation Potential:** The measure of tendency of a metallic electrode to lose electrons when in contact with a solution of its own metal salt.

- **Reduction Potential:** The measure of tendency of a metallic electrode to gain electrons when in contact with a solution of its own metal salt.

- **Reference Electrodes**: They are standard half-cells having constant electrode potentials. They are used to measure half-cell potentials of various metals placed in their own salt solution.

⇒ **Examples:** Standard hydrogen electrode and saturated calomel electrode.

- **Electromotive Force (E_{cell})**: It is the potential difference of two half-cells, which drives (motivates) the electrons to flow from one half-cell to the other half-cell.

- **EMF Expression**: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

  where E_{cathode} is the cathode half-cell potential and E_{anode} is the anode half-cell potential.

- Electrochemical cell is a device in which chemical energy is converted into electrical energy.

- The electrochemical cell consists of two half cells namely an anode half-cell and a cathode half-cell.

- In the anode half-cell, the anode undergoes oxidation and in the cathode half-cell, the cathode undergoes reduction. The electron transfer in the oxidation and reduction reactions is utilized as a source of producing electrical energy in electrochemical cell.

GALVANIC CELL

- **Definition:** Galvanic cell is an electrochemical cell, which converts chemical energy into electrical energy. It uses two different metals as anode and cathode (Galvanic means dissimilar).

⇒ **Example:** Zinc-copper cell.

- **Construction**: In a galvanic cell, a zinc rod is partially immersed in 1M $ZnSO_4$ solution and a copper rod is partially immersed in 1M $CuSO_4$ solution (Fig. 2.1a).

- The two solutions are interconnected by a salt bridge. The salt bridge consists of ammonium nitrate or potassium chloride in agar-agar gel.

- Salt bridge provides electrical contact between the two half cells. It also helps to maintain electrical neutrality by allowing the migration of ions.

- The practical example of galvanic cell is Daniel cell in which the two solutions are separated by a porous pot. The two solutions can seep through the pot and come in contact with each other automatically. Here the porous pot acts as salt bridge (Fig. 2.1b).

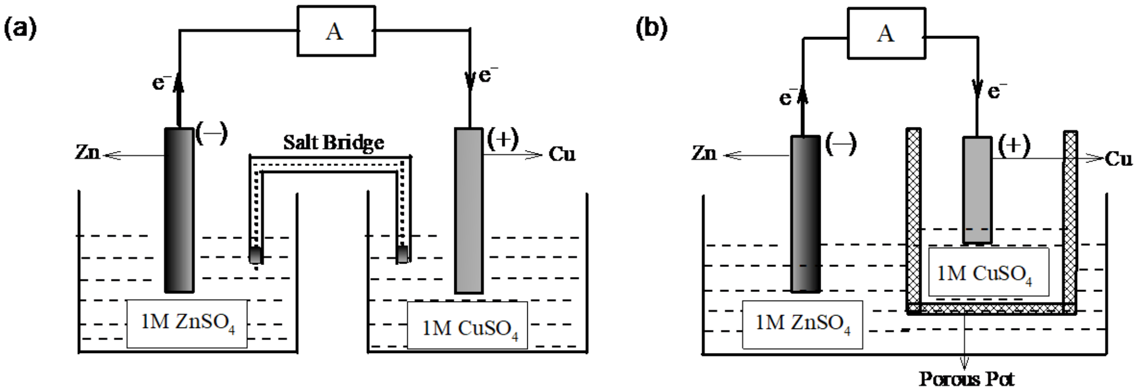


Fig. 2.1: (a) Galvanic Cell (b) Daniel Cell

- **Working**: If zinc and copper rods are connected from outside, flow of electrons takes place from zinc to copper. This is because, zinc atoms are oxidized and copper atoms are reduced.

- The flow of electrons is indicated by ammeter placed in the circuit.

- **Electrode Reactions**

- At anode, zinc undergoes oxidation with the liberation of electrons.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad \text{(Oxidation)}$$

- At cathode, reduction of copper ions to copper takes place.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{(Reduction)}$$

- The net cell reaction is:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

ELECTROCHEMICAL CELL REPRESENTATION

A cell consists of two half cells namely anode and cathode half cells.

(ii). A salt bridge is indicated by two vertical lines (‖) separating the two half-cells.

(ii). The anode half-cell must be represented always on the left side while the cathode half-cell must be represented always on the right side of the salt bridge.

(iii). The anode half-cell must be written by writing metal first and then electrolyte. The two must be separated by a vertical line or a semicolon.

Example: M/M^{n+} or $M; M^{n+}$

(iv). The cathode half-cell must be written by writing electrolyte first and then the metal. The two must be separated by a vertical line or a semicolon.

Example : M^{n+}/M or $M^{n+} ; M$

(v). The electrolyte may be represented by whole formula or its ionic species. The concentration of the electrolyte may also be represented in bracket.

Applying the above rules to a galvanic cell, we can represent it as:

$$Zn / ZnSO_4\ (1M) \parallel CuSO_4\ (1M) / Cu.$$

or $$Zn / Zn^{2+}\ (1M) \parallel Cu^{2+}\ (1M) / Cu.$$

or $$Zn ; Zn^{2+}\ (1M) \parallel Cu^{2+}\ (1M) ; Cu.$$

EMF SERIES AND ITS SIGNIFICANCE

Table 2.1: Standard electrode potential (Half-cell potential) of some metals with respect to SHE at 25°C

Half Cell Reaction	E° (Volts) vs SHE	Half Cell Representation	
$Li^+ + e^- \Leftrightarrow Li$	−3.01	Li^+ / Li	Anodic
$Mg^{2+} + 2e^- \Leftrightarrow Mg$	−2.37	Mg^{2+} / Mg	↑
$Al^{3+} + 3e^- \Leftrightarrow Al$	–1.66	Al^{3+} / Al	
$Zn^{2+} + 2e^- \Leftrightarrow Zn$	–0.76	Zn^{2+} / Zn	
$Fe^{2+} + 2e^- \Leftrightarrow Fe$	–0.44	Fe^{2+} / Fe	
$2H^+ + 2e^- \Leftrightarrow H_2$	0.0	$2H^+ / H_2$	
$Cu^{2+} + 2e^- \Leftrightarrow Cu$	+0.34	Cu^{2+} / Cu	
$Ag^+ + e^- \Leftrightarrow Ag$	+0.80	Ag^+ / Ag	↓
$\frac{1}{2} F_2 + e^- \Leftrightarrow F^-$	+2.65	$\frac{1}{2} F_2 / F^-$	Cathodic

- **Definition:** The arrangement of various metals in increasing order of their standard reduction potentials is called as electrochemical series or electromotive force series (EMF series).

1. RELATIVE EASE OF OXIDATION (or) REDUCTION

- The positive sign of reduction potential in EMF series indicates that the electrode reaction occurs in forward direction, i.e., reduction direction.

⇒ **Example:** The fluoride has higher positive value of standard reduction potential (+2.65V) and shows higher tendency towards reduction.

- The negative sign of reduction potential indicates that the electrode reaction occurs in opposite direction i.e., backward direction.

⇒ **Example:** Lithium has the highest negative reduction potential (-3.01V) and shows higher tendency to lose electrons.

2. DISPLACEMENT OF ONE SPECIES BY THE OTHER

- A metal with more negative reduction potential can displace those metals with less negative or positive potentials from their own salt solution.

⇒ **Example:** We can know whether copper will displace zinc from solution or vice versa.

- We know that $E^o_{Cu^{2+}/Cu} = +.34\text{V}$ and $E^o_{Zn^{2+}/Zn} = -0.76\text{V}$. Therefore Cu^{2+} has much greater tendency to get Cu–form than Zn^{2+} for getting Zn–form. In other words zinc will displace copper from its salt solution.

3. CALCULATION OF STANDARD EMF OF THE CELL

- Using E° values of anode half cell and cathode half cell, the standard EMF of a cell can be calculated by using the following expression.

$$E^o_{Cell}\text{ (Standard EMF of cell)} = E^o_{Cathode} - E^o_{Anode}$$

4. PREDICTING FEASIBILITY (OR) SPONTANEITY OF THE CELL REACTION

- In a reversible cell, when the cell yields electrical energy, there is a fall in free energy (or) $-\Delta G = nFE_{cell}$.

⇒ If ΔG = Negative; E_{cell} = Positive. Then the cell reaction is spontaneous (feasible).

⇒ If ΔG = Positive; E_{cell} = Negative. Then the cell reaction is non spontaneous (not feasible).

⇒ If $\Delta G = 0$; $E_{cell} = 0$. Then the cell reaction has the equilibrium.

5. DETERMINATION OF EQUILIBRIUM CONSTANT FOR THE REACTION

- Standard electrode potential can be used to determine equilibrium constant for the reaction.

We know that,

$$\begin{aligned} -\Delta G^\circ &= RT\ \text{In}\ k \\ -\Delta G^\circ &= 2.303\ RT \log k \\ \log k &= \frac{-\Delta G^o}{2.303RT} \\ \log k &= \frac{nFE^o_{Cell}}{2.303RT} \qquad \left[\because -\Delta G^o = nFE^o\right] \end{aligned}$$

- So, from the value of E° for a cell reaction, its equilibrium constant (k) can be calculated.

BATTERIES: TERMINOLOGY

Battery: Battery is an electrochemical device in which the active electrode materials undergo oxidation and reduction reaction in presence of suitable electrolyte to produce electric current.

Components of a Battery

Anode - Negative plate
Cathode - Positive plate
Electrolyte - Medium for charge transfer
Separator - Avoids short – circuit of electrodes
Container - Holds the above components

Discharging: It is an *electrochemical process* by which a battery delivers current to an external circuit at the cost of the consumption of electrode materials.

Charging: It is an *electrolytic process* by which a constant current is passed through a battery in order to regenerate the active materials back into their original form.

Primary Cells: They are unchargeable cells because the active materials consumed during the discharge process cannot be regenerated by passing electric current.

Examples: Dry cell, $\text{Zn}-\text{HgO}$ cell.

Secondary Batteries: They are known as chargeable batteries because the active materials consumed during the discharge can be regenerated back into their original form by passing electric current.

Examples: Lead-acid accumulator, Nickel-cadmium batteries.

Fuel Cells: They are primary cells in which the active materials in gaseous form are supplied continuously into the cell to produce electric current.

Examples: Hydrogen-oxygen fuel cell, Methanol fuel cell

Cycle Life: The number of times a battery can be discharged and charged before the failure occurs in the electrode materials to produce electric current is known as cycle life.

Capacity: The amount of constant current delivered by a battery for a definite period is known as its capacity. It is expressed in ampere-hour, Ah. For example, if a battery has the capacity of 50 Ah, it is capable of delivering a current of 5 ampere for 10 hours or 10 ampere for 5 hours or 50 amperes for 1 hour.

Open Circuit Voltage (OCV): It refers to the cell voltage (emf) of a fully charged battery.

Closed Circuit Voltage (CCV): It refers to the cell voltage of a completely discharged battery.

Power: The cell voltage at which a battery delivers a constant current to an external circuit is known as operating cell voltage. The product of operating cell voltage and the constant current is known as power.

Power Density: The amount of power produced by unit kilogram weight of a battery is known as power density. It is expressed in watt/kg.

Energy Density: The amount of energy (power) obtained for an hour by unit kilogram weight of a battery is known as energy density. It is expressed in watt.hr/kg.

Internal Resistance: Internal resistance is the resistance offered by all the components of a battery. It can be determined by measuring the cell voltage of battery at different discharge current densities. The cell voltage (CV) versus current yields a straight line and slope of it gives internal resistance (IR) of the battery.

Shelf life: A good battery must have long shelf life. It should not undergo any self-discharge when not in use.

LEAD-ACID ACCUMULATOR

COMPONENTS OF A LEAD-ACID ACCUMULATOR:

Anode	Negative plate; Pb-Sb grid filled with spongy lead
Cathode	Positive plate; Pb-Sb grid filled with PbO_2
Electrolyte	21.4% H_2SO_4 (sp.gr = 1.25–1.26 at 25ºC)
Separator	Nylon cloth
Container	Polypropylene (PP)
Cell representation	Pb, $PbSO_4$ / H_2SO_4(21.4%) / $PbSO_4$, PbO_2
OCV	2.10V
CCV	1.78V
Energy density	44 watt hr / kg

CONSTRUCTION:

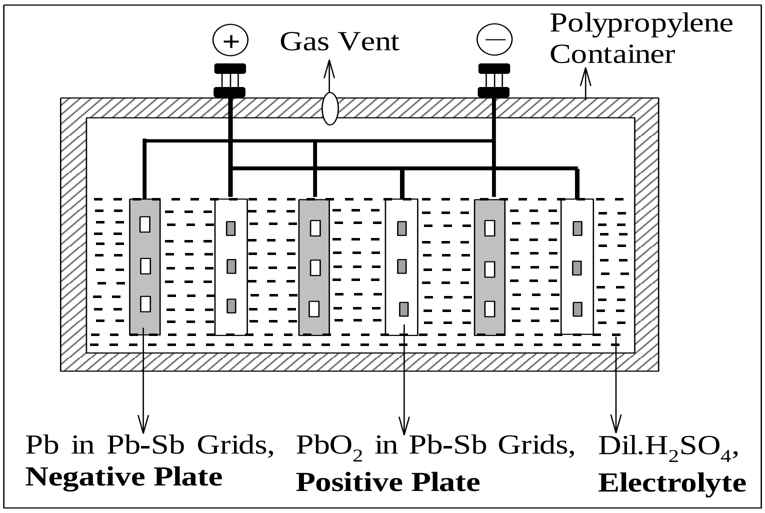


Fig. 2.2: Lead Acid Accumulator

CHEMISTRY DURING DISCHARGE:

When a battery delivers current to an external circuit, the process is known as discharging. During the discharge in a lead-acid battery, the lead anode undergoes oxidation and PbO_2 cathode undergoes reduction.

At anode, lead oxidizes into Pb^{2+} with the liberation of electrons. But the SO_4^{2-} ions of the electrolyte react with Pb^{2+} and make it as $PbSO_4$.

$$\boxed{\begin{array}{lcll} Pb & \longrightarrow & Pb^{2+} + 2e & \\ Pb^{2+} + SO_4^{2-} & \longrightarrow & PbSO_4 & \\ \hline Pb + SO_4^{2-} & \longrightarrow & PbSO_4 + 2e & \quad ...(1) \\ \hline \end{array}}$$

At cathode, PbO_2 gains the electrons and gets reduced into Pb^{2+} ions in presence of acid. Further the SO_4^{2-} ions of the electrolyte react with this Pb^{2+} ion and make it as $PbSO_4$

$$\boxed{\begin{array}{lcll} PbO_2 + 4H^+ + 2e & \longrightarrow & Pb^{2+} + 2H_2O & \\ Pb^{2+} + SO_4^{2-} & \longrightarrow & PbSO_4 & \\ \hline PbO_2 + 4H^+ + SO_4^{2-} + 2e & \longrightarrow & PbSO_4 + 2H_2O & \quad ...(2) \\ \hline \end{array}}$$

The net cell reaction during discharge (1) + (2) gives

$$\boxed{\mathbf{Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O}}$$

Note:

$$Pb^{4+} + 2O^{2-} + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O$$

CHEMISTRY DURING CHARGING:

During the discharge, (i) both the electrodes becomes $PbSO_4$ and (ii) specific gravity of acid decreases due to the formation of H_2O.

At one stage, the $PbSO_4$ of two electrodes fails to produce the electric current. For further use, $PbSO_4$ should be converted back into their original form. This is possible by reversing the anode and cathode reactions. In order to reverse these reactions, an external current is supplied through battery by connecting the positive plate to the positive terminal of external source and negative plate to negative terminal of the external source, so that the system acts as an electrolytic cell.

At positive plate, oxidation occurs:

$$\boxed{PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e}$$

Note:

$$Pb^{2+} + SO_4^{2-} + 4H^+ + 2O^{2-} \longrightarrow [Pb^{4+} + 2e] + 2O^{2-} + SO_4^{2-} + 4H^+ \longrightarrow PbO_2 + 2e + SO_4^{2-} + 4H^+$$

At negative plate, reduction occurs:

$$\boxed{PbSO_4 + 2e \longrightarrow Pb + SO_4^{2-}}$$

Note:

$$Pb^{2+} + SO_4^{2-} + 2e \longrightarrow Pb + SO_4^{2-}$$

The net cell reaction during charging is

$$\boxed{\mathbf{2\,PbSO_4 + 2\,H_2O \longrightarrow Pb + PbO_2 + 2\,H_2SO_4}}$$

Applications:

- ✓ A battery with 50 Ah capacities is used for SLI (starting-lighting-ignition) purposes in cars
- ✓ A battery with 1000 Ah capacity is used as emergency power supply in hospitals, telephone exchanges, for train lighting and as standby power supply for computers (UPS)

NICKEL-CADMIUM BATTERIES.

Nickel-cadmium (NICAD) batteries are rechargeable alkaline batteries.

COMPONENTS OF A NICAD BATTERY:

Anode	Cadmium as cadmium hydroxide
Cathode	Nickel as nickel hydroxide, $Ni(OH)_3$
Electrolyte	Aqueous KOH (6M)
Cell representation	Cd, Cd $(OH)_2$/ aq.KOH / Ni, Ni $(OH)_3$
OCV	1.34 to 1.40V
Energy density	50 watt hr / kg

TYPES OF NICKEL-CADMIUM BATTERIES:

Ni-Cd batteries are manufactured in two different types.

(1) Pocket plate cells

(2) Sintered plate cells

1. POCKET PLATE CELLS

Characteristics: Pocket plate cells are highly reliable and have long shelf life. They are manufactured with the capacities 10–1000 Ah.

Fabrication of Electrodes: The electrodes are fabricated by using the perforated two-nickel plated steel strips. The two strips are folded in the form of packets and are filled with suitable active electrode materials.

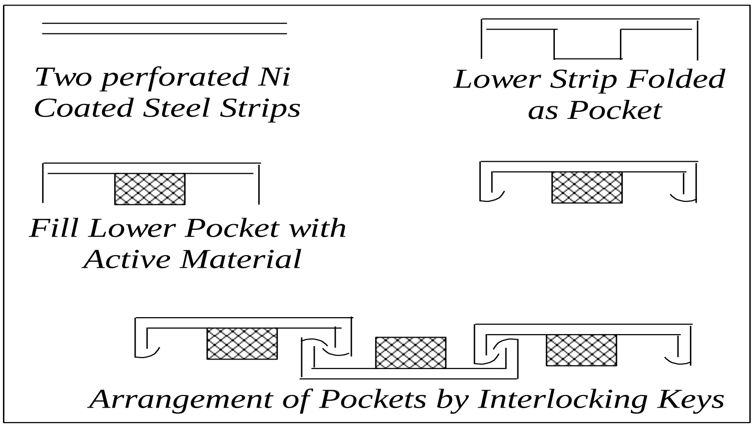


Fig. 2.3: Fabrication of Pocket Plate Cells

The active materials for the negative electrode consists of 78% $Cd(OH)_2$ + 20% Fe + 1% Ni + 1% Graphite. *Iron* increases the electrical conductivity of *cadmium* during discharge process. Presence of small amount of *nickel and graphite* increases the shelf life of batteries.

The active materials for the positive electrode consists of 80% $Ni(OH)_2$ + 18% Graphite + 2% $Co(OH)_2$ + a trace amount of $Ba(OH)_2$. *Graphite* increases the electrical conductivity of *nickel* and the presence of *cobalt and barium* compounds increases the percentage usage of nickel metal.

2. SINTERED PLATE CELLS

Characteristics: Sintered plate cells are characterized by good cycle life, 1000–2000 cycles and have flat discharge curve. They are manufactured with different sizes and capacities.

Fabrication of Electrodes: The electrodes are fabricated by using the sintered metals of thickness of 0.5–1.0mm with the porosity 80–85% and surface area 0.25–0.5m^2/gm.

The two sintered metals, nickel and cadmium are placed in $Ni(NO_3)_2$ and $Cd(NO_3)_2$ solutions respectively. Then a vacuum pump is used to suck the solution into all the pores. The electrodes are then treated chemically, thermally and electrochemically to cause the solutions to precipitate nickel as $Ni(OH)_2$ and cadmium as $Cd(OH)_2$. The complete cycle is repeated 3-10 times to obtain high loading of active materials. Then the electrodes are charged before the cell is assembled.

CHEMISTRY DURING DISCHARGE:

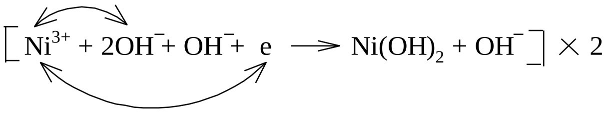
At anode, Cadmium is oxidized into Cd^{2+} ion with the liberation of electrons. The OH^- ions of the electrolyte make it as $Cd(OH)_2$.

$$\begin{array}{l} Cd \longrightarrow Cd^{2+} + 2e \\ Cd^{2+} + 2\,OH^- \longrightarrow Cd(OH)_2 \\ \hline Cd + 2\,OH^- \longrightarrow Cd(OH)_2 + 2e \qquad \ldots(1) \\ \hline \end{array}$$

At cathode, +3 oxidation state of $Ni(OH)_3$ gets reduced into +2 oxidation state of $Ni(OH)_2$.

$$\boxed{2\,Ni(OH)_3 + 2e \longrightarrow 2\,Ni(OH)_2 + 2\,OH^- \qquad ...(2)}$$

Note:



$$\left[Ni^{3+} + 2OH^- + OH^- + e \longrightarrow Ni(OH)_2 + OH^-\right] \times 2$$

The net reaction during discharge (1) + (2) gives

$$\boxed{\mathbf{Cd + 2\,Ni(OH)_3 \longrightarrow Cd(OH)_2 + 2\,Ni(OH)_2}}$$

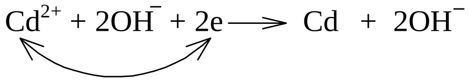
CHEMISTRY DURING CHARGING:

The active materials of the electrode are charged by passing external current through the battery in the opposite direction of discharge current.

At the negative plate, reduction occurs

$$\boxed{Cd(OH)_2 + 2e \longrightarrow Cd + 2\,OH^- \qquad ...(3)}$$

Note:

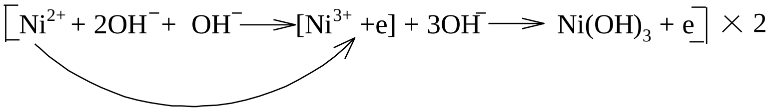


$$Cd^{2+} + 2OH^- + 2e \longrightarrow Cd + 2OH^-$$

At the positive plate, oxidation occurs

$$\boxed{2\,Ni(OH)_2 + 2\,OH^- \longrightarrow 2\,Ni(OH)_3 + 2e \qquad ...(4)}$$

Note:



$$\left[Ni^{2+} + 2OH^- + OH^- \longrightarrow [Ni^{3+} + e] + 3OH^- \longrightarrow Ni(OH)_3 + e\right] \times 2$$

The net reaction during charging (3)+(4) gives

$$\boxed{\mathbf{Cd(OH)_2 + 2\,Ni(OH)_2 \longrightarrow Cd + 2\,Ni(OH)_3}}$$

Applications: Nickel-cadmium batteries are used for

- ✓ Emergency power supply in hospitals, train lighting etc.
- ✓ Military applications.
- ✓ And used in small electronics equipment.

LITHIUM BATTERIES

UNIQUE PROPERTIES OF LITHIUM METAL AS ANODE

Lithium metal has certain unique properties.

- ✓ Lithium has high electrochemical equivalent. 1 gram equivalent (7 gram) of lithium is capable of producing one Faraday electric current
- ✓ Lithium has high negative electrode potential (−3.01V) with respect to standard hydrogen electrode. This makes use of lithium for constructing high cell voltage cells
- ✓ Since lithium metal reacts vigorously with water, aprotic (non-aqueous) organic solvents are used in battery systems. Further organic solvents are low boiling liquids, the lithium battery systems can be operated over wide range of temperatures
- ✓ Lithium is of light weight metal. Hence it is capable of producing high energy density batteries

Lithium Battery is a Cell of Future (or) Advantages of lithium cells over other conventional batteries:

- ✓ Lithium cells have high cell voltage (3.0 to 3.9V)
- ✓ Lithium cells have higher energy densities (400watt hr/kg) than any other battery systems
- ✓ Lithium cells can be operated over wide range of temperature (+60ºC to –40ºC)
- ✓ Lithium cells produce flat discharge curves during discharge at different current densities
- ✓ Lithium cells have good power density and good shelf life

CLASSIFICATION OF LITHIUM PRIMARY CELLS:

Lithium primary cells are classified into three types on the basis of nature of cathode and electrolyte.

1. Lithium – soluble cathode cells

Eg.: Lithium / Thionyl chloride cells

2. Lithium – solid cathode cells

Eg.: Lithium / Manganese dioxide cells

3. Lithium – solid electrolyte cells

Eg.: Lithium / Iodine cell

Li/SOCl₂ CELL

It is an example of soluble cathode cells.

COMPONENTS OF LITHIUM-THIONYL CHLORIDE CELL:

Anode	Pure Li-foil
Cathode	Porous carbon, bonded with Teflon
Electrolyte	Li $AlCl_4$ in $SOCl_2$ solution. (When cathode is placed in electrolyte, $SOCl_2$ gets absorbed preferentially into pores by the carbon).
OCV	3.6V
Energy density	350 – 400 watt hr / kg
Cell representation	$Li/LiAlCl_4$, $SOCl_2$ / $SOCl_2$, C

CHEMISTRY DURING DISCHARGE:

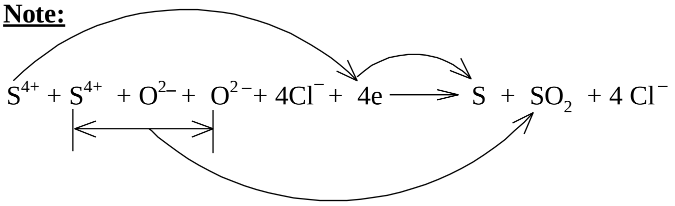
At anode, lithium oxidizes into Li^+ ions with the liberation of electrons.

$$\boxed{4\,Li \longrightarrow 4\,Li^+ + 4e}$$

At cathode, $SOCl_2$ gets reduced into sulphur

$$\boxed{2\,SOCl_2 + 4e \longrightarrow S + SO_2 + 4\,Cl^-}$$

Note:



The net cell reaction is

$$\boxed{\mathbf{4\,Li + 2\,SOCl_2 \longrightarrow S + SO_2 + 4\,LiCl}}$$

APPLICATIONS:

Lithium–thionyl chloride system is used (i) for military applications where high energy density is required (ii) as power source for small electronic equipment.

LITHIUM-ION BATTERIES

COMPONENTS OF LITHIUM-ION BATTERIES:

Lithium-ion cell has three layers.

(i) ***A negative electrode plate (Anode):*** Graphitic carbon usually denoted as C_6, which acts as host solid electrode

(ii) A positive electrode plate (Cathode): It is made from lithium liberating compounds such as lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel oxide ($LiNiO_2$) etc.

(iii) A separator: Micro porous polyethylene membrane

(iv) Electrolyte: $LiPF_6$ or $LiBF_4$ dissolved in Organic solvent

CHEMISTRY DURING CHARGING AND DISCHARGING:

The process of lithium ion moving into negative electrode (C_6) from the positive electrode ($LiCoO_2$) is known as insertion or intercalation (Fig.2.6).

Charging: When a cell is subjected for charging, the lithium ions are extracted from the positive electrode and inserted into the negative electrode. The positive electrode compensates the removal of lithium ions by the oxidation of its transition metal ($Co^{3+} \rightarrow Co^{4+}$).

$$\boxed{\begin{array}{l} LiCoO_2 \xrightarrow[\textit{Oxidation}]{\textit{Extraction}} xLi^+ + xe + Li_{(1-x)}CoO_2 \\ xLi^+ + xe + C_6 \xrightarrow[\textit{Reduction}]{\textit{Intercalation}} Li_xC_6 \\ LiCoO_2 + C_6 \xrightarrow{\textit{Charging}} Li_xC_6 + Li_{(1-x)}CoO_2 \end{array}}$$

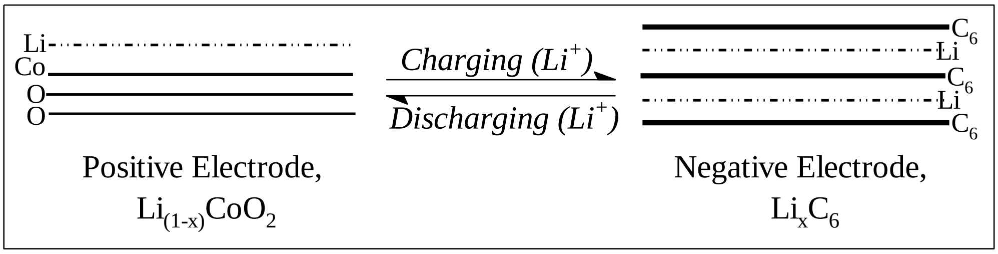


Fig. 2.4: Schematic layer of $LiCoO_2$ and LiC_6

Discharging: When a cell starts to deliver current to en external circuit, the process is known as discharging. During the discharge, the lithium ions are shuttled from the negative electrode through the electrolyte back to the positive electrode. The positive electrode accepts lithium ions by the reduction of its transition metal ($Co^{4+} \rightarrow Co^{3+}$).

$$\boxed{\begin{array}{l} Li_xC_6 \xrightarrow{\textit{Oxidation}} xLi^+ + xe + C_6 \\ xLi^+ + xe + Li_{(1-x)}CoO_2 \xrightarrow{\textit{Reduction}} LiCoO_2 \\ Li_xC_6 + Li_{(1-x)}CoO_2 \xrightarrow{\textit{Discharging}} LiCoO_2 + C_6 \end{array}}$$

FEATURES (or) ADVANTAGES OF LITHIUM-ION CELLS

- ✓ High energy density 160Wh/Kg
- ✓ High OCV of 3.6V or even 3.7V

- ✓ No memory effect. The cell can be charged any time
- ✓ Flat discharge voltage allowing the device to stable power throughout the discharge period
- ✓ High charge currents (0.5−1A) that lead to small charging times (around 2−4 hours)
- ✓ Recommended temperature range 0−40˚C

APPLICATIONS:

Major applications of lithium−ion batteries include

- ✓ Mobile phones: ~ 55% of total production
- ✓ Notebook PC's: ~ 25% of total production
- ✓ Cameras, Camcorders, MP3, Games, etc.: ~ 20% of total production

FUEL CELLS

A fuel cell is a device that converts a fuel and air (O_2) directly into electricity, heat and water by means of simple electrochemical reactions. In a fuel cell, the electricity can be generated as long as the fuel and oxygen are supplied into the cell.

COMPONENTS:

A fuel cell consists of a liquid or a solid electrolyte sandwiched between the two porous electrodes namely anode (−ve) and cathode (+ve). *Porous electrodes are used in fuel cells to provide a large surface area for smooth access of the reactants and prompt removal of products.* A catalyst such as Pt, Pd, Mg or Ni is often used to initiate and speed up the reactions at the electrodes.

In a fuel cell, a fuel is sent always through the anode and the oxygen supplied always through the cathode. The electrolyte carries the charged particles from anode to cathode and vice versa.

A fuel cell will also have a "fuel reformer" which can use hydrogen fuel from any hydrocarbon fuel (natural gas, methanol, or even gasoline).

A single fuel cell can generate a tiny amount of direct current but a large number of such fuel cells in the form "stack" can provide the power output from few watts to mega watts.

THEORETICAL BASIS:

The maximum amount of electrical energy generated in a fuel cell corresponds to Gibbs free energy, ΔG.

$$W_{eletrical} = -\Delta G$$

The theoretical potential of fuel cell, E, is given by:

$$E \equiv \frac{-\Delta G}{nF}$$

where n is the number of electrons involved in the cell reaction (n = 2) and F is the Faraday's constant (96,485 Coulombs).

Since ΔG, n, F are known, the theoretical hydrogen/oxygen fuel cell potential can also be calculated:

$$E \equiv \frac{-\Delta G}{nF} = \frac{2{,}73{,}340\ \text{J.mol}^{-1}}{2\times 96485\ \text{Amp.sec.mol}^{-1}} = 1.23\,Volts$$

HYDROGEN-OXYGEN FUEL CELL

CONSTRUCTION AND DESCRIPTION:

The hydrogen–oxygen fuel cell (H_2-O_2 fuel cell) uses a pure hydrogen gas as fuel. The cell consists of two porous carbon electrodes impregnated with a finely divided platinum or nickel as catalyst with an electrolyte of 25−40% KOH.

The cell develops an emf of ~1.23V. The efficiency of H_2–O_2 cell is 70% and the operating temperature is 60-70ºC. The cell power output range is 300 watts to 5 kilowatts.

The cell may be represented as: C, Pt or Ni / KOH / C, Pt or Ni

WORKING:

In H_2-O_2 fuel cell, the pure hydrogen gas is supplied through anode and O_2 gas is supplied through the cathode. Presence of Pt (or) Ni catalyst initiates the oxidation of H_2 gas and makes to split up into H^+ ions and electrons. These electrons are shuttled to the cathode through an external source to produce electric current. The H^+ ions migrate towards cathode through the electrolyte and get reduced into H_2O in presence of O_2.

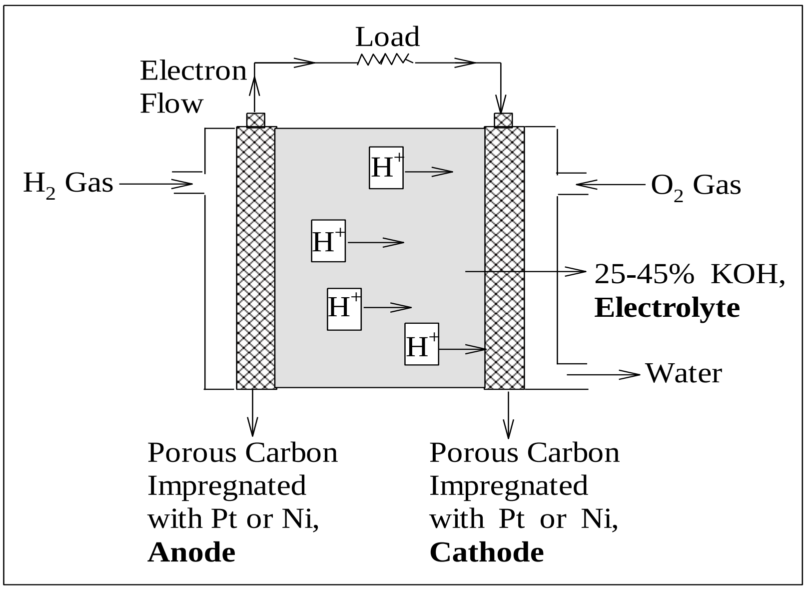


Fig.2.5: Hydrogen-oxygen fuel cell

At anode,

$$\boxed{\begin{array}{l} H_2 \longrightarrow 2H^+ + 2e \\ 2\,H^+ + 2OH^- \longrightarrow 2\,H_2O \\ \hline H_2 + 2OH^- \longrightarrow 2\,H_2O + 2e \quad \ldots(1) \\ \hline \end{array}}$$

At cathode,

$$\boxed{1/2\,O_2 + H_2O + 2e \longrightarrow 2OH^- \quad \ldots(2)}$$

The net cell reaction (1) + (2) gives,

$$\boxed{\mathbf{H_2 + 1/2\,O_2 \longrightarrow H_2O}}$$

ADVANTAGES:

H_2–O_2 fuel cell

- ✓ is highly reliable
- ✓ does not cause noise or thermal pollution
- ✓ does not form any effluents (iv) produces water of potable quality
- ✓ has efficiency 70%

APPLICATIONS:

H_2–O_2 fuel cell is used in

- ✓ Apollo spacecraft to produce electricity and H_2O
- ✓ Military and other commercial vehicles of all types

SOLID OXIDE FUEL CELL (SOFC)

DESCRIPTION AND CONSTRUCTION:

Solid oxide fuel cell (SOFC) uses natural gas or coal gas or reformed gas ($CO+H_2$) as fuel. SOFC consists of three major components (Fig.2.4).

COMPONENTS OF SOLID OXIDE FUEL CELL:

Anode	The most commonly used anode material is a ceramic–metallic composite, referred to as “cermet”.
Cathode	The most commonly used cathode material is Lanthanum Manganite ($LaMnO_3$). It is often doped with strontium and referred to as “LSM” ($La_{1-x}Sr_xMnO_3$).
Electrolyte	A thin film (20 to 40 microns thick) Yttria–Stabilized–Zirconia (YSZ) is used as electrolyte.

The cell develops an emf of ~1.0V. Efficiency is 60% and operating temperature is 800-1000ºC. Cell power output is up to 100kW.

The cell may be represented as Ni–YSZ/YSZ/LSM

WORKING:

The primary reaction in SOFC is reduction. LSM catalyses oxygen molecule to undergo reduction reaction and gives O^{2-} ions. The oxygen anion migrates through YSZ electrolyte towards the anode. Presence of nickel in anode catalyses hydrogen gas to react with O^{2-} ions and conducts electrons to an external circuit to produce electricity.

At cathode, $\frac{1}{2} O_2 + 2e \rightarrow O^{2-}$

At anode, $H_2 + O^{2-} \rightarrow H_2O + 2e$

The net cell reaction is, $\frac{1}{2} O_2 + H_2 \rightarrow H_2O$

When a fuel contains CO, it also reacts with O^{2-} to give CO_2 and electrons.

At anode, $CO + O^{2-} \rightarrow CO_2 + 2e$

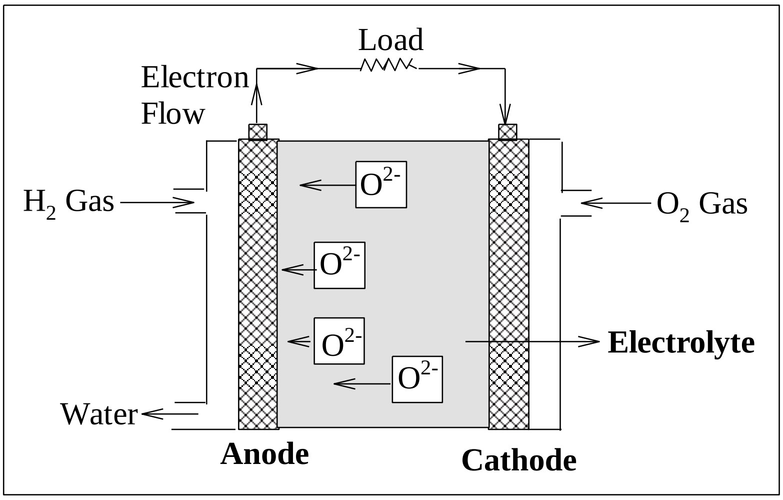


Fig. 2.6: Solid oxide fuel cell

ADVANTAGES:

- ✓ High tolerance to impurities avoids the use of fuel reformer.
- ✓ High operating temperature avoids the use of expensive catalyst like platinum.

APPLICATIONS:

- ✓ SOFC can be used as stationary generator to power homes, office buildings etc.
- ✓ SOFC can be used as power unit to run air conditioners, on-board electronics in automobiles.

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DEPARTMENT OF CHEMISTRY

UNIT – 3 – Phase Equilibria – SCY1213

INTRODUCTION: PHASE EQUILIBRIA

Phase rule was discovered by J.W. Gibbs in 1875 and is known as Gibbs Phase Rule.

For a heterogeneous system in equilibrium at a definite temperature and pressure, Gibbs phase rule relates that the number of degrees of freedom equals to the difference in the number of components and the number of coexisting phases plus two provided the equilibrium is not influenced by external effects such as gravity, electrical and magnetic forces, surface tension, etc.

❖ MATHEMATICAL STATEMENT OF PHASE RULE

The phase rule is mathematically stated as:

$$F = C - P + 2$$

Where,

- ⇒ P is the number of Phases present in equilibrium.
- ⇒ C is the number of Components for the system.
- ⇒ F is the number of Degrees of Freedom for the equilibrium.
- ⇒ 2 indicate the variables: Temperature and Pressure.

TERMS INVOLVED IN PHASE RULE

1. PHASE

Phase is a homogeneous, physically distinct, and mechanically separable part of a system, which is separated from other parts of system by definite boundaries.

❖ EXAMPLES

(i) **Freezing water system:** Freezing water system consists of three phases namely liquid water, solid ice and water vapour. Each phase is physically distinct and homogeneous.

(ii) **Liquids:** If two liquids are miscible (alcohol and water), they are considered as one liquid phase only. If two liquids are immiscible (Oil and water), they are considered as two separate phases.

(iii) **Gases:** A pure gas or a mixture of any number of gases is considered as a single phase. This is because gases are completely miscible in all proportions.

- ⇒ Pure oxygen gas – Single phase.
- ⇒ Mixture of CO and N_2 – Single phase
- ⇒ Mixture of CO (g) and H_2O (g) – Single phase

(iv) Solids: Each solid is considered as a separate phase. For example, a heterogeneous mixture of $CaCO_3$ and CaO consists of two solid phases. Each allotrope of a substance is considered as a single phase. For example, carbon exhibits allotropy graphite and diamond. They are considered as two separate phases.

(v) Solution: A solution (solute and solvent) is considered as a single phase only (Glucose in water).

2. COMPONENTS

The number of components of a system is the minimum number of chemical constituents required to express the composition of all the phases present in the system.

While expressing the chemical composition of all the phase present in the system,

⇒ *all the selected or chosen constituents must be included and*
⇒ *for this purpose positive, negative or zero quantities of constituents may be used*

❖ EXAMPLES

(i) The freezing water system: This system consists of three phases namely ice, water and water vapour. All the three phases are different physical form of same chemical substance (water). Hence this is considered as one-component system.

(ii) A system of saturated solution of NaCl: This system consists of three phases namely solid $NaCl$, $NaCl$ solution and water vapour. The chemical composition of all the three phases can be expressed in terms of $NaCl$ and H_2O. Hence it is a two-component system.

(iii) Thermal decomposition of $CaCO_3$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

This system consists of three phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2. Though the system has three different constituents, it is considered as a two-component system.

This is because the chemical composition of all the three phases can be expressed in terms of any two of the three chemical constituents present.

$CaCO_3$ and CaO are chosen as Two Components		**$CaCO_3$ and CO_2 are chosen as Two Components**		**CaO and CO_2 are chosen as Two Components**	
Phase	**Chemical Composition**	**Phase**	**Chemical Composition**	**Phase**	**Chemical Composition**
$CaCO_3$	$CaCO_3 + 0CaO$	$CaCO_3$	$CaCO_3 + 0CO_2$	$CaCO_3$	$CaO + CO_2$
CaO	$0CaCO_3 + CaO$	CaO	$CaCO_3 - CO_2$	CaO	$CaO + 0CO_2$
CO_2	$CaCO_3 - CaO$	CO_2	$0CaCO_3 + CO_2$	CO_2	$0CaO + CO$

(iv) Dissociation of NH_4Cl in vacuum

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

This system consists of two phases namely, solid NH_4Cl and gaseous mixture containing NH_3 and HCl. The composition of both the phases can be expressed in terms of only one constituent namely, NH_4Cl. Hence it is a one-component system.

Phase	Chemical Composition
Solid NH_4Cl	xNH_4Cl
Gaseous phase xNH_4Cl	$xNH_3 + xHCl$

If the concentration of NH_3 is not equal to that of HCl i.e., $NH_{3(g)} \neq xHCl_{(g)}$, then the system becomes two component system. Suppose y mole of HCl is added to xNH_4Cl, then the chemical composition of solid and gaseous phases is expressed in terms of NH_4Cl and HCl as follows.

Phase	Chemical Composition
Solid NH_4Cl	$x\ NH_4Cl + 0\ HCl$
Gaseous phase $x\ NH_4Cl + y\ HCl$	$x\ NH_3 + x\ HCl + y\ HCl$

3. DEGREE OF FREEDOM (or) VARIANCE OF SYSTEM

The number of degrees of freedom of a system is the minimum number of independent variable factors such as temperature, pressure and concentration (composition) required to describe the system completely.

A system having one, two, three and zero degrees of freedom are usually called *univariant, bivariant, trivariant and invariant system* respectively.

❖ EXAMPLES

(i) Consider a one component system consisting of two phases

$$\text{Water} \rightleftharpoons \text{Water vapour}$$

$$P = 2\ ;\ C = 1$$
$$F = C - P + 2$$
$$F = 1 - 2 + 2$$
$$F = 1$$

To define such a system, only one variable factor (either temperature or pressure) is needed. Hence the system is ***univariant.***

(ii) Consider a one component system consisting of one phase: Water vapour.

$$\begin{aligned} P &= 1 ; C = 1 \\ F &= C - P + 2 \\ F &= 1 - 1 + 2 \\ F &= 2 \end{aligned}$$

To define such a system, two variable factors (temperature and pressure) are needed. Hence the system is ***bivariant.***

(iii)Consider a one component system:

$$\textit{Ice} \rightleftharpoons \textit{Water} \rightleftharpoons \textit{Water vapour}$$

$$\begin{aligned} P &= 3 ; C = 2 \\ F &= C - P + 2 \\ F &= 1 - 3 + 2 \\ F &= 0 \end{aligned}$$

To describe this equilibrium system, no need to specify any variable factors, because all the three phases can occur in equilibrium only at a particular temperature and pressure. Hence this system does not have any degree of freedom ***(invariant or zero variant).***

USES OF PHASE RULE

⇒ The phase rule takes no account of the nature or amount of substances.

⇒ Phase rule is applicable to macroscopic systems. Therefore, it is not necessary to have information about molecular structure.

⇒ It gives information about the behaviour of systems when they are subjected to changes in variables such as temperature, pressure and concentration.

LIMITATIONS OF PHASE RULE

⇒ The phase rule takes into account only the variable factors like temperature, pressure and the composition. The influences of factors such as electric, magnetic, gravitational, surface forces etc. are ignored.

⇒ The phase rule is applicable only to heterogeneous systems in equilibrium.

⇒ In phase rule, time is not a variable factor because this rule applies to a system in equilibrium. The equilibrium state is independent of time factor.

PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against another. If temperature is plotted against pressure, it is known as temperature-pressure diagram. If temperature is plotted against composition, it is known as temperature–composition diagram.

❖ SIGNIFICANCE

They help in studying and controlling the various processes such as phase separation, solidification of metals, and change of structure during heat treatment like annealing, quenching, tempering etc.

ONE COMPONENT SYSTEM: WATER SYSTEM

The water system is an example of one component system. It consists of three phases namely solid ice, liquid water and water vapour. The phase diagram of water system is given in Fig. 3.1.

Table 3.1: Important data for constructing phase diagram of water system

S. No.	Parameters	Temperature	Pressure
1	Boiling point	100°C	1 atm
2	Triple point	0.0075°C	4.58 mm
3	Critical point	374°C	218 atm

❖ SALIENT FEATURES OF PHASE DIAGRAM OF WATER SYSTEM

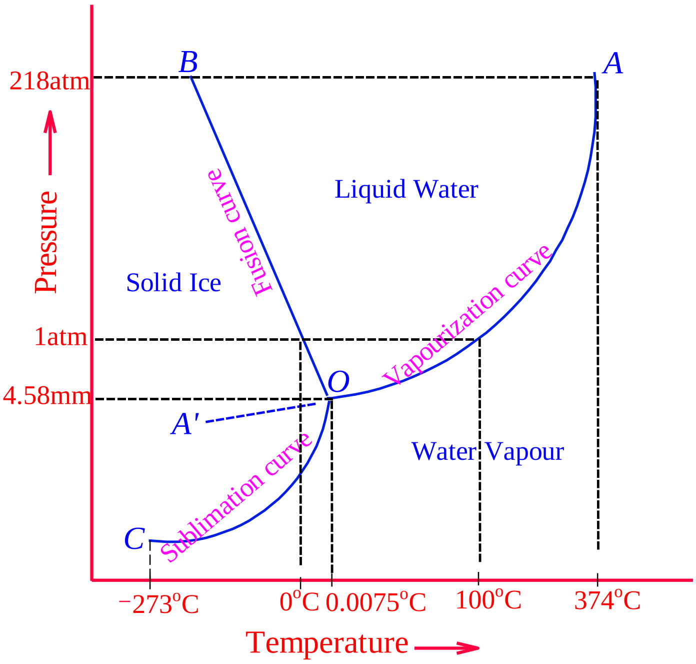

Fig. 3.1: The Phase Diagram of Water System

1. CURVES

The phase diagram consists of three curves *OA*, *OB* and *OC*. Each curve separates two phases and hence the system is “univariant” along the curve.

$$F = C - P + 2$$
$$F = 1 - 2 + 2$$
$$F = 1$$

Curve *OA*: Curve *OA* is the *vaporization curve* because it separates the liquid region from vapour region. Along the curve *OA*, water and water vapour are in equilibrium (water ↔ water vapour). The curve *OA* ends at the point *A*, which corresponds to the critical temperature (374°C) and critical pressure (218.5atm) of water. Beyond the point *A,* the liquid and vapour phases merge into each other to form a single homogeneous phase.

Curve *OB*: Curve *OB* is the *fusion or melting curve* because it separates ice and water phases (ice ↔ water). The curve *OB* is slightly inclined towards pressure axis. This shows that melting point of ice decreases with the application of pressure.

Curve *OC:* Curve *OC* is the *sublimation curve* because it separates ice and water vapour phases (ice ↔ water vapour). At the lower limit, the curve *OC* terminates at absolute zero (−273°C) where no vapour can be present and only ice exists.

2. POINT 'O' (TRIPLE POINT)

The three curves *OA, OB,* and *OC* meet at a point *O,* at which solid ice, liquid water and water vapour are simultaneously in equilibrium. This is called triple point.

$$\textit{Solid ice} \rightleftharpoons \textit{Liquid water} \rightleftharpoons \textit{Water vapour}$$

At the triple point, the system is 'invariant'. The triple point of water system corresponds to a temperature of 0.0075°C and a pressure of 4.58 mm mercury.

$$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 3 + 2 \\ F &= 0 \end{aligned}$$

3. AREAS

The curve is divided into three areas *AOB, BOC* and *COA.* Each area represents a single phase and hence the system is 'bivariant'.

$$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 1 + 2 \\ F &= 2 \end{aligned}$$

4. CURVE *OA′* (META STABLE EQUILIBRIUM)

The curve *OA'* represents the vapour pressure curve of super cooled water. Super cooling means, cooling of water below its freezing point without the separation of solid. Super cooled water is highly unstable and it can be converted into solid by a slight disturbance. Hence the system along the curve *OA'* is said to be in "meta stable equilibrium".

TWO COMPONENT ALLOY SYSTEMS: CLASSIFICATION

Based on mutual solubility and reactive ability, the two-component system is classified into the following three types:

1. SIMPLE EUTECTIC FORMATION

The two solid substances can form a simple eutectic under the following conditions:

⇒ The two solid metals must be completely miscible in the liquid state but completely immiscible in the solid state.

⇒ They should not chemically react with each other.

Therefore, *eutectic has the same composition both in liquid and solid states.* Also the eutectic has a sharp melting and freezing point as the pure metals. Hence eutectic composition is a unique mixture of two solids, which has the lowest melting point.

❖ **Examples:** Lead – Silver system; Bismuth – Cadmium system.

❖ **Uses of eutectic system**

⇒ De-silverisation of lead (Enrichment of silver from argentiferous lead ore) is based on the formation of simple eutectic.

⇒ The principle of a simple eutectic system is used for preparing solders (Eg: Pb-Sn solder), which are used for joining two metal pieces together.

2. FORMATION OF COMPOUND WITH CONGRUENT MELTING POINT

When two solid substances combine in a definite proportion, one or more stable compounds are formed.

These compounds melt at constant temperature to give liquid melt of the same composition.

The temperature at which a compound melts to give liquid phase of same composition is known as congruent melting point.

❖ **Examples:** Zinc – Magnesium system; Tin – Magnesium system.

3. FORMATION OF COMPOUND WITH INCONGRUENT MELTING POINT

There are solid substances which combine together to form one or more unstable compounds.

Further, they decompose into a new solid phase and a liquid melt of different composition.

The temperature at which the unstable compound decomposes into a new solid phase and a liquid melt (having different composition from solid phase) is known as incongruent melting point.

❖ **Examples:** Sodium – Potassium system; Gold – Antimony system.

4. SOLID SOLUTION FORMATION

When two different metals dissolve each other in liquid and or in solid state, the resulting phase is called solid solution.

Solid solution is formed when the solvent and solute atoms have similar sizes and electron structure.

- **Examples**: Copper – Nickel system.

REDUCED PHASE RULE

A solid−liquid alloy system has practically no gaseous phase. Hence the effect of pressure is negligible on this type of equilibrium.

Therefore, to construct the usual phase diagram with two axes, the vapour phase is neglected. Such a solid-liquid system is called "condensed system".

In condensed system measurements are made at constant pressure. This reduces the degree of freedom of the system by one. Therefore, the phase rule equation for two-component alloy system is written as: $F = C - P + 1$. This equation is known as "reduced phase rule equation".

THERMAL ANALYSIS

Thermal analysis involves the study of cooling curve of various compositions of two solids during solidification.

COOLING CURVE OF A PURE METAL (Fig. 3.2a)

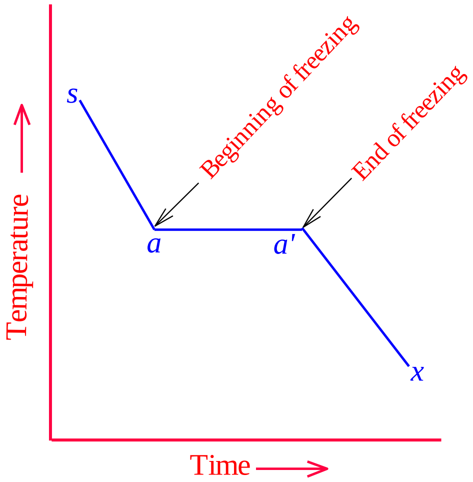

Fig. 3.2a: Cooling Curve of Pure Metal

S : Represents the pure metal is in molten state.

Sa : Along *sa*, the temperature of the melt decreases gradually with time.

A : The point ‘*a’* indicates the temperature at which the molten metal starts freezing at its surface.

aa’ : Along *aa’,* the liquid melt and solid metal are in equilibrium. Further the temperature remains constant until the liquid melt is completely solidified because the liquid melt and solid metal have same chemical composition.

a’ : Indicates the end of freezing.

a’x : Along *a’x*, the temperature of solid metal again decreases with time.

❖ COOLING CURVE OF A MIXTURE OF SOLID *A* AND SOLID *B* (Fig. 3.2b)

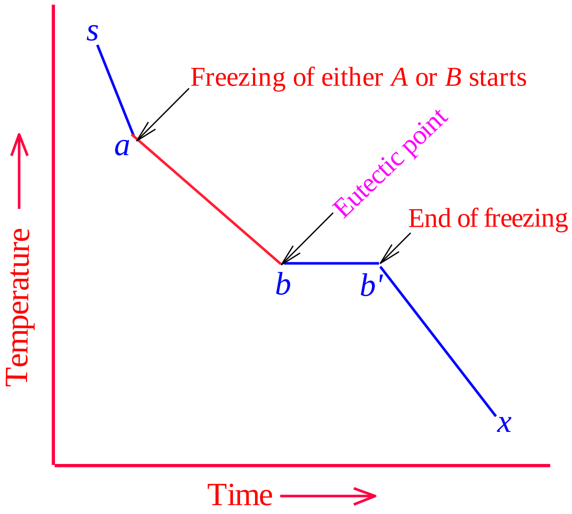

Fig. 3.2b: Cooling Curve of a Mixture of Two Solids A and B

S : Represents a mixture of solid *A* and solid *B* is in fused state.

Sa : Along s*a*, the temperature of the mixture containing *A* and *B* decreases with time.

A : The point ‘*a’* indicates the temperature, at which freezing of base metal (either *A* or *B* depends upon their freezing point) starts from the liquid mixture.

ab : Along *ab*, the liquid melt and solid metal *A* (or solid metal *B*) are in equilibrium. Further, the line *ab* indicates the composition of molten mixture progressively changes due to continuous separation of solid *A* (or solid *B*) with time. Because of two different chemical composition of the liquid mixture (containing *A* and *B*) and solid metal (either *A* or *B*), the temperature of the liquid mixture decreases at a different rate.

B : The point at which the liquid mixture (containing both A and B) starts freezing into solid *A* and solid *B* (eutectic mixture).

bb’ : Along *bb’,* the liquid mixture and solid *A* and solid *B* are in equilibrium.

b’ : Indicates the end of freezing of eutectic mixture.

b’x : Along *b’x*, the temperature of solids again decreases with time.

❖ COOLING CURVE OF EUTECTIC MIXTURE

Since eutectic behaves like a pure solid metal, it also has same type of cooling curve as pure solid metal.

❖ CONSTRUCTION OF SIMPLE EUTECTIC DIAGRAM (Fig. 3.4c)

So, it is possible to construct a complete phase diagram for the two-component system on the basis of large number of cooling curves of various compositions (Fig.3.3c).

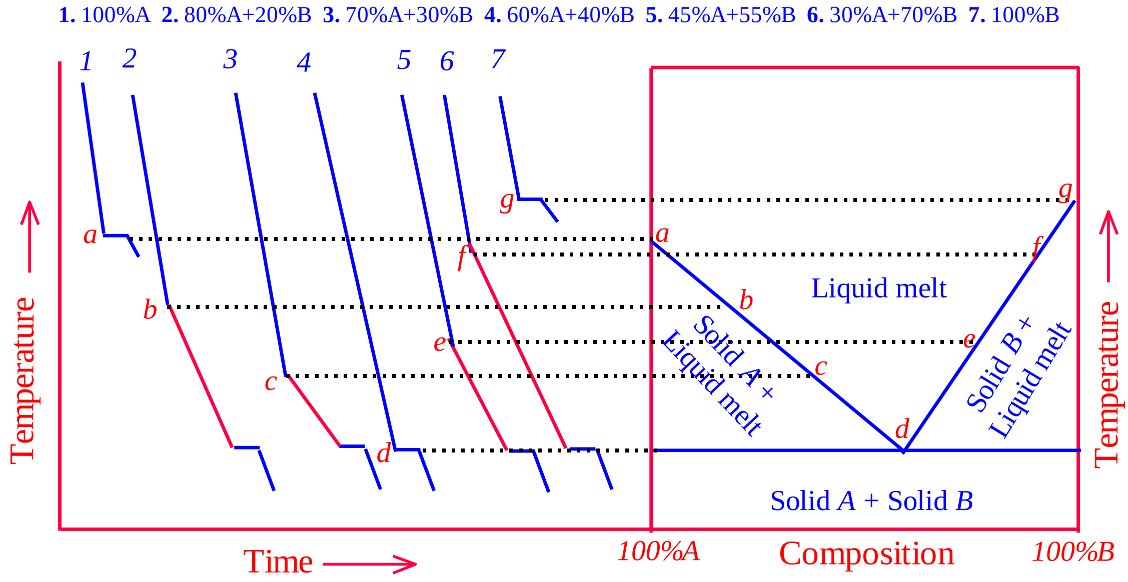

Fig. 3.3c: Cooling Curves of Various Compositions of Two Solids (1) 100% A (2) 80%A+20% B (3) 70%A+30%B (4)60%A+ 40% B (5) 45%A+55%B (6) 30%A+70% (7) 100%B

In eutectic phase diagram:

⇒ Each curve corresponds to a definite composition of *A* and *B*.

⇒ The break or discontinuity in the graph (*a, b, c, d, e, f, g, h*) denotes phase transformation (freezing point of either *A or B*).

⇒ The cooling curve of eutectic composition (curve *4*) is similar to those of pure substances (curve *1* and *7*).

⇒ The eutectic phase diagram is obtained by plotting various compositions of two substances against the discontinuity (freezing point), which is nothing but characteristic temperature.

❖ SALIENT FEATURES

Curves: The eutectic phase diagram consists of two curves *abcd,* and *gfed.* Along the curve, two phases (Solid Liquid melt) are in $\rightleftharpoons$ equilibrium and hence the system is 'univariant' (F = 2–2+1 = 1).

Point *O* (Eutectic Point): The curve *abcd* and *gfed* intersect at *d* which is called eutectic point. At the eutectic point three phases are in equilibrium. Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0).

$$\text{Liquid melt} \rightleftharpoons \text{Solid } A + \text{Solid } B$$

Areas: The eutectic phase diagram consists of four distinct areas (i) Above *abcdefg* has a single phase (molten *A* and *B*) (ii) Below *abcd* (solid *A* + liquid melt) (iii) Below *gfed* (solid *B*+ liquid melt) and (iv) Below the point *d* (solid *A* + solid *B*).

SIMPLE EUTECTIC SYSTEM: LEAD-SILVER SYSTEM

Important data for constructing phase diagram of Pb-Ag system

S. No.	Parameters	Temperature/Composition
1.	Melting point of Lead *(Pb)*	327°C
2.	Melting point of Silver *(Ag)*	961°C
3.	Eutectic Temperature	303°C
4.	Eutectic Composition	97.4% *Pb* + 2.6% *Ag*

❖ SALIENT FEATURES OF PHASE DIAGRAM OF Pb-Ag SYSTEM

1. CURVES

Curve *AO*: Pure *Ag* melts at 961°C. Addition of *Pb* lowers the freezing point of *Ag* along the curve *AO*. Therefore *AO* is the freezing point curve of silver. Along *AO*, solid *Ag* and liquid melt are in equilibrium. Hence the system along the curve is 'univariant' (F = C–P+1 = 2–2+1 = 1).

Curve *BO*: Pure *Pb* melts at 327^{0}C. Addition of *Ag* lowers the freezing point of *Pb* along the curve *BO*. Therefore *BO* is the freezing point curve of *Pb*. Along *BO*, solid *Pb* and liquid melt co-exist and hence the system is 'univariant' (F = C–P+1 = 2 – 2 + 1 = 1).

2. POINT *O* (EUTECTIC POINT)

The curve *AO* and *BO* intersect at *O* which is called eutectic point. At this point three phases are in equilibrium.

$$\text{Liquid melt} \rightleftharpoons \text{Solid } Ag + \text{Solid } Pb$$

Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0). Below the point *O*, both silver and lead exist in the solid state.

Therefore, eutectic point is the lowest temperature at which a mixture of two solids melts (eutectic = easy melting). The corresponding temperature and composition are called “eutectic temperature” and “eutectic composition” respectively.

The eutectic point of *Pb-Ag* system corresponds to a temperature 303°C and composition 97.4%*Pb*+2.6%*Ag*.

3. AREAS

The area above *AOC* has a single phase (molten *Pb* and *Ag*). Applying the reduced phase rule F = C–P+1 = 2–1+1 = 2, the system is bivariant.

The area below *AO* (solid *Ag* + liquid melt), below *BO* (solid *Pb* + liquid melt) and below *O* (solid *Ag* + solid *Pb*) have two phases and hence the system is univariant (F = C–P+1 = 2–2+1 = 1).

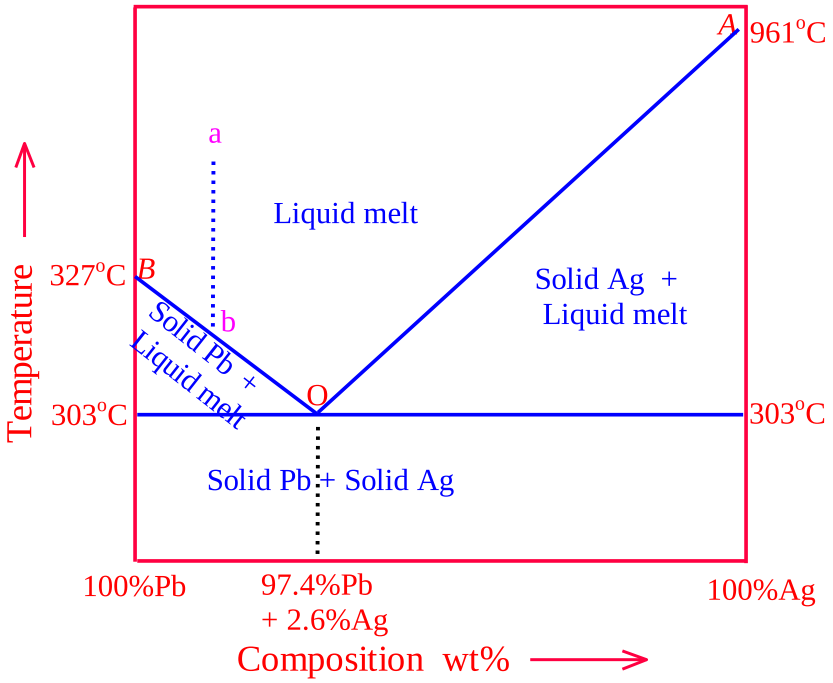

Fig. 3.4: The Lead-Silver System

❖ APPLICATION OF Pb-Ag SYSTEM

PATTINSON’S PROCESS

The process of recovery of silver from argentiferous lead is called as de-silverisation. Argentiferous lead consisting of a very small amount (0.1%) of silver. Desilverisation of lead is based on the formation of eutectic mixture. Argentiferous lead is heated to a temperature well above its melting point, so that the system consisting of only one liquid phase say, by the point *a*. When the liquid melt is allowed to cool, the temperature of the melt falls along the line *ab*. As soon as point *b* is reached, lead is separated out as solid. On repeating the process of melting and cooling, more and more lead is separated along *BO*. Finally, at *O*, an eutectic mixture consisting of 2.6%Ag and 97.4%Pb is obtained. The eutectic alloy is then chemically treated to recover the silver.

CONGRUENT SYSTEM: ZINC-MAGNESIUM SYSTEM

⇒ *When two components combine chemically to form a compound which melts to give a liquid melt of same chemical composition is known as congruent system and its corresponding temperature is known as congruent melting point temperature.*

⇒ Examples: Zn-Mg system

⇒ The zinc–magnesium system is an example of two component system which forms a compound with congruent melting point.

⇒ The phase diagram appears to be made up of two simple eutectic diagrams.

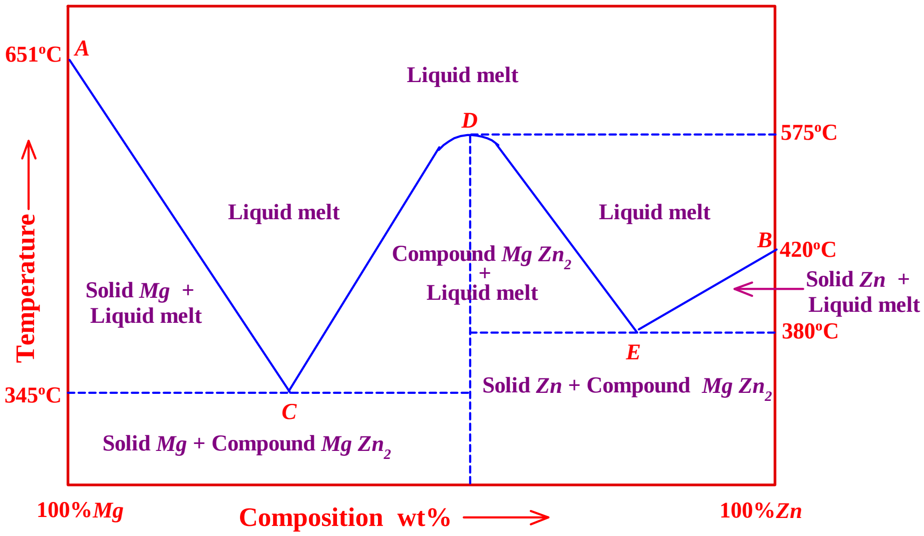

Fig. 3.5: The Zinc-Magnesium System

Salient features of phase diagram of zinc-magnesium system:

(i) Curves

⇒ The points *A* and *B* represent the melting point of pure magnesium (651°C) and pure zinc (420°C) respectively.

⇒ ***Curve AC:*** The curve *AC* represents the variation of melting point of magnesium on the addition of zinc and and hence the curve *AC* is the freezing point curves of magnesium.

⇒ ***Curve BE:*** The curve *BE* represents the variation of melting point of zinc on the addition of magnesium, and hence the curve *BE* is the freezing point curve of zinc.

⇒ ***Curve CDE:*** Addition of zinc to magnesium or magnesium to zinc leads to the formation of a compound $MgZn_2$ at the points *C* and *E*. Hence, the curve *CDE* is the melting point curve of the compound *D* is its melting point.

⇒ Since along the curves two phases are in equilibrium, and hence the system is univariant [$F = C - P + 1 = 2 - 2 + 1 = 1$].

(ii) Maximum Point *D* (Congruent Melting Point)

⇒ The maximum point *D* on the curve *CDE* is the melting point of the pure compound $MgZn_2$.

⇒ Since the compound has the same composition both in liquid and solid states at *D*, it is the congruent melting point of the compound.

Compound	Congruent Melting Point
$MgZn_2$	575°C

⇒ At the congruent melting point, the two component system becomes one component system because both the liquid and solid phases can be represented by the component $MgZn_2$. Hence at the point *D*, the system is non-variant [F = C – P +1 = 1 – 2+ 1 = 0].

(iii) Eutectic Points *C* and *E*

⇒ There are two eutectic points in the phase diagram.

⇒ At the eutectic point *C*, solid *Mg* and solid $MgZn_2$ and liquid melt exist in equilibrium.

⇒ At the eutectic point *E*, solid *Zn* and solid $MgZn_2$ and liquid melt exist in equilibrium.

⇒ The degrees of freedom at eutectic points is non-variant [$F = C – P$ +1 = 2 – 3+ 1 = 0].

(iv) Areas

⇒ The area above the curves *AC*, *CDE*, and *BE* represents the solution of magnesium and zinc (the liquid melt). The single phase system at any point in this area is bivariant [$F = C – P$ +1 = 2 – 1+ 1 = 2].

⇒ The areas below *AC*, below the points *C* and *E*, below *CDE* and below *BE* have two phases each and hence the system is univariant [$F = C – P$ +1 = 2 – 2+ 1 = 1].

INCONGRUENT SYSTEM: SODIUM POTASSIUM SYSTEM.

⇒ *When two components combine chemically to form a compound which melts incongruently (decompose) to give a new solid of different composition from that of solid compound is known as incongruent system and its corresponding temperature is known as incongruent melting point or peritectic temperature.*

⇒ Examples: Na-K system

Salient features of phase diagram of sodium-potassium system:

(i) Curves: There are three main curves in the system a fourth one is hypothetical curve.

Curve *AC*: This curve is known as ***freezing point curve of potassium*** and shows the effect of addition of sodium on the melting point (depression of freezing point) of potassium (63.8˚C).

Along this curve, two phases (solid *K* and a liquid melt of *K* and *Na*) are in equilibrium, and hence the system is monovariant ($F = C - P + 1 = 2 - 2 + 1 = 1$).

Curve *BD*: This curve is known as ***freezing point curve of sodium*** and shows the effect of addition of potassium on the melting point (depression of freezing point) of sodium (97.8˚C). Along this curve, two phases (solid *Na* and a liquid melt of *Na* and *K*) are in equilibrium, and hence the system is monovariant ($F = C - P + 1 = 2 - 2 + 1 = 1$).

Curve *DC*: This curve is known as ***freezing point curve of incongruent compound Na_2K*** and shows the effect of addition of potassium on the melting point (depression of freezing point) of Na_2K. Along this curve, two phases (solid Na_2K and a liquid melt of *Na* and *K*) are in equilibrium, and hence the system is monovariant ($F = C - P + 1 = 2 - 2 + 1 = 1$).

Curve *DE*: It is the ***hypothetical congruent point curve of the compound Na_2K.*** If the compound Na_2K does not melt incongruently (does not decompose) at the point *D*, then it will melt at *E* congruently without changing in composition. Along this curve, two phases (solid Na_2K and solid *Na*) are in equilibrium, and hence the system is monovariant ($F = C - P + 1 = 2 - 2 + 1 = 1$).

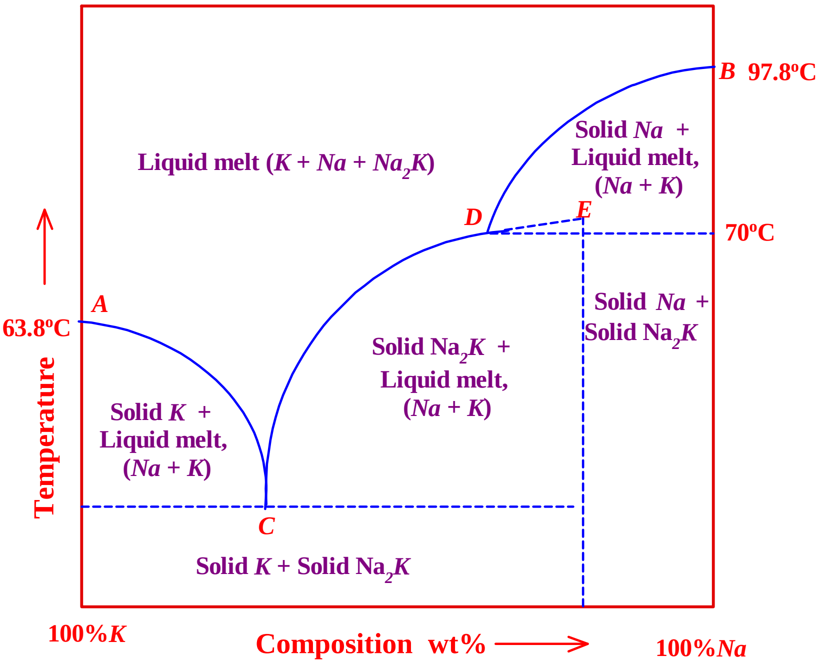

Fig. 3.6: The Sodium-Potassium System

(ii) Points

Point *C*: It is the ***eutectic point.*** At this point two phases: solid *K* and Na_2K are in equilibrium with the liquid melt containing *K* and *Na*). Hence, the degree of freedom at this point is zero and hence the system is invariant ($F = C - P + 1 = 2 - 3 + 1 = 0$).

Point *D*: It is the ***incongruent point.*** At this point the compound Na_2K melts to give a new solid phase. so, there are three phases (solid Na_2K, new solid Na and the liquid melt containing K and N) are in equilibrium. Hence the system at this point is invariant ($F = C - P + 1 = 2 - 3 + 1 = 0$).

Point *E*: It is the ***hypothetical congruent point of the compound Na_2K and behaves as one component system.*** At this point, the compound Na_2K is in equilibrium with its melt. Hence the system at this point is invariant ($F = C - P + 1 = 1 - 2 + 1 = 0$).

(iii) Areas:

The system consisting of five areas namely (i) below the curve *AC* (Solid *K* + Liquid melt) (ii) below the curve *BD* (Solid *Na* + Liquid melt) (iii) Below the point *C* (Solid *K* + Solid Na_2K) (iv) Below the point *D* (Solid Na_2K and Liquid melt), below the point *E* (solid Na_2K and Solid *Na*) and each area represents two phases, hence system is monovariant ($F = C - P + 1 = 2 - 2 + 1 = 1$).

But the above the curve *ACDB*, the system consisting of only one phase (Liquid melt) and hence the system is bivariant ($F = C - P + 1 = 2 - 1 + 1 = 2$).

SOLVED PROBLEMS

1. Is it possible to have a quadruple point in phase diagram of a one-component system?

"No". Quadruple point means 4 phases are simultaneously in equilibrium.

$$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 4 + 2 \\ F &= -1 \end{aligned}$$

F = – 1 is meaningless. Hence the answer is "No".

---

2. How many number of phases, components and degrees of freedom are available in the following systems:

(i) $BaCO_3\,(s) \rightleftharpoons BaO\,(s) + CO_2\,(g)$

(ii) $MgCO_3\,(s) \rightleftharpoons MgO\,(s) + CO_2\,(g)$

(iii) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

All the above systems have 2 solid phases and one gaseous phase.

Number of phases, P = 3
Number of components, C = 2
Number of degrees of freedom, F = C – P + 2
F = 2 – 3 + 2
F = 1(univariant)

---

3. How many phases, components, and degrees of freedom are present in:

(i) Water at 0.0075°C and 4.58mm Hg
(ii) Water) $\rightleftharpoons$ Water vapour at 30°C
(iii) Pb–Ag alloy system at constant pressure [composition 2.6%Ag and 303°C]

(i) This indicates triple point of water system,. At the triple point, solid ice, liquid water and water vapour are simultaneously in equilibrium.

Number of phases, P = 3
Number of components, C = 1
Number of degrees of freedom, F = C – P + 2
F = 1 – 3 + 2
F = 0 (invariant)

(ii) Water ↔ Water vapour at 30°C.

Number of phases, P = 2
Number of components, C = 1
Number of degrees of freedom, F = C – P + 2
F = 1 – 2 + 2
F = 1(univariant)

(iii)This indicates eutectic point of Pb-Ag system. At the eutectic point, solid Ag, solid Pb and liquid melt are in equilibrium.

Number of phases, P = 3
Number of components, C = 2
Number of degrees of freedom, F = C – P + 1
F = 2 – 3 + 1
F = 0 (invariant)

---

4. In the phase diagram of water, point out the phase in equilibrium with (i) One degree of freedom and (ii) No degrees of freedom.

(i)
Number of phases, P = ?
Number of components, C = 1
Number of degrees of freedom, F = 1
F = C – P + 2
P = C + 2 – F
P = 1 + 2 – 1
P = 2 (bivariant)

Any two phases can be in equilibrium.

Water ⇄ *Water vapour*
Ice ⇄ *Water*
Ice ⇄ *Water vapour*

(ii)
Number of phases, P = ?
Number of components, C = 1
Number of degrees of freedom, F = 0
F = C – P + 2
P = C + 2 – F
P = 1 + 2 – 0

P = 3 (trivariant)

All the three phases are simultaneously in equilibrium.

Solid ice ⇌ *Liquid water* ⇌ *Water vapour*

---

5. Fe(s) + H_2O (g) ↔ FeO(s) + H_2 (g). Calculate P, C and F for the above system.

Number of phases, P = 3 (2 solids; 1 gaseous)
Number of components, C = 3 (Fe, O_2 and H_2)
Number of degrees of freedom, F = C – P + 2
F = 3 – 3 + 2
F = 2 (bivariant)

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UNIT – 4 – Synthesis of Nanomaterials – SCY1213

INTRODUCTION: NANOMATERIALS

Nanoscience is a blend of chemistry, physics, biology and material science.

Nanochemistry is a branch of nanoscience which deals with synthesis and characterization of materials at nanoscale. They find applications from nanoelectronics to nanomedicine.

Nanometer is so small that if you imagine ten hydrogen atoms placed in a line touching each other, it will measure one nanometer. A bacterial cell measures a few hundred nanometers (200 nm) across and a human hair measure about 50,000nm across. The smallest things seeable with the unaided human eye are 10,000nm across.

With only reduction in size and no change in substance, the characteristics such as electrical conductivity, colour, melting point, strength, we usually consider as constant for a given material can all change.

Nanotechnology is the manipulation of individual molecules or groups of atoms to make useful materials and devices. Nanotechnology can create a computer laptop screen that has the thickness and weight of a piece of paper, micro devices to make toxic waste inert, nanodevices to perform surgery or to detect cancer cells inside the human blood stream etc.

DEFINITION AND CLASSIFICATION BASED ON DIMENSIONS

In scientific language, nano is “billionth” on some unit scale.

Nanometer: It is a billionth of a meter

$$1nm = \frac{1}{1,000,000,000}\, m = 10^{-9}\, m$$

Nanotechnology: Nanotechnology refers to the manipulation of self-assembly of individual atoms or molecules into structure to create materials and devices with new and vast different properties.

***Nanochemistry**:* Nanochemistry is the science of tools, technologies, and methodologies performed at nanoscale for chemical synthesis, analysis and biochemical diagnostics.

Nanomaterials: Materials which possess an average size of less than 100nm at least in one coordinate (dimension) are called nanomaterials ***or nanostructured materials.***

***Bottom-up nanofabrication**:* The building of nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

Examples: Chemical vapour deposition; Sol-gel process; Chemical reduction
***Top-down nanofabrication**:* The process of making nanostructures starting with larger structures and taking parts away is called top-down approach.

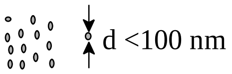
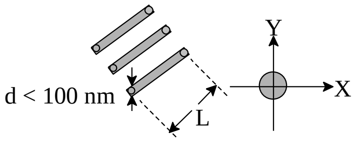
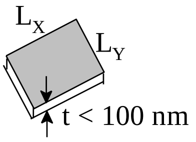
***Examples**:* Lithography; Ball milling; Epitaxy

Classification of nanomaterials on the basis dimensions:

- Nanomaterials can be classified as: zero dimensional (0-D), one dimensional (1-D), and two dimensional (2-D) objects.

- This classification is based on the number of dimensions, which are not confined to the nanoscale range (1–100 nm).

Table 5.1: Classification of nanomaterials on the basis of dimensions

S.No.	Reduction in size in different coordinates	Nanoobjects	Examples
1.	0-Dimensional nanomaterials: All dimensions *x*, *y*, *z* are at nanoscale.		Nanoparticles; Quantum dots.
2.	1-Dimensional nanomaterials: Two dimensions *x*, *y* are at nanoscale and other dimension, length (*L*) is not at nanoscale.		Nanotubes; Nanorods; Nanowires.
3.	2-Dimensional nanomaterials: One dimension, thickness, *t* is at nanoscale and other two dimensions, Lengths along L_X and L_Y are not at nanoscale.		Nanofilms; Nanocoatings.

SIZE DEPENDENT PROPERTIES

1. Chemical Properties

Size reduction in bulk materials leads surface to volume effects. It has been observed that the surface area to volume ratio increases with decrease of particle size diameter. Therefore, size reduction in Nanomaterials leads to more number of surface atoms with enhanced surface area. This effect leads more reactivity and catalytic activity of materials in nanoform in turn increases the reaction rate and efficiency of various chemical reactions.

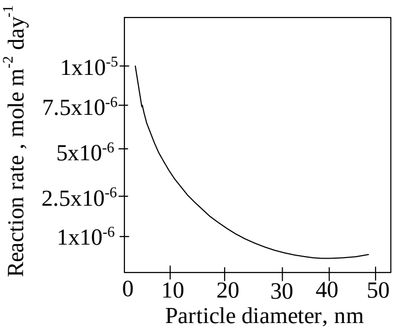


Fig. 4.1: Reaction Rate versus Particle Size Diameter

Examples: Au and Ag in bulk form are chemically inert. But they become good catalyst in nanoform.

2. Thermal Properties

The melting point of bulk material is directly related with the bond strength. In bulk materials all the atoms are compactly packed and eletrovalently bonded and hence they exhibit higher melting points.

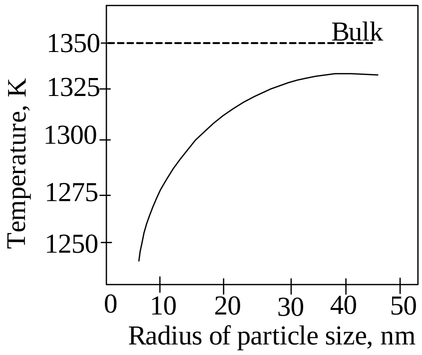


Fig. 4.2: Temperature versus Particle Size Diameter

In Nanomaterials, surface atoms are not bonded in direction normal to surface plane and hence surface atoms will have more freedom to move. Hence the melting point of Nanomaterials is size dependent and it decreases with decrease of particle size diameter.

Examples: Bi (in bulk form: 660K): Bi (6nm: 500K); Bi (4nm: 480K) and Bi (2nm: 400K).

3. Electronic Properties:

In bulk materials, conduction of electron is delocalized (i.e: the electrons can move freely in all directions). When the scale is reduced to nanoscale, quantum confinement dominates. Due to electron confinement, the energy bands are replaced by discrete energy states of electrons, which make the conducting materials to behave like semiconductors or insulators.

For 0-D nanomaterials, all the dimensions are at nanoscale and hence electrons are confined in 3-D space. Therefore, no delocalization occurs. For 1-D nanomaterials, electron confinement occurs in 2-D space and electron delocalization occurs along the axis of Nanowires / Nanotubes / Nanorods.

Examples: Si and Ge are well known semiconductors in single crystal bulk form. But in nanoform, due to electron confinement, they do not show semiconducting properties.

4. Optical Properties:

When a beam of visible light falls on certain substances, they absorb light radiations and get excited. In order to come back to their original state, they emit energy in the form of light radiations. This phenomenon is known as photoluminescence.

Because of quantum confinement, size reduction in Nanoparticles shifts the emission of light towards shorter wavelength (Blue shift).

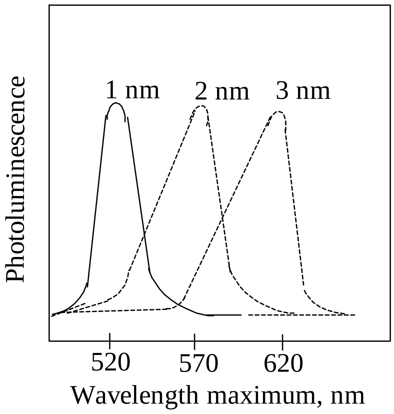


Fig. 4.3: Effect of Particle Size Diameter on Wavelength

Examples:

CdS (Bulk) + hγ → CdS* (Excited state)
CdS* (Excited) → CdS (Ground state) + Energy as red light
CdS* (6nm) (Excited) → CdS (6nm) (Ground state) + Energy as orange light
CdS* (4nm) (Excited) → CdS (4nm) (Ground state) + Energy as yellow light
CdS* (2nm) (Excited) → CdS (6nm) (Ground state) + Energy as blue/white light

Table 4.1: Differences between Molecules, Nanomaterials and Bulk Materials

S. No.	Property	Molecules	Nanomaterials	Bulk Materials
1.	Size	Exhibit few Angstrons (Å)	Exhibit 1 – 100 nm at least in one dimension	Exhibit more than Microns (μ)
2.	Number of constituents	Consist of more than one atom.	Made up of one to several thousand depends upon their size.	Consist of infinite number of atoms and/or molecules.
3.	Electronic structure	Confined.	Confined.	Continuous.
4.	Geometric structure	Well defined and predictable.	Well defined and predictable.	Depends upon crystal structure.
5.	Tools for characterizat-ion	SEM; TEM.	SEM; TEM.	SEM; X-ray diffraction etc. depends upon the properties of bulk.
6.	Examples	O_2; C_2H_2; KCl.	Fullerene; Carbon nanotubes.	Bulk copper; gold.

NANOPARTICLES: SYNTHESIS BY CHEMICAL REDUCTION METHOD

Particles or powders with grain size (diameter) less than 100 nm are called nanoparticles.

APPLICATIONS OF NANOPARTICLES

The most commercially used nanoparticles are (i) metal nanoparticles, (ii) metal oxide nanoparticles, (iii) mixed oxide nanoparticles.

1. METAL NANOPARTICLES

(a) Since Ag nanoparticles has good antibacterial properties, it is used in refrigerators, air-conditioners, water purifiers etc.

(b) Au – nanoparticles are used to produce silicon nanowire and in medicine.

2. METAL OXIDE NANOPARTICLES

ZnO, TiO_2 nanoparticles are used as sunscreen cosmetics because they absorb *uv* and give protection to skin.

3. MIXED OXIDE NANOPARTICLES

Antimony-Tin-Oxide (ATO), Indium-Tin-oxide (ITO) nanoparticles are used in car windows to reduce solar heat radiations.

PROPERTIES OF NANOPARTICLES

The most claimed properties of nanoparticles are:

- ✓ As the particle size decreases, surface to volume ratio increases. This enhances catalytic activity of nanoparticles
- ✓ Size reduction influences optical properties of nanoparticles. For example, CdS in bulk appears as red, but 6 nm size of CdS shows orange colour, 4 nm size shows yellow and 2 nm size appears as white
- ✓ Size reduction also influences thermal properties like melting point. Melting point decreases with the particle size reduction.

SYNTHESIS OF NANOPARTICLES BY CHEMICAL REDUCTION METHOD

Group VI metal halides like $CrCl_3$, $MoCl_3$, WCl_4 can be reduced into their corresponding metals by using $NaBEt_3H$ (sodium tri-ethoxy boron hydride) with toluene as solvent at room temperature.

When M = Cr or Mo, then x = 3

$$MCl_x + xNaBEt_3H \xrightarrow{\text{Toluene}} M + xNaCl + xBEt_3 + x/2\ H_2$$

$$CrCl_3 + 3NaBEt_3H \xrightarrow{\text{Toluene}} Cr + 3NaCl + 3BEt_3 + 3/2\ H_2$$

$$MoCl_3 + 3NaBEt_3H \xrightarrow{\text{Toluene}} Mo + 3NaCl + 3BEt_3 + 3/2\ H_2$$

When M=W, then x = 4

$$WCl_4 + 4NaBEt_3H \xrightarrow{\text{Toluene}} W + 4NaCl + 4BEt_3 + 2H_2$$

NANOPOROUS MATERIALS: SYNTHESIS BY SOL-GEL METHOD

Materials which have pore size less than 100 nanometers are known as nanoporous materials.

There are two types of nanoporous materials namely

(i) Micro porous materials: Pore size < 2nm

Examples: Zeolites and their derivatives

(ii) Meso porous materials: Pore size > 2nm to < 50nm

Examples: Aerogels and xerogels

PROPERTIES AND APPLICATIONS OF NANOPOROUS MATERIALS

1. Nano porous materials have the surface area of 500–1000m^2/gm, which enhances the chemical reactivity and catalytic activity of various reactions.

2. Since they have very low thermal conductivity values (presence of air in the pores makes the porous material less conductive), they are used as thermal insulators.

3. Because of high porosity (90-99%), they are extensively used in membrane technology.

4. They are of light weight materials (Density: 0.003-0.8gm/cc).

AEROGEL AND XEROGEL

Aerogel: It is a highly porous structure of gel network. It can have porosity as high as 99% and surface area 1000m^2/gm. Its average pore size is 2-50nm.

Xerogel*:* It is a porous collapsed gelled sphere.

Examples

- ✓ Inorganic aerogels: SiO_2, TiO_2, ZrO_2
- ✓ Mixed oxide aerogels: SiO_2-TiO_2, SiO_2-ZrO_2
- ✓ Organic aerogels: Resorcinol-Formaldehyde(RF), Melamine-Furfural(MF)

SOL-GEL PROCESS (SYNTHESIS OF NANOPOROUS MATERIALS)

BASIC PRINCIPLE:

Sols are particles in liquid. Gels are nothing but a continuous network of particles with porous structure filled with a liquid.

A sol-gel process involves the formation of sols in a liquid and then converting the sol particles into a porous network filled with a liquid. By drying the liquid, it is possible to obtain a thin film or monolithic solid is known as aerogel.

PRECURSORS:

The precursors used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides, $M(OR)_4$. They readily react with water to form gels.

Examples:

- ✓ Tetra methoxy silane (TMOS), $[Si(OCH_3)_4]$
- ✓ Tetra ethoxy silane (TEOS), $[Si(OC_2H_5)_4]$
- ✓ Tetra butoxy titanate, $[Ti(OC_4H_9)_4]$

PROCESS: (Synthesis of silica aerogel)

The process consists of four main steps:

1. Hydrolysis of precursors
2. Condensation followed by polycondensation
3. Gelation
4. Super critical drying

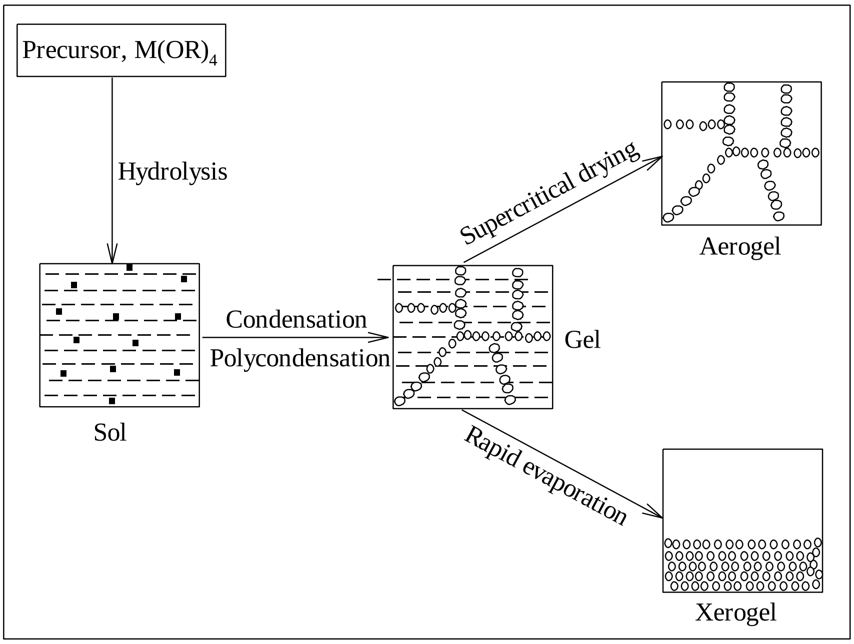


Fig. 4.4: Sol-gel Process

***1. Hydrolysis**:* It occurs through the addition of water and to form silanol, (Si–OH) particles.

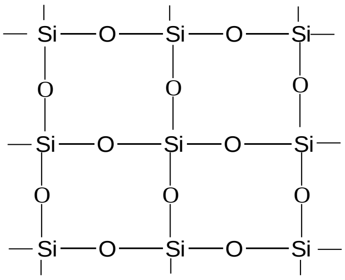
$$(RO)Si(OR)_3 + HOH \rightarrow HO\text{–}Si\text{–}(OR)_3 + R\text{–}OH$$

2. Condensation: The self-condensation of silanol groups produces siloxane linkages, (Si–O–Si) filled with byproducts of water and alcohol.

$(OR)_3–Si–OH + HO–Si–(OR)_3 \rightarrow (OR)_3–Si–O–Si–(OR)_3 + H_2O$

$(OR)_2–OH –Si–OR + HO–Si–(OR)_3 \rightarrow (OR)_2–OH–Si–O–Si–(OR)_3 + ROH$

3. Polycondensation: The condensation process continues to form poly condensed silica gel with Si–O–Si linkages.



4. Drying: The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78bar and 294ºC respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.

NANOWIRES: SYNTHESIS BY VLS MECHANISM

Nanowires are one dimensional cylindrical solid with an aspect ratio (length/diameter) of greater than 20 with a diameter ranging from 10 – 100 nm.

Applications: (i) Nanowires are used in electron devices like field effect transistors, in sensors, and detectors (ii) Nanowires replace copper in computers and in electronics.

Synthesis of Nanowires by Vapour–Liquid–Solid Mechanism

A well accepted mechanism for the growth of nanowires through gas phase reaction is vapour-liquid-solid (VLS) process. To grow any nanowire, the material used must be soluble in the catalyst nanoparticles. For example, to grow silicon nanowire, gold nanoparticles is used because silicon vapour is soluble in gold nanoprticles. To grow gallium nitride nanowire, iron nanoparticles is used because the reactants gallium and nitrogen are soluble in iron nanoparticles.

VLS mechanism follows two step processes:

(i) In the first step, diffusion of vapour phase (reactants) takes place into the liquid phase (catalyst nanoparticles).

(ii) In the second step, super saturation of reactants occurs in the liquid phase which causes the precipitation of solid phase (nanowire).

Synthesis of Silicon Nanowire

To grow silicon nanowire, gold nanoparticles is used as catalyst. The substrate is first covered with a coating of gold nanoparticles and heated to a temperature in a furnace so that it becomes liquid. Simultaneously the precursor (raw material), SiH_4 is introduced into the furnace where it vapourises to form silicon vapour. During the reaction, silicon vapour diffuses and dissolves in molten gold nanoparticles. When the concentration of silicon becomes supersaturated, the excess material (silicon) precipitates and grows as nanowires.

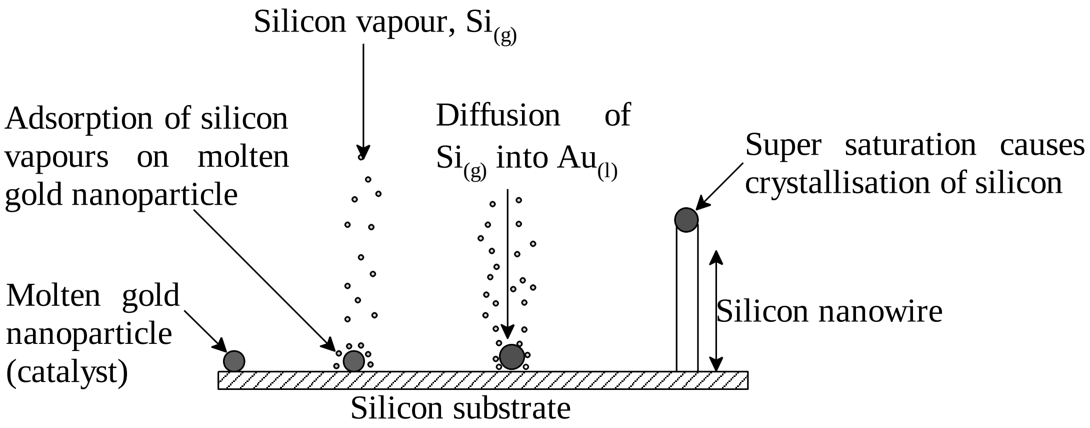


Fig. 4.5: Vapour-Liquid-Solid Mechanism for the Synthesis of Nanowires

CARBON NANOTUBES (CNTS): SINGLE WALLED AND MULTI WALLED NANOTUBES

When a graphite sheet is folded into a cylinder or tube, it is considered as carbon nanotube.

In carbon nanotubes, each atom is bonded to three other carbon atoms by strong covalent bonds and forms a lattice in the shape of hexagons except near the end. At each end, the carbon atoms form pentagon (half of the number in fullerene) and different number of hexagon so that pentagons can fit on tubes properly. Some of the cylinders are closed at the ends and some of them are open. It was first discovered by S. Iijima in 1991.

1. SINGLE-WALLED CARBON NANOTUBES (SWCNT) AND MULTI-WALLED CARBON NANOTUBES (MWCNT)

If a nanotube has a single cylinder of graphene sheet, it is known as single-walled carbon nanotube (SWCNT). If a nanotube has a number of concentric rings of graphene sheets, it is known as multi-walled carbon nanotube (MWCNT).

SWCNT		MWCNT	
Diameter	1–2nm	Outer diameter	2–20nm
		Inner diameter	1–3nm
Length	1–100μm	Length	1–100μm
		Inter tubular distance	0.34nm

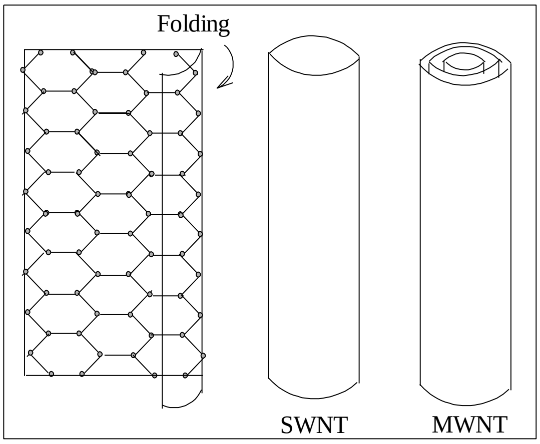


Fig. 4.6: Illustration of SWCNT and MWCNT

APPLICATIONS OF CNTS

1. ***Catalyst Supports:*** CNTs can be used as catalyst supports because they can provide advantages of large surface areas, high chemical stability and controlled surface chemistry.

2. ***Hydrogen Storage:*** Recently carbon nanotubes have been proposed to store hydrogen in hydrogen–oxygen fuel cell.

3. ***AFM Probe Tips:*** To characterize surface of material *'Probes'* are used. CNTs are widely used as materials for the manufacture of AFM (atomic force microscope) probes.

4. ***Drug Delivery:*** CNTs can be widely used as drug carriers for drug delivery, as they can easily adapt themselves and enter the nuclei of the cell.

5. ***Actuators / Artificial Muscles:*** An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move.

6. ***Chemical Sensors / Biosensors:*** Devices used to detect changes in physical and chemical quantities are called sensors. CNTs act as sensing materials in pressure, thermal, gas, optical, mass, position, stress, strain, chemical, and biological sensors.

7. ***Field Emission:*** The high current density, low turn-on and operating voltage, and steady, long-lived behavior make CNTs ideal field emitters.

8. ***Touch Screens:*** Very thin CNT films (10 or 20nm) are transparent to visible light and can conduct enough electricity to make them useful for many applications which include thin film solar cells, organic LEDs, and touch screens.

9. ***Structural and Mechanical Applications:*** CNTs are characterized with superior mechanical properties such as stiffness, toughness, and strength. These properties lead in the production of very strong, lightweight materials that can be used in areas such as building, structural engineering and aerospace.

10. ***Aerospace Components:*** CNTs have good fatigue strength over a long time which makes use of them as aircraft components.

SYNTHESIS OF CNTS BY ELECTRIC ARC DISCHARGE METHOD AND LASER ABLATION METHOD

1. Electric Arc Discharge Method (or) Plasma Arcing

Carbon nanotubes are commonly prepared by striking or producing an arc between graphite electrodes in an inert atmosphere. The following are the conditions required for CNT formation.

Electrodes	Pure graphite
Diameter of electrodes	5 to 20μm
Gap between the electrodes	1mm
Current	50 to 120Amperes
Voltage	20 to 25V
Inert gas pressure	100 to 500torr (No CNT forms if P<100torr)
Temperature rise during arc discharge	3000 to 3500˚C

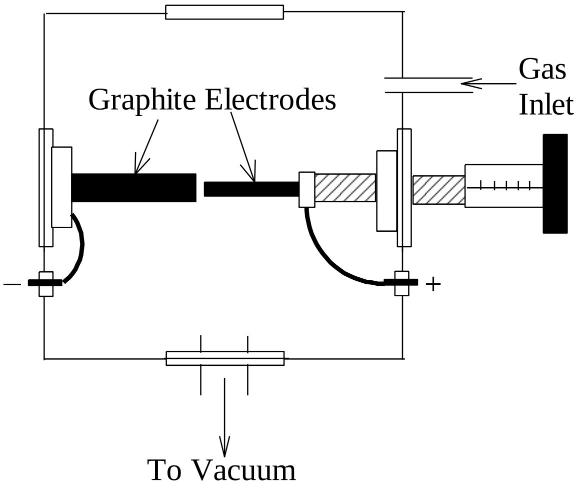


Fig. 4.7: Synthesis of Carbon Nanotubes by Electric Arc Discharge Method

In this method, a potential of 20–25V is applied across the pure graphite electrodes of 5–20μm diameter and separated by 1mm at 500torr pressure of flowing helium gas.

Under these conditions carbon atoms are ejected as vapour from the positive electrode and forms nanotube on the negative electrode. To produce SWCNT a small amount of Co, Ni, or Fe is incorporated as catalyst in the central region of the positive electrode. Presence of catalyst controls the anode reaction and releases carbon ions in a controlled manner so that it forms a SWNT at the negative electrode. If no catalysts are used, the tubes formed are multi-walled types. The arc discharge method can produce SWCNT of diameter 1–5nm with a length of 1μm.

2. Synthesis of Carbon Nanotubes by Laser Ablation Technique

Laser ablation is used to prepare high quality SWNT. The laser ablation apparatus consists of (i) a furnace, (ii) a quartz tube with a window, (iii) a graphite target doped with small amount of catalytic metals like cobalt and nickel, (iv) flow systems for argon gas to maintain constant pressures (100 Torr; 1 Torr = 10^{-3} atm) and flow rates ($1 cm.s^{-1}$) and (v) a water–cooled copper collector placed somewhat outside the furnace.

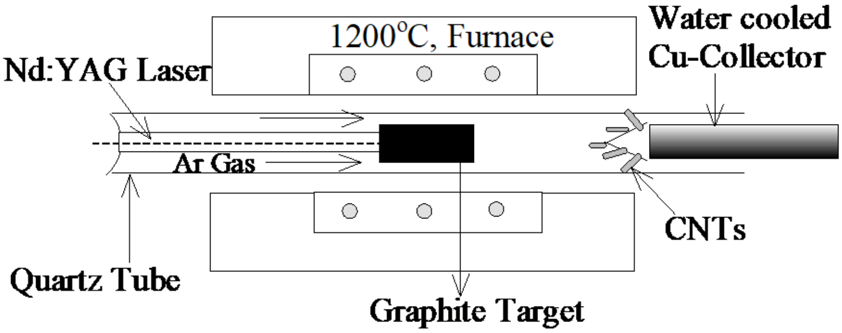


Fig. 4.8: Synthesis of Carbon Nanotubes by Laser Ablation Method

A pulsed or continuous laser beam of Nd:YAG (Neodymium-doped-yttrium aluminium garnet, $Nd:Y_3Al_5O_{12}$) or CO_2 is introduced through the window of quartz tube focused onto the graphite target, located at the center of the furnace.

The furnace temperature is maintained at 1200°C. The laser vapourises graphite and produces carbon molecules and atoms. The argon gas sweeps the carbon atoms from the high temperature zone to the colder copper collector, where they condense and grow as carbon nanotubes. The argon flow rate and pressure are typically $1 cm.s^{-1}$ and 500 Torr respectively.

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DEPARTMENT OF CHEMISTRY

UNIT – 5 – Polymer Chemistry – SCY1213

INTRODUCTION TO POLYMERS

Polymers (derived from Greek words, poly–many; mers–units or parts) are macromolecules formed by the combination of large numbers of small molecules known as monomers. Polymers have high tensile strength and they are all non-magnetic solids. Further the covalent bonds of all polymers prevent electrical conduction. The properties of polymers depend upon molecular configuration, the degree of polymerization, branching and cross linking. Polymers are finding many applications in industrial areas like automobiles, defense, electrical and electronic goods, computer components etc.

NOMENCLATURE OF POLYMERS

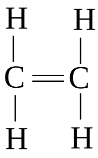
1. MONOMER

- **Definition:** Monomer is a simple molecule consisting of two or more bonding sites through which it interacts with other simple molecules to form a polymer.

- All simple molecules do not qualify as monomers. The essential requirements of a simple molecule to qualify as a monomer are:

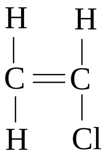
  - It must possess at least two active centres (bonding sites) in the form of double bonds. (or)
  - It must have at least two reactive, same or different functional groups.

- **Examples of Type-I Monomers**



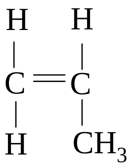
$H_2C{=}CH_2$

Ethylene



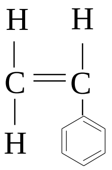
$H_2C{=}CHCl$

Vinylchloride



$H_2C{=}CH(CH_3)$

Propylene



Styrene

- **Examples of Type-II Monomers**

$H_2N{-}(CH_2)_6{-}NH_2$

Hexamethylene diamine

$HOOC{-}(CH_2)_4{-}COOH$

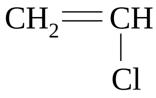
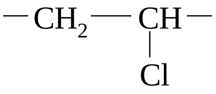
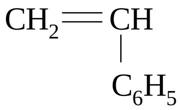
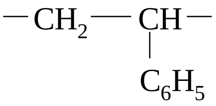
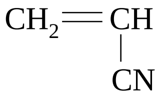
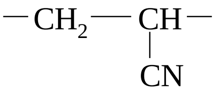
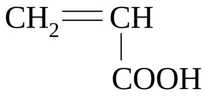
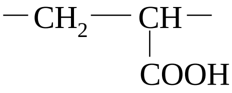
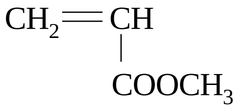
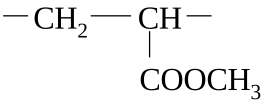
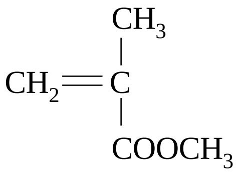
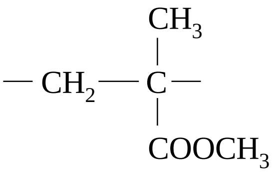
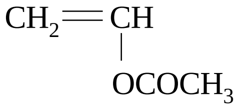
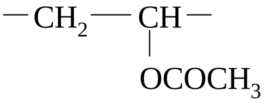
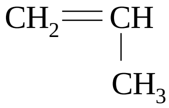
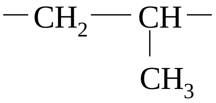
Adipic acid

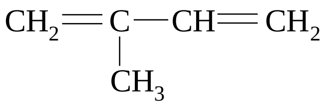
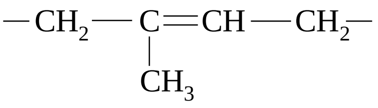
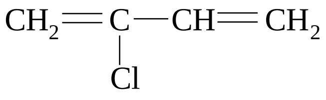
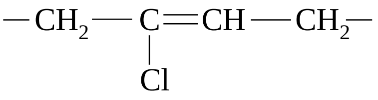
2. POLYMER

- **Definition:** Polymer is a macromolecule formed by the combination of large number of one or more types of small molecules of low molecular weight called monomer.

- Some monomers and the repeating unit in the polymers are summarised in Table 5.1.

Table 5.1: List of Monomers and the Repeating Unit of their Corresponding Polymers

S. No.	Monomer	Repeating unit of the Polymer
1	$CH_2{=}CH_2$ Ethylene	$-CH_2-CH_2-$ Polyethylene (PE)
2	 $CH_2{=}\underset{\substack{\vert\\ Cl}}{CH}$ Vinyl chloride	 $-CH_2-\underset{\substack{\vert\\ Cl}}{CH}-$ Polyvinylchloride (PVC)
3	 $CH_2{=}\underset{\substack{\vert\\ C_6H_5}}{CH}$ Styrene	 $-CH_2-\underset{\substack{\vert\\ C_6H_5}}{CH}-$ Polystyrene (PS)
4	 $CH_2{=}\underset{\substack{\vert\\ CN}}{CH}$ Acrylonitrile	 $-CH_2-\underset{\substack{\vert\\ CN}}{CH}-$ Polyacrylonitrile (PAN)
5	 $CH_2{=}\underset{\substack{\vert\\ COOH}}{CH}$ Acrylic acid	 $-CH_2-\underset{\substack{\vert\\ COOH}}{CH}-$ Polyacrylic acid (PAA)
6	 $CH_2{=}\underset{\substack{\vert\\ COOCH_3}}{CH}$ Methyl acrylate	 $-CH_2-\underset{\substack{\vert\\ COOCH_3}}{CH}-$ Polymethyl acrylate (PMA)
7	 $CH_2{=}\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ COOCH_3}}{C}}$ Methyl methacrylate	 $-CH_2-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ COOCH_3}}{C}}-$ Polymethyl methacrylate (PMMA)
8	 $CH_2{=}\underset{\substack{\vert\\ OCOCH_3}}{CH}$ Vinyl acetate	 $-CH_2-\underset{\substack{\vert\\ OCOCH_3}}{CH}-$ Polyvinyl acetate (PVAc)
9	 $CH_2{=}\underset{\substack{\vert\\ CH_3}}{CH}$ Propylene	 $-CH_2-\underset{\substack{\vert\\ CH_3}}{CH}-$ Polypropylene (PP)

10	$CH_2=CH-CH=CH_2$ Butadiene	$-CH_2-CH=CH-CH_2-$ Polybutadiene
11	 $CH_2=\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CH=CH_2$ Isoprene	 $-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH-CH_2-$ Polyisoprene
12	 $CH_2=\underset{\displaystyle Cl}{\underset{\vert}{C}}-CH=CH_2$ Chloroprene	 $-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{C}}=CH-CH_2-$ Polychloroprene

DEGREE OF POLYMERISATION (DP)

- **Definition:** The number of repeating unit in a polymer is known as degree of polymerisation.

- Degree of polymerisation ban be calculated from the following expression:

$$\text{Degree of polymerisation} = \frac{\text{Molecular weight of the polymer}}{\text{Molecular weight of the monomer}}$$

- Polymers with low degree of polymerisation are known as oligo polymers or oligomers. Their molecular weight ranges from 500–5000. Polymers with high degree of polymerisation are known as high polymers. The molecular weight of such polymers ranges from 10,000–2,00,000.

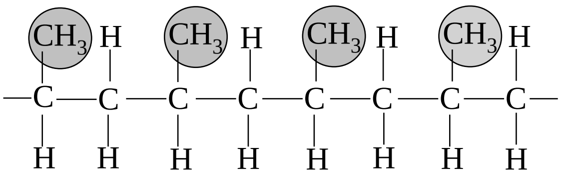
TACTICITY OF POLYMERS

- **Definition:** The orientation of monomeric units (or functional groups) in a polymer can take place in an orderly or disorderly manner with respect to main chain is known as tacticity.

- Tacticity results three types of stereo-regular polymers.

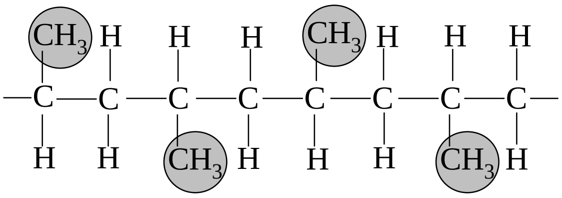
1. **Isotactic Polymer:** The functional groups are arranged on the same side with respect to the main chain.

❖ **Examples:** Polypropylene, Cis–Polyisoprene.



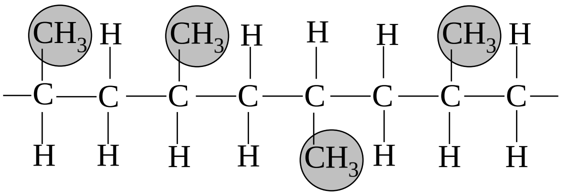
2. **Syndiotactic Polymer:** The functional groups are arranged in alternative sequence with respect to the main chain.

- **Examples:** Polypropylene, Trans–Polyisoprene.



3. **Atactic Polymer:** The functional groups are arranged randomly with respect to the main chain.

- **Examples:** Polypropylene.



CLASSIFICATION OF POLYMERS

Table 5.2: Classification of Polymers in Different Manner

S. No.	Classification	Definition	Examples
On the basis of occurrence			
1	Natural polymers	They are available in nature.	Cellulose; Starch; Natural rubber.
2	Synthetic polymers	They are chemically modified natural polymers.	Polyethylene; Polyvinyl chloride.
On the basis of type of atom in the backbone of polymers			
1	Organic polymers	The backbone contains only C-atoms.	Polyethylene; Polyvinyl chloride.
2	Inorganic polymers	The backbone contains atoms like O, N, S other than carbon.	Silicones; Phosphazine.
On the basis of arrangement of monomers in polymer chain			
1	Homopolymers	Polymers containing same type of monomers. $—M—M—M—M—M—$	Polyethylene; Polypropylene.
2	Copolymers (or) Heteropolymers	Polymers containing different type of monomers. $—M_1—M_2—M_1—M_2—M_1—M_2—$	Nylon 6:6; Phenol formaldehyde.

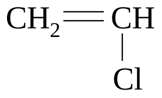
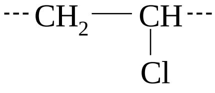
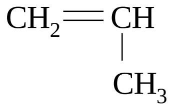
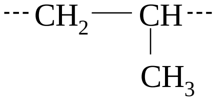
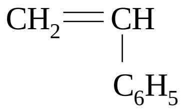
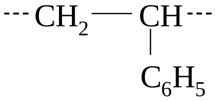
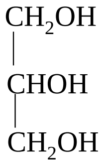
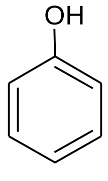
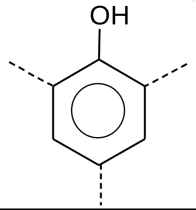
On the basis of tacticity of polymers			
1	Isotactic polymer	Functional groups are arranged on the same side with respect to the main chain.	Cis–Polyisoprene.
2	Syndiotactic Polymer	Functional groups are arranged in alternative sequence with respect to the main chain.	Trans–Polyisoprene.
3	Atactic Polymer	Functional groups are arranged randomly with respect to the main chain.	Polypropylene
On the basis of thermal behaviour of polymers			
1	Thermoplastic polymers	They soften on heating and become hard and rigid on cooling. Repeated heating and cooling do not affect the structure of polymer chains.	Polyethylene; Polyvinyl chloride.
2	Thermosetting polymers	They get hardened permanently on heating. Once set, they cannot be softened again.	Phenol formaldehyde resin (Bakelite); Urea formaldehyde resin.
On the basis of end use and applications			
1	Plastics	Plastics are high molecular weight organic materials. Plastics can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst.	Polyethylene; Polyvinyl chloride.
2	Elastomers	Polymers show good strength and elongation.	Natural rubber; Buna-S; Butyl rubber.
3	Fibers	When a polymer is drawn into long filament whose length is at least 100 times of its diameter.	**Natural fibers:** Wood. Silk, Cotton. **Synthetic fiber:** Terylene.
4	Liquid resins	When a polymer is used as adhesive, sealants in liquid form, it is known as liquid resins.	Epoxy adhesive; Polysulphide sealant.

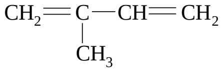
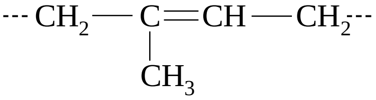
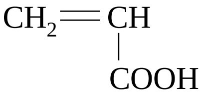
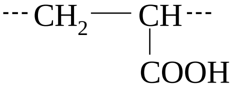
FUNCTIONALITY

Definition: The number of bonding sites or reacting functional groups present in a monomer is known as monomer functionality.

Table 5.3: Examples of Functionality of Monomers

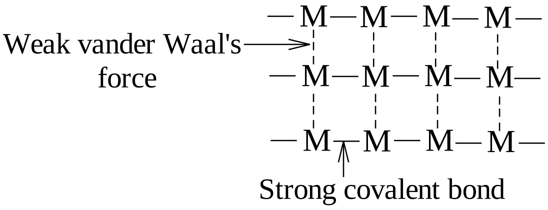
S.No.	Monomer	Functionality
1	$CH_2=CH_2$ Ethylene	Breaking of double bond in the ethylene monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer. $---CH_2-CH_2---$

2	 $CH_2=\underset{Cl}{\underset{\vert}{CH}}$ Vinyl chloride	Breaking of double bond in the vinyl chloride monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.  $\cdots CH_2-\underset{Cl}{\underset{\vert}{CH}}\cdots$
3	 $CH_2=\underset{CH_3}{\underset{\vert}{CH}}$ Propylene	Breaking of double bond in the propylene monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.  $\cdots CH_2-\underset{CH_3}{\underset{\vert}{CH}}\cdots$
4	 $CH_2=\underset{C_6H_5}{\underset{\vert}{CH}}$ Styrene	Breaking of double bond in the styrene monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.  $\cdots CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}\cdots$
5	$H_2N-(CH_2)_6-NH_2$ Hexamethylene diamine	Presence of two reactive functional groups in hexamethylene diamine monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.
6	$HOOC-(CH_2)_4-COOH$ Adipic acid	Presence of two reactive functional groups in adipic acid monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.
7	 $\begin{matrix}CH_2OH\\ \vert\\ CHOH\\ \vert\\ CH_2OH\end{matrix}$ Glycerol	Presence of three reactive functional groups in glycerol monomer provides three bonding sites for polymerisation to occur. Hence its functionality is **three** and it is a tri-functional monomer.
8	 Phenol	Presence of alternate double bonds in phenol monomer provides three bonding sites for polymerisation to occur. Hence its functionality is **three** and it is a tri-functional monomer. 
9	$CH_2=CH-CH=CH_2$ Butadiene	Rearrangement of alternate double bonds in butadiene monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.

		$\cdots CH_2-CH=CH-CH_2\cdots$
10	 $CH_2=\underset{\underset{CH_3}{\mid}}{C}-CH=CH_2$ Isoprene	Rearrangement of alternate double bonds in isoprene monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.  $\cdots CH_2-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2\cdots$
11	 $CH_2=\underset{\underset{COOH}{\mid}}{CH}$ Acrylic acid	Breaking of double bond in the acrylic acid monomer provides two bonding sites for polymerisation to occur. Hence its functionality is **two** and it is a bi-functional monomer.  $\cdots CH_2-\underset{\underset{COOH}{\mid}}{CH}\cdots$

1. Significance of Bi-functional Monomers

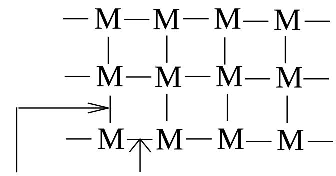
- If the functionality of monomer is two, then such a monomer produces only straight chain (or linear chain) polymers. Each monomeric unit in the linear chain polymer is held by strong covalent bond forces (primary bond) whereas the different chains are held together by weak Vander Waal's forces of attraction (secondary bond).



- Therefore, there is no restriction in the movement of one polymer chain over another chain. Such linear types of polymers have less strength, low heat resistance and they are soft and flexible.

2. Significance of Tri-functional Monomers

- If the functionality of monomer is three, then such a monomer produces cross-linked three-dimensional network polymers. All the monomers in the polymer are connected to each other by strong covalent bond forces and hence the movement of polymer chain is totally restricted. Such cross-linked polymers have very high strength, hardness, toughness, heat resistance and insoluble in almost all organic solvents.



TYPES OF POLYMERIZATION

Definition: The reaction by which monomers combine to give polymer is known as polymerisation.

1. ADDITION (OR) CHAIN GROWTH POLYMERISATION

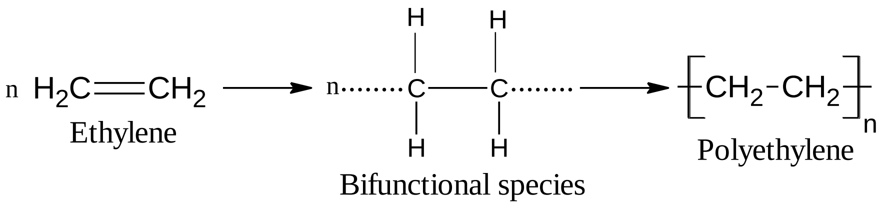
- Monomers having multiple bonds (double or triple bond) undergo addition polymerisation. Monomers combine to give addition polymer through addition reaction and no other by-products.

- Therefore, molecular weight of the resulting polymer will be an integral multiple of the molecular weight of monomers.

1. Polymerisation of Ethylene

- Polyethylene is obtained by polymerisation of ethylene monomers. The ethylene monomer can be obtained by dehydrogenation of ethane and by dehydration of ethyl alcohol.

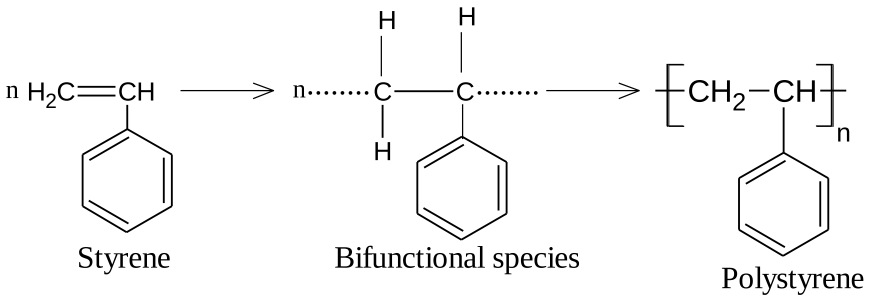
- The first step in the polymerisation is molecular rearrangement to produce a bi-functional molecule. In presence of suitable catalysts, these activated molecules join together to form a long chain polyethylene.



$$n\,H_2C{=}CH_2 \longrightarrow n\cdots\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdots \longrightarrow \left[CH_2-CH_2\right]_n$$

2. Polymerisation of Styrene

- Polystyrene is obtained by polymerisation of styrene monomers. The styrene monomer is obtained by catalytic dehydrogenation of ethyl benzene. In presence of light, heat or a suitable catalyst, styrene monomers join together to form long chain polystyrene.

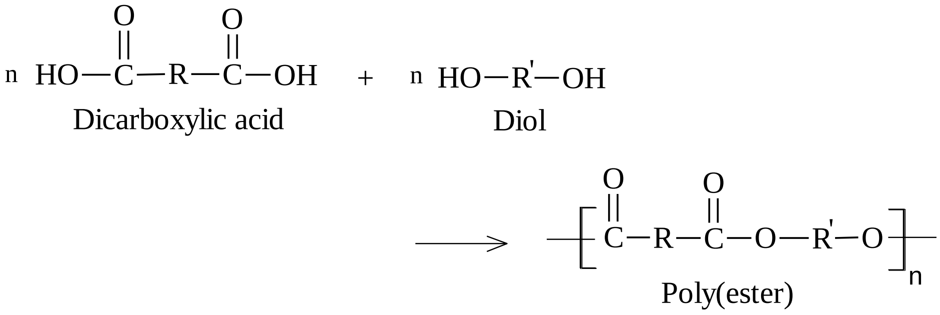


2. CONDENSATION (OR) STEP POLYMERISATION

- Monomers having same type or different type of functional groups undergo condensation polymerisation. The polymerisation proceeds by step wise reaction between reactive functional groups and small molecules are eliminated. Therefore, molecular weight of polymer will not be an integral multiple of the molecular weight of monomers. Condensation polymers are hard, strong and more brittle. They are insoluble in almost all organic solvents because of strong bonds and cross linking.

1. Polyesters

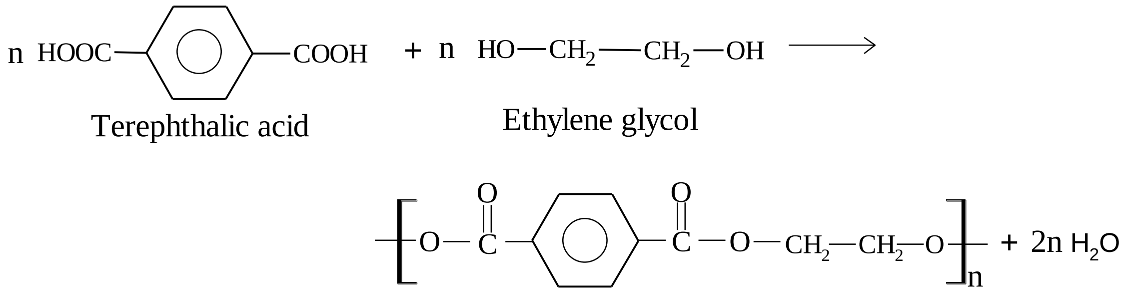
- Polyester is obtained by the reaction of a dicarboxylic acid with a diol.



$$n\ HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH + n\ HO-R'-OH \longrightarrow -\!\!\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O\right]\!\!-_n$$

❖ Example of Polyester: Dacron (Terylene)

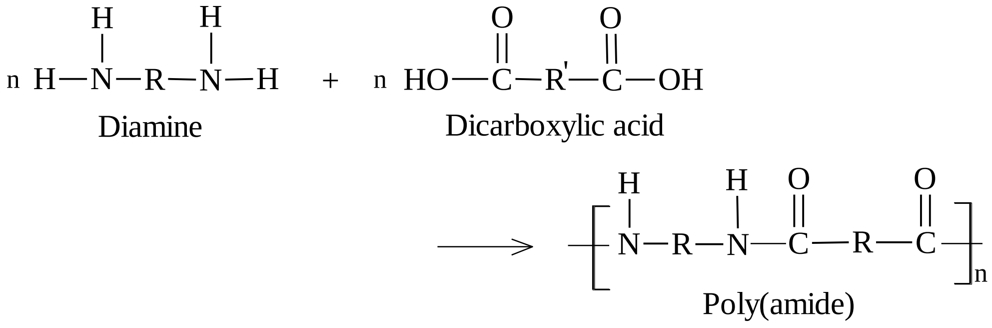
- Dacron (Terylene) is formed by the condensation of ethylene glycol and terephthalic acid. It is used as a synthetic fibre.



Terylene (Dacron)

2. Polyamides

- Polyamides are obtained by the condensation of a diamine with dicarboxylic acid.



$$n\ H-\underset{}{\overset{H}{\overset{|}{N}}}-R-\overset{H}{\overset{|}{N}}-H + n\ HO-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-OH \longrightarrow -\!\!\left[\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}\right]\!\!-_n$$

❖ Example of Polyamide: Nylon 6,6

- Nylon 6, 6 is obtained by condensation polymerisation of hexamethylene diamine and adipic aicd.

$$n\,H_2N\text{—}(CH_2)_6\text{—}NH_2 \;+\; n\,HOOC\text{—}(CH_2)_4\text{—}COOH$$

Hexamethylene diamine   Adipic acid

$$\longrightarrow \left[HN\text{—}(CH_2)_6\text{—}NH\text{—}CO\text{—}(CH_2)_4\text{—}CO\right]_n$$

Nylon 6,6

Table 5.4: Typical Examples of Condensation Polymerisation

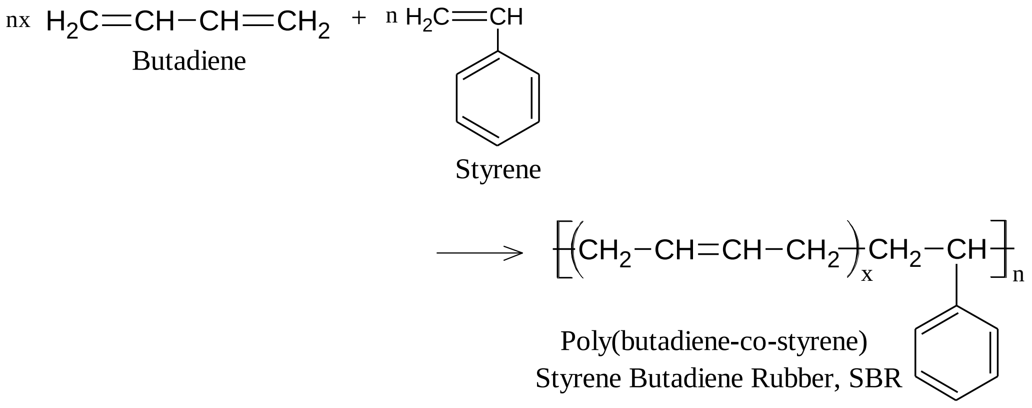
S. No.	Chemical Reaction	Type of chain	Linking Group	Name of Polymer Product
1	Dicarboxylic acid + Glycol	Polyesters	– CO – O –	Dacron
2	Dicarboxylic acid + Diamine	Polyamides	– CO – NH –	Nylon 6,6
3	Bisphenol + Sepoxide	Polyethers	– O –	Epoxy resin
4	Diisocyanate + Glycol	Polyurethanes	– NH – CO – O –	Elastomers
5	Bisphenol + Phosgene	Polycarbonate	– O – CO – O –	Lexan

3. COPOLYMERISATION

- Copolymerisation is the joint polymerisation of two or more different monomers. In this process no side products are formed. Copolymerisation can be used to obtain polymeric materials with new properties.Chemical and geometrical shape of polymers can be varied by copolymerisation reaction. Hence it is used to produce unsymmetrical or irregular shape polymers. Copolymerisation is superior to other polymerisation reaction because the reaction can control various polymer properties such as hardness, toughness, flexibility, heat resistance, solubility, crystallization tendency, etc.

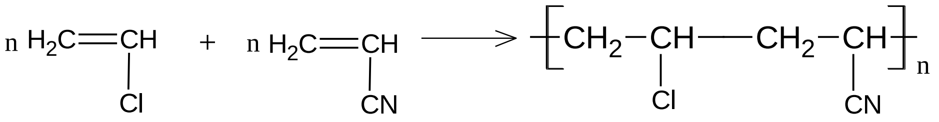
1. Copolymerisation of styrene and butadiene

- Copolymerisation of styrene and butadiene forms styrene-butadiene rubber (SBR) which has superior properties than ordinary synthetic butadiene rubber. Styrene butadiene rubber (SBR) consists of about 75% butadiene and 25% styrene.



2. Copolymerisation of acrylonitrile and vinyl chloride

- Copolymerisation of acrylonitrile and vinyl chloride is readily soluble in acetone but polyvinyl chloride and polyacrylonitrile are soluble only at higher temperatures.



$$n\,H_2C{=}\underset{\displaystyle Cl}{\underset{|}{CH}} + n\,H_2C{=}\underset{\displaystyle CN}{\underset{|}{CH}} \longrightarrow \left[CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right]_n$$

Vinyl chloride Acrylonitrile Poly(vinylchloride-co-acrylonitrile)

4. COORDINATION (OR) ZEIGLER-NATTA POLYMERISATION

- Coordination polymerisation is nothing but addition polymerisation using coordination complex of transition metal halide and an organometallic compound as catalyst (Zeigler-Natta catalyst). By using suitable catalyst, solvent, temperature, it is possible to produce stereo regular polymers such as isotactic, syndiotactic and atactic. The atactic polymer is soft and flexible and the other two are dense.

- A typical example of Zeigler-Natta catalyst is the coordination complex of titanium trichloride and trialkyl aluminium.

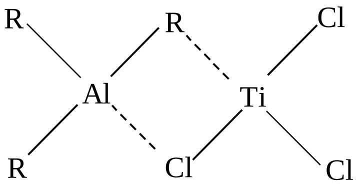


Table 5.5: Differences between Addition Polymerisation and Condensation Polymerisation

S.No.	***Addition/Chain Polymerisation***	***Condensation/Step Polymerisation***
1.	Monomers having multiple bonds undergo chain polymerisation. **Examples:** Acetylene; Vinyl compounds.	Monomers having same or different functional groups undergo step polymerisation. **Examples:** Glycol; Hydroxy acid.
2.	During polymerisation, monomers add to the polymer one at a time. Therefore, number of monomeric units decreases steadily throughout the reaction.	During polymerisation, any two monomers or functional groups react and produce polymer. Therefore, monomers disappear early in the reaction.
3.	*High polymer is formed at once.*	*The molecular weight of the polymer increases steadily throughout the reaction.*
4.	Molecular weight of the polymer will be an integral multiple of the monomer.	*Molecular weight of the polymer need not be an integral multiple of monomer.*
5.	*Longer reaction times give high yield.*	*Longer reaction times are essential to obtain high molecular weight.*

6.	*Mostly thermoplastics are produced.*	*Mostly thermosetting plastics are produced.*
7.	***Examples:*** *Polymerisation of ethylene, vinyl chloride etc.*	***Examples:*** *Polymerisation of phenol and formaldehyde.*

MECHANISM OF POLYMERIZATION: FREE RADICAL MECHANISM - CATIONIC MECHANISM - ANIONIC MECHANISM

1. FREE RADICAL MECHANISM

- Free radical mechanism follows three main steps:

  (i) Chain initiation

  (ii) Chain propagation and

  (iii) Chain termination.

1. Chain Initiation

- Chain initiation involves two reactions:

(i) Production of primary free radical by homolytic dissociation of thermal initiator.

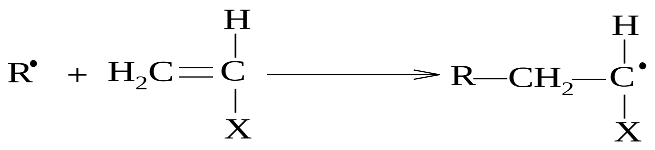
$$\underset{\text{Acetylperoxide}}{CH_3COO\text{-}OOCCH_3} \xrightarrow{70\text{-}90^\circ C} \underset{\text{Primary free radical}}{2CH_3COO^\bullet \text{ (or) } 2R^\bullet}$$

$$\underset{\text{Benzoylperoxide}}{C_6H_5COO\text{-}OOCC_6H_5} \xrightarrow{80\text{-}95^\circ C} \underset{\text{Primary free radical}}{2C_6H_5COO^\bullet \text{ (or) } 2R^\bullet}$$

$\bullet$ represents free radical.

(ii) Addition of this free radical to the first monomer to produce chain initiating species.

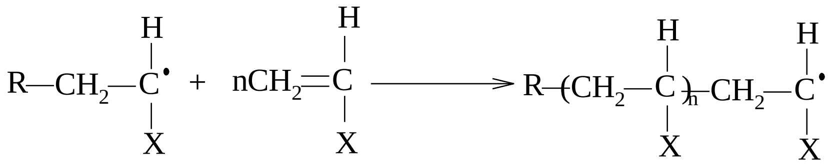
$$\underset{\substack{\text{Primary}\\\text{Free Radical}}}{R^\bullet} + \underset{\substack{\text{First}\\\text{Monomer}}}{M} \longrightarrow \underset{\substack{\text{Chain Initiating}\\\text{Species}}}{R\text{—}M^\bullet}$$



$$R^\bullet + H_2C{=}\overset{\overset{\large H}{|}}{\underset{\underset{\large X}{|}}{C}} \longrightarrow R\text{—}CH_2\text{—}\overset{\overset{\large H}{|}}{\underset{\underset{\large X}{|}}{C^\bullet}}$$

2. Chain Propagation

- Propagation consists of the growth of chain initiating species by successive addition of large number of monomer molecules one by one.



$$R-CH_2-\overset{H}{\underset{X}{C^{\bullet}}} + nCH_2=\overset{H}{\underset{X}{C}} \longrightarrow R\!-\!(CH_2-\overset{H}{\underset{X}{C}})_n-CH_2-\overset{H}{\underset{X}{C^{\bullet}}}$$

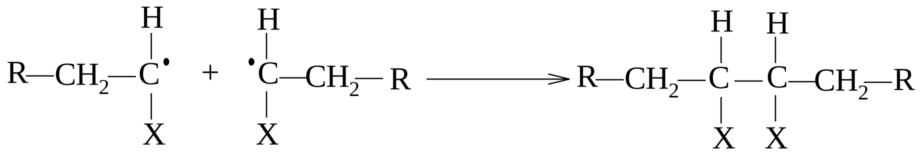
Growing Chain (Living Polymer)

- The growing chain of the polymer is known as ***living polymer.***

3. **Chain Termination**

- Termination of living polymer may occur due to:

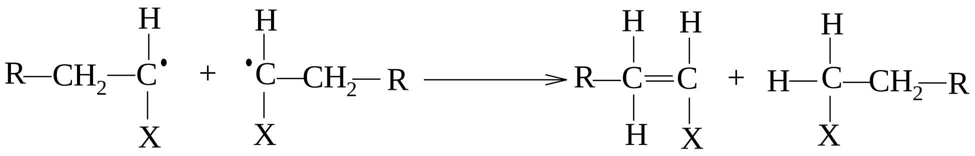
- **Combination or Coupling** of free radical of one chain end to another free radical forming a macromolecule.



$$R-CH_2-\overset{H}{\underset{X}{C^{\bullet}}} + {}^{\bullet}\overset{H}{\underset{X}{C}}-CH_2-R \longrightarrow R-CH_2-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-CH_2-R$$

Dead Polymer

- **Disproportionation** involves transfer of a hydrogen atom of one chain end to another to form two macromolecules (one saturated and another unsaturated).



$$R-CH_2-\overset{H}{\underset{X}{C^{\bullet}}} + {}^{\bullet}\overset{H}{\underset{X}{C}}-CH_2-R \longrightarrow R-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{X}{C}} + H-\overset{H}{\underset{X}{C}}-CH_2-R$$

Unsaturated polymer

Saturated polymer

- The product of addition polymerisation is called as ***dead polymer.***

2. ANIONIC MECHANISM

- Monomers containing electronegative groups like Cl^-, CN^- at one of the carbon atoms connected by the double bond follow this mechanism.

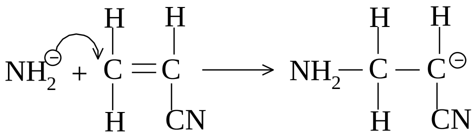
- The catalysts used to initiate the reaction are KNH_2, $NaNH_2$ (Lewis bases).

❖ **Examples:** Vinyl chloride, Acrylonitrile.

1. **Chain Initiation**

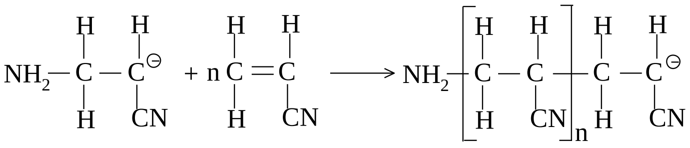
- It involves the formation of chain initiating ***carbanion***.

$$KNH_2 \longrightarrow K^{\oplus} + NH_2^{\ominus}$$


Chain initiating carbanion

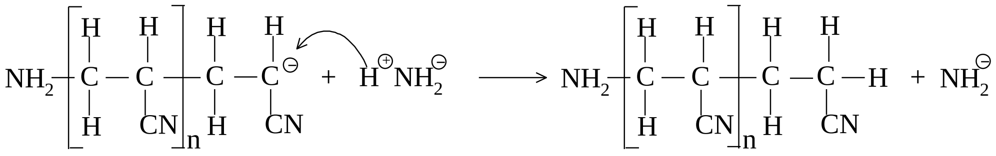
2. Chain Propagation

- ➢ It involves the growth of chain initiating ***carbanion*** by successive addition of large number of monomers one by one. The growth involves the transfer of negative charge along the chain.



3. Chain Termination

- ➢ Termination of growing chain occurs by the reaction of growing ***carbanion*** chain with the medium of the polymerisation like ammonia.



3. CATIONIC MECHANISM

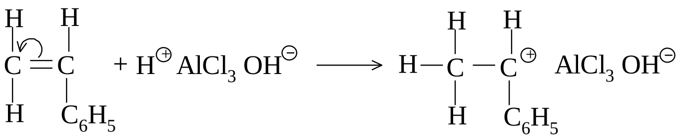
- ➢ Monomers containing electropositive groups like CH_3, C_6H_5 at one of the carbon atoms connected by the double bond follow this mechanism. The catalysts used to initiate the reaction are $AlCl_3$, BF_3 (Lewis acids).

❖ **Examples:** Isoprene, Styrene.

1. Chain Initiation

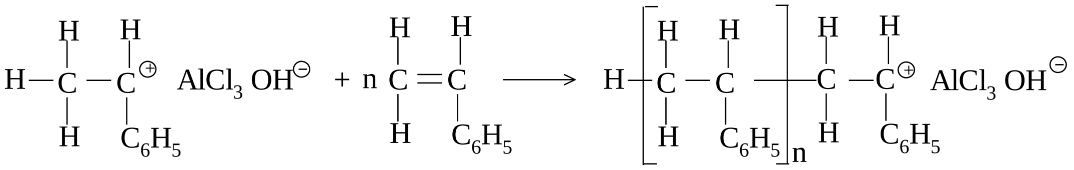
It involves the formation of chain initiating ***carbonium ion***.

$$AlCl_3 + H_2O \longrightarrow H^{\oplus}\,AlCl_3\,OH^{\ominus}$$


Chain initiating carbonium ion

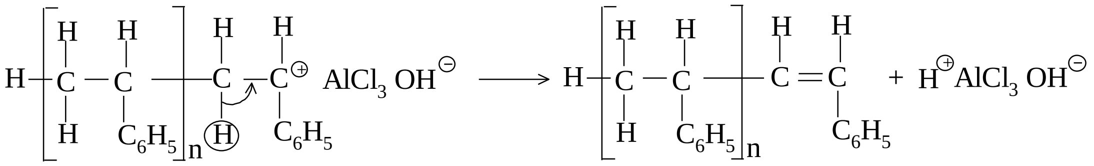
2. Chain Propagation

- It involves the growth of chain initiating ***carbonium*** ion by successive addition of large number of monomers one by one. The growth involves the transfer of positive charge along the chain.



3. Chain Termination

- It involves the splitting of the catalyst from the growing chain of polymer.



PLASTICS: TYPES - THERMOPLASTICS AND THERMOSETTING PLASTICS

- ***Plastics*** are high molecular weight organic materials which can be moulded into any definite shape by the application of heat and pressure in the presence of a catalyst.

- ***Resin*** is the major part of a plastic, which actually undergoes polymerisation reaction during the moulding operation.

- Based on thermal behaviour, resins are classified into two types. (i) Thermoplastic resins and (ii) Thermosetting resins. On the basis of the type of resin used in plastic preparation, the plastic itself is called thermoplastics and thermosetting plastics.

- **Thermoplastic Resins:** They soften on heating and become hard and rigid on cooling. They are soft, weak and less brittle. They are soluble in some organic solvents because of their weak intermolecular forces.

- **Thermosetting Resins:** They get hardened on heating. Once set, they cannot be softened again. They are hard, strong and more brittle. They are insoluble in almost all organic solvents because of strong bonds and cross linking.

Table 5.6: Differences between Thermoplastics and Thermosetting Plastics

S.No.	***Thermoplastics***	**Thermosetting Plastics**
1	Thermoplastics are formed by addition polymerisation.	Thermosetting plastics are formed by condensation polymerisation.

2	They consist of linear structure held by weak Vander Waals forces.	They consist of 3-dimensional network structure joined by strong covalent bonds.
3	They soften readily on heating because secondary bond forces between the individual chains can break easily by heat and pressure. They become hard and rigid on cooling because the broken bonds are re-established on cooling.	Thermosetting plastics get harden or gain strength on heating. Once set they cannot be softened again because the cross-links and bonds retain their strength on heating.
4	By reheating to a suitable temperature, they can be softened, reshaped and reused.	They cannot be remoulded and reused, because the cross-links and bonds retain their shape and structure on heating.
5	They are soft, weak and less brittle.	They are hard, strong and more brittle.
6	They can be reclaimed from wastes.	They cannot be reclaimed from wastes.
7	They are soluble in some organic solvents because of their weak intermolecular forces.	They are insoluble in almost all organic solvents because of strong bonds and cross linking.
8	**Examples:** PE, PVC.	***Examples:*** *Bakelite; Epoxy resin.*

PROPERTIES: STRENGTH – CRYSTALLINE AND AMORPHOUS STATE – AVERAGE MOLECULAR WEIGHT – POLYDISPERSITY

1. STRENGTH OF POLYMERS

The strength of polymeric materials depends upon: (a) Molecular weight (b) Molecular shape (c) Cross linking.

(i) Molecular weight: The strength of a polymer increases with increase of molecular weight. The molecular weight in turn depends upon degree of polymerization.

(ii) Molecular shape: In linear polymers, the polymer chains are held by weak vander waals forces of attraction and hence they have relatively lower strength. However the strength of such polymers can be increased by side chain substitution or by introducing bulkier groups.

For example, polyethylene is a simple linear polymer due to its symmetrical structure and has lower strength. But in polyvinyl chloride, presence of chlorine increases intermolecular forces of attraction between the polymer chains and thereby making the polymer very hard and tough.

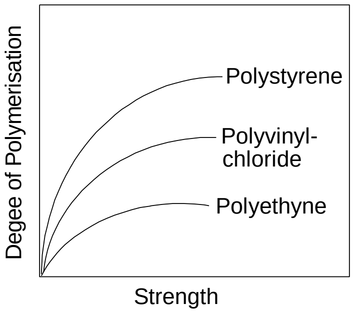


Fig. 5.1: Strength of Polymers

(iii)Crosslinking: Cross linked polymers are very strong and hard because all the atoms in the polymer structure are interconnected by strong covalent bonds.

2. PHYSICAL STATE OF POLYMERS

Relative arrangement of polymer chains with respect to each other results in two physical state of polymers. (i) Amorphous polymers and (ii) Crystalline polymers.

(i) Amorphous polymers: It is characterized by completely random arrangement of polymer chains. Polymers with low degree of symmetry generally form amorphous structure. Amorphous region in a polymer provides flexibility. Example: Polyvinyl acetate.

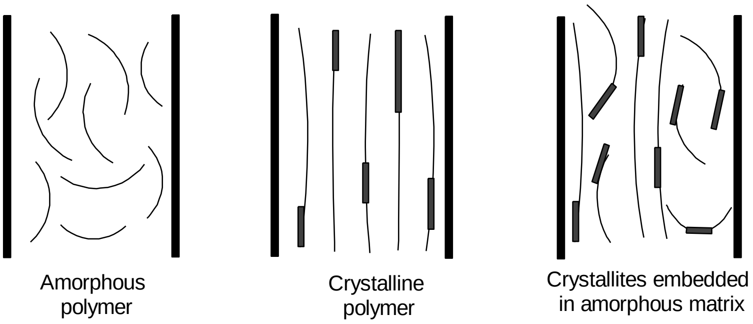


Fig. 5.2: Physical State of Polymers

(ii) Crystalline polymers: It is characterized by completely regular arrangement of polymer chains. Polymers with high degree of symmetry generally form crystalline structure. Crystallites in polymers provide hardness, rigidity and heat resistance.

A complete crystalline polymer tends to become brittleness because of regular arrangement of polymer chains. It increases intermolecular forces of attraction and making it close denser packing. Crystallisation tendency of can be decreased by copolymerization. So, by controlling the extend of copolymerization, the amorphous and crystalline region in a polymer can be adjusted in order to get required polymer strength and heat resistance.

3. GLASS TRANSITION TEMPERATURE (T_g)

It is the temperature below which a polymer is hard and above which it is soft. The hard and brittle state is known as glassy state and the soft and flexible state is rubbery or visco–elastic state. Glass transition temperature decides whether a polymer will behave like glass or rubber. Polystyrene (T_g = 100°C) and PVC (T_g = 80°C) are hard and stiff materials at room temperature whereas low density polyethylene (T_g = −105°C) and polyethyl acrylate (T_g = −70°C) are soft and rubbery.

Factors affecting glass transition temperature:

1. **Crystallinity:** In crystalline polymers, the polymer chains are arranged in an orderly manner. The regular arrangement of polymer chains increases intermolecular forces of attraction in turn cause high T_g.
2. **Cross-linking:** The presence of cross-linking between the polymer chains restricts the movement (rotation) of chains in turn raises T_g.
3. **Molecular weight:** In general, T_g of polymers increases with increase of molecular weight up to a particular value and beyond that there is no change in T_g occurs.

4. **Plasticisers:** Addition of a plasticiser reduces the intermolecular forces of attraction present between the polymer chains in turn decreases T_g.

5. **Tacticity:** Isotactic polymers have higher T_g because of regular arrangement of functional groups with respect to main chain than that of syndiotactic polymers and atactic polymers. Polymers are normally a mixture consisting of different chain lengths. Hence it is not possible to assign a definite molecular weight to a polymer. In practice, statistical methods are adopted for assigning average molecular weight of polymers.

4. NUMBER AVERAGE MOLECULAR WEIGHT ($\overline{M_n}$)

- It is defined as the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

- If a polymer mixture contains n_1 molecules with molecular weight M_1, n_2 molecules with molecular weight M_2 .... till n_i molecules with molecular weight M_i then,

$$\overline{M_n} = \frac{n_1M_1 + n_2M_2 + \cdots + n_iM_i}{n_1 + n_2 + \cdots + n_i}$$

$$\overline{M_n} = \frac{\sum n_iM_i}{\sum n_i}$$

5. WEIGHT AVERAGE MOLECULAR WEIGHT ($\overline{M_w}$)

- It is defined as the ratio of sum of weights of individual polymer molecules to the total weight of polymer molecules in the mixture.

- In a polymer mixture, if w_1 is the weight of polymer with molecular weight M_1, w_2 is the weight of polymer with molecular weight M_2 .... till w_i is the weight of polymer with molecular weight M_i then,

$$\overline{M_w} = \frac{w_1M_1 + w_2M_2 + \cdots + w_iM_i}{w_1 + w_2 + \cdots + w_i}$$

$$\overline{M_w} = \frac{\sum w_iM_i}{\sum w_i}$$

- But, number of moles $n = \frac{w}{M}$ and $w = nM$. Therefore, replacing w_1 *by* n_1M_1, w_2 *by* n_2M_2, …. and w_i *by* n_iM_i, then we have:

$$\overline{Mw} = \frac{n_1M_1^2 + n_2M_2^2 + \cdots + n_iM_i^2}{n_1M_1 + n_2M_2 + \cdots + n_iM_i}$$

$$\overline{M_w} = \frac{\sum n_iM_i^2}{\sum n_iM_i} = \frac{\sum n_iM_i}{\sum n_i}$$

6. VISCOSITY AVERAGE MOLECULAR WEIGHT

- From the measurements of the viscosity of polymer solutions, it is possible to determine the average molecular weight of the polymer. The molecular weight of a polymer is proportional to the intrinsic viscosity of its solution (η_i) when the polymer molecular chain is extended to its full contour length.

- The relationship between intrinsic viscosity and molecular weight is given by Mark-Hownik's equation.

  $$\eta_i = KM^{\alpha}$$

  Where,
  - ✓ K and α are constants that depend on the polymer, solvent and temperature.
  - ✓ M is the average molecular weight of the polymer.

  (or) $$\log M = \frac{\log \eta_i - \log K}{\alpha}$$

- The intrinsic viscosity of the polymer can be determined by U-tube viscometer.

  $$\eta_i = \frac{1}{C} \times \left[\frac{\eta}{\eta_o} - 1 \right]$$

  Where,
  - ✓ η_o and η are the viscosity of the solvent and the solution respectively.
  - ✓ C is the concentration of the polymer, usually in wt. %.

7. POLYDISPERSITY INDEX

- The ratio of weight average molecular weight ($\overline{M_w}$) to number average molecular weight ($\overline{M_n}$) is known as polydispersity index or distribution ratio.

  $$\text{Polydispersity index} = \frac{\overline{M_w}}{\overline{M_n}}$$

- The weight average molecular weight ($\overline{M_w}$) is always greater than the number average molecular weight ($\overline{M_n}$) for polydisperse systems.

- For monodisperse system, $\overline{M_w} = \overline{M_n}$.

- The deviation of ratio from the unity is taken as a measure of polydispersity of the polymer sample. Higher value of the ratio indicates greater polydispersity. It means all the molecules of the polymers will not have identical molecular weight (M).

COMPOUNDING OF PLASTICS

Compounding is a process by which specific type of additives are added into the resin in order to incorporate certain properties to plastics.

S. No.	Additives	Examples	Functions
1.	Resins	Thermoplastic resins and Thermosetting resins	They are basic binding materials and hold other constituents together. They are the major part of plastics Thermosetting resins are generally supplied as linear polymers, comparatively low molecular weight. This is because at this stage they are fusible and hence mouldable. The conversion of this form into crosslinked form takes place during moulding itself in presence of catalyst
2.	Plasticizers	Dioctylphthalate (DOP); Adipate; Oleate; Organic phosphates	They improve flow for processing by reducing the intermolecular forces of attraction. Also, they reduce the brittleness of the products
3.	Fillers or Extenders	**Particulate fillers** – Mica, Quartz **Fibrous fillers**–Nylon, Arylics	They increase tensile and compressive strength of the plastics. Also, they reduce shrinkage during setting of the plastics
4.	Lubricants	Waxes, Oils, Soaps	They make the moulding process easier and provide glossy finish to the final product
5.	Stabilizers	Stearates of lead, barium and cadmium	They increase the thermal stability during processing
6.	Pigments	TiO_2–White; Cr_2O_3–Green; Carbon black – Black	They provide pleasing colour to the plastics
7.	Anti-oxidants	Phenylparanaphthylamine ;	They protect against oxidative degradation
8.	Catalysts	H_2O_2, Benzoyl peroxide	They are added only in the case of thermosetting resins in order to accelerate the polymerization of fusible resin into cross-linked infusible form during moulding operation

MOULDING OF PLASTICS: COMPRESSION MOULDING – INJECTION MOULDING - EXTRUSION MOULDING

1. COMPRESSION MOULDING

PRINCIPLE:

The principle of compression moulding is to keep the moulding compound in mould cavity and subjected to heat and pressure simultaneously so that setting and curing of the product takes place in the hot mould itself.

PROCESS:

This technique is used to produce articles from thermosetting materials. The mould used in this technique consists of a hydraulic press, a bottom mould and a top mould. The bottom mould contains a cavity while the top mould has a projection which exactly fits into the cavity. The gap between the projected top mould and the cavity in the bottom one gives the shape of the article.

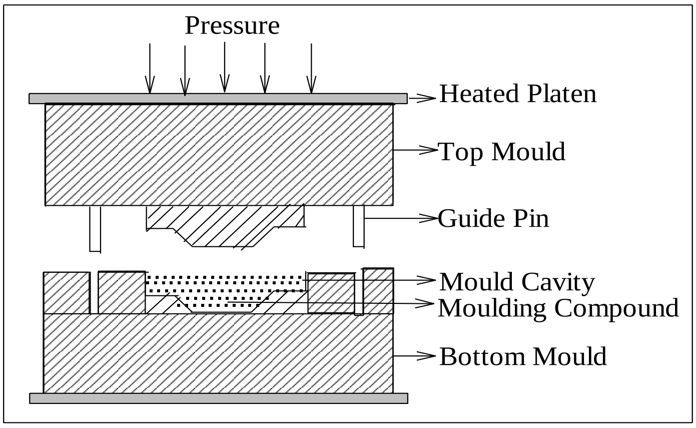


Fig. 5.3: Compression Moulding

The process is carried out by using a hydraulic press with heated plates. The moulding compound is subjected to heat and pressure in a single stroke.

The moulding temperature and pressure can be as high as 200ºC and 70kg/cm^2 respectively. Under the influence of heat, the compacted mass gets cured and hardened. Finally, it is released as a moulded product.

ADVANTAGES:

- ✓ Low mould cost
- ✓ Relatively low pressure (70kg/cm^2) is required

DISADVANTAGES:

- ✓ Low production rate
- ✓ Wastes cannot be reclaimed

APPLICATIONS: Compression moulding is used for the manufacture of electrical plugs and sockets; Gramophone records; Anti-vibration mounting pads.

2. INJECTION MOULDING

PRINCIPLE:

The principle of injection moulding is to inject the molten polymer under the great pressure into a closed, cooled mould where it solidifies to give the product in definite shape.

PROCESS:

This technique is used to produce articles from thermoplastic materials. The system consists of two parts namely a cold movable mould and a stationary horizontal cylinder. The compounded material (charge) is fed into the horizontal cylinder through hopper, where it gets softened by means of electrical heating. Then the molten plastic material is injected under a high pressure of 1500kg/cm^2 into a cold movable mould where it solidifies and takes the shape of the mould.

ADVANTAGES:

- ✓ The process involves high speed production
- ✓ The wastes can be reclaimed and reused

DISADVANTAGES:

- ✓ The capital cost is more
- ✓ Relatively very high pressure (1500kg/cm^2) is required for injecting the charge into the mould

APPLICATIONS: Injection moulding is used for the fabrication of computer parts; Radio and TV cabinets.

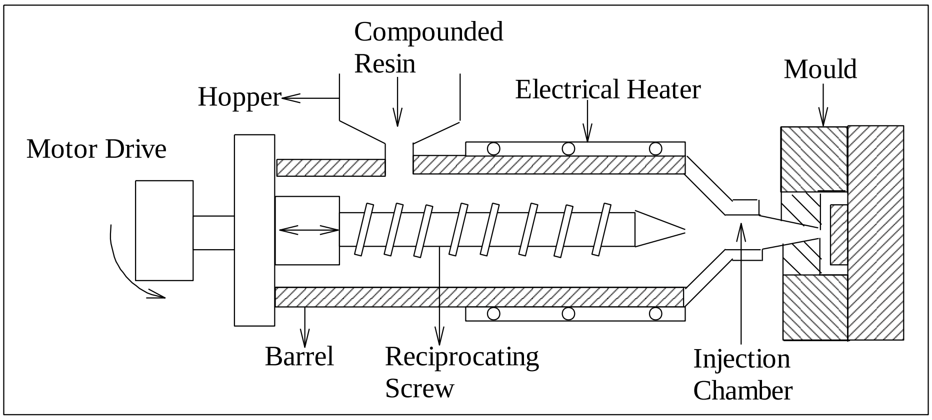


Fig. 5.4: Injection Moulding

3. EXTRUSION MOULDING

PRINCIPLE:

The extrusion process consists of forcing the molten plastic material by means of pressure through a die to give an extruded product of constant cross section.

PROCESS:

The extruder is divided into four zones.

(i) ***Feed zone***: The first zone is known as feed zone in which the predetermined proportion of resin and other additives is added through a hopper into the cylinder. To preheat this mixture, it is conveyed to the next subsequent zone

(ii) ***Compression zone:*** The second zone is known as compression zone in which the mixture is softened by means of electrical heater. Then the softened material is compressed to obtain a uniform and homogeneous mixture and to remove any air bubbles if any present

(iii) ***Metering zone***: Here the compressed mixture is forced at a controlled rate with constant temperature and pressure into a die by means of screw arrangement

(iv) ***Die zone***: The fourth zone is known as die zone which produces the product of uniform cross section. The finished product that extrudes out is cooled by atmospheric exposure or by spraying water. A long conveyor carries away continuously the cooled product.

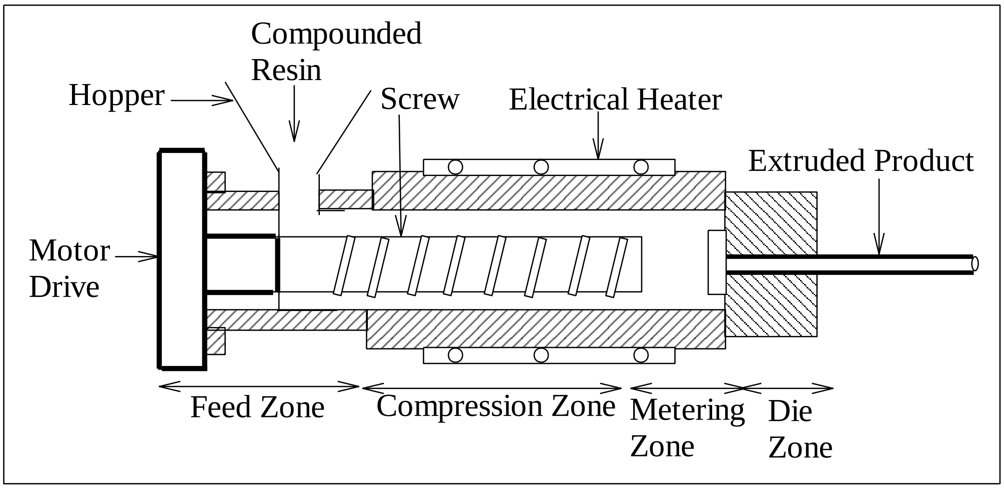


Fig. 5.5: Extrusion Moulding

APPLICATIONS: This method is mainly used for continuous moulding of thermoplastic material into articles of uniform cross section like tubes, rods and pipes.

Table 5.7: Comparison of Compression Moulding and Injection Moulding

S.No.	Compression moulding	Injection moulding
1	Compression moulding is used for fabricating mainly thermosetting materials	Injection moulding is used for fabricating thermoplastic materials
2	It involves low production rate	It involves high speed production
3	The process is associated with low mould cost	Cost of the equipment is relatively high
4	Wastes produced in the process cannot be reclaimed	The process involves low loss of materials
5	Relatively low pressure is used (70 kg/cm^2)	High pressure is used (1500 kg/cm^2)

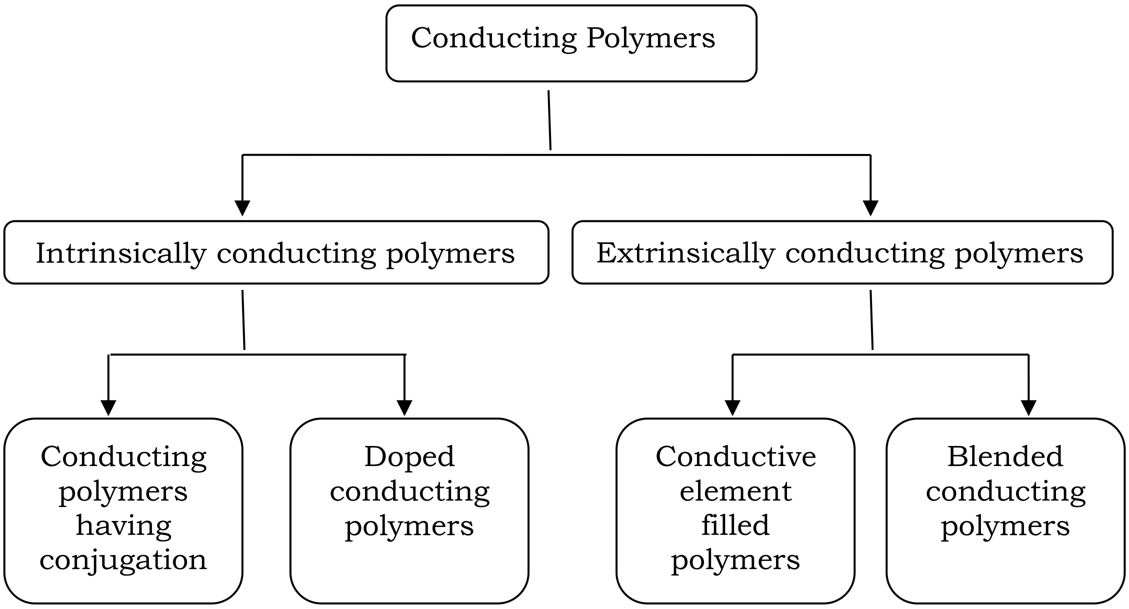
INTRODUCTION TO CONDUCTING POLYMERS

Definition: Conducting polymers are poly conjugated polymers, which are able to conduct electricity because of their conjugated π-bonding system.

Examples: Polyacetylene; Polyaniline; Polythiophene, Polypyrrole

CLASSIFICATION OF CONDUCTING POLYMERS

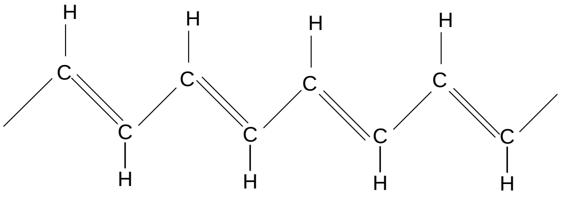
Conducting polymers are classified into the following types:



1. Intrinsically Conducting Polymers

(i) Conjugated conducting polymers: Conjugated conducting polymers have a frame work of alternating single and double bonds.

Example: Trans-Polyacetylene.



(ii) Doped conducting polymers: The conductivities of conjugated polymers can be improved by the process known as doping. Doping of conjugated polymers involves either partial oxidation or partial reduction. Dopants like I_2, Br_2 (X) etc. can be added to produce p-type conductivity. Dopants like Li, Na (M) etc. can be added to produce n-type conductivity.

2. Extrinsically Conducting Polymers

(i) Conductive element filled polymers: A conductive element filled polymer is obtained by blending an insulating polymer with conductive elements like carbon black, metallic oxides etc. in order to make it conducting. The minimum concentration of conductive element required to make an insulating polymer conducting is known as percolation threshold.

(ii) Blended conducting polymers: A blended conducting polymer is obtained by blending a conventional polymer with a suitable conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties.

DOPING OF CONDUCTING POLYMERS

Doping of conjugated polymers involves partial oxidation (removal of electrons from the π-bonding system of the polymer backbone) or partial reduction (addition of electrons to π-bonding system of the polymer backbone).

Examples of p-type dopants: I_2, Cl_2, AsF_5, BF_6 etc.

Examples of n-type dopants: Na, K, Li, Tetra butyl ammonium etc.

FACTORS INFLUENCING THE CONDUCTIVITY OF POLYMERS

The conductivity of organic polymers is influenced by various factors, listed below.

(i) ***Conjugation length of the polymer chain**:* The conductivity of a conducting polymer increases with increase in the chain length or conjugation.

(ii) ***Doping level**:* The conductivity of a conducting polymer increases with increase in doping level, but after some time, it becomes saturated.

(iii) ***Temperature**:* The conductivity of conducting polymers increase with increase in temperature. At some high temperature, conductivity becomes constant.

(iv) ***Frequency of current**:* The conductivity of conducting polymers also depends on the frequency of current, because doping is the transport mechanism of these materials.

APPLICATIONS OF CONDUCTING POLYMERS

1. Conducting polymer like polyaniline is used in rechargeable batteries and is capable of producing current density up to $50mA/cm^2$.

2. Conducting polymers are also used for making analytical sensors for pH, O_2, NO_x, SO_2, NH_3 and glucose.

3. The membranes made of conducting polymers show selective permeability for ions and gases hence they are used for control release of drug.

4. Conducting polymers are used making electronic displays and optical fibres.

5. Conducting polymers are used in light emitting diodes, information storage devices, optical computers etc.

6. Conducting polymers are used as conducting tracks on printed circuit boards.

7. Conducting polymers are also used in fuel cells as electro-catalytic materials.

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