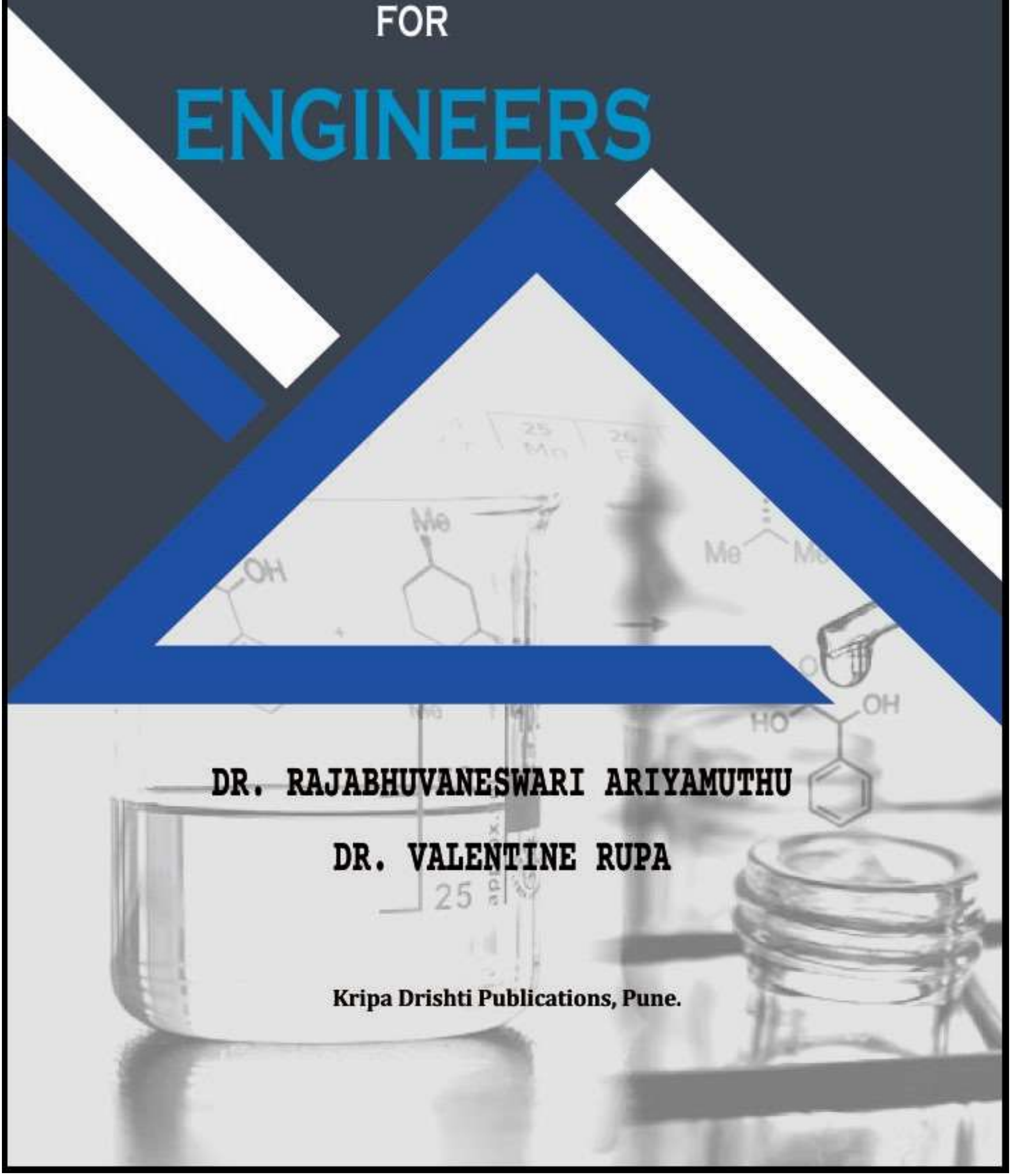
CHEMISTRY
FOR
ENGINEERS



DR. RAJABHUVANESWARI ARIYAMUTHU

DR. VALENTINE RUPA

Kripa Drishti Publications, Pune.

CHEMISTRY
FOR
ENGINEERS

Dr. Rajabhuvaneswari Ariyamuthu

Dr. Valentine Rupa

Kripa-Drishti Publications, Pune.

Book Title: **Chemistry for Engineers**

Authors by: **Dr. Rajabhuvaneswari Ariyamuthu,**
Dr. Valentine Rupa

1st Edition

ISBN: **978-93-90847-88-4**

Published: **Jan 2022**

Publisher:

Kripa-Drishti Publications
A/ 503, Poorva Height, SNO 148/1A/1/1A,
Sus Road, Pashan- 411021, Pune, Maharashtra, India.
Mob: +91-8007068686
Email: editor@kdpublications.in
Web: https://www.kdpublications.in

PREFACE

We are happy to present the first edition of Chemistry for engineers. This book is an introduction to fundamental concepts and the applications of chemistry for engineers.

This book comprises of five units which covers the entire engineering chemistry syllabus. Topics like Water treatment, surface chemistry and catalysis, Alloys and phase rule, Fuels and combustion and Energy storage Devices have been written in a simple manner. All the topics in the book are covered comprehensively and explained with illustrations. The simple language used throughout the book will help the students in grasping the concept of the subject easily. Figures and tables are incorporated where ever necessary to make the concept clearer.

Authors hope that this book will be useful for both students and teachers. Suggestions for improvement will be gratefully acknowledged.

Acknowledgement

We owe our heartfelt thanks to GOD almighty, for his grace to complete this book successfully. We thank our parents for their love and support which helped us to complete this work in time, for whom we remain the primary source of inspiration.

INDEX

Chapter 1

Water and Its Treatment

1.1 Hardness:

a. Definition:

If the water produces lather with soap, it is soft water. If the water does not produce lather with soap, it is called as hard water. The property is known as hardness. Hard water will produce a scummy white precipitate. The hardness is due to Ca^{2+}, Mg^{2+} and SO 2- 4, Cl-, CO_2-, H_3 CO - ion3s. And their salts.

1.1.1 Test for Hardness:

- Eriochrome Black – T indicator gives red color in hard water.
- With soap, hard water gives a scummy precipitate.

$2C_{17}H_{35}COONa + CaCl_2$ ❼ $(C_{17}H_{35}COO)\ {}_2Ca + {}_2NaCl$

(Sodium stearate) (Scummy precipitate)

1.1.2 Types of Hardness:

Temporary Carbonate hardness: The hardness due to carbonates and bicarbonates can be removed by simple boiling. So, they are known as temporary or carbonate or alkaline hardness.

$Ca\ (HCO_3)_2$ (On heating) ❼ $CaCO_3 + H_2O + CO_2$

Sulphate cannotbe removed by simple boiling. They need special methods like lime soda process and zeolite process.Non-alkaline hardness.

$CaCl_2 + Na_2CO_3$ ❼ $CaCO_3 + 2NaCl$ (Lime soda process) $CaSO_4$

$+ Na_2Ze$ (Zeolite) ❼ $CaZe + Na_2SO_4$ (Zeolite process)

1.1.3 Units of Hardness:

- ppm
- mg/L
- Degree Clarkes
- Degree French

1 ppm – 1 part by weight of CaCO3 equivalent hardness/106 parts of water 1 mg/L – 1mg of $CaCO_3$ / 1 Lr of water Clarkes Degree - ^{0}Cl-1 part of $CaCO_3$ equivalent hardness /70,000 parts of water1 Degree French – ^{0}F - 1 part of CaCO3 equivalent hardness/10^5 parts of water.

Therefore, 1ppm = 1mg/L = 0.07 ^{0}Cl = 0.1^{0}F

1.1.4 $CaCO_3$ Equivalence:

Hardness is expressed in $CaCO_3$ equivalence. Because,

- It has the highest molecular weight of 100 and the lowest equivalent weight of 50, making it the most insoluble and prone to precipitation. Because these are whole integers, they are relatively simple to utilize in calculations.

1.1.5 Estimation of Hardness by EDTA Method:

A. Aim:

To estimate the amount of hardness present in the given water sample.

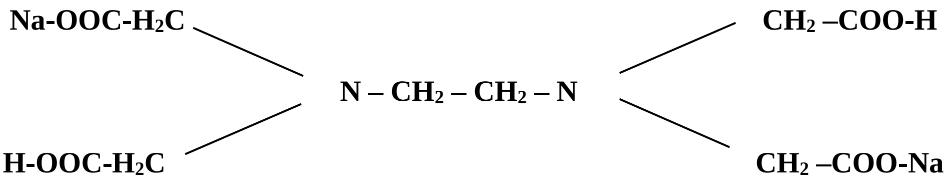
B. Chemicals required:

- Standard hard water – 1 g $CaCO_3$ + dil. HCl – made up to 1 L.
- EDTA solution – 4 g of EDTA sodium salt / 1 L of water
- EBT Indicator – 0.5 g EBT / 100 ml alcohol
- Ammonia buffer - 67.5 g Ammonium chloride +570ml Ammonia-- made up to 1L

C. Principle:

EDTA stands for Ethylene Diamine Tetra Acetic acid. As it is insoluble in water, we use itsdisodium salt.

Structure of EDTA:



By nature, Eriochrome Black T indicator is blue in colour. When EBT indicator is added to watersample, it forms a wine red colored unstable Ca-Mg-EBT complex. This reaction is carried out under a basic P^H of 8- 10 using ammonia buffer.

Ca^{2+} / Mg^{2+} in water + EBT -❼ [Ca / Mg –EBT] unstable wine red complex

When EDTA is titrated against the complex, EDTA replaces all the EBT and forms a stable Ca /Mg –EDTA complex. The liberated EBT indicates the end point as steel blue.

[Ca / Mg –EBT] + EDTA ❼ [Ca /Mg –EDTA] + EBT

(Wine red/unstable) (Stable) (Steel blue)

So, the end point is the colour change from wine red to steel blue.

D. Short Procedure:

Sr. No.	**Content**	**Titration-I Standardization of EDTA**	**Titration-II Total Hardness**	**Titration-III permanent Hardness**
1	Burette	EDTA	Standard EDTA	Standard EDTA
2	Pipette (20 ml)	Std. Hard water	Sample water	Boiled water
3	Additional solution	10ml of NH_3 buffer	10ml of NH_3buffer	10ml of NH_3 buffer
4	Indicator	EBT	EBT	EBT
5	Endpoint	Wine red to steel blue	Wine red to steelblue	Wine red to steelblue
6	Volume	V_1	V_2	V_3

E. Calculation:

Step1 – Standardization of EDTA

1 ml of Std. Hard water = 1 mg of $CaCO_3$ (Given)

So, 20 ml of Std. Hard water = 20 mg of $CaCO_3$

V_1 ml of EDTA is required for = 20 mg of $CaCO_3$

Therefore,

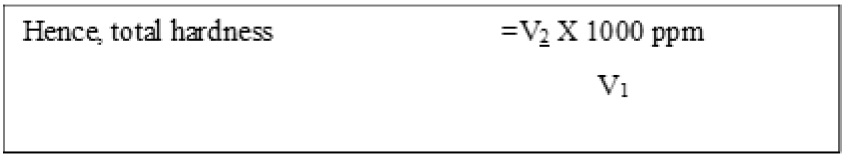
$$\boxed{\text{1ml of EDTA} = 20 / V_1 \text{ mg of } CaCO_3}$$

Step 2: Finding Total hardness:

20ml of sample water required = V_2 ml of EDTA

= V_2 X 20 mg of $CaCO_3$

V_1



Hence, total hardness =V_2 X 1000 ppm

V_1

Therefore, 1000ml of sample requires = V_2 X 20 X 1000 mg of $CaCO_3$

V_1 20

Step 3: Finding Permanent hardness:

20ml of boiled water required = V_3 ml of EDTA

Hence permanent hardness =V_3 X 1000 ppmV_1

V_1

V_3 X 20 mg of $CaCO_3$

V_1

Therefore, 1000ml of boiled sample requires = V_3 X 20 X 1000 mg of $CaCO_3$

V_1 20

Step 4: Temporary hardness = Total hardness – permanent hardness

1.2 Boiler Troubles:

1.2.1 Definition:

A "boiler" is a device that produces steam in industries. To make steam, water is fed into the boiler and heated. "Boiler feed water" is the water that is fed into the boiler.

1.2.2 Requirements for Boiler Water:

Sr. No.	Requirements for Boiler Water	If Not, it will Cause
1	Salts that cause hardness aren't present.	Sludge and scale
2	Silica is oil and grease-free.	Foaming

Sr. No.	Requirements for Boiler Water	If Not, it will Cause
3	dissolved salts, suspended contaminants, and alkalis-free	Caustic embrittlement
4	Suspended salts, free of dissolved gases	Boiler corrosion

If untreated water is injected directly into the boiler, it can result in sludge, scale, priming, foaming, caustic embrittlement, and boiler corrosion, all of which are known as boiler problems.

Sludge and scale:

A. Definition:

If the water contains hardness-causing salts such as $MgSO_4$, MgC_{l2}, $CaSO_4$, $Ca (HCO_3)_2$, the salts precipitate as the water evaporates.

Sludge is a loose, slimy, non-adherent precipitate that forms when they combine.

Scale is a hard, thick, adhering precipitate that forms when they come together.

B. Reasons for sludge and scale:

Sludge: $MgCl_2$, $MgSO_4$, $CaCl_2$ Scale: $CaCO_3$,

$MgCO_3$, $Ca (HCO_3)_2$

C. Disadvantages of scales and sludges:

- Wastage of fuel:

The heat conductivity of scales is low. As a result, heat transfer from the boiler to the interior water may be insufficient. Overheating is required to deliver a constant supply of heat to water, which results in fuel waste. The wastage of fuel depends on the thickness and nature of the scale which is shown in the table.

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel (%)	10	15	50	80	150

- **Decrease in efficiency:**

Choking can occur when scaling deposits in the valves and condensers of boilers and heat exchangers. The boiler and heat exchangers' efficiency suffers as a result.

- **Boiler explosion:**

Thick scales can shatter due to overheating, resulting in the unexpected contact of high-heated boiler material with water. This results in the creation of a significant amount of steam and high pressure. This results in an explosion.

D. Examples of Scale deposits:

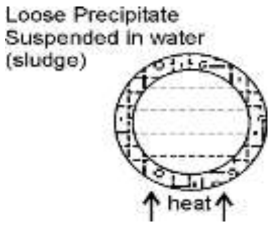
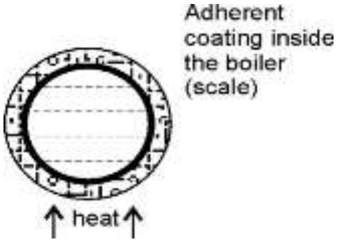
Sr. No.	Name of the deposit	Properties
1	$CaCO_3$ Deposit	It is formed due to decomposition of calcium bicarbonate. It has lower solubility and forms tenacious scale. The liberated CO_2 produces carbonic acid and produces boiler corrosion.
2	$CaSO_4$ deposit	At high temperature and high pressure boilers, It forms harder and denserdeposit.
3	$Mg(OH)_2$ deposit	It is formed due to decomposition of magnesium bicarbonate. It reacts withwater and liberates corrosive HCl.
4	SiO_2 deposit	It forms a hard, porcelain coating on the boiler surface.
5	Fe deposit	It causes dark colored magnetic deposits.

Prevention of Scales:

- Scales can be removed with a scraper, wire brush, or mechanical scrubber at an early stage.
- Brittle scales are removed using thermal shocks.
- Using external treatments (e.g., ion exchange demineralization, zeolite softening)
- Internal treatment with boiler chemicals (e.g. carbonate, phosphate, Calgon, EDTA)
- Through the use of acid

E. Differences between sludge and scale:

Sr. No.	Sludge	Scale
1	A non-adherent, loose deposit on the inside walls of the boiler.	Precipitate that is hard, thick, and sticky.
2	$MgSO_4$, $MgCl_2$, and other salts	$CaSO_4$, $Ca(HCO_3)_2$, and other salts
3	They reduce boiler efficiency to a lesser extent due to weak conductivity, producing pipeline clogging.	They limit boiler efficiency to the highest extent possible due to inadequate conductivity, resulting in reduced fuel economy, faulty boiling, boiler explosion, and so on

Sr. No.	Sludge	Scale
4	It can be avoided by replacing concentrated hard water with fresh water regularly. The "blowdown" approach is the name for this procedure.	It can be prevented by special methods like Special procedures can be used to prevent it, such as • External ion exchange treatment, • Internal carbonate, phosphate, and Calgon conditioning • Methods of mechanical hard scrubbing • Thermal jolts
5	Diagram: 	

1.3 External Treatment Methods:

External treatment is the process of removing pollutants and salts from boiler feed water before it is sent to the boiler.

1.3.1 Zeolite (Permutit) Softening Process:

a. Setup:

- Zeolite is a naturally occurring hydrated sodium alumino silicate silicate.
- These zeolites are made up of green sand. They have a non-porous surface.
- The general formula for zeolites is $xSiO_2$. yH_2O ($x = 2$ to 10; $y = 2$ to 6) Na_2O Al_2O_3
- Permutit refers to porous and gel-structured synthetic zeolites.
- Water softening is done with these zeolites and permutit.
- Na_2Ze is the symbol for synthetic zeolite.

A. Principle:

- These zeolites only hold the sodium ions loosely. Calcium and magnesium ions found in the water rapidly replace them. When hard water passes through a cylinder containing a bed of sodium zeolite, the sodium ion exchanges with the Ca2+ and Mg2+ ions in the water to form Calcium and Magnesium zeolite.
- Zeolite softeners may be of pressure type or gravity type.

B. Reactions:

$CaSO_4 + Na_2Ze$ ❼ $CaZe + Na_2SO_4$

$MgSO_4 + Na_2Ze$ ❼ $MgZe + Na_2SO_4$

$CaCl_2 + Na_2Ze$ ❼ $CaZe + 2\ NaCl$

$MgCl_2 + Na_2Ze$ ❼ $MgZe + 2\ NaCl$

The resulting water is fortified with a high concentration of sodium salts that do not induce hardness. However, it is not suitable for use in a boiler.

Regeneration:

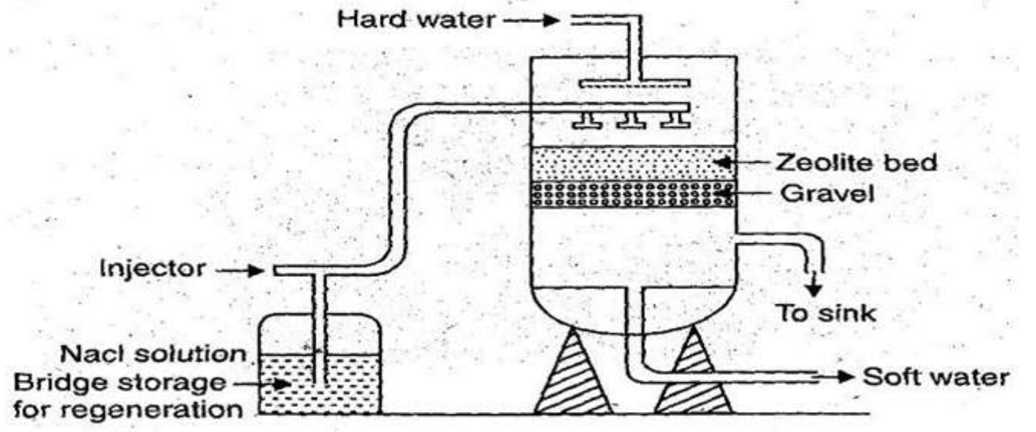
- After a long period of use, all of the zeolite sodium ions are depleted.
- No sodium ions will be present to exchange the calcium and magnesium ions. As a result, they must be regenerated. The exhausted zeolite is regenerated by soaking it in a 10% NaCl solution.

C. Regeneration reaction:

The regeneration step comprises of a) backwashing b) salting c) rinsing before reuse.

$CaZe + 2\ NaCl$ ❼ $Na_2Ze + CaCl_2$

$MgZe + 2\ NaCl$ ❼ $Na_2Ze + MgCl_2$



Zeolite softener

D. Advantages of zeolite process:

- The hardness of the output water will be between 1 and 2 ppm.
- The process is inexpensive because the zeolite may be renewed.
- It's simple to use.
- This configuration just requires a little amount of room.
- During this process, no sludge is generated.

E. Disadvantages of zeolite process:

- Turbid water can't be treated since it clogs the zeolite bed's pores.
- Acidic water cannot be handled because it degrades the zeolite structure.
- Water containing Fe and Mn cannot be treated due to the difficulty of regeneration.
- Because brackish water contains Na+ ions, it cannot be treated. As a result, the ion exchange reaction will not take place.
- Boiler corrosion and caustic embrittlement can occur when softened water contains more dissolved sodium salts.

1.3.2 Ion Exchange Method - (Demineralization):

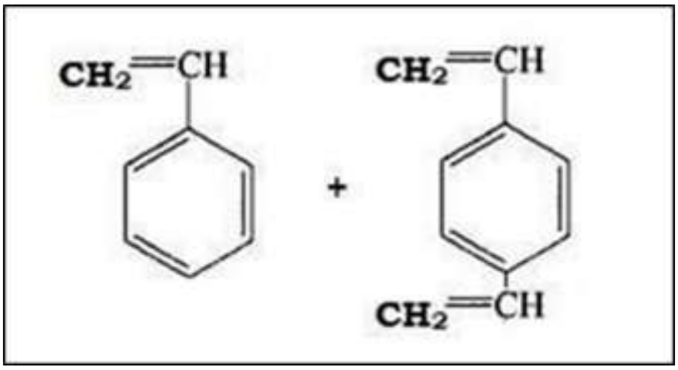
A. Working:

All cations and anions are eliminated here. It employs two cation exchange and anion exchange cylinders, both of which are filled with resins.

Resins are organic polymers with long chains that are insoluble and cross-linked. There are two kinds.

- RH_2 (e.g., sulfonated coals, RSO_3H) cation exchange resins
- Resins for ion exchange. Amines $R\text{-}NH_2$ (e.g., urea-formaldehyde)

$R(OH)_2$ (e.g., urea-formaldehyde) $R(OH)_2$ (e.g., urea-formaldehyde Styrene and divinylbenzene are copolymerized to make the resins.



When the resulting polymer is acid-treated, it transforms into cation exchange resin. An anion exchange resin is formed when the polymer is treated with bases and ammonium chloride.

Water is poured into the cylinder –I, which contains RH_2 Resins that replace all cations.

$RH_2 + CaCl_2$ ❼ $R\,Ca + 2\,HCl$

$R'(OH)_2 + 2\,HCl$ ❼ $R'Cl_2 + 2H_2O$

The cation-free water is pumped into cylinder II, which replaces all of the anions. As a result, the resulting water is free of all ions.

B. Regeneration:

When all the resins are consumed after a lengthy period of use, there will be no H+ or OH – ions to exchange the undesirable ions. As a result, they must be regenerated. HCl regenerates cation resins, while NaOH regenerates anion resins.

$R\,Ca + 2\,HCl$ ❼ $RH_2 + CaCl_2$

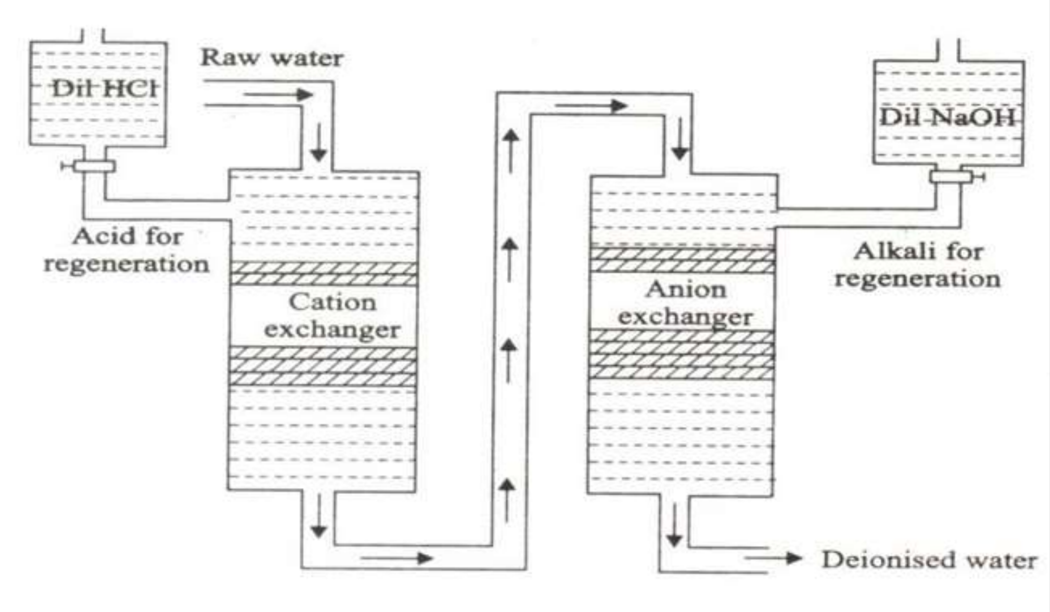
$R'Cl_2 + 2NaOH$ ❼ $R'(OH)_2 + 2NaCl$

C. Advantages of Ion exchange method:

- It can also be utilized in high-pressure boilers.
- It can handle both acidic and alkaline water.
- We can obtain pure water with a hardness of only 2 ppm.

D. Ion exchange method drawbacks:

- Expensive
- Cannot be used for turbid water because Fe and Mn form complexes with resins.
- Cannot be used for turbid water because they clog the resins.



E. Differences between soft water and demineralized water.

<table>
<tr><th>Sr. No.</th><th colspan="4">Soft water</th><th>Demineralized water</th></tr>
<tr><td>1</td><td colspan="4">It lacks the hardness-producing calcium and magnesium ions, but it may contain other ions such as K+, Na+, Cl-, and others.</td><td>Demineralized water is devoid of all ions, including those that cause hardness.</td></tr>
<tr><td>2</td><td>Softening involves hardness-causing ions.</td><td>removal</td><td>2</td><td>Softening involves hardness-causing ions.</td><td>Removal</td></tr>
</table>

Differences between Zeolite and ion exchange process:

Sr. No.	Zeolite Process	Ion Exchange Process
1	It solely exchanges cations.	It is a cation and anion exchanger.
2	Zeolite is used to fill the cylinder. $xSiO_2.yH_2O$. Na_2O. Al_2O_3. $xSiO_2.yH_2O$	Cation exchange resin (RH_2) is used in the cylinders. For regeneration, anion exchange resins such as $R(OH)_2$ HCl and NaOH are utilized.
3	For regeneration, NaCl is utilized.	Demineralization is the process of removing all ions from water.

Sr. No.	Zeolite Process	Ion Exchange Process
4	Only hardness-causing ions are removed during softening.	There are no dissolved salts in the treated water. They might not cause any issues with the boiler.
5	The treated water includes a high concentration of dissolved sodium salts, causing caustic embrittlement in boilers.	The setup and operational costs are both quite substantial.
6.	The costs of setup and operation are both minimal.	The hardness could be as high as 2 ppm.
7	The hardness could be as high as 10 ppm.	Acidic water can be handled.
8	Acidic water cannot be handled because the zeolite decomposes.	It is a cation and anion exchanger.

1.4 Internal Treatment Methods:

The residual salts that are not removed by external methods can be removed by adding some chemicals directly into the boiler water. These chemicals are known as *Boiler compounds*. This method is known as Internal treatment (or) sequesterisation. E.g., Carbonate conditioning, Aluminate conditioning Phosphate conditioning, Calgon conditioning, colloidal conditioning, EDTA conditioning in general, internal treatment methods are followed by blow down operation.

1.4.1 Carbonate Conditioning:

For low-pressure boilers, carbonate conditioning is utilized. Here, salts like CaSO4 are transformed to $CaCO_3$, which is easily removed. However, surplus Na_2CO_3 in high-pressure boilers is hydrolyzed and transformed to NaOH. Caustic embrittlement and boiler corrosion are the results. As a result, it is less preferred.

$CaSO_4 + Na_2CO_3$ ❼ $CaCO_3 + Na_2SO_4$

1.4.2 Phosphate Conditioning:

For high-pressure boilers, phosphate conditioning is utilized. There is no risk of CO2 liberation, caustic embrittlement, or boiler damage, hence it is preferable to carbonate conditioning.

A pH range of 9.5–10.5 is advised for best outcomes.

$3CaSO_4 + 2\ Na_3PO_4$ ❼ $Ca_3\ (PO_4)_2 + 3\ Na_2SO_4$

Three types of Phosphate salts are used:

Sr. No.	**Salt**	**Name**	**Used for Treating**
1	Na_3PO_4	Trisodium Phosphate	Highly acidic water
2	Na_2HPO_4	Di sodium hydrogen Phosphate	Slightly acidic water
3	NaH_2PO_4	Sodium dihydrogen phosphate	Highly alkaline water

1.4.3 Calgon Conditioning:

Calgon is the brand name for sodium hexametaphosphate, also known as $Na_2 [Na_4 (PO_3)_6]$.

- It creates a soluble compound with calcium ions.
- As a result, sludge disposal is not an issue.
- It's appropriate for both high and low-pressure boiler.

$2CaSO_4 + Na_2 [Na_4 (PO_3)_6]$ ❼ $Na_2 [Ca_2 (PO_3)_6] + 2 Na_2SO_4$

1.4.4 Aluminate Conditioning by Sodium Aluminate:

Sodium aluminate ($NaAlO_2$) gets hydrolyzed inside the boiler giving aluminium hydroxide ($Al (OH)_3$) and sodium hydroxide (NaOH).

$NaAlO_2 + 2H_2O$ ❼ $Al (OH)_3 + NaOH$

The sodium hydroxide formed would react with Mg ions forming $Mg(OH)_2$.

$MgCl_2 + 2NaOH$ ❼ $Mg (OH)_2 + 2NaCl$

Suspended particles such as oil, silica, and other colloidal contaminants were captured by the flocculant precipitates of $Mg(OH)_2$ and $Al(OH)_3$.

Blow-down operations might be used to remove the loose precipitate.

1.4.5 Colloidal Conditioning:

Colloidal conditioning is used in low-pressure boilers to prevent scale development by coating scale-forming precipitates with organic compounds such as kerosene, tannin, agar-agar, and so on. This turns the scale into sludge, which is then removed via blowdown operations.

1.4.6 EDTA Complex Metric Conditioning:

i) At basic PH, EDTA is added to boiler water.

ii) EDTA binds the scale forming cations to form soluble complex. Thus scale formation is prevented.

$[\mathrm{Ca}^{2}+ / \mathrm{Mg}^{2}+] + \mathrm{EDTA}$ ❼ $[\mathrm{Ca} / \mathrm{Mg} – \mathrm{EDTA}]$

1.5 Desalination of Brackish Water by Reverse Osmosis Method:

Desalination is the process of removing common salt ($NaCl$) from water. Water can be divided into three categories based on the number of dissolved solids in it. Sea and brackish water are converted to freshwater via reverse osmosis.

Sr. No	Type of water	Dissolved Solids
1	Fresh water	Less than 1000 ppm
2	Brackish water	1000 ppm – 35,000 ppm
3	Sea water	More than 35,000 ppm

1.5.1 Osmosis:

When two different concentrated solutions are separated by a semi permeable membrane, due to osmotic pressure, low concentrated solvent flows to higher one. This is known as osmosis.

1.5.2 Reverse Osmosis:

When we provide excess and opposing Hydrostatic pressure of 15–40 kg/ cm^2 to counteract the osmotic pressure, however, the more concentrated solvent flows to the lower one. Reverse osmosis is the term for this process. Only water passes over the membrane during the RO process, which prevents salt migration. As a result, this procedure is also known as "Super filtering." Polymethacrylate, cellulose acetate, and cellulose butyrate make up the membrane.

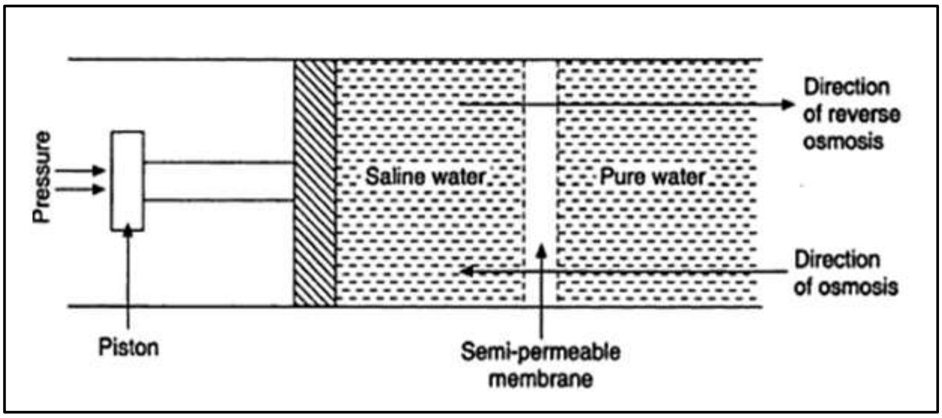
A. Advantages of Reverse Osmosis:

- The life time of membrane is quite high. (2- 3 years)
- Removes ionic, non-ionic and colloidal silica impurities, which cannot be removed by demineralization method.
- Low capital cost.
- Simple operational procedure.

- The membrane can be replaced within a few minutes, thereby providing uninterrupted water supply.
- This method is also used to remove bio-molecules, proteins, sugar etc.

B. Disadvantages:

- Periodical cleaning of membrane is needed.
- Pretreatment for bacterial removal is needed.

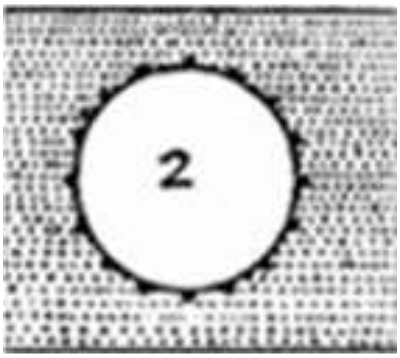


Chapter 2

Surface Chemistry and Catalysis

2.1 Adsorption:

It is the process of concentration of gas/liquid on the surface of solid/liquid due to weak or strong forces of attraction. (e.g.) Adsorption of H_2 on Nickel.

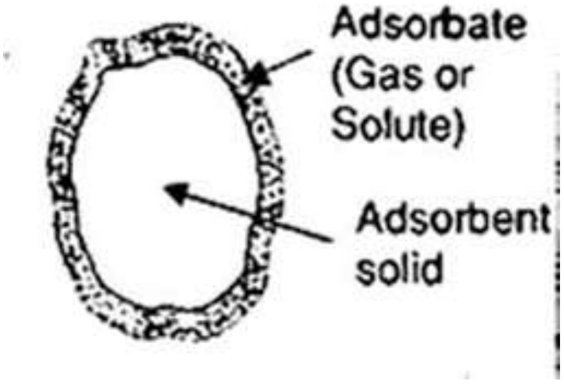


a. Adsorbent:

The surface on which adsorption takes place is known adsorbent. (e.g.) Nickel, Charcoal.

b. Adsorbate:

Adsorbate is the substance that is adsorbed on the adsorbent. (e.g.) H_2 is a gas



2.1.1 Absorption:

Absorption is a phenomenon in which gas/liquid steadily penetrates throughout the solid/body. Liquid's Ink absorption on the surface of chalk, for example.

2.1.2 Sorption:

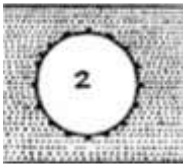
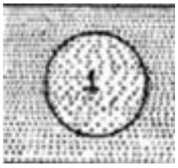
It is the process in which both adsorption and absorption take place simultaneously.

E.g., NH_3 in water in presence of charcoal.

2.1.3 Desorption:

It is reverse process of adsorption. i.e., removal of adsorbate from the adsorbent surface.

A. Differences between adsorption and absorption:

Sr. No.	Adsorption	Absorption
1	Surface phenomenon	a mass phenomenon
2	It is the concentration of gas/liquidon adsorbent	It is the concentration of gas/liquid throughout the body of adsorbent
3	Fast process	Slow process
4	Equilibrium is easily achieved in a quick process	It takes some time
5	It depends upon the surface of adsorbent	No such effect
6	E.g., Adsorption of water vapour onsilica gel	Absorption of water vapour by CO_2
7		

B. Types of Adsorption

- **Physical adsorption/ Phys sorption:**

'Physisorption' is a process in which a gas, solid, or liquid is retained to a solid surface by weak van der walls forces. (e.g.) On charcoal, H_2

- **Chemical adsorption/Chemisorption:**

Chemisorption is a process in which a gas, solid, or liquid is retained to a solid surface by strong chemical covalent interactions. H_2 on nickel, for example.

- **Differences between the Physical adsorption and Chemical adsorption:**

Sr. No.	Physisorption	Chemisorption
1	Vander Waal's forces are weak, which causes adsorption.	Because of the strong covalent bonds.
2	Adsorption is a multilayered process.	Adsorption is a monolayer process.
3	Adsorption can be reversed completely.	Adsorption is a process that cannot be reversed.
4	The equilibrium is quickly established.	It takes time to reach a state of equilibrium.
5	There is no surface compound generated.	The complex formation on the surface is formed.
6	The activation energy (Ea) is minimal.	The activation energy (Ea) is very high.
7	Adsorption heat (H) is minimal (20-40kcal/mol).	Adsorption heat (H) is high (200-400kcal/mol).
8	Adsorption reduces as temperature rises.	When the temperature rises, adsorption rises, then fall.
9	As pressure rises, so does adsorption.	It is pressure-independent.
10	Its nature is non-specific and non-selective.	It is specific and selective.
11	e.g., - H_2 on charcoal.	e.g., H_2 on nickel.

C. Factors influencing the adsorption of gases on solid:

Adsorption of gases on solids: (Occultation)

(i) Nature of gases:

Because of I) critical temperature (ii) Vander Waal's forces, easily liquefiable gases like HCl and NH_3 adsorbed more readily than permanent gases like N_2, H_2, O_2, and so on. Example,

Gas	**SO_2**	**NH_3**	**CO_2**	**N_2**	**H_2**
CT (K)	430	406	304	120	33
Amount of gas Adsorbed (mL)	380	180	48	8	4.5

(ii) Nature and surface area of adsorbent:

The larger the pores on the adsorbent, the higher the surface area, the stronger the adsorption. Charcoal and Silica gel, for example.

(iii) Heats (or) Enthalpy of adsorption:

When 1 g mole of a gas is adsorbed on a solid surface, energy is released. It is small in physical adsorption due to weak Vander Waal's forces, but it is substantial in chemical adsorption due to the creation of chemical bonds.

(iv) Reversible character:

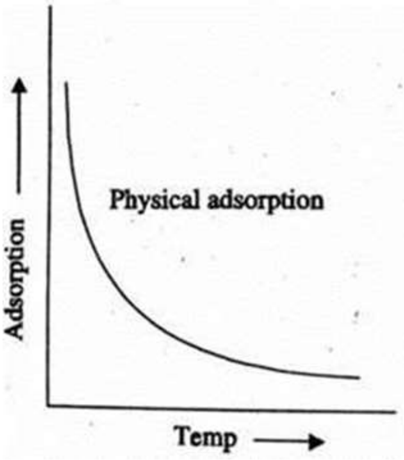
The process of physical adsorption is reversible. Under the right temperature and pressure, the gas adsorbed on a solid can be removed. Because a surface compound is created, chemical adsorption is not reversible.

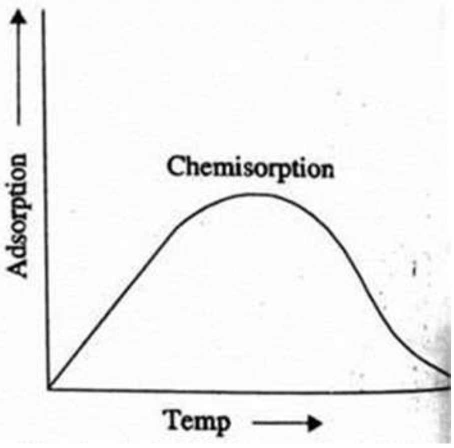
(v) Effect of pressure:

Physical adsorption happens quickly at low pressures and accelerates as pressure rises. Chemical adsorption: Because chemisorption's are pressure-independent, there is no such impact.

(vi) Effect of temperature:

Physical adsorption happens quickly at low temperatures and slows down as the temperature rises. Chemical adsorption: As the temperature rises, it climbs, then declines.





(vii) Thickness of adsorbed layer of gas:

Physisorption produces multilayer adsorption. Chemisorption involves monolayer adsorption.

(viii) Effect of activation of adsorbent:

The surface increases as a result of activation.

(ix) Creation of rough surface:

- By rubbing the solid adsorbent mechanically,
- By subjecting to some chemical reactions on the solid adsorbent.

(x) Increasing effective area of the surface:

- By sub dividing the solid adsorbent into fine particles.
- By heating of solid adsorbent in superheated steam now its pores are opened and adsorption increases.

D. Adsorption of Solute from Solution:

An adsorbent adsorbs substances (solutes) from the solution in two ways.

- Solid substances adsorb dissolves substances from solutions.
- E.g. Activated charcoal adsorbs coloring matter present in sugar solution.
- An adsorbent also adsorbs certain substance from the solution in preference to other substances.
  E.g. Charcoal adsorbs non-electrolytes more readily than electrolytes from a solution.

E. Factors Influencing Adsorption of Solutes from Solutions:

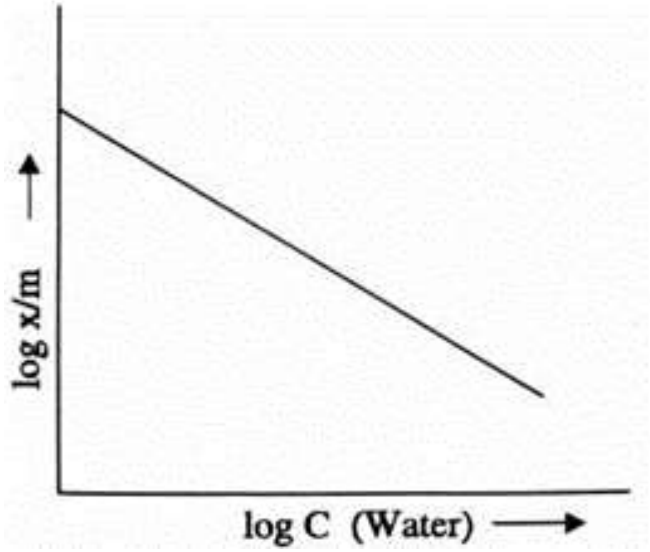
- **Effect of Concentration:**

Temperature and concentration affect the amount of solute adsorption from a solution. The Freundlich adsorption isotherm explains the effect of concentration,

$$\frac{x}{m} = KC1/\mathrm{n}$$

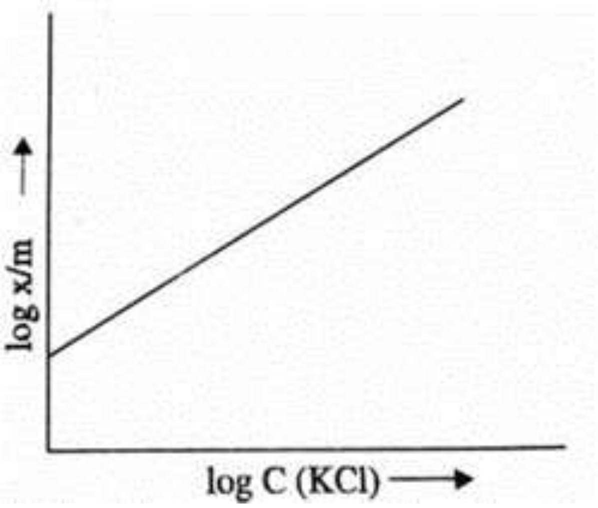
- **Negative adsorption:**

The concentration of the solution rises due to the adsorption of the solvent from the solution.



- **Positive adsorption:**

The concentration of the solution decreases due to the adsorption of the solute from the solution.



- **The area of adsorbent**

The total amount of solute adsorbed increases as the surface area of the adsorbent grows.

- **The nature of the solute adsorbed**

When the molecular weight of the solute is high, the amount of adsorption is usually greater.

F. Adsorption Isotherm:

It may be mathematical relationship or of graphical relation between adsorption and pressure at constant temperature is known as adsorption isotherm.

$$\frac{S}{N} = KP^{1/n} \text{ (at constant T)}$$

Where, x = amount of Adsorbate

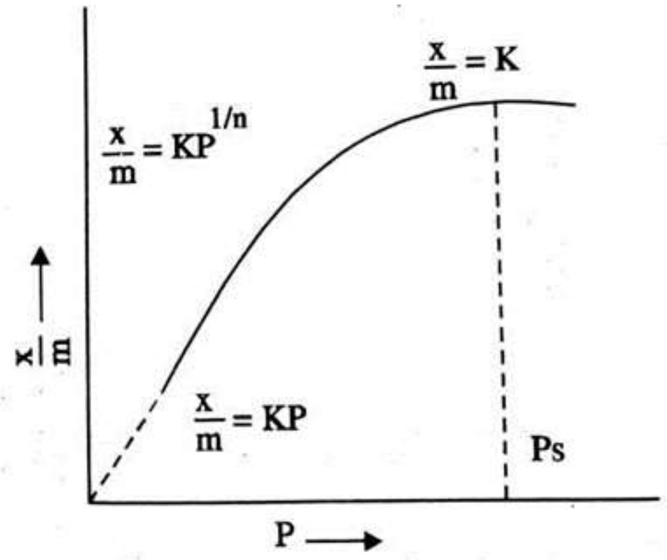
m = amount of adsorbent x / m

x/m= extent of adsorption

P= pressure

n = whole number

K = adsorption coefficient

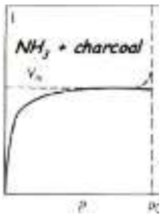
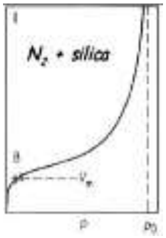
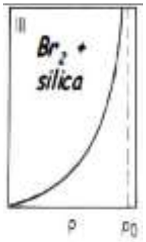
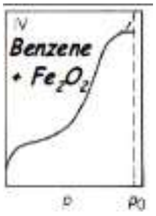
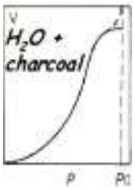


To convert the equation as y = mx + C form, taking log on both sides, log (x / m) =log k + (1/n) log P (at constant T)

Where y = log (x / m); m = (1/n); C = log k

So, the plot will be a line with slope 1/n and intercept log k.

G. Different types of adsorption isotherm curves: (P_0 = Saturation pressure)

Type	I	II	III	IV	V
Model Graph					
Adsorbate	N_2	N_2	I_2 Vapours	Benzene Vapours	Water vapours
Adsorbent	Charcoal	Non poroussilica gel	Porous Silica gel	Porous Ferric oxidegel	Porous Charcoal
Temperature	-183^{0}C	-195^{0}C	83^{0}C	50^{0}C	100^{0}C
Characteristics	Chemisorp-tion (monolayer)	Physisorp-tion (Multilayer)	Physisorption (Multilayer)	Condensation in pores/Capillaries	Condensation in pores/Capillaries
Explanation	Saturation monolayer formation at the	Multilayer forms after the completion ofmonolayer	Multilayer forms beforethe completion of monolayer	Saturation at the multilayer formation	Multilayer formed at beginning adsorption process is the of
Diagram					

H. Freundlich’s Adsorption Isotherm:

Adsorption isotherm is the relationship between adsorption and pressure at a constant temperature. It could be a graphical or mathematical link

$$\frac{S}{N} = KP1/n \text{ (at constant T)}$$

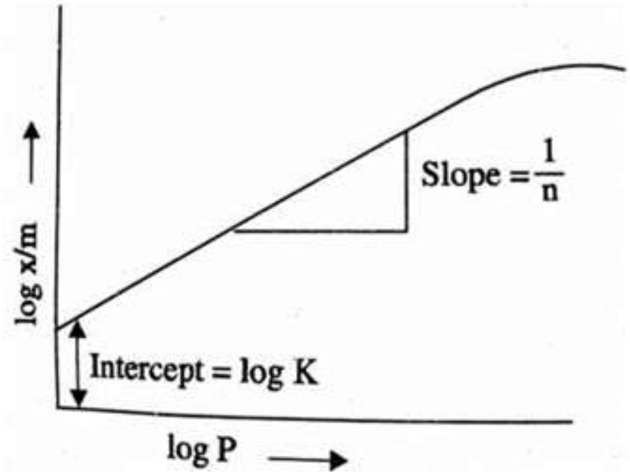
To convert the equation as y = mx + C form, taking log on both sides, log

(x / m) = log k + (1/n) log P (at constant T)

Where y axis = log (x / m); m = (1/n);

C = log k; x axis= log P

So, the plot will be a line with slope 1/n and intercept log k.



From the above graph, there may be three cases:

Case 1: At low pressure, adsorption is proportional to pressure.

$$\frac{S}{N} \infty P^1$$

$$\frac{S}{N} = KP^1$$

Case 2: At high pressure, adsorption is almost constant.

$$\frac{S}{N} = \mathrm{K}$$

$$\frac{S}{N} = \mathrm{K\ P}^0$$

Case 3: At intermediate pressure.

$$\frac{S}{N} = K\ P^{1/n}$$

This is known as Freundlich adsorption isotherm.

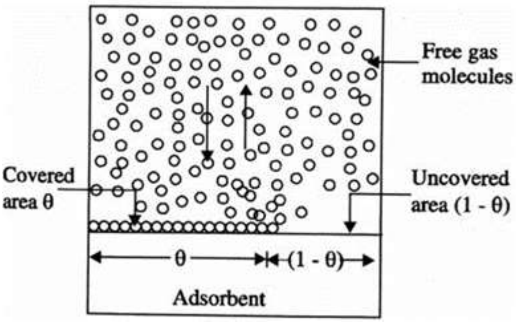
Limitations of Freundlich isotherm:

- It is only an empirical formula and it has no theoretical basis.
- It is deviated at high pressure.
- It is not good at high concentration.
- n and K are temperature dependent.

I. Derivation of Langmuir Adsorption Isotherm:

Postulates:

- Surface valencies are not met in the adsorbent.
- Adsorbate is a monolayer adsorbate.
- On the surface, the adsorbate is evenly dispersed.
- There is no interaction between gas molecules nearby.
- The gas molecules on the surface do not move.



Derivation:

1. As per dynamic equilibrium,

Gas + Solid $\underset{k_d}{\overset{k_a}{\rightleftharpoons}}$ G – S where, k_a = Adsorption rate constant k_d
k_d = Desorption rate constant

2. Let us consider,

Total area of adsorbent = 1cm^2

Surface area adsorbed by gas molecule = θ Then,

Surface area available for adsorption = (1-θ)

The rate of $adsorption\ R_a = k_a(1-\theta)P$ $\ldots\ldots(1)$

Rate of $desorption\ R_d = k_d\theta$ $\ldots\ldots(2)$

At Equilibrium $R_a = R_d$ $\ldots\ldots(3)$

$$k_d\theta = k_a(1-\theta)P$$

$$k_d\theta = k_aP - k_aP$$

$$k_d\theta + k_aP\theta = k_aP$$

$$\theta(k_d + k_aP) = k_aP$$

$$\theta = k_aP \qquad \text{......}(4)$$

Equ. (4) ÷ k_d; we get $k_d + k_aP$

$$\theta = \frac{\left({k_a}/{k_d}\right)P}{\left({k_d}/{k_d}\right) + \left({k_a}/{k_d}\right)P} \qquad \therefore \frac{k_a}{k_d} = Adsorption\ coefficient$$

$$\theta = \frac{KP}{1 + KP} \qquad \text{......}(5)$$

The amount of gas adsorbed x is proportional to θ,

$$x \propto \theta$$

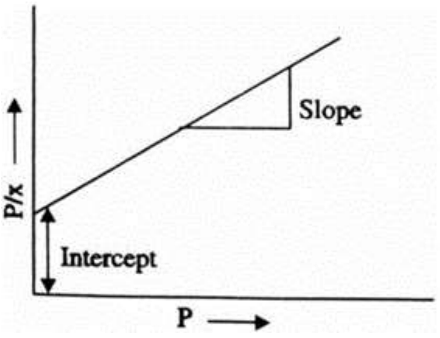
$$x = \frac{KP}{1 + KP} \cdot K\ ; \qquad 1 + KP = \frac{KK'P}{x}$$

Where K' is new constant. This equation gives the relation between the amounts of gas adsorbed to the pressure of the gas at constant temperature. It is known as langumuir adsorption isotherm.

Rearranging the equation 5.

$$1 + KP = \frac{K'KP}{x}$$

$$\frac{1}{K'K} \quad \frac{K}{K'K} + P = \frac{P}{s} \quad \text{--6}$$



A plot of P vs $\frac{P}{}$ gives a straight line with a slope of $\frac{k}{k'k'}$ and an intercept of $\frac{1}{k'k'}$

Case 1: it low. Pressure: P is very low,

$$\frac{1}{K'K}+\frac{KP}{KK'}=\frac{P}{x} \qquad \dots\dots(6)$$

P term is negligible,

$$\frac{1}{K'K}=\frac{1}{x}$$

$$x=K'KP$$

$$x=P \qquad \dots\dots(7)$$

Case 2: At high pressure,

$$P \ggg$$

$$x=KP^0 \qquad \dots\dots(8)$$

At intermediate pressure equation becomes

$$x=KP^n \qquad n=0\ to\ 1$$

Case 3: At normal pressure,

At intermediate pressure equation 8 becomes

$x = K'P^{n}$, where n= 0 to 1

This proves that at normal pressure, Langmuir adsorption resembles Freundlich isotherm.

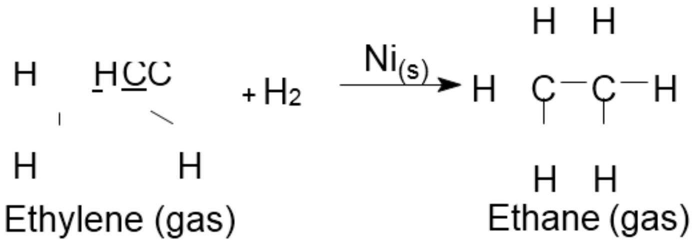
Limitations:

At low pressures, Langmuir adsorption works well, but at high pressures, it fails. Only monolayer adsorption is explained by Langmuir adsorption.

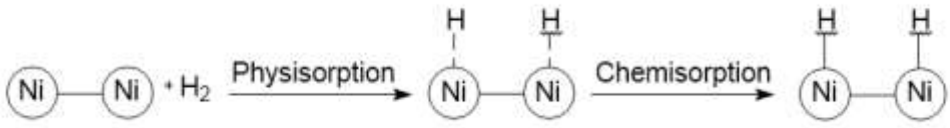
- **Role of Adsorbent in Catalysis Reactions (Or) Adsorption (Or) Contact Theory:**

Catalyst impact on heterogeneous materials

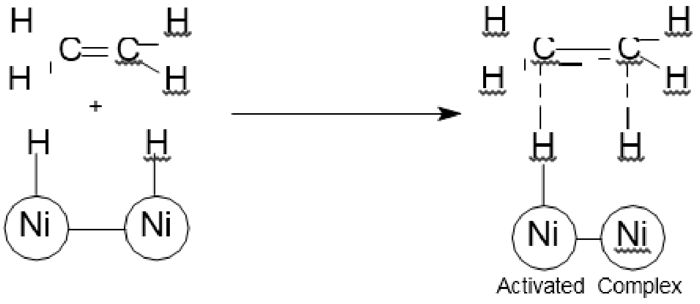
The many processes involved in heterogeneous catalysis are illustrated using the example of ethylene hydrogenation with a Ni catalyst.



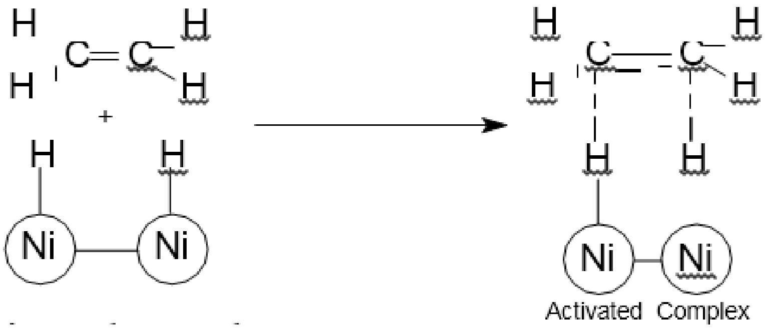
Step I Adsorption of reactant molecules
Active centers in the catalyst surface adsorbs the gaseous reactant.



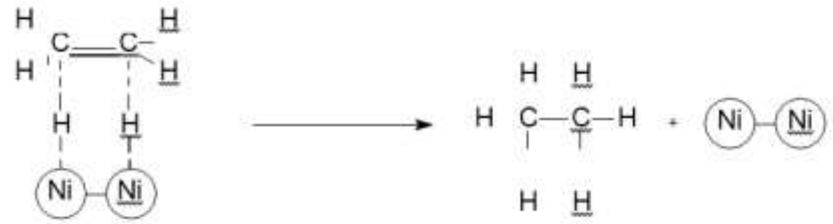
Step II Formation of activated complex



Step III Decomposition of activated complex

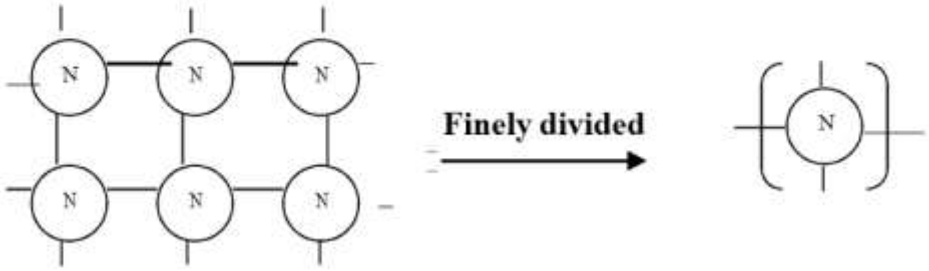


Step IV Desorption of activated complex



- **Finely divided state of catalyst is more efficient:**

E.g.

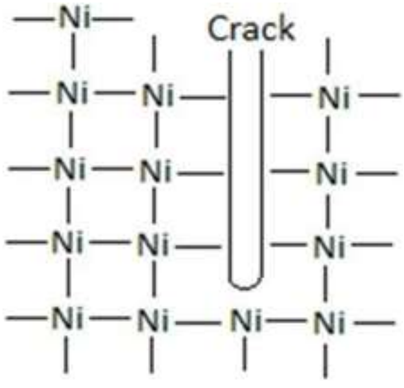


Free valencies in combined state = 10 Divided state valencies = (6 x 4) =24

As the catalyst's fineness improves, the free surface area expands, and the number of free valencies expands.

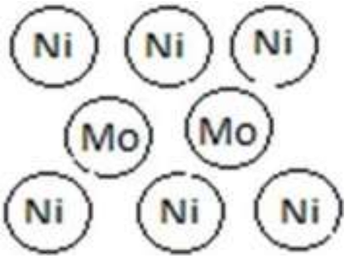
- **Enhanced activity of a rough surfaced catalyst:**

It possess “Cracks”, “Peaks”, “Corners” etc., and consequently have larger number of active centers. These active centers increase the rate of reaction.



- **Action of promoters:**

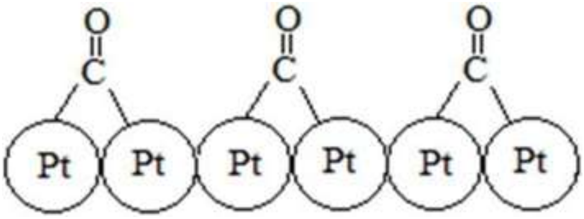
Promoter chemicals are compounds that improve the activity of a catalyst. Promoters alter the spacing of the lattice.



Promoters increases the peaks and cracks

- **Action of catalytic poisons:**

A drug that destroys the catalyst's action is known as catalytic poison. This is known as catalytic poisoning. The poison's preferential adsorption reduces several free valencies (or active centers) of catalysts. As a result, the rate of reaction slows.



- **Specific action of the catalyst:** Adsorption is influenced by the characteristics of both the adsorbent (catalyst) and the adsorbate (reactants). As a result, various catalysts will have varying affinities for identical reactants. As a result, the catalyst's effect is quite particular.
- **Ion exchange method (Demineralization):** Ion exchange resins absorb the cations and anions contained in hard water.

Role of Adsorbents in Pollution Abatement Treatment of Polluted Water and Air.

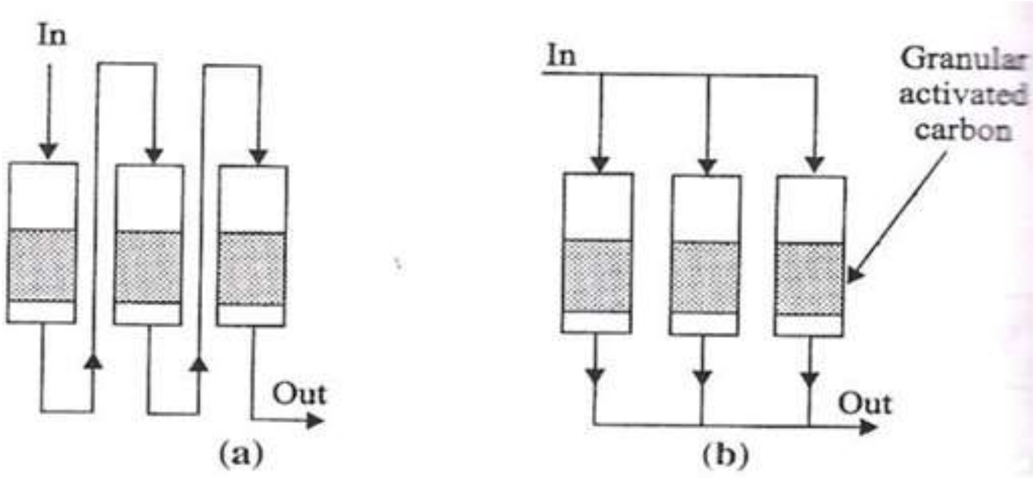
Using Granular Activated Carbon (GAC):

When interacting dirty water or air with GAC, a fixed-bed column is commonly used. It can be used in a single, series, or parallel configuration. There are two key types among the different types.

a. Down flow carbon contactors.
b. Up flow carbon contactors.

a. Down flow Carbon Contactors:

It usually consist of two (or) three columns operated in series (or) in parallel.



Down flow in series **Down flow in parallel**

The water or air is applied to the top of the column and withdrawn at the bottom. The AC is held in place with an under drain system at the bottom of the column. Provision for back washing and surface washing is usually necessary to limit the headless build up due to the removal of particle material with the carbon column.

Advantage:

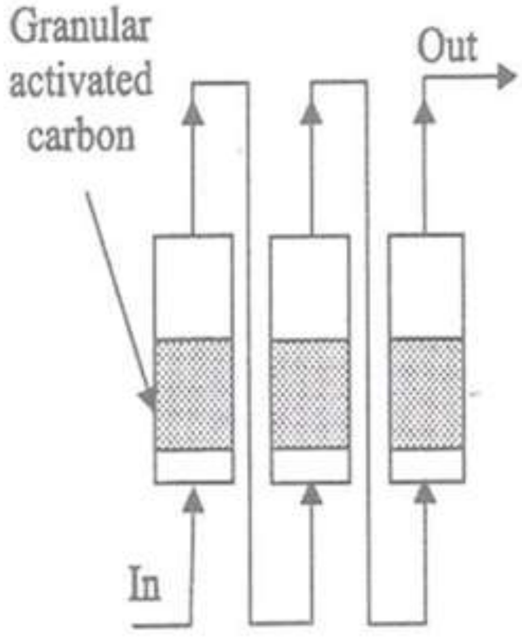
Organic material adsorption and suspended solids filtering are combined in a single process.

Disadvantages:

- Because of the deposition of suspended contaminants on the contactor's surface, down flow filters may require more regular backwashing.
- Plugging of carbon pores may necessitate early carbon removal for regeneration, reducing the carbon's useful life.

b. Up flow Carbon Contactors:

In the up flow columns, the polluted water or air moves upward from the base of the column.



Up flow expanded in series

Advantage:

- As the carbon adsorbs organic materials, the apparent density of the carbon particles increases and encourages migration of the heavier or spent carbon downward.

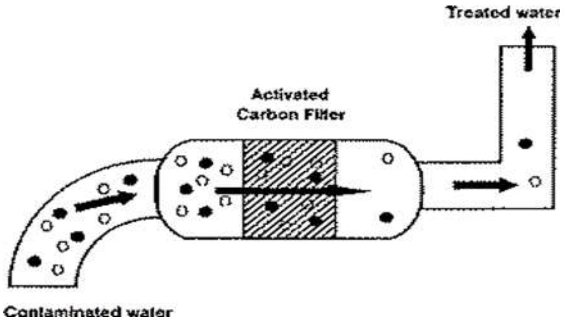
Disadvantage:

- Because up-flow columns expand rather than compress carbon, there may be more carbon fines in the effluent than down-flow columns.
- The fines can escape through the passages established by the expanding bed.

Using Powdered Activated Carbon:

In this method powdered activated carbon is added directly into the effluent.

- Activated carbon powder is applied directly to the wastewater in this procedure.
- In the contact aeration tank, powdered activated carbon and a coagulant are combined.
- It is then transferred to the clarifying tank, where gravity causes the heavier carbon to settle.
- The used carbon can be recycled.
- A filtration column filters the water from the clarity tank.



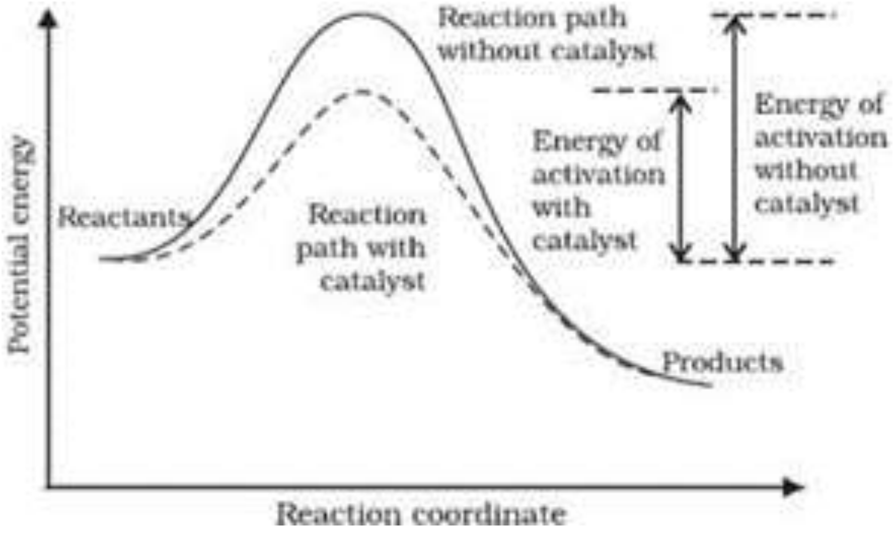
Flow diagram of water treatment using powdered activated carbon

2.2 Catalysis:

The process of altering (increasing or decreasing) the rate of a chemical reaction with the help of a catalyst is known as catalysis.

2.2.1 Effect of Catalyst:

A catalyst increases the rate of reaction by lowering the energy barrier between the reactant and product.



2.2.2 Types of Catalysis:

A. Homogeneous Catalysis:

It is a process in which the catalyst and the reactants are in the same phase.

Examples

Homogeneous catalysis in gas phase,

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{[NO]_{(g)}} 2SO_{3(g)}$$

Homogeneous catalysis in liquid phase,

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \xrightarrow{[H^+/OH^-]} CH_3COOH_{(l)} + CH_3OH_{(l)}$$

B. Heterogeneous Catalysis:

It is a process in which the catalyst and the reactants are in different phase.
Examples

Heterogeneous catalysis in gaseous and solid phase,

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{[Pt]_{(s)}} 2SO_{3(g)}$$

Heterogeneous catalysis in liquid and solid phase,

$$2H_2O_{2(l)} \xrightarrow[{[Pt]_{(s)}}]{} 2H_2O_{(l)} + O_{2(g)}$$

C. Difference between homogeneous and heterogeneous catalysis:

Sr. No.	Homogeneous catalysis	Heterogeneous catalysis
1.	The reactant, the product, and the catalyst are all in the same phase.	The reactant, product, and catalyst are all in distinct stages of development.
2.	Catalyst is non-regenerable.	It is possible to regenerate the catalysts.
3.	The catalyst has low thermal stability	The catalyst's heat stability is poor.
4.	Low temperatures and pressure are used in the reactions.	High temperatures and pressures are used in reactions.
5.	The pace of the reaction increases as the temperature rises.	The pace of the reaction increases as the temperature rises.
6.	The physical nature of the catalyst has no bearing on its selectivity.	The physical nature of the catalyst affects its selectivity.

2.2.3 Acid-Base Catalysis:

Acids and bases catalyze a vast number of homogeneous catalytic processes. Acid-base catalysis is the study of the kinetics of chemical events.

A. Examples:

Inversion of cane sugar,

$$CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Hydrolysis of an ester,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

B. Classification of acid base catalysis Acid catalysis:

A proton (H+) can catalyze a reaction - specifically, proton catalyzed reactions.

A bronsted acid (proton donors) can also catalyze a process - general acid catalysis.

Base Catalysis

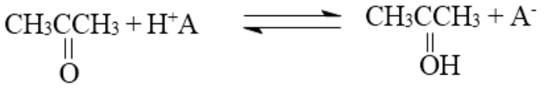
A hydroxide ion (OH-) can catalyze a reaction - specifically, hydroxide catalyzed reactions. Or

A bronsted base (proton donors) can catalyze a process - this is known as general base catalysis.

C. Mechanism of Acid-Base catalysis:

Acid catalysis:

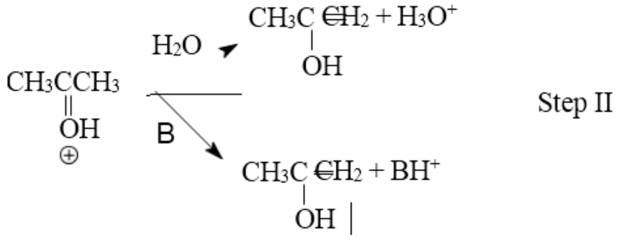
Step I: Addition of H+ ion to the substrate forming intermediate complex. (E.g. keto-enol tautomerism of acetone)



$$CH_3\underset{\underset{O}{\|}}{C}CH_3 + H^+A \rightleftharpoons CH_3\underset{\underset{OH}{\|}}{C}CH_3 + A^-$$

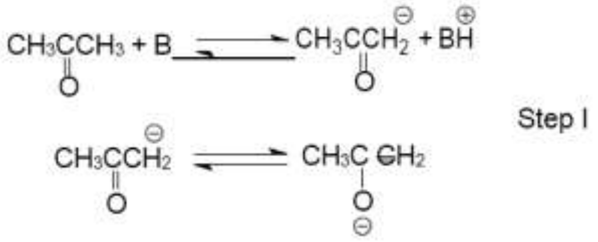
Step I

Step II: Removal of proton from intermediate complex by water or base.



Base catalysis:

Step I: Removal of H+ ions from the reactant forming intermediate complex.



Step II: Addition of proton to the intermediate complex.

D. Kinetics of acid-base catalysis:

Kinetics of acid-base catalysis is explained by the following mechanism.

Step I: Involves transfer of the H^+ ions from an acid AH^+ to the substrate S.

$$S + AH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A \qquad \text{Step I}$$

Step II: Involves reaction of the acid form of the substrate with water to give products.

$$SH^+ + H_2O \overset{k_2}{\rightleftharpoons} P + H_3O^+ \ \text{Step II}$$

Applying steady state approximation to the intermediate $[SH^+]$

$$\frac{d[SH^+]}{dt} = 0 = k_1[S][AH^+] - k_{-1}[A][SH^+] - k_2[SH^+] \qquad ---1$$

The reactions are carried out at low concentration hence concentration of water is not taken into account in equation 1.

$$k_1[S][AH^+] = k_{-1}[A][SH^+] + k_2[SH^+]$$

$$[SH^+] = \frac{k_1[S][ÆK^+]}{k_{-1}[Æ]+k_2} \qquad ---2$$

The rate of formation of product is given by

$$\frac{d[P]}{dt} = k_2[SH^+] \qquad ---3$$

Substituting 2 in 3

$$Rate = \frac{d[P]}{dt} = \frac{k_2k_1[S][ÆK^+]}{k_{-1}[Æ]+k_2} \qquad ---4$$

Two cases are applied on equation 4.

Case 1 When $k_2 >> k_{-1}[A]$, $k_{-1}[A]$ is negligible, so the above equation 4 becomes

$$Rate = \frac{k_2k_1[S][AH^+]}{k_2}$$

$$Rate = k_1[S][AH^+] \qquad ---5$$

In this case the reaction is general acid catalyzed

Case II: When $k\text{-}1[A] >> k_2$, k_2 is negligible, the equation 4 becomes

$$Rate = \frac{k_2k_1[S][ÆK^+]}{k_{-1}[Æ]} \qquad ---6$$

The ionization constant of the acid AH^+ is

$$AH^{+} \rightleftharpoons [H^{+}] + [A]$$

$$K = \frac{[H^{+}][A]}{[AH^{+}]}$$

$$[A] = \frac{K[\text{Æ}K^{+}]}{[K^{+}]} \qquad \text{---}7$$

Equation 7 is substitute in 6

$$Rate = \frac{k_2 k_1 [S][AH^{+}]}{K[AH^{+}]}$$

$$k \;{}_{1}\; \frac{\quad}{[H^{+}]}$$

$$Rate = \frac{k_2 k_1 [S]|H^{+}|}{k_{-1} K}$$

In this case the reaction is specifically hydrogen-ion catalyzed, because the equation contains $[H^{+}]$

E. General applications of catalysis:

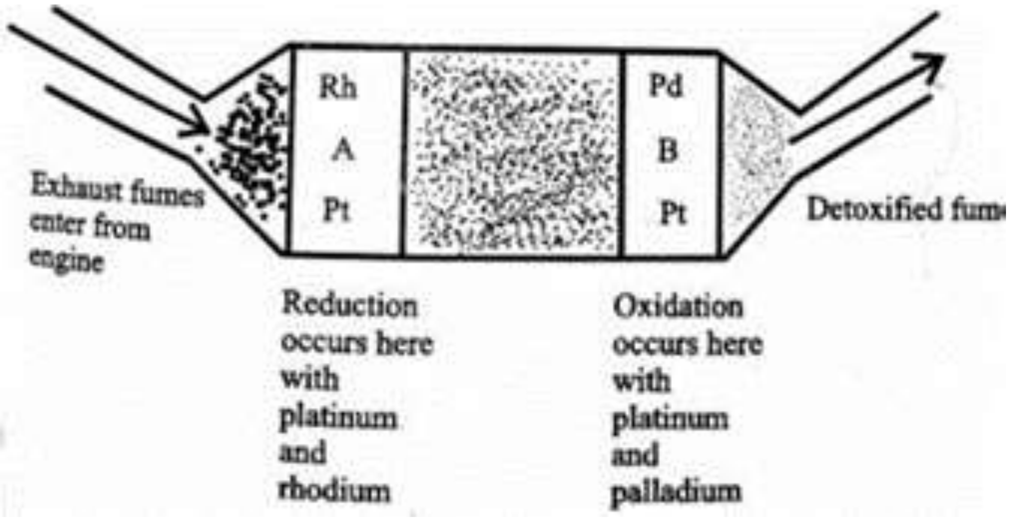
- It boosts the productivity of industrial processes.
- Catalysts are used to make a variety of fine compounds.
- Shape-specific catalysis is a possibility.
- Zeolites are utilized as a catalyst in hydrocarbon cracking.
- Catalyst is used in petroleum catalytic cracking.
- They are necessary for the operation of fuel cells.
- In the hydrogenation of oils, a nickel catalyst is used.
- Green chemistry makes use of catalysts.

2.4 Catalytic Converter:

- It is a device that is used to reduce IC engine emissions
- When the supply of oxygen in the IC engine is reduced, poisonous gases are released.
- Catalytic converters oxidize and decrease these gases to less hazardous byproducts.

A. Construction:

- The honeycomb inside is coated with aluminum oxide and contains metals such as platinum, palladium, and rhodium.
- It has a metal casing with a ceramic honeycomb-like interior with insulating layers.



B. Working:

- The exhaust fumes are allowed inside compartment A where the reducible impurities are reduced.
- The remaining gases are allowed through the compartment B where all the oxidisable impurities are oxidized.
- There are no hazardous byproducts in the emitted fume.

C. Function of Catalytic Converter:

Reduction of nitrogen oxides into elemental nitrogen and oxygen

$NOx \longrightarrow Nx + Ox$

Oxidation of CO to CO_2

Oxidation of hydrocarbons into CO_2 and H_2O

2.5 Enzyme Catalysis:

Enzymes (or) biological catalyst are complex organic substances of high molecular weight proteins derived from living organisms. Examples

A. Conversion of starch into maltose:

$$2(C_6H_{10}O_2) + nH_2O \xrightarrow{\text{Diatase}} nC_{12}H_{22}O_{11}$$

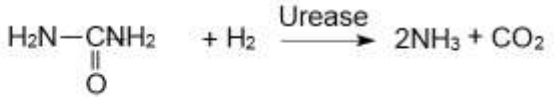
B. Inversion of cane sugar: The enzyme invertase catalyses the conversion of sugar into glucose and fructose.

C. Conversion of glucose into ethanol: The enzyme zymase catalysis the conversion of glucose into ethanol.

$C_6H_{12}O_6$ zymase→ $2C_2H_5OH + 2CO_2$

D. Hydrolysis of urea:

The enzyme urease converts urea in ammonia.



$$H_2N-\underset{\underset{O}{\|}}{C}NH_2 \quad + H_2 \xrightarrow{Urease} 2NH_3 + CO_2$$

2.5.1 Characteristics of Enzyme Catalysis:

- **Enzymes are most efficient catalysts:** Enzyme catalyzed reactions proceed at higher rates than the reactions catalyzed by inorganic catalysts. Enzymes lower the activation energy of a reaction.

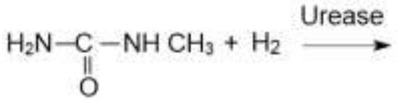
$2H_2O_2 \longrightarrow 2H_2O + O_2$

Activation Energy without catalyst = 18 kCal/mol

Activation Energy with colloidal platinum = 11.7 kCal/mol

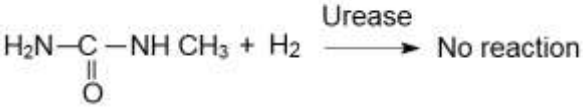
Activation Energy with enzyme catalyst > 2 kCal/mol

- **Enzyme catalyzed reactions are more specific:** Enzymes are highly specific in catalyzing reactions. An enzyme catalyzes only a particular reaction.



$$H_2N-\underset{\underset{O}{\|}}{C}-NH\,CH_3 + H_2 \xrightarrow{Urease}$$

$2NH_3 \quad + CO_2$



$$H_2N-\underset{\underset{O}{\|}}{C}-NH\,CH_3 + H_2 \xrightarrow{Urease} \text{No reaction}$$

Methy Urea

- **Rate of the enzyme catalyzed reactions is maximum at optimum temperature:** The rate of enzyme-catalyzed processes increases as temperature rises, yet enzymes denature at high temperatures. At the ideal temperature, the rate is at its highest. For example, the optimum temperature for enzyme processes in the human body is 37 degrees Celsius. Because enzymatic reactions do not occur at high temperatures, high body temperatures are hazardous.

- **Rate of the enzyme catalyzed reactions is maximum at optimum pH:** At a specific pH, known as optimal pH, the rate of enzyme-catalyzed processes is at its highest. Below and above the optimal pH, the rate declines. Many enzymes in the human body, for example, are highly active at pH 7.4.
- **Catalytic activity of the enzymes is enhanced by activators (or) Co-enzymes:** The catalytic activity of enzymes is increased when activators (metal ions Na+, Mn^2+, Co^2+, Cu^2+, etc.) (or) co-enzymes (small molecules) are added.
- **Enzymes are poisoned by other substances:** The catalytic activity is inhibited by the addition of other substances. E.g. Heavy metal ions (Ag^+, Hg^{2+}) react with the SH group of the enzyme and inhibit theenzyme activity.

2.6 Michelis-Menten Equation:

The following mechanism is proposed by Michaelis and Menten to explain the enzyme catalyzed reactions. Let the enzyme E react with the substrate S resulting in the formation of intermediate complex X in first step.

$$E + S \xrightarrow{k1} X \qquad \text{Step I}$$

The intermediate complex and S (or) may dissociate back into E form product P.

$$X \xrightarrow{k_2} E + S \qquad \text{Step II}$$

$$X \xrightarrow{k_3} P \qquad \text{Step III}$$

k1, k2 and k3 are rate constant of the respective reactions.

The rate of formation of complex X is given by the following equation.

$$\frac{d[X]}{dt} = k_1[E][S] - k_2[X] - k_3[X]$$

$$= k_1[E][S] - (k_2 + k_3)[X] \qquad \text{--1}$$

Where, [E][S] and [X] = Molar concentrations of the enzyme, substrate and intermediate complex. Rate of formation of the product is given by the following

$$\frac{d[P]}{dt} = k_3 [X] \qquad \text{---2}$$

Since, $[E_0] = [E] + [X]$ ------------------- 3

Applying equation 3 in 1 gives,

$$\frac{d[X]}{dt} = \mathbf{0} \qquad \mathbf{5}$$

Applying steady state, equation 5 may be applied on 4

$$k_1\{[E_0] - [X]\}[S] = (k_2 + k_3)[X] \qquad \text{---6}$$

$$k_1[E_0][S] - k_1[X][S] = (k_2 + k_3)[X]$$

$$k_1[E_0][S] = k_1[X][S] + (k_2 + k_3)[X]$$

$$k_1[E_0][S] = \{k_1[S] + (k_2 + k_3)\}[X]$$

$$[X] = \frac{k_1[E_0][S]}{k_1[S] + k_2 + k_3} \qquad \text{---7}$$

Dividing equation 7 by $k_1[E_0]$ gives

$$[X] = \frac{[E_0]}{1 + \frac{k_2 + k_3}{k_1[C]}} \qquad \text{---8}$$

Substituting [X] in equation 2 gives

$$\frac{d[P]}{dt} = k_3 \frac{[E_0]}{1 + \frac{k_2 + k_3}{k_1[S]}} \qquad \text{---9}$$

$$\frac{k_2 + k_3}{k_1} = K_N = \mathit{Michaelis\ constant}$$

$$\frac{d[P]}{dt} = \frac{k_3[E_0]}{1 + \frac{K_m}{[S]}} \qquad \text{--10} \quad \text{(or)} \qquad \mathit{Rate} = \frac{k_3[E_0][S]}{[S] + K_m}$$

Equation 10 is called Michaelis-Menten equation

Case (i) At low concentration of substrate

When the concentration of the substrate [S] is less than K_m

$[S] << K_m$ then

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{K_m} \qquad \text{---}11$$

Case (ii) At high concentration of substrate

When the concentration of the substrate [S] is higher than K_m

$[S] >> K_m$ then

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{|S|}$$

$$\frac{d[P]}{dt} = k_3[E_0] \qquad \text{---}12$$

- **Effect of substrate concentration on rate:**

The order of the reaction changes with increase in the concentration of substrate.

(i) At low concentration of substrate:

When the substrate concentration is low most of the active sites in the enzyme are unoccupied. At this moment, rate of the reaction increase with increase in the concentration of the substrate. It is a first order reaction with respect to substrate.

(ii) At high concentration of substrate:

When all the active sites are occupied, further increase in concentration of enzyme has no effect on the rate. The reaction becomes zero order with respect to substrate.

2.6.1 Significance of Michaelis-Menten Equation:

The equation can be simplified by assuming that all the enzyme has reacted with the substrate. In that case the rate is maximum.

$[E_0] = [X]$

Substituting the above equation in equation 2 gives

$$\frac{d[P]}{dt} = k_3 [E]_0 = v_{Nas} \qquad ---13$$

Where, v_{Nas} = maximum rate

The Michaelis-Menten equation can be written as

$$Rate = \frac{v_{Nas}[S]}{[S] + K_N}$$

If $K_N = [S]$, then

$$Rate = \frac{v_{Nas}[S]}{[S] + [S]}$$

$$Rate = \frac{v_{Nas}[S]}{2[S]}$$

$$Rate = \frac{1}{2} v_{Nas}$$

When the Michaelis-Menten constant is equal to concentration of the substrate, rate of the reaction is half the maximum rate.

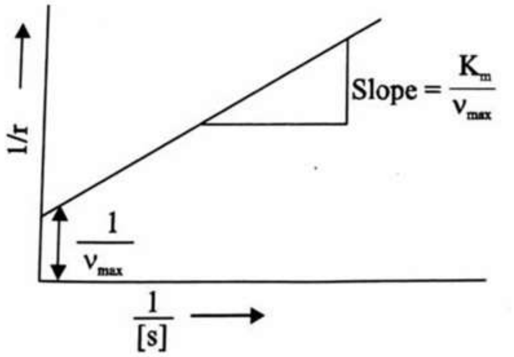
2.6.2 Determination of the Michaelis-Menten Constant (K_m):

Line weaver-Burk equation is used to determine the value of the Michaelis-Menten constant.

$$\frac{1}{rate} = \frac{1}{v_{Nas}} + \frac{K_N}{v_{Nas}[S]}$$

The plot of reciprocal of rate vs concentration of substrate gives a straight line with intercept

$\frac{(1)}{rate}$ and slope $\frac{K^N}{vNax}$



Turn over number (k_3):

The number of molecules of substrate converted into products in unit time by one molecule of enzyme.

2.6.3 Factors Affecting Enzyme Catalysis:

A. pH: Enzymes work best at neutral pH, but at low and high pH, they become denatured.

B. Temperature: At high temperatures, enzymes work more quickly.

C. Salt Concentration: A high salt concentration boosts the enzyme's activity.

D. Activators and Inhibitors: Activators are small chemicals that boost the enzyme's activity. Inhibitors are small molecules that inhibit the enzyme's activity. Inhibitors are tiny chemicals that reduce the enzyme's activity.

Chapter 3

Alloys

Metals are generally insoluble in common solvents such as water and alcohol, but they can dissolve in another metal when molten, resulting in a homogenous liquid combination. This cooling forms into an alloy, which is a solid blend of metals. Most metals, such as tin and lead, can be mixed in any proportion to make alloys. Metals, as well as metal and non-metal components, combine to produce alloys. It is evident from the foregoing description that an alloy contains at least one metal.

3.1 Definition:

An alloy is a "homogeneous solid solution of two or more distinct elements, at least one of which is fundamentally a metal," according to the definition. Amalgams are alloys that contain mercury as a component element. Base metals are metals that are present in surplus amounts, while alloying elements are metals that are present in less levels.

3.2 Properties of Alloy:

- Alloys are harder, good strength less malleable and ductile.
- Alloys have low electrical conductivity and low melting point than pure metals.
- Alloys resist corrosion and the action of acids.

3.3 Importance (or) Need (or) Purpose of Making Alloys:

- In general, pure metals have qualities such as a high melting point, high density, malleability, ductility, and good thermal and electrical conductivity.
- As previously stated, alloying metal with another metal (or) non-metal can improve its qualities. The following are the reasons why alloys are created:

A. To Increase the Hardness of Metals:

Pure metals are soft in general, but their alloys are tough.

Examples:

- Gold and silver are soft metals that are hardened by alloying with copper.
- A 0.5 percent arsenic addition hardens lead, which is used to create bullets.

B. To Increase the Strength of Metals:

Pure metals are weaker than their alloyed counterparts.

Examples:

The strength of the pure iron metal is lower, but it is increased when it is alloyed with carbon.

C. To Lower the Melting Points of Metals:

Alloying makes the metal easily fusible.

Examples:

Wood's metal (a lead, bismuth, tin, and cadmium alloy) melts at 60.5° C, well below the melting temperatures of any of its component metals.

D. To Resist the Corrosion of Metals:

Metals, in pure form, are quite reactive and easily corroded by surroundings, thereby their life isreduced. If a metal is alloyed, it resist corrosion.

Examples:

Pure iron rusts, however, it resists corrosion when alloyed with carbon(or) chromium (stainless steel).

E. To Modify Chemical Activity of Metals:

Alloying can increase or decrease the chemical activity of a metal.

Examples:

Aluminum amalgam is more active than sodium amalgam, although sodium amalgam is less active than sodium.

F. To modify the colour of metals:

By alloying with other metals, dull-colored metals can be enhanced.

Examples:

Brass is a white alloy made up of copper (red) and zinc (silver-white).

G. To Get Good Casting of metals:

Some metals expand on solidification but are soft and brittle. The addition of other metals produce alloys which are hard, fusible and expand on solidification and thus give good casting.

Examples:

An alloy of lead with 5% tin and 2% antimony is used for casting printing type, due to its goodcasting property.

3.4 Functions (or) Effect of Alloying Elements:

Small amounts of specific metals, such as Ni, Cr, Mo, Mn, Si, V, and Al, are added to steel to give it unique attributes including hardness, tensile strength, corrosion resistance, and coefficient of expansion. Such products are known as special steels (or) alloy steels.

Such products are known as special steels (or) alloy steels.

Element	Effect on Properties	Uses of Alloys
1. Nickel	i) Fine grains are created. ii) Co-efficient of expansion decrease and corrosion resistance increases.	It's used to make balance wheels.
2. Chromium	Tensile strength, depth hardening, and corrosion resistance are increased.	To make medical instruments, cutlery, and connecting rods, among other things
3. Manganese	i) Hot shortness is removed. ii) Resistance to abrasion is increased.	Grinding wheels, steering spindles, and rails are all made with this material.
4. Vanadium	i) Reversible stresses are produced. ii) Tensile strength and abrasion resistance are improved.	Axles, crankpins, massive locomotive forgings, piston rods, and other components.
5. Molybdenum	Because phases are stable, cutting hardness increases at high temperatures.	For the production of high-speed tools.
6. Tungsten	(i) Grain structure is refined. (ii) Magnetic receptivity and cutting hardness are both improved.	To make cutting tools, permanent magnets, and other items

Element	Effect on Properties	Uses of Alloys
7. Nickel and Chromium	Corrosion resistance and tensile strength have both been improved.	For the production of stainless steel.

3.5 Heat Treatment of Alloys (Steel):

The process of heating and cooling of solid steel articles under well-controlled conditions," according to the definition of heat treatment. Certain physical qualities are affected after heat treatment without changing the chemical composition.

3.5.1 Purpose of Heat Treatment:

- Grain structure refinement, as well as improvements in magnetic and electrical properties.
- Gases that have been trapped must be released.
- Internal stress and strain are alleviated.
- Increases corrosion and fatigue resistance.

3.5.2 Types of Heat Treatment of Alloys (Steel):

The different heat-treatment processes are as follows:

1. Annealing
2. Hardening
3. Tempering
4. Normalizing
5. Case-Hardening
a) Carburizing b) Nitriding c) Cyaniding

3.6 Annealing:

Softening is referred to as annealing. This is accomplished by heating the metal to a high temperature and then cooling it slowly in a furnace.

A. Purpose:

- It increases the machinability.
- It also removes the imprisoned gases.

B. Annealing can be done in two ways:

- Low temperature annealing (or) process annealing.
- High temperature annealing (or) full annealing.

3.6.1 Types of Annealing:

A. Low temperature annealing (or) process annealing:

It involves in heating steel to a temperature below the lower critical temperature followed by slowcooling.

Purpose:

- It increases machinability by reducing internal tension and strain.
- • It improves ductility and resilience to shock.
- • It softens the skin

B. High temperature annealing (or) full-annealing:

It entails heating the steel to a temperature of 30 to 50 degrees Celsius above the higher critical temperature, maintaining it there for long enough to allow internal changes to occur, and then cooling it to room temperature.

Purpose:

- It increases the ductility and machinability.
- It makes the steel softer, together with an appreciable increase in its toughness.

C. Hardening (or) Quenching:

It's the process of heating steel above its critical temperature and then rapidly cooling it in oil, brine water, or another fluid. Steel's hardness is increased via hardening. The steel produced will be tougher if it is cooled at a faster rate. Low-carbon steels cannot be toughened, whereas medium and high-carbon steels may.

Purpose:

- It improves steel's wear resistance, ability to cut other metals, and strength, but it also makes it more brittle.
- • It improves abrasion resistance, allowing it to be used in cutting instruments.

D. Tempering:

- It's the technique of heating hardened steel to a temperature below its hardening temperature and then cooling it gently in the air. The temperature at which hardened steel is re-heated is crucial in tempering since it determines how the final qualities evolve. Thus
- Reheating temperatures should not exceed 400°C to maintain strength and hardness.
- The reheating temperature should be between 400 and 600° C to improve ductility and toughness.

Purpose:

- It relieves any stress and strains that may have accumulated during the quenching process, as well as reduces brittleness and some hardness.
- It improves ductility and toughness.
- Tempering is required for all cutting instruments, such as blades, cutters, and tool-bites.

E. Normalizing:

It's the process of heating the steel to a specific temperature (greater than its higher critical temperature) and then allowing it to cool in the air. Normalized steel is not as soft as annealed steel, but it takes significantly less time to normalize than annealing.

Purpose:

- It restores the steel structure's uniformity.
- It improves the grain structure.
- It relieves internal tension and stress.
- It improves the toughness of the skin.
- Normalized steel can be used in engineering projects.

Case- Hardening (or) Surface Hardening:

Case–hardening is the process of creating a hard, wear-resistant surface over a strong, tough, and ductile core. Low-carbon, low-alloy steel is the ideal choice for this. The following are the various case-hardening procedures:

- **Carburizing:**

The mild steel item is placed in a cast-iron box with little charcoal bits (carbon material). It is then heated to around 900 to 950°C and kept at that temperature for long enough for the carbon to be absorbed to the appropriate depth.

After that, the object is allowed to cool slowly within the iron box. The article's outside surface is made of high-carbon steel with a carbon content of 0.8 to 1.2 percent.

Purpose: To produce hard-wearing surface on steel article.

- **Nitriding:**

Nitriding is the process of heating the metal alloy in presence of ammonia at a temperature of about 550°C. The nitrogen (obtained by the dissociation of ammonia) combines with the surface of the alloy to formhard nitride.

Purpose: To get super-hard surface

- **Cyaniding:**

The process of cyaniding involves dipping pre-heated steel in a cyanide bath containing sodium cyanide, sodium carbonate, and sodium chloride.

Carbon and nitrogen are dispersed through the surface of steel during this process, hardening it. The disadvantage is that cyanide baths are a poisonous substance.

3.7 Classification (or) Types of Alloys:

Based on the type of base metals, alloys are classified into two types:

- Ferrous alloys. (e.g.) nichrome, stainless steel
- Non-ferrous alloys. (e.g.) brass, bronze

A. Ferrous Alloys (or) Alloy Steels:

Ferrous alloys are the type of steels in which the elements like Al, B, Cr, Co, Cu, Mn are present insufficient quantities, in addition to carbon and iron, to improve the properties of steels.

B. Properties of Ferrous alloys:

- It possesses a high yield point and strength, as well as adequate formability, ductility, and weldability.
- It resists corrosion and abrasion well.
- There is less distortion and cracking.
- The strength of high-temperature materials is increased.

C. Important Ferrous Alloys:

- **Nichrome:**

Nichrome is an alloy of nickel and chromium. Its composition are

Metal	Composition
Iron	60%
Nickel	12%
Chromium	26%
Manganese	2%

Properties:

- It has a high melting point and exhibits good resistance to oxidation and heat.

- It can endure temperatures of up to 1100°C.
- It has great resistance to electricity.

Uses:

It's commonly utilized in the production of,

- Stove resistance coils and heating elements
- An electric ironing board and other electrical household gadgets.
- Parts for boilers, steam lines, gas turbines, aero-engine valves, retorts, and annealing boxes
- Machines (or) equipment that is subjected to extremely high temperatures.

3.8 Stainless Steels (or) Corrosion Resistant Steels:

These are alloy steels that contain chromium together with other elements like nickel, molybdenum, and so on.

Chromium is effective at a concentration of 16 percent (or) higher. Stainless steel has a carbon content of up to 1.5 percent.

Stainless steel is resistant to corrosion caused by both ambient gases and other chemicals. The creation of a dense, non-porous, robust coating of chromium oxide on the metal's surface protects it from corrosion. If this coating fractures, the oxygen in the air heals it immediately.

A. Types of Stainless Steels:

There are two main types of stainless steels.

- Heat treatable stainless steels.
- Non-heat treatable stainless steels.

B. Heat Treatable Stainless Steels:

Composition:

Heat - treatable stainless steels mainly contain upto 1.2% of carbon and less than 12-16% of chromium.

Properties:

- Heat - treatable stainless steels are magnetic, tough and can be worked in cold condition.
- They can be used up to 800°C.
- They have good resistant towards weather and water.

Uses:

They are used in making surgical instruments, scissors, blades, etc.

C. Non - Heat Treatable Stainless Steels:

These steels possess less strength at high temperature. They are more resistant to corrosion. There areof two types of Non-Heat Treatable Stainless Steel according to their composition:

(i) Magnetic typeComposition:

It contains 12 - 22% of chromium and 0.35% of carbon.

Properties:

- It can be forged, rolled and machined by the use of specially designed tools.
- It has better corrosion resistance than heat-treatable stainless steel.

Uses:

It is used in making chemical equipment’s and automobile parts.

(ii) Non-Magnetic Type:

Composition:

It contains 18 - 26% of chromium, 8 - 21% of nickel and 0.15% of carbon.

The total percentage of Crand Ni in such steel should be more than 23%.

18/8 Stainless Steel:

The steel having 18% Cr and 8% Ni are known as 18/8 stainless steel. It is the most widely usedstainless steel.

Properties:

- It shows maximum corrosion resistance
- Corrosion resistance can be further increased by adding small amounts of molybdenum.

Uses:

It is used in making household utensils, sinks, dental and surgical instruments.

3.9 Phase Rule:

Introduction:

All chemical reactions are broadly classified into 2 types:

Irreversible Reactions: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

Reversible reactions:

Homogeneous reversible reactions

Eg: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Heterogeneous reversible reactions

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

The reversible reactions are represented by 2 arrows in the opposite directions. The homogeneous reversible reactions can be studied by the law of mass action and the heterogeneous reversible reactions usingthe phase rule, given by Willard Gibbs (1874) which is defined as,

Phase Rule:

If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as: $F = C - P + 2$

3.9.1 Explanation of Terms with Examples:

A. Phase (P):

PHASE is defined as, "any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries".

- **Gaseous Phase (g):**

All gases are completely miscible and have no boundaries between them. Hence all gases constitute asingle phase.

Eg: Air, a mixture of O_2, H_2, N_2, CO_2 and water vapor, etc., constitutes a single phase.

- **Liquid Phase (l):**

The number of liquid phases depends on the number of liquids present and their miscibility's. If two liquids are immiscible, they will form two separate liquid phases.

(e.g.) Benzene – Water system.

If two liquids are completely miscible, they will form only one liquid phase. *(e.g.) Alcohol – Water* System.

- **Solid Phase (s):**

Every solid constitutes a separate single phase.

(e.g.) *Decomposition of* $CaCO_3$

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)}$$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous CO_2.

B. Other Examples:

A water system has 3 phases namely one solid, one liquid and one gaseous phase.

$$\mathbf{Ice(s)\quad Water\ (l) \rightleftharpoons Vapour\ (g)}$$

A solution of a substance in a solvent constitutes only one phase. *(e.g.)* Sugar solution in water.

An emulsion of oil in water forms two phases

$$\mathbf{MgCO_3\ (s) \rightleftharpoons MgO\ (s) + CO_2\ (g)}$$

It involves 3 phases, solid $MgCO_3$, solid MgO and gaseous CO_2.

Rhombic Sulphur (s) ——> Monoclinic Sulphur (s). It forms 2 phases.

Consider the following heterogeneous system.

$$\mathbf{CuSO_4(s) + 5H_2O\ (l) \rightleftharpoons CuSO_4.\ 5H_2O(s)}$$

It involves 3 phases namely, 2 solids and 1 liquid phase.

3.9.2 Component (C):

The term component is meant "the smallest number of independent variable constituents, taking part in the state of equilibrium, by mean of which the composition of each phase can be expressed in the form of the chemical equation".

Examples:

Consider a water system consisting of three phases.

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water (l)} \rightleftharpoons \textbf{Vapour (g)}$$

The chemical composition of all the three phases is H_2O. Hence the number of component is one.

Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapor, but the chemical composition is only Sulphur. Hence it is a one component system.

Thermal decomposition of $CaCO_3$

$$\mathbf{CaCO_3 s)} \rightleftharpoons \mathbf{CaO\ (s) + CO_2(g)}$$

The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2 and 2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When $CaCO_3$and CaO are considered as components, the chemical equations are:

Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
CaO	$0CaCO_3 + CaO$
CO_2	$CaCO_3 – CaO$

$$\mathbf{PCl_5(s)} \rightleftharpoons \mathbf{PCl_3\ (l) + Cl_2(g)}$$

This system has 3 phases and 2 components namely, PCl_3 and Cl_2.

An aqueous solution of NaCl is a two component system. The constituents are NaCl and H_2O

$$\mathbf{CuSO_4.\ 5H_2O(s)} \rightleftharpoons \mathbf{CuSO_4.\ 3H_2O(s) + 2H_2O\ (g)}$$

It is also a two component system as components are $CuSO_4.3H_2O$ and H_2O.

In the dissociation of NH_4Cl, the following equilibrium occurs.

$$\mathbf{NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)}$$

The system consists of 2 phases namely solid NH_4Cl and the gaseous mixture containing NH_3 + HCl.When $NH_3$and HCl are present in equivalent quantities the composition of both the phases can be representedby NH_4Cl and hence the system will be a one component system.

3.9.3 Degree of Freedom (F):

Degree of freedom is defined as, "the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely".

A system having 1, 2, 3 or 0 degrees of freedom are called as univariate, bivariate, trivariant andnon-variant systems respectively.

Examples:

Consider the following equilibrium

$$\mathbf{Ice(s) \rightleftharpoons Water\ (l) \rightleftharpoons Vapour\ (g)}$$

These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

Consider the following equilibrium

$$\mathbf{Liquid\ Water\ (l) \rightleftharpoons Water\text{-}\ vapor\ (g)}$$

Here liquid water is in equilibrium with water vapor. Hence any one of the degrees of freedom suchas temperature (or) pressure has to be fixed to define the system. Therefore, the degree of freedom is one. For a gaseous mixture of N_2 and H_2, both the pressure and temperature must be fixed to define thesystem. Hence, the system is bivariate.

3.9.4 Phase Diagram:

Phase diagram is a graph obtained by plotting one degree of freedom against the other.

A. Types of Phase Diagrams:

- **P-T Diagram:**

If the phase diagram is plotted between temperature and pressure, the diagram is called P -T diagram.P -T diagram is used for one component system.

- **T-C Diagram:**

If the phase diagram is plotted between temperature and composition, the diagram is called T-C diagram. T- C diagram is used for two component system

Uses of Phase Diagram:

It helps in

- Predicting whether a eutectic alloy (or) a solid solution is formed on cooling a homogeneous liquidcontaining mixture of two metals.
- Understanding the properties of materials in the heterogeneous equilibrium system.
- Studying of low melting eutectic alloys, used in soldering.

3.9.5 Applications of Phase Rule - to One Component System:

A. The Water System:

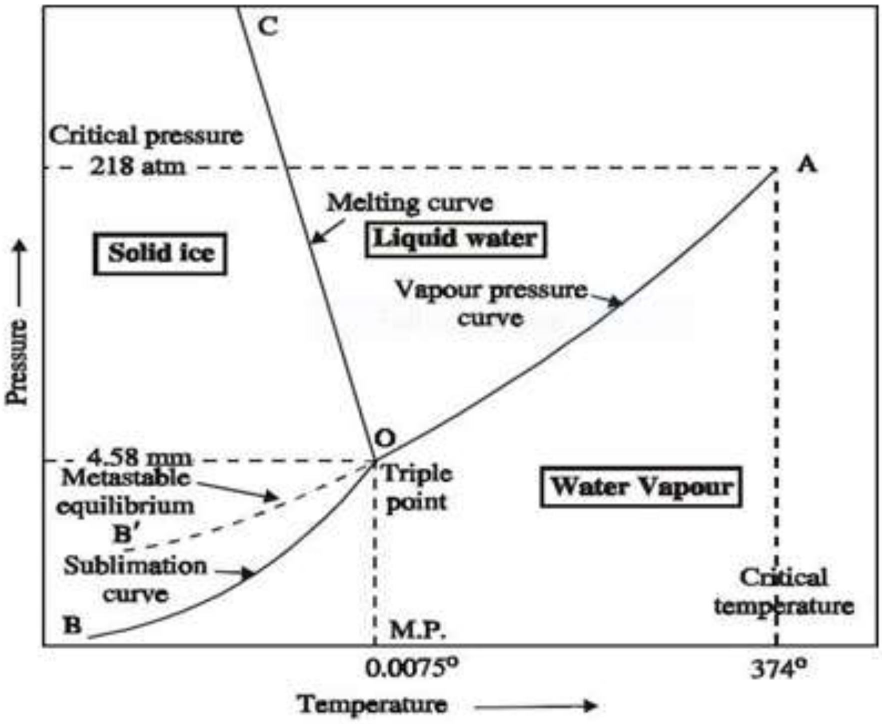
Water exists in 3 possible phases, namely solid ice, liquid water and water-vapor. Hence, there canbe three forms of equilibria, each involving two phases such as.

Solid Ice $\rightleftharpoons$ **Liquid Water Liquid**

Water $\rightleftharpoons$ **Water- vapor**

Solid Ice $\rightleftharpoons$ **Water- vapor**

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.



B. Curve OA:

- The curve OA is called vaporization curve, it represents the equilibrium between water and vapor.
- At any point on the curve the following equilibrium will exist.

$$\textbf{Liquid Water} \rightleftharpoons \textbf{Water- vapor}$$

- This equilibrium (i.e. line OA) will extend up to the critical temperature (374°C).
- Beyond the critical temperature the equilibrium will disappear and only water vapor will exist.

C. Curve OB:

- The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapor.
- At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Water- vapor}$$

- This equilibrium (i.e. line OB) will extend up to the absolute zero (− 273°C)
- Beyond absolute zero only solid ice will exist and no water-vapor.

D. Curve OC:

- The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water.
- At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Liquid Water}$$

- The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

E. Curve OB′ (Metastable Equilibrium):

The curve OB′ is called vapor pressure curve of the super-cooled water (or) metastable equilibriumwhere the following equilibrium will exist.

$$\textbf{Super- cooled water} \rightleftharpoons \textbf{Water- vapor}$$

- Sometimes water can be cooled below its freezing point (0°C) without the formation of ice, this water iscalled super-cooled water.
- Super cooled water is unstable and it can be converted into solid ice by "seeding" (or) by slightdisturbance.
- **Along the curves OA, OB, OC and OB′:**

The no. of phases (P) is 2, component(C) is 1 and the degree of freedom of the system is one i.e., univariant.This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 2 + 2;\ F = 1}$$

Therefore, either temperature (or) pressure must be fixed to define the system.

- **Point 'O' (Triple point):**

The three curves OA, OB and OC meet at a point „O", where three phases namely solid ice, liquid waterand water-vapor are simultaneously at equilibrium. This point is called triple point, at this point the following equilibrium will exist

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water (l)} \rightleftharpoons \textbf{Vapour(g)}$$

At this point the no. of phases (P) is 3, component(C) is 1 and the degree of freedom of the system is zeroi.e., nonvariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 3 + 2;\ F = 0}$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

- **Areas:**

Areas AOC, BOC, AOB represents liquid water, solid ice and water-vapor respectively where the no. of phases (P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariate. Thisis predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 1 + 2;\ F = 2}$$

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.

3.9.6 Two Component Alloy System (or) Multi Component Equilibria:

A. Reduced Phase Rule (or) Condensed System:

The maximum number of degrees of freedom for a two component system will be three, when the system exists as a single phase.

$$\mathbf{F = C - P + 2;\ F = 2 - 1 + 2;\ F = 3}$$

In order to represent the conditions of equilibrium graphically, it requires three co-ordinates, namely P, T and C.

This requires three dimensional graph, which cannot be conveniently represented on paper. Therefore, any two of the three variables must be chosen for graphical representation. A solid-liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible.

Therefore, experiments are conducted under atmospheric pressure. Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignoredis called a condensed system. Since the pressure is kept constant, the phase rule becomes

$$\mathbf{F' = C - P + 1}$$

This equation is called reduced phase rule (or) condensed phase rule.

B. Classification of Two Component System:

Based on the solubility and reactive ability, the two component systems are classified into three types.

- Simple eutectic formation.
    - Formation of compound with congruent melting point.
    - Formation of compound with incongruent melting point.
- Formation of solid solution.

(i) Simple Eutectic Formation:

A binary system having two substances, which are completely miscible in the liquid state, but completelyimmiscible in the solid state, is known as eutectic (easy melt) system.

They do not react chemically. Of the different mixtures of two substances, a mixture having the lowest melting point is known as the eutectic mixture.

- **Formation of compound with congruent melting point:**

The binary alloy system with two substances form one or more compounds with definite proportions.

Of the compounds, a compound is said to have congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

- **Formation of compound with incongruent melting point:**

Of the above compounds, a compound is said to have incongruent melting point, if it decomposes completely at a temperature below its melting point forming a new solid phase with adifferent composition from that of the original.

(ii) Formation of solid solution:

A binary system in which two substances, especially metals, are completely miscible in both solid andliquid states form solid solutions and their mixing takes place in the atomic levels. This happens only when the atomic radius of the two metals not differ by more than 15%.

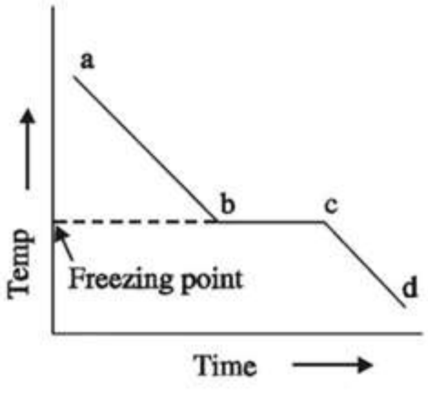
C. Experimental Method of Construction of a Simple Eutectic Phase Diagram:

Thermal Analysis (or) Cooling Curves:

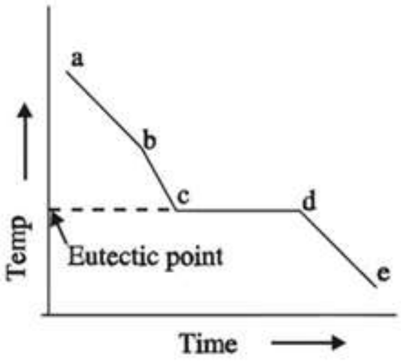
Thermal analysis is a method of studying the cooling curves of various compositions of a system duringsolidification. The shapes of the freezing point curves for any system (involving metals) can be determined by thermal analysis. The form of cooling curves indicates the composition of the solid.

Example 1:

A pure solid substance in the fused state is allowed to cool slowly and the temperature is noted at different time intervals. Then a graph is plotted between temperature and time and it is the cooling curve for the pure solid substance.



Cooling curve of pure solid



Cooling curve of a mixture A+B

Initially the rate of cooling of liquid melt is continuous from „**a**‟ till the point „**b**‟, where solid beginsto appear. Then the temperature remains constant until the liquid melt is completely solidified and solidification completes at the point „**c**‟.

The horizontal line „**bc**‟ represents the equilibrium between the solid and liquid melt. After the point„ **c**‟, along the curve „**cd**‟ cooling of solid mass begins and the temperature begins to decrease.

Example 2:

If a mixture of two substances (say A and B) in the fused state are allowed to cool slowly, the coolingcurve is obtained as above:

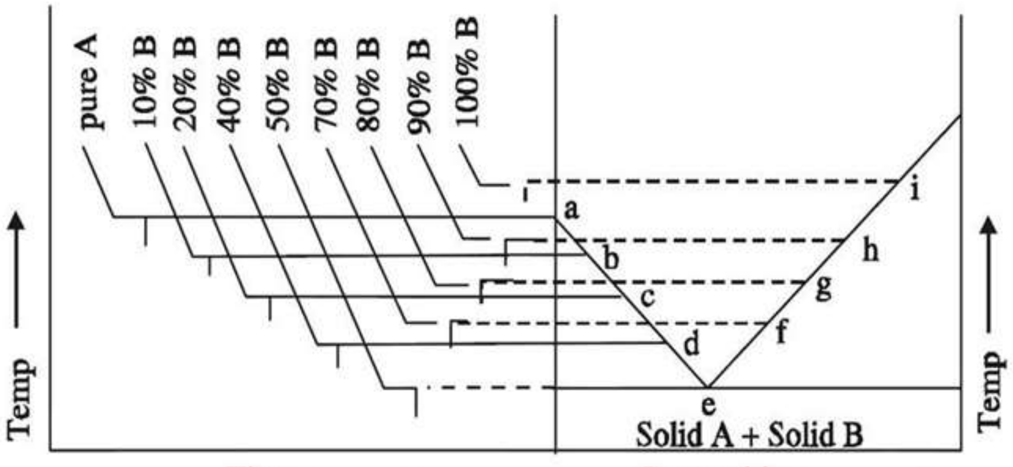
Initially the rate of cooling of liquid melt is continuous from **'a'** till the point **'b'**. When it reaches thepoint **'b'** one substance (either A or B) begins to solidify out of the melt.

This is indicated by a break where the rate of cooling is different. On further cooling at the break point **'c'** the second substance also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms theeutectic mixture along the line **'cd'**.

After the break point **'d'** cooling of solid mass begins. The temperature of horizontal line „**cd**‟ gives the eutectic temperature.

The experiment are repeated for different compositions of A and B and the various cooling curves are recorded.

From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temperature in Y-axis.



Cooling curve of various compositions of two solids

Uses of Cooling Curves:

- Melting point and eutectic temperature can be noted.
- Percentage purity of the compounds can be noted.
- The behavior of the compounds can be clearly understood.
- The composition corresponding to its freezing point yields the composition of the alloy.
- The phase diagram for any two component system can be obtained.

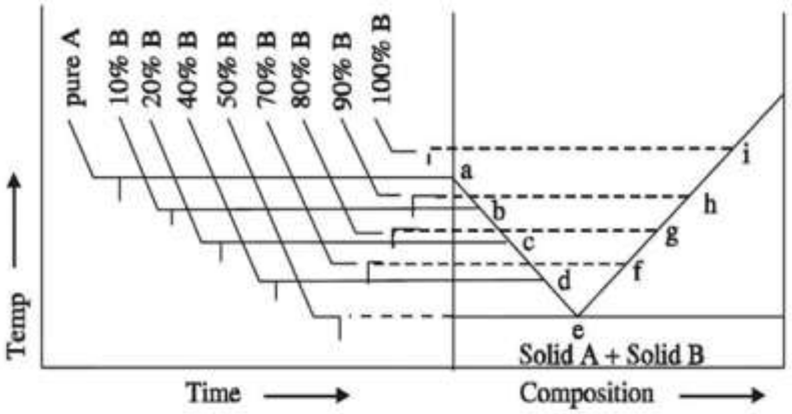
D. Binary Alloy System (or) the Simple Eutectic System:

The Lead-Silver System:

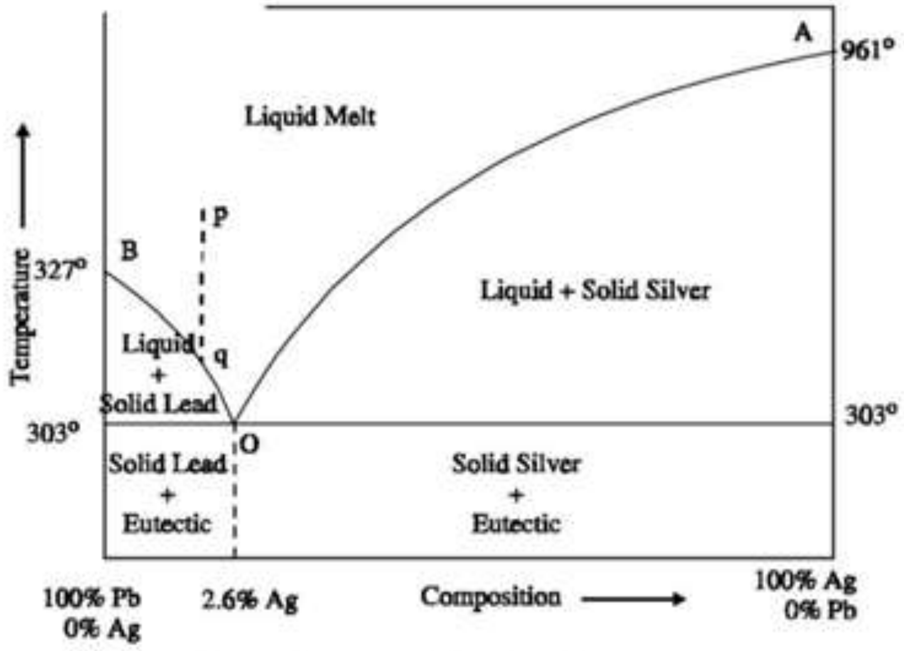
The Lead-Silver system is studied at constant pressure and the vapour phase is ignored. Hence thecondensed phase rule is used:

$$\mathbf{F' = C - P + 1}$$

The phase diagram of lead-silver system is shown as follows. It contains curves, areas and eutectic point.



Cooling curve of various compositions of two solids



Phase diagram of Lead - Silver system

E. Curve AO:

The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along thiscurve AO, solid Ag and the melt are in equilibrium.

Solid Ag Liquid Melt

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

F. Curve BO:

The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C).

The curve BO shows the melting point depression of Pb by the successive addition of Ag. Along with this curve

Solid Pb Liquid Melt

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

Along the curves AO and BO:

The system is univariant which means either temperature (or) composition must be fixed to define the system.

Point ‘O’ (Eutectic point):

The curves AO and BO meet at point „O‟ at a temperature of 303°C, where three phases (solid Ag,solid Pb and their liquid melt) are in equilibrium.

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

According to reduced phase rule equation.

$$F' = C - P + 1; F' = 2 - 3 + 1; F' = 0$$

The system is non-variant. The point „O‟ is called eutectic point or eutectic temperature and its corresponding composition,97.4%Pb + 2.6%Ag, is called eutectic composition. Below this point the eutectic compound and the metal solidify.

Area: The area above the line AOB has a single phase (molten Pb+Ag) or liquid melt. According to reduced phase rule the degree of freedom.

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

The system is bivariate which means both the temperature and composition have to be fixed to define the system completely.

The area below the line AO (solid Ag + liquid melt), below the line BO (solid Pb + liquid melt) and below the point „O‟ (Eutectic compound + solid Ag or solid Pb) have two phases and hence the system is univariant

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1.$$

Application of Pattinson’s process for the desilverisation of Argentiferous lead:

The argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point, so that the system has only the liquid phase represented by the point „**p**‟ in the phasediagram.

It is then allowed to cool where the temperature decreases along the line „**pq**‟. As soon as the point„ **q**‟ is reached, Pb is crystallized out and the solution will contain relatively increasing amounts of „Ag‟. On further cooling, more and more of „Pb‟ is separated along the line „BO‟. The melt continues to be richer andricher in Ag until the point „O‟ is reached, where the percentage of Ag rises to 2.6%. Thus, the process of raising the relative proportions of Ag in the alloy is known as Pattinson‟s process.

Uses of Eutectic System:

- Suitable alloy composition can be predicted.
- Making solders, used for joining two metal pieces together.

G. Differences between Melting point, Eutectic point and Triple point:

Melting Point: It is the temperature at which the solid and liquid phases, having the same composition,are in equilibrium.

$$\textbf{Solid A} \rightleftharpoons \textbf{Liquid A}$$

Eutectic Point: It is the temperature at which two solids and a liquid phase are in equilibrium

$$\textbf{Solid A + Solid B} \rightleftharpoons \textbf{Liquid}$$

Triple Point:

It is the temperature at which three phases are in equilibrium.

$$\textbf{Solid} \rightleftharpoons \textbf{Liquid} \rightleftharpoons \textbf{Vapour}$$

- All the eutectic points are melting points
- All the melting points need not be eutectic points.

Similarly, all the eutectic points are triple points, but all the triple points need not be eutectic.

Chapter 4

Fuels and Combustion

4.1 Fuel:

Fuel is a combustible substance with carbon as its principal element that produces a substantial quantity of heat when burned. The atoms of carbon, hydrogen and other elements mix with oxygen during the combustion of a fuel, releasing heat in the process.

$$C + O_2 \rightarrow CO_2 + 94 \text{ k cals.}$$

$$2H_2 + O_2 \rightarrow 2H_2O + 68.5 \text{ k cals.}$$

Coal and crude petroleum oil are the primary sources of energy. These are stored fuels that are found in the Earth's crust and are known as fossil fuels since they are made up of fossilized plant and animal remains.

Classification of Fuel: Fuels can be classified:

Types of Fuel	Natural or Primary Fuels	Artificial or Secondary Fuels
Solid	Wood, peat, coal, lignite, dung	Coke, charcoal, petroleum
Liquid	Crude oil	Tar, kerosene, diesel, Petrol
Gas	Natural gas	Coal gas, water gas, bio Gas, coke oven gas,producer gas, CNG, LPG

4.2 Primary Solid Fuel – Coal:

Coal is a major solid fuel that is created by the transformation of vegetative matter under certain suitable conditions.

- **Coalification (or) Metamorphism:**

Coalification or coal metamorphism is the process of converting (or altering) vegetative matter to anthracite (coal).

4.2.1 Classification of Coal:

The rank of coal is used to classify it. The maturity of coal is indicated by its rank.

Carbon content, calorific value, hardness, moisture content, H, O, N, S content, and volatile matter increases are used to classify various varieties of coal.

The gradual transformation of wood into anthracite produces

- Decrease in moisture content,
- Decrease in volatile content,
- Decrease in hydrogen, oxygen, nitrogen and sulphur contents,
- Increase in carbon content,
- Increase in hardness,
- Increase in calorific value

4.3 Analysis of Coal:

To assess the quality of coal, the following two types of analysis are made.

4.3.1 Proximate Analysis:

It involves the determination of percentage of (i) Moisture content (ii) Volatilematter (iii) Ash content (iv) Fixed carbon in coal.

A. Moisture Content:

About 1 gm of powdered coal sample is taken in a crucible and is heated at $100 - 105°C$ in an electric hot-air oven for 1 hour.

The loss in weight of the sample is found out and the percentage of moisture is calculated as

$$Percentage\ of\ moisture = \frac{Loss\ in\ weight}{weight\ of\ sample} \times 100$$

Volatile malter

B. Volatile Matter:

After the analysis of moisture content, the crucible with residual coal sample is covered with a lid, and is heated at 950 ± 20°C for 7 minutes in a muffle furnace.

The loss in weight of the sample is found out and the % of volatile matter is calculated as loss in weight of the coal.

$$Percentage\ of\ volatile\ matter = \frac{Loss\ in\ weight}{weight\ of\ coal\ sample} \times 100$$

C. Ash Content:

After the analysis of volatile matter, the crucible with residual coal sample is heated without lidat 700 ± 50°C for half an hour in a muffle furnace. The loss in weight of the sample is found out and the % of ash content is calculated as

$$Percentage\ of\ ash\ content = \frac{weight\ of\ ash\ content}{weight\ of\ coal\ sample} \times 100$$

D. Fixed Carbon:

It is determined by subtracting the sum total of moisture, volatile and ash contents from 100.

$$= 100 - \%\ of(moisture + volatile\ matter + ash)$$

Significance (or) Importance of Proximate Analysis:

Sr. No.	Analysis	Significance
1	**Moisture content**	• Because a high proportion of moisture is undesirable, • It lowers the calorific value of coal; • The majority of the energy supplied will be squandered due to evaporation. • It raises transportation costs • It emits smoke
2	**Volatile matter**	• Because a high percentage of volatile materials is unfavorable, • It lowers the calorific value of coal; • It produces a smoky, sooty flame; • Coking is impossible; • Toxic gases are released
3	**Ash content**	• The presence of a large percentage of ash is undesirable because • It lowers the calorific value of coal; • It forms clinkers, which disrupt oxygen delivery; • It produces flying ash, which pollutes the air and land; • It raises transportation, handling, and storage expenses; • It adds to the cost of ash disposal.

Sr. No.	Analysis	Significance
4	**Fixed carbon**	• Because it is desirable to have a high percentage of fixed carbon, • The higher the proportion of fixed carbon in coal, the higher its calorific value; • The percentage of fixed carbon aids in furnace construction.

4.3.2 Ultimate Analysis:

It involves the determination of percentage of (i) carbon and hydrogen contents, (ii) nitrogencontent (iii) Sulphur content (iv) ash content (v) oxygen content

A. Carbon and Hydrogen Contents:

In a combustion apparatus, a known amount of coal sample is burned in an O2 stream. According to the following equations, the carbon and hydrogen in the coal sample are transformed into CO_2 and H_2O, respectively.

$$C + O_2 \longrightarrow CO_2 \uparrow$$

$$H_2 + 1/2\ O_2 \longrightarrow H_2O \uparrow$$

The CO_2 and H_2O vapors are absorbed in KOH and anhydrous $CaCl_2$ tubes of known weights, respectively.

The generation of CO_2 causes the weight of the KOH tube to increase, whereas the formation of H_2O causes the weight of the $CaCl_2$ tube to increase. The percent of carbon and hydrogen present in the coal can be determined using the weights of CO_2 and H_2O produced.

$$\%\ of\ carbon\ = \frac{Increase\ in\ weight\ of\ bulb\ K_0H \times 12}{weight\ of\ coal\ sample\ \times f4} \times 100$$

$$\%\ of\ Hydrogen\ = \frac{2}{18} \times \frac{Increase\ in\ weight\ coal_2\ bulb}{weight\ of\ coal\ sample\ taken}$$

B. Nitrogen Content:

Kjeldahl's technique is used to figure out how much nitrogen is in something. In a long-necked flask (called Kjeldahl's flask), a known amount of powdered coal sample is heated with con. H2SO4 in the presence of K2SO4 (catalyst). The nitrogen in the coal is transformed to ammonium sulfate, resulting in a clear solution

$N_2 + 3H_2 + H_2SO_4 \longrightarrow (NH_4)_2 SO_4$

The ammonia is distilled over and absorbed in a known volume of standard N/10 HCl after the clear solution is boiled with excess NaOH.

$$(NH_4)_2 SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

Titrating unused N/10 HCl against standard N/10 NaOH yields the volume of unused N/10 HCl. As a result, the amount of acid neutralized by ammonia freed from coal may be calculated.

$$\%\ of\ Nitrogen\ = \frac{1.4 \times volume\ of\ and\ used \times Normality\ of\ and}{weight\ of\ coal\ sample\ taken}$$

C. Sulphur Content:

In a bomb calorimeter, a known amount of coal sample is burned. Sulfur is transformed into sulfate during this process, which is then removed with water. Sulfates are precipitated as $BaSO_4$ after the extract is treated with $BaCl_2$ solution. Filtered, dried, and weighed precipitate The amount of sulfur in the coal is determined using the weight of $BaSO_4$ obtained:

$$\%\ of\ Sulphure\ = \frac{volume\ of\ BaSo_4 precipitated \times 13.73}{weight\ of\ coal\ sample\ taken}$$

D. Ash Content:

Determination of ash content is carried out as in proximate analysis

$$\%\ of\ Oxygen\ = 100 - \%\ of\ (C + H + N + S)$$

E. Oxygen Content:

The percentage of oxygen is calculated as follows.

Significance (or) Importance of Ultimate Analysis

Sr.No.	Analysis	Significances
1	**Carbon and hydrogen contents**	The higher the percentage of carbon and hydrogen in coal, the better its quality and calorific value. The percent of the carbon in coal is useful in coal categorization because it minimizes the size of the combustion chamber required.
2	**Nitrogen content**	The presence of nitrogen in coal is undesirable since it has no calorific value. The nitrogen level of good coal should be very low
3	**Sulphur Content**	Its presence in coal is undesirable because • The combustion products of sulfur, i.e., SO_2 and SO_3 are toxic and have corrosion effects on equipment. • The coal containing sulfur is not suitable for the preparation of metallurgical coke as it affects the properties of the metal.
4.	**Ash Content**	The presence of a large percentage of ash is undesirable because • It lowers the calorific value of coal; • It forms clinkers, which disrupt oxygen delivery; • It produces flying ash, which pollutes the air and land; • It raises transportation, handling, and storage expenses; • It adds to the cost of ash disposal.
5.	**Oxygen Content**	• Lower the % of oxygen higher is its calorific value. • As the oxygen content increases its moisture-holding capacity increases, and the calorific value of the fuel is reduced.

4.4 Carbonization:

When coal is heated rapidly in the absence of air (a process known as destructive distillation), it is transformed into coke, a glossy, thick, porous, and cohesive mass.

Carbonization is the term for the process of turning coal into coke.

Types of carbonization (i) Low temperature carbonization (ii) High temperature carbonization

Sr.No.	Low Temperature Carbonization	High Temperature Carbonization
1	It is carried out at 500 - 700˚C	It is carried out at 900 - 1200˚C
2	Produces soft semi coke	Produces hard metallurgical coke
3	Yield of coke 75 – 85 %	The yield of coke 65 – 75 %
4	Used for domestic purpose	Used for metallurgy
5	Volatile matter is 5 – 15%	Volatile matter is 1-3%
6	Low calorific value	High calorific value
7	Strength of coke is low	The strength of coke is high

A. Caking Coals and Coking Coals:

When coals are burned to a high temperature, the mass becomes malleable, pliable, and fuses to form a cohesive mass. Caking coals are the name for this sort of coal. The coals are called Coking Coals if the mass formed is hard, porous, and strong.

Coking coals have a reduced volatile matter content and are used to make metallurgical coke. As a result, all coking coals are also caking coals, but not all caking coals are coking coals.

B. Secondary Solid Fuel - Metallurgical Coke:

When bituminous coal is heated rapidly in the absence of air, the volatile content exits and the mass transforms into Metallurgical Coke, which is hard, strong, porous, and coherent

Requisites (or) characteristics of good metallurgical coke:

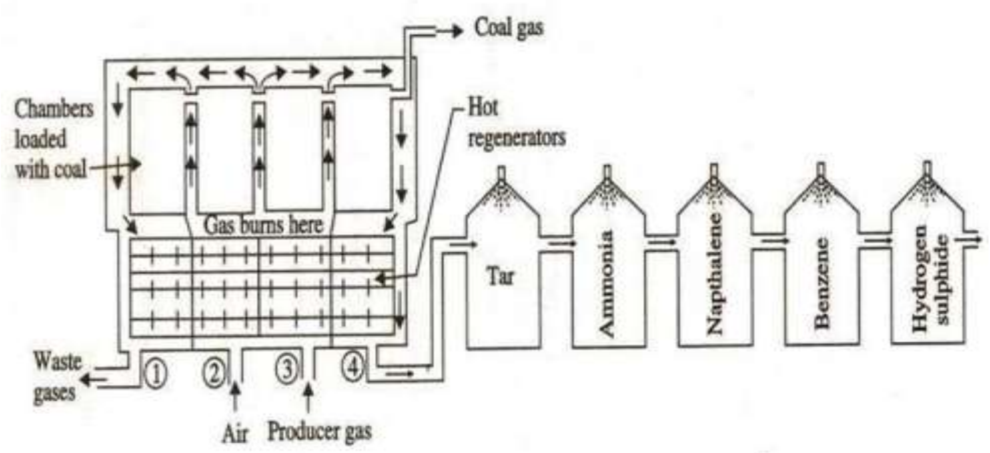
Sr.No.	Requisites	Explanation
1	**Purity**	It ought to be quite high. Moisture, ash, sulfur, and phosphorus are examples of impurities that can contaminate metals and diminish their calorific value.
2	**Porosity**	Coke should be porous, allowing oxygen to come into direct touch with carbon.
3	**Strength**	It should be high toto withstand a heavy load.
4	**Calorific value**	It needs to be quite high.
5	**Combustibility**	The coke should be easy to burn.
6	**Reactivity**	Because low reactive cokes produce high temperatures, the reactivity of the coke should be below low.
7	**Cost**	It should be inexpensive and easily accessible.

C. Manufacture of Metallurgical COKE (Otto-Hoffman’s by-Product Oven):

There are several different types of ovens used to make metallurgical coke. However, Otto-by-product Hoffman's oven is the most crucial.

Objectives and Advantages:

- Increase the thermal efficiency of the carbonization process and,
- Recover the valuable by products (like coal gas, ammonia, benzol oil, etc.,
- Heating is done externally by producer gas hence we can save fossil fuel
- The carbonization time is less.



a. The oven is made up of several silica chambers. Each chamber is approximately 10 to 12 meters long, 3 to 4 meters tall, and 0.4 to 0.45 meters broad. Each chamber is equipped with a charging hole at the top, as well as a gas off-take valve and an iron door at each end for releasing coke.
b. The silica chamber is filled with coal, and the chambers are closed. The preheated air and producing gas mixture are burned in the interspaces between the chambers to raise the temperature to 1200°C.
c. The air and gas are warmed by passing them through the second and third hot regenerators. The temperature is raised to 1000°C by allowing hot flue gases produced during carbonization to pass through the first and fourth regenerators. The 2nd and 3rd regenerators are used to heat the entering air and gas combination, while the 1st and 4th regenerators are heated by hot flue gases.
d. The direction of input gases and flue gases is frequently adjusted for efficient heating. The regenerative system of heat economy is defined as the recycling of flue gases to produce heat energy. The coke is removed and quenched with water once the operation is finished.
e. Carbonization takes between 12 and 20 hours to finish. The yield of coke is approximately 70%. Flue gas can be used to recover important by-products such as coal gas, tar, ammonia, H2S, and benzol, among others.

Recovery of by – products:

Sr.No.	By – products	Recovered by
1	**Tar**	To dissolve tar, sprinkle Liquid Ammonia over it. The NH_3 is recovered once more by boiling the solution.
2	**Ammonia**	Water is sprayed. Ammonia is transformed to NH_4OH here.
3	**Naphthalene**	Naphthalene is condensed by spraying cold water on it.
4	**Benzene**	Benzene is converted to a liquid by spraying it with petroleum.
5	**Hydrogen Sulphide**	The residual gases are subsequently filtered by a moist Fe_2O_3 purifier. $H2_S$ is kept in this case.
6	**Gaseous fuel**	Coal gas is the final gas left over, and it is used as a gaseous fuel.

4.5 Primary Liquid Fuels – Petroleum/Crude Oil:

Crude oil is a mixture of paraffinic, olefinic, and aromatic hydrocarbons with trace amounts of organic molecules such as nitrogen, oxygen, and sulfur. Petroleum's chemical make-up is rough as follows:

Constituents	Percentage (%)
C	80-87
H	11-15
S	0.1-3.5
N and O	0.1-0.5

There are three types of petroleum:

- Paraffinic based – straight chain hydrocarbons
- Naphthenic based – Cycloparaffins and aromatic
- Mixed based – both paraffinic and naphthenic

4.5.1 Refining of Petroleum (or) Crude Oil:

Refining petroleum is the process of eliminating impurities such as water, Sulphur, and dissolved salts like MgCl2 from crude oil and dividing them into separate factions with varying boiling points. The following are the four steps in the refining process.

Sr.No.	Various Steps	Process
1.	Separation of water (Cottrell's Process)	The crude oil is pumped between two electrodes that are both strongly charged. When colloidal water droplets clump together to create big drops, they are isolated from the oil.
2.	Removal of harmful sulfur compounds	Copper oxide is used to eliminate Sulphur compounds. Filtration is used to separate the copper sulfide that has developed.
3.	Electrical Desalting	This technique comes after electrolysis, which removes dissolved ions from oil such as NaCl, $MgCl_2$, and others.
4.	Fractional Distillation	The fumes are passed at the bottom of the fractionating column after the refined crude oil is heated to 4000C. There are multiple horizontal stainless-steel trays in the column. The vapors are condensed and collected according to their boiling temperatures as they pass through the trays.

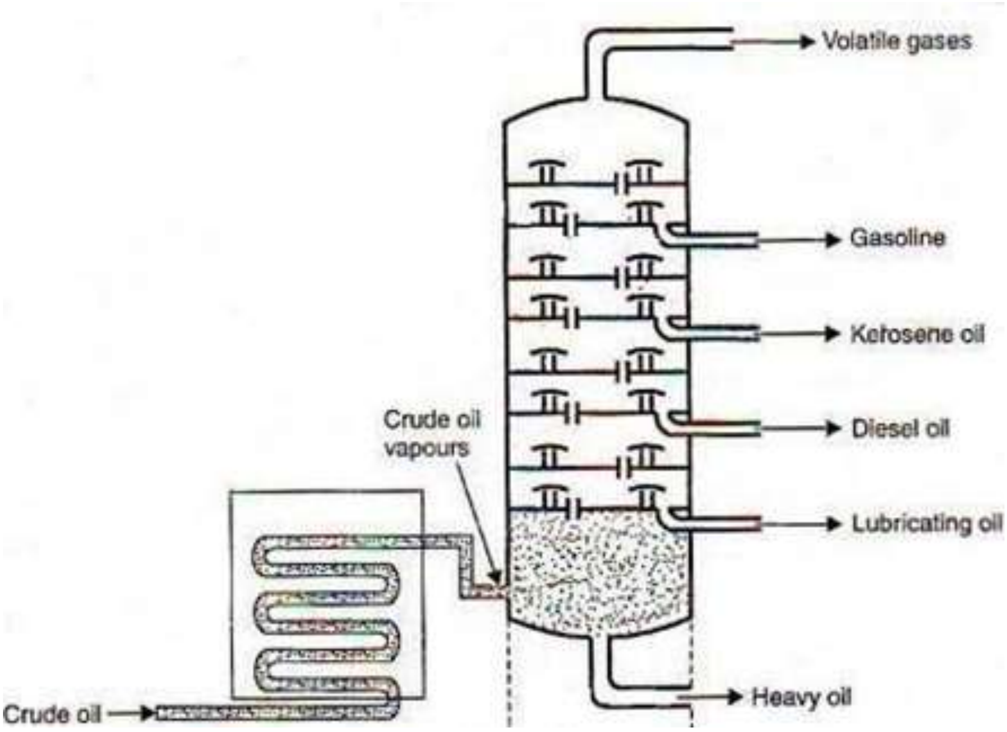


Figure 4.1: Fractional Distillation of Crude Petroleum

When the oil vapors rise in the fractionating column, they cool down and condense on distinct trays. Lower trays condense fractions with greater boiling points, while higher trays condense fractions with lower boiling points. Straight-run gasoline is the gasoline derived from fractional distillation. The table shows the various fractions produced from various trays.

Name of the fraction	**B. Pt. (˚C)**	**C-atoms**	**Uses**
Uncondensed gases	Below 30	C1-C4	Liquefied petroleum gas
Petroleum ether	30-70	C5–C7	As a solvent
Gasoline or petrol	40-120	C5–C9	Fuel for IC engines.
Naphtha or solvent spirit	120-180	C9–C10	As a solvent, dry cleaning
Kerosene oil	180-250	C10–C16	Fuel for stoves, jet engines
Diesel oil	250-320	C15–C18	Diesel engine fuel
Heavy oil	320-400	C17–C30	Fuel for ships, production of gasoline by cracking

Sr.No.	**Name of the Fraction**	**Uses**
1	Lubricating oil	As lubricants
2	Petroleum jelly or Vaseline	Used in medicines and cosmetics
3	Grease	As lubricant
4	Paraffin wax	Used in candles, boot polishes
5	Pitch above 400˚C	Used for making roads and water proofroofing.

4.6 Manufacture of Synthetic Petrol:

Straight-run gasoline is a type of gasoline made via fractional distillation of crude petroleum oil. As the consumption of gasoline grows, the amount of straight-run gasoline available is insufficient to fulfill the needs of the current community. As a result, we must devise a method for synthesizing petrol.

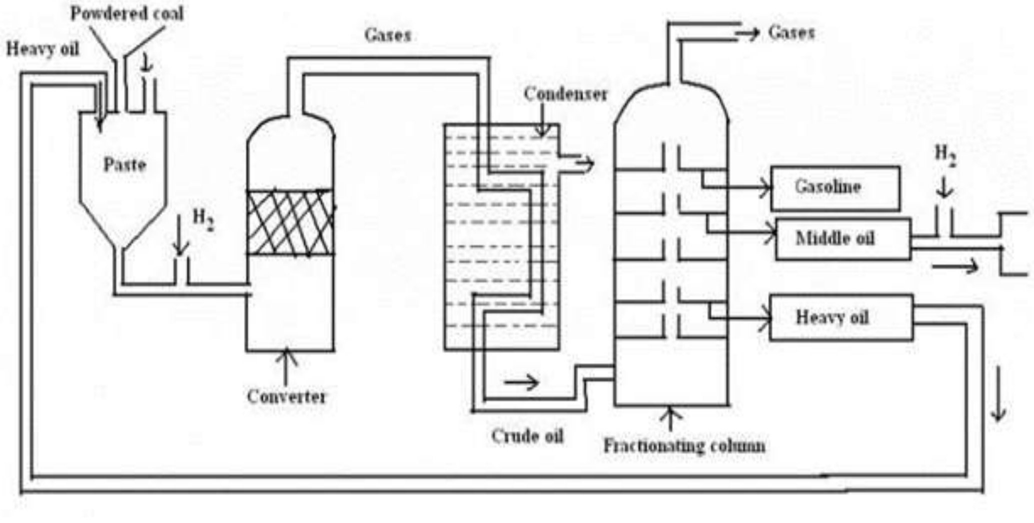
A. Hydrogenation of Coal (or) Synthetic Petrol:

Coal has roughly 4.5 percent hydrogen, but petroleum has about 18 percent. As a result, coal is a hydrogen-deficient substance. Coal is transformed into gasoline when heated with hydrogen to a high temperature under high pressure. Hydrogenation of coal (or synthetic petrol) is the process of making liquid fuels from solid coal. The hydrogenation of coal can be accomplished in two ways.

- Bergius process (or direct method).
- Fischer-Tropsch process (or indirect method).

B. Bergius Process (or) Direct Method:

a. In this process, finely powdered coal is mixed with heavy oil to make a paste, and then a catalyst powder (tin or nickel oleate) is added.
b. The paste is pumped into the converter with hydrogen gas, where it is heated to 400°C under a pressure of 200–250 atm.
c. During this process, hydrogen reacts with coal to produce saturated higher hydrocarbons, which then decompose at higher temperatures to produce a mixture of lower hydrocarbons.
d. The mixture is passed through a condenser, which extracts the crude oil.
e. After that, the crude oil is fractionated into I gasoline, (ii) middle oil, and (iii) heavy oil.
f. More gasoline is produced in the middle vapor phase. The heavy oil is recycled and mixed with fresh coal dust to make a paste.
g. The yield of gasoline is roughly 60%



4.7 Knocking:

Knocking is an explosion (unwanted sound) caused by a quick rise in pressure inside the engine. It's found in both gasoline and diesel engines.

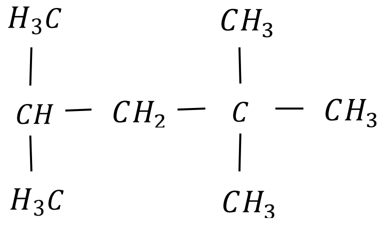
A. Causes of knocking in S.I. (Spark Ignition) Engine [Petrol Engines]:

A 1:17 combination of gasoline vapor and the air is used as fuel in a petrol engine. An electric spark ignites this combination after it has been crushed. The oxidation reaction's result (combustion) raises pressure and forces the piston down the cylinder. Knocking is not a concern if the combustion happens regularly.

However, due to undesired chemical elements in gasoline, the rate of combustion (oxidation) may not be consistent in some situations. The rate of fuel ignition steadily rises, until the final component of the fuel-air mixture ignites instantly, resulting in an explosive sound known as "Knocking." The "Octane number" is used to rate the performance of a knocking petrol engine.

B. Octance Number or Octance Rating:

The octane number is defined as „"the percentage of iso-octane present in a mixture of iso-octane and n-heptane.



$$\begin{array}{ccccccc} H_3C & & & & CH_3 & & \\ | & & & & | & & \\ CH & - & CH_2 & - & C & - & CH_3 \\ | & & & & | & & \\ H_3C & & & & CH_3 & & \end{array}$$

Iso-octane (Octane number -93)

$CH_3 - (CH_2)_5 - CH_3$

n-Leplane (Octane number -

C. Structure Knocking Property is based on the Chemical:

Fuel hydrocarbons' knocking tendency is mostly determined by their chemical structures. The knocking quality of the fuel lowers the engine's efficiency. As a result, good gasoline should be resistant to knocking. In the following order, the knocking tendency decreases.

Straight Chain Paraffins > Branched Chain Paraffins > Cycloparaffins > Olefins > Aromatics.

Thus olefins of the same carbon-chain length possess better anti-knock properties than the corresponding paraffins.

Reduction of Knocking (or) Improvement of Anti-Knocking Characteristics:

- Blending low octane numbered gasoline with high octane numbered fuel
- Adding anti-knock chemicals like Tetra-Ethyl Lead (TEL)
- Aromatic phosphates are now commonly utilized as antiknock agents because they do not pollute the environment with lead.
- Using correct cracking techniques.

D. Leaded petrol:

Gasoline's anti-knock qualities can be improved by adding appropriate additives. Tetraethyl lead (TEL) (C2H5)4Pb is a common addition in gasoline. As a result, leaded petrol is defined as gasoline containing tetraethyl lead,

E. Mechanism of Knocking:

TEL lowers the likelihood of hydrocarbons to knock. Knocking works based on a free radical mechanism, which leads to a chain reaction that ends in an explosion. Knocking will stop if the chains are terminated before they expand. TEL decomposes thermally to create ethyl free radicals, which mix with the knocking process's increasing free radicals to inhibit chain growth.

F. Disadvantages of using TEL:

TEL is transformed to lead oxide and metallic lead when leaded gasoline is used as a fuel. This lead deposits on the spark plug and cylinder walls, shortening the life of the engine. To avoid this, TEL is combined with a little amount of ethylene dibromide. This ethylene dibromide interacts with lead and lead oxide to form volatile lead bromide, which escapes with exhaust fumes. However, this pollutes the atmosphere. As a result, aromatic phosphates are now used in place of TEL.

$$Pb + \begin{array}{l} CH_2-Br \\ | \\ CH_2\quad Br \end{array} \longrightarrow PbBr_2 \uparrow + CH_2=CH_2$$

4.8 Knocking in Diesel Engine:

a. The diesel and air are not sent at the same time in a diesel (compression) engine.
b. Compressed air is delivered initially. The temperature rises to roughly 500 degrees Celsius as a result of the compression. The diesel oil is now being sprayed. This raises the temperature and pressure even further. The piston is pushed by the expanding gases, and the power stroke begins.
c. "Ignition lag" refers to the time interval between diesel injection and ignition.
d. If there are any impurities in the diesel, the ignition will be delayed. The accumulated pion of vapor increases as a result of the delayed ignition lag, significantly increasing the pressure and knocking ensues.
e. The "cetane number" is used to rate the knocking of a diesel engine.

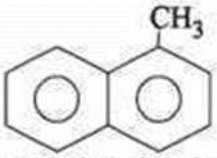
A. Cetane Number or Cetane Rating:

"The proportion of hexadecane present in a mixture of hexadecane and -methyl naphthalene with the same ignition lag as the fuel under test," according to the cetane number.

$CH_3-(CH_2)_{14}-CH_3$

n – cetane (hexa decane)

(cetane number = 100)



α-methyl naphthalene

(cetane number = 0)

The cetane number was created to express diesel's knocking characteristics. Because cetane (hexadecane) (C16H34) has a small ignition lag, its cetane number is 100. -Methyl naphthalene, on the other hand, has a considerable ignition lag and hence has a zero cetane number.

The cetane number decreases in the following order.

Straight chain paraffins > Cycloparaffins > Olefins > Branched paraffins > Aromatics:

The cetane number of a diesel oil can be increased by adding additives called dopes. Ex: Ethyl nitrate, Iso-amyl nitrate.

B. Differences between petrol (gasoline) and Diesel:

Sr.No.	Petrol	Diesel
1.	Fuel for SI engines	Fuel for CI engine
2	Low boiling fraction	High boiling fraction
3	Liberates more pollutants	Less pollutants
4	It is rated by octane number	It is rated by cetane number
5	Knocking is due to premature ignition	Knocking is due to delayed ignition lag
6	Knocking is prevented by anti-knocking agent (e.g., TEL)	Knocking is prevented by dopes (e.g., Iso amyl nitrate)

C. Secondary Gaseous Fuels - Compressed Natural Gas (CNG):

Compressed Natural Gas is the name given to natural gas that has been compressed (CNG). Methane is the most common component in CNG. Natural gas is the primary source. Natural gas can be kept as compressed natural gas (CNG) at 3,000 or 3,600 psi in a vehicle's tank or as liquefied natural gas (LNG) at approximately 20-150 psi. The following is the average CNG composition:

Constituents	Percentage (%)
Methane	88.5
Ethane	5.5
Propane	3.7

Constituents	Percentage (%)
Butane	1.8
Pentane	0.5

Properties:

- CNG is the cheapest, cleanest and least environmentally impacting alternative fuel.
- Vehicles that run on compressed natural gas emit less carbon monoxide and hydrocarbons (HC).
- It is less expensive than petrol and diesel.
- The temperature at which CNG ignites is around 550°C.
- It takes more air to ignite CNG.

D. Advantages of CNG over LPG:

- CNG emits fewer pollutants than LPG and is both cheaper and cleaner.
- Because CNG has a high octane rating, it has higher thermal efficiency.
- It produces no sulfur or nitrogen emissions.
- It is much easier to mix with air than other gaseous fuels.
- The noise level is significantly lower than diesel.
- CNG vehicles emit 40% less nitrogen oxide and 90 percent less carbon monoxide.

Comparison of emission levels between CNG - driven vehicles and petrol driven vehicles

Pollutants	Emission levels	
	Petrol driven vehicle	CNG driven vehicle
CO (g/km)	0.92	0.05
HC (g/km)	0.36	0.24

4.9 Liquefied Petroleum Gas (LPG):

Because it can easily liquefy under pressure, it may be stored and transported in cylinders at a low cost.

The following is the average LPG composition

Constitute	Percentage (%)
n-Butane	38.5
Isobutane	37

Constitute	Percentage (%)
Propane	24.5
Calorific value	25,000kcal/m

Uses: (1) It is used as a domestic and industrial fuel (2) It is also used as a motor fuel.

Advantages of LPG over Gaseous Fuels:

- LPG (hydrocarbons) has a higher calorific value than other gaseous fuels containing H_2 or CO because it is made up of hydrocarbons, which burn cleanly and leave no residue. The calorific value is seven times that of coal gas and three times that of natural gas.
- It has a high thermal efficiency and heating rate
- It is simple to manipulate
- It poses a lower health risk, even if it leaks, and
- It does not contain CO, making it less harmful.

Disadvantages of LPG over other gaseous fuels:

- Leakage is difficult to detect due to its weak odor.
- It has a low octane rating.
- Handling must be performed under extreme stress.
- LPG is only recommended for engines with a high compression ratio.

4.9.1 Combustion of Fuels:

A. Introduction:

Combustion is a quick exothermic oxidation process in which fuel burns in the presence of oxygen, releasing heat and light in the process.

The goal of combustion is to extract as much heat as possible from a flammable substance in the shortest length of time. The majority of combustion compounds are carbon and hydrogen-rich.

They undergo thermal decomposition during burning, yielding simpler molecules that are oxidized to CO_2, H_2O, and other compounds.

$$C + O_2 \longrightarrow CO_2\text{; Exothermic.}$$

$$H_2 + ½O2 \longrightarrow H_2O\text{; Exothermic.}$$

Since the above reactions are exothermic, large quantity of heat is given out.

B. Calorific Value:

The efficiency of a fuel can be understood by its calorific value. The calorific value of fuel is defined as the total amount of heat liberated, when a unit mass of fuel is burnt completely.

C. Units of Calorific Values:

The quantity of heat can be measured by the following units:

- Calorie.
- Kilocalorie.
- British Thermal Unit (B.T.U).
- Centigrade Heat Unit (C.H.U).

Calorie:

It is defined as the amount of heat required to raise the temperature of 1 gram of water through 1°C (15 to 16°C).

4.9.2 Higher and Lower Calorific Values (Dulong's Formula):

A. Higher (or) Gross Calorific Value (GCV):

It is defined as the total amount of heat produced, when a unit quantity of the fuel is completely burnt and the products of combustion are cooled to room temperature. GCV (or) HCV.

B. Lower (or) Net Calorific Value (NCV):

It is defined as the net heat produced, when a unit quantity of the fuel is completely burnt and the products of combustion are allowed to escape. Thus * ( ) †

$$Ncv = Gcv - Latent\ leat\ of\ condensation\ of\ steam\ produced$$

$$Ncv = Gcv - mass\ of\ gydrogen \times 9 \times Latent\ Leat\ of condensation\ of\ steam$$

4.9.3 Flue Gas Analysis (Orsat's Method):

Flue gases are a mixture of gases (such as CO2, O2, CO, and others) that emerge from the combustion chamber.

The study of flue gas can reveal whether the combustion process is full or incomplete. The flue gas analysis is carried out using Orsat's instrument.

A. Description of Orsat's Apparatus:

A horizontal tube makes up the structure. A U-tube holding fused CaCl2 is linked to one end of this tube through a 3-way stop cock. A graded burette is attached to the other end of this tube.

To maintain the temperature of the gas constant, the burette is encircled by a water jacket. A rubber tube connects the lower end of the burette to a water reservoir. The reservoir can be raised or lowered to change the amount of water in the burette. For absorbing CO_2, O_2, and CO, the horizontal tube is additionally attached to three distinct absorption bulbs I, II, and III.

- **Bulb:** It contains potassium hydroxide solution, and it absorbs only CO_2.
- **Bulb:** It contains alkaline pyrogallol solution, and it absorbs CO_2 and O_2.
- **Bulb:** It contains ammoniacal cuprous chloride solution and it absorbs CO_2, O_2 and CO.

B. Precautions:

- Care must be taken in such a way that, the reagents in the absorption bulb 1, 2 and 3 should bebrought to the etched marked level one by one by raising and lowering reservoir bottle.
- By lifting the reservoir bottle, all of the air insides are released into the atmosphere; CO_2, O_2, and CO must be critical that CO_2, O_2, and CO are absorbed in that order only.
- Because the CO concentration of flue gas is very low, it must be measured extremely carefully.

C. Working:

The reservoir is raised and the 3-way stop-cock is opened to the atmosphere until the burette is full with water and the air is excluded from the burette. The 3-way stop-cock is now linked to the flue gas supply, and the flue gas is sucked into the burette while the reservoir is raised and lowered to adjust the volume of flue gas to 100 ccs. After then, the three-way stop cock is closed.

a. Absorption of CO_2: The stopper of the absorption bulb-I, which is filled with KOH solution, is opened, and all of the gas is forced into bulb-I by raising the water level in the burette. The flue gas enters Bulb-I, where CO_2 in the flue gas is absorbed by KOH. The gas is sent to the burette once more. To guarantee total CO_2 absorption, this process is performed multiple times. The volume of CO_2 in 100 ccs of flue gas decreases as the volume of flue gas decreases in the burette.

b. **Absorption of O_2:** The Bulb-I stop-cock is closed, while the bulb-II stop-cock is opened. The flue gas is sent to the absorption bulb-II, where alkaline pyrogallol absorbs the O_2 present in the flue gas. The volume of O_2 in the flue gas in the burette decreases as the volume of flue gas in the burette decreases.

c. Absorption of CO: The stop-cock on bulb II is now closed, while the stop-cock on bulb III is now open. The leftover gas is transferred to the absorption bulb-III, where ammoniacal cuprous chloride absorbs CO from the flue gas. The volume of CO is indicated by the decrease in flue gas volume in the burette. After the absorption of CO_2, O_2, and CO, the residual gas in the burette is referred to as nitrogen.

D. Significance (or) Uses of Flue Gas Analysis:

- A flue gas examination can reveal if a combustion process is full or incomplete.
- If the flue gases contain a significant amount of CO, it shows that incomplete combustion is taking place, as well as a lack of O2.
- If there is a significant amount of O2 in the flue gases, it indicates that complete combustion is taking place and that an excess of O2 is being provided.

E. Ignition Temperature:

The ignition temperature is the lowest temperature to which the fuel must be heated to burn smoothly. The igniting temperature of liquid fuels is referred to as a flashpoint. Examples,

Sr. No.	Type of fuel	Ignition Temperature (^oC)
1	Solid coal	300
2	Liquid fuels	200 – 450
3	Gaseous fuels	800

Spontaneous Ignition Temperature is the lowest temperature at which the fuel spontaneously ignites without any external heat (SIT). Pulverized coal, oil rags, and cotton wastes take a long time to oxidize. If the heat generated cannot escape, the temperature in the system will continue to rise until SIT is reached, at which point the system will spontaneously catch fire.

SIT's Importance: A low SIT rating indicates that the fuel is ready to ignite and poses a fire threat.

4.9.4 Explosive Range (Limits of Inflammability*):*

Fuel must be combined with air in the appropriate proportions to burn. The fuel must be present in a specific range in the fuel-air mixture. The mixing of gaseous fuels has two extreme limits: a) upper limit and b) lower limit. The area encompassed by these two extremes (upper and lower) is referred to as the explosive range or inflammability limits.

Significance: The amount of fuel present in the fuel-air mixture should not fall below the lower limit or rise above the upper limit for continuous burning.

Petrol, for example, has an explosive range of 2–4.5. This means that the mixture will ignite when the concentration of petrol vapor in the petro-air mixture is between 2 and 4.5 by volume. The burning will be improper if it is less than 2% or more than 4.5 percent by volume.

Example:

Sr. No.	**Fuel**	**Explosive Range %**
1	Hydrogen	4 – 75
2	Carbon monoxide	13 – 74
3	Acetylene	3 – 80
4	Natural gas	5 – 14

Power Alcohol:

Power alcohol is created when ethyl alcohol is combined with petrol at a concentration of 5-10%.

The following two steps are involved in the production of power alcohol.

Step1: Manufacture of ethyl alcohol.

The fermentation of carbohydrates in the presence of yeast can produce ethyl alcohol. Only around 20% of the alcohol produced by this fermentation is consumed.

$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2C_2H_5OH + 2C0_2$
(Glucose Sugar) (Ethyl alcohol)

Fractional distillation can enhance the concentration of alcohol up to 97.6%, resulting in rectified spirit.

Step2: Ethyl alcohol is converted to power alcohol.

However, for usage in IC engines. By eliminating the final remnants of water from rectified spirit, 100 percent alcohol (absolute alcohol) is created. The following method can be used to do this.

In the presence of a dehydrated environment, alcohol is distilled. Alcohol is distilled in the presence of a dehydrator that traps the water. To make power alcohol, absolute alcohol is blended with petrol at a concentration of 5-10%.

Properties:

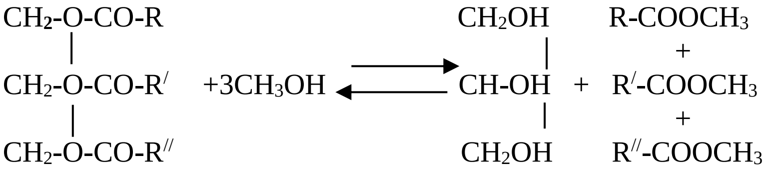
- The calorific value of power alcohol is lower (7000kcal/kg).
- • It has a high octane rating (90).
- • It has good anti-knocking characteristics.

Biodiesel:

Vegetable oils are mostly triglycerides, with a few diglycerides, free fatty acids, and phospholipids thrown in for good measure. Stearic acid and palmitic acid are long-chain fatty acids that makeup triglycerides. Vegetable oils have a higher viscosity and molecular weights in the range of 600 to 900, which are roughly three times higher than diesel fuels.

4.9.5 Manufacture: Trans-Esterification or Alcoholics:

It entails treating vegetable oil, sunflower oil, palm oil, soya bean oil, mustard oil, and other oils with a high concentration of methanol in the presence of a catalyst to produce monomethyl esters of long-chain fatty acids and glycerin. After allowing it to sit for a while, the glycerin separates. The alcoholics reaction is denoted by



$$\begin{array}{l} CH_2\text{-O-CO-R} \\ | \\ CH_2\text{-O-CO-R}' \\ | \\ CH_2\text{-O-CO-R}'' \end{array} + 3CH_3OH \rightleftharpoons \begin{array}{c} CH_2OH \\ | \\ CH\text{-OH} \\ | \\ CH_2OH \end{array} + \begin{array}{c} R\text{-}COOCH_3 \\ + \\ R'\text{-}COOCH_3 \\ + \\ R''\text{-}COOCH_3 \end{array}$$

Methyl esters of fatty acids (Bio diesel)

Methyl esters of fatty acid thus formed are called bio- diesel.

Biodiesel is defined as mono alkyl esters of long chain fatty acids derived from vegetable oils or fats. It is a pure fuel before blending with conventional diesel fuel. It can be blended with petroleum diesel.

ISBN: 978-93-90847-88-4

Chapter 5

Energy Sources and Storage Devices

Syllabus:

Nuclear fission - controlled nuclear fission - nuclear fusion - differences between nuclear fission and fusion - nuclear chain reactions - nuclear energy - light water nuclear power plant - breeder reactor - solar energy conversion - solar cells - wind energy. Batteries, fuel cells and super capacitors: Types of batteries – primary battery (dry cell) secondary battery (lead acid battery, lithium-ion- battery) fuel cells – H_2-O_2 fuel cell.

5.1 Nuclear Fission:

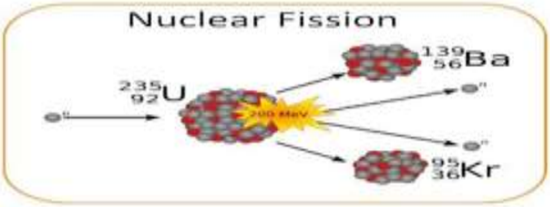
The process of dividing a heavy nucleus into two or smaller nuclei while simultaneously liberating a huge quantity of energy is known as nuclear fission.

Example:

$${}_{92}U^{235} + {}_{0}n^{1} \rightarrow [{}_{92}U^{236}] \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3{}_{0}n^{1} + 200.5 \text{ MeV (Energy)}$$

A. Mechanism of Nuclear Fission:

When a slow-moving neutron bombards U-235, unstable U-236 is generated. With the emission of a large quantity of energy and a few neutrons, this nucleus disintegrates into two equal nuclei**.**



B. Characteristics of nuclear fission reaction: (Part-B):

- The nucleus of the heavy nucleus separates into two or more nuclei.
- Each nucleus produces two or more neutrons when it fissions.
- The nuclear fission reaction produces a large amount of energy.

- The fission pieces are all radioactive, emitting gamma rays.
- Nuclear fission products have atomic weights ranging from 70 to 160.
- Because the neutron is one of the fission products, all fission processes are self-propagating chain reactions.
- By absorbing neutrons using Cd or Boron, nuclear processes can be regulated.
- The nucleus is not struck by every secondary neutron emitted in the fission event. Some neutrons are ejected into the atmosphere. As a result, a chain reaction cannot continue.
- The multiplication factor is the number of neutrons produced by single fission. A nuclear chain reaction does not occur when it is less than 1.

5.2 Nuclear Fusion:

Nuclear energy is defined as the act of combining lighter nuclei to generate heavier nuclei while simultaneously liberating a massive amount of energy.

Example:

Fusion reaction in sun (Thermonuclear reactions)

$$4\,{}_{1}H^{1} \longrightarrow {}_{2}He^{4} + 2\,{}_{+1}e^{0} + \text{Energy}$$

A. Characteristics of nuclear fusion:

- The amount of nuclear fusion that can occur has no limit; nonetheless, it is only conceivable when the distance between the nuclei is on the order of one Fermi.
- Fusion produces four times the amount of energy than fission does.
- A sufficient quantity of kinetic energy must be delivered to promote the fusion reaction, and nuclear fusion can only occur with lighter nuclei.

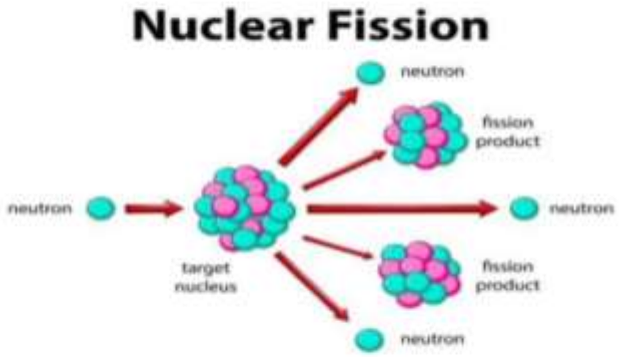
Differences between nuclear fission and nuclear fusion: (Part-B):

Sr. No.	Nuclear fission	Nuclear fusion
1	It is the nucleus. Breaking of heavier	It is the combination nuclei of lighter
2	It emits radioactive rays.	It does not emit radioactive rays.
3	It happens at room temperature.	It takes place at a temperature of over 10^6 degrees Celsius.) extremely high
4	The fission product has a lower mass number and atomic number than the heavier nucleus.	The fusion product has a larger mass number and atomic number than the beginning elements.

Sr. No.	**Nuclear fission**	**Nuclear fusion**
5	It sets off a chain reaction.	It does not give a rise to a chain reaction
6	Neutrons are emitted as a result of this process.	Positrons are emitted.
7	It can be managed.	It is uncontrollable.
8	Example: $92U^{235} + 0n^{1} \rightarrow [92U^{236}] \rightarrow$ ${}_{56}Ba^{141} + {}_{36}Kr^{92} + 3{}_{0}n^{1} +$ Energy	Example: $4{}_{1}H^{1} \longrightarrow 2He^{4} + 2{}_{+1}e^{0} +$ Energy

5.3 Nuclear Chain Reaction:

A fission reaction, where the neutrons from the previous step continue to propagate and repeat the reaction is called nuclear chain reaction.



A. Reason for Less Energy:

Some neutrons generated during the fission of U235 may escape into the air, while others may be absorbed by the impurity U239 present. As a result, the chain will be broken, and the amount of energy released will be less than anticipated.

How to improve the amount of energy?

For a nuclear chain reaction to continue, sufficient amount of U^{235} must be present to capture the neutrons.

B. Critical Mass:

Critical mass is the smallest amount of fissionable material required to keep the nuclear chain reaction going. U-235 has a critical mass of 1 to 100 kg.

- **Super critical mass:**

It's called supercritical mass when the mass of a fissionable substance exceeds the critical mass.

- **Sub critical mass:**

Subcritical mass is defined as the mass of a fissionable material that is smaller than the critical mass. The super- and sub-critical masses may obstruct the chain reaction's propagation.

5.4 Nuclear Energy:

Nuclear fission energy, also known as nuclear energy, is the energy released by nuclear fission.

A. Cause of the release of energy:

The total of the masses of the products exceeds the sum of the masses of the reactants by a small amount. According to Einstein's equation, E= mc2, the mass loss is turned into energy.

Where m- loss in mass, c- velocity, E- energy

B. Hazards of using nuclear energy:

- Nuclear radiation damages the structure of human cells, resulting in disorders such as cancer and blindness.
- In the human body, it causes genetic diseases.
- It makes the younger generation sterile.

C. Types of nuclear fission reaction:

a. Uncontrolled nuclear fission reaction. Example- Atom bomb
b. Controlled nuclear fission reaction. Example- Nuclear power plant.

5.5 Light Water Nuclear Power Plant (Part-B):

A nuclear reactor is an arrangement or piece of equipment that is used to carry out fission reactions under controlled conditions.

The energy released by the nuclear reactor's fission reaction can be utilized to generate steam, which can then be used to power turbines and generate electricity.

Components of a Nuclear Reactor:

a. Fuel rods
b. Control rods
c. Moderators
d. Coolant
e. Pressure vessel
f. Protective shield
g. Heat exchanger
h. Turbine

a. Fuel rods:

The fissionable material used in the nuclear reactor is enriched U-^{235}. It is used in the form of rods or strips.

Example: U^{235}, Pu^{239}

Function:

It generates both fuel and neutrons. A nuclear chain reaction is started by this neutron.

b. Control rods:

Movable rods consisting of cadmium (Cd) or boron (B) are suspended between fuel rods to adjust the rate of U-235 fission.

The extra neutrons are absorbed by these rods. As a result, the fission reaction continues at a constant rate. These rods can be lifted and lowered as needed.

If the rods are put deeply enough into the reactor, they absorb more neutrons, slowing down the reaction. The rods will absorb fewer neutrons if they are pushed outwards, and the reaction will be very quick.

$${}^{113}_{43}Cd + {}^{1}_{0}n \rightarrow {}^{114}_{43}Cd + \gamma$$

$${}^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{11}_{5}B + \gamma$$

Example: Cadmium, Boron

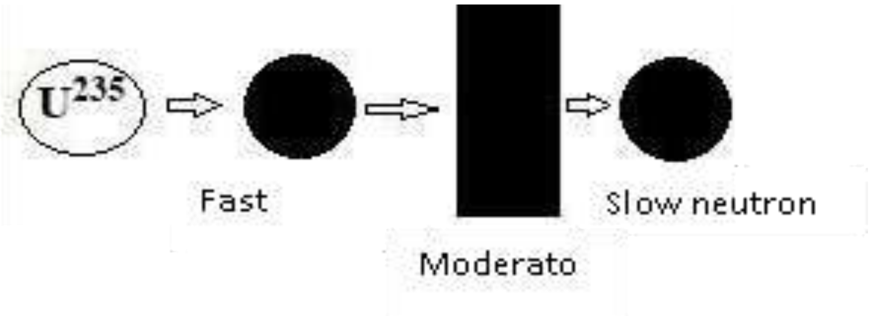
Function: It controls the nuclear chain reaction and avoids the damage to the reactor.

c. Moderators:

The substances used to slow down the neutrons are called moderators.

Example: Ordinary water, Heavy water, graphite, beryllium.

Function: The kinetic energy of fast neutron (1meV) is reduced to slow neutrons (0.25 eV).



d. Coolant:

The coolant circulates in the reactor core to absorb the heat created during the fission reaction. It enters from the bottom and exits from the top. Steam is created by the heat transferred by the exiting liquid.

Example: Water (act as coolant and moderator), Heavy water, liquid metal (Na or K)

Function: It cools the fuel core.

e. Pressure vessel:

It encloses the core and also provides the entrance and exit passages for coolant.

Function: It withstands the pressure as high as 200 atm.

f. Protective shield:

The moderator, control rods, and fuel element are all housed in a concrete shielded chamber (10m thick).

Function: In the event of a radioactive leak, the environment and the operating personnel are safeguarded.

g. Heat exchanger:

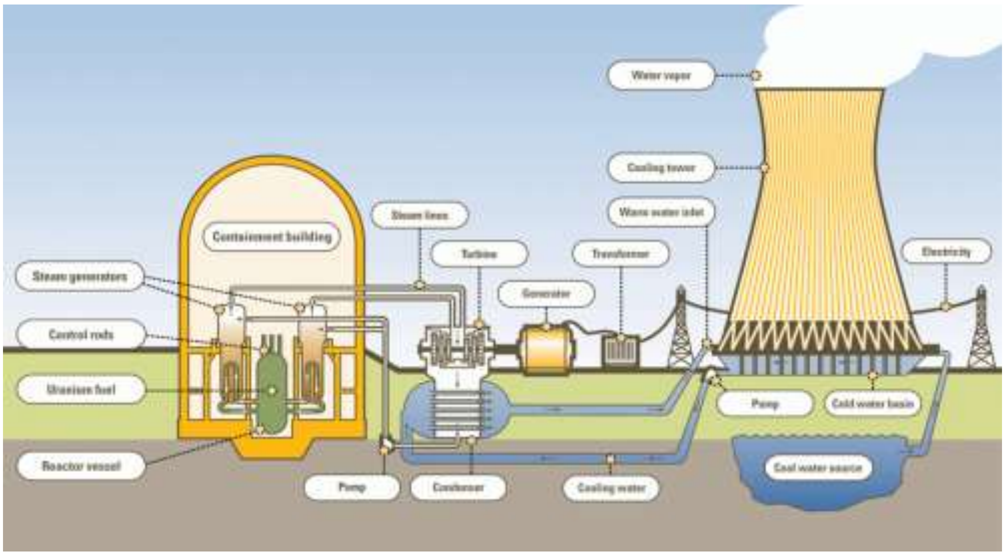
It uses the heat released from the reactor core to boil water and produce steam at a pressure of 400 kilograms per square meter.

H. Turbine:

The steam produced in the heat exchanger powers a steam turbine, which in turn powers a generator to generate electricity.

Working of light water nuclear reactor:

It is the one in which U-235 fuel rods are submerged in water. Here water acts as coolant and moderator.



Light water nuclear power plant

The fission process is regulated by automatically inserting and removing B10 control rods from the gap between the fuel rods. The coolant absorbs the heat that is emitted (light water).

The heated coolant is then passed through a heat exchanger containing seawater and turned into steam. The turbines are powered by steam, which generates energy.

5.6 Breeder Reactor:

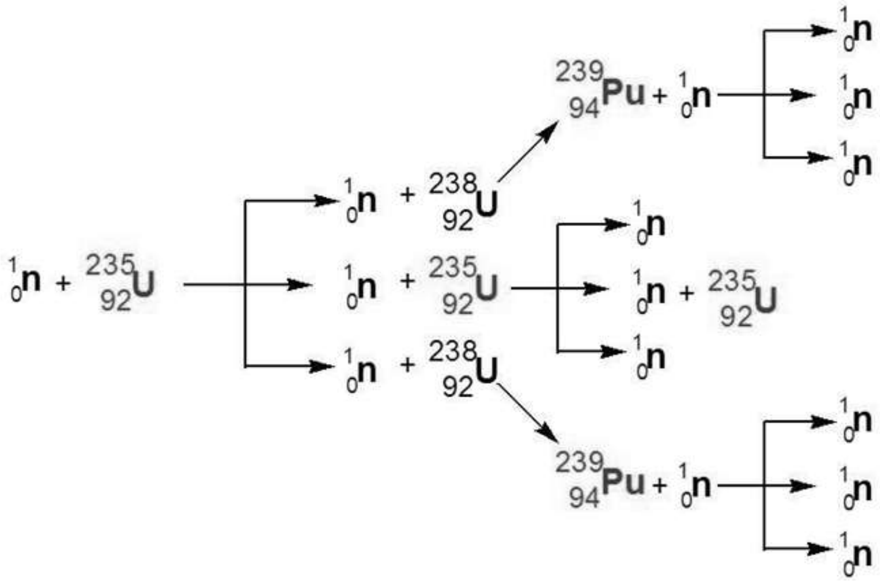
Non-fissionable material (U238, Th232) is converted into fissionable material in a breeder reactor (U235, Pu239). As a result, the reactor generates or creates more fissionable material than it consumes.

A. Illustration:

$$U^{238}_{92} + n^{1}_{0} \rightarrow Pu^{239}_{94} + 2e^{-}$$

$$Pu^{239}_{94} + n^{1}_{0} \rightarrow Fission\ products + 3n^{1}_{0}$$

During the fission of U239 in a breeder reactor, three neutrons are emitted. Only one neutron out of the three is used in the propagation step. The remaining two neutrons are free to interact with U238. One fissionable atom of U235 yields two fissionable atoms of Pu239 as a result. As a result, the breeder reactor generates more fissile material than it consumes. Pu239 is classified as a secondary or man-made fuel.



B. Significance:

- Fertile materials are non-fissionable materials such as U238 and Th232.
- Fissile materials are those that can be fissioned, such as U235 and Pu239
- The breeder reactor's efficiency is higher because fissile materials are regenerated.

Solar energy (Part-B)

5.6.1 Solar Energy Conversion:

It's the transformation of direct sunlight into more usable forms. It happens as a result of the following two mechanisms.

- Thermal conversion
- Photo conversion

A. Thermal conversion:

It entails thermal energy absorption in the form of infrared radiation.

Solar energy is a valuable source of low-temperature heat that can be used to heat buildings, water, and refrigeration systems.

- **Methods of thermal conversion:**

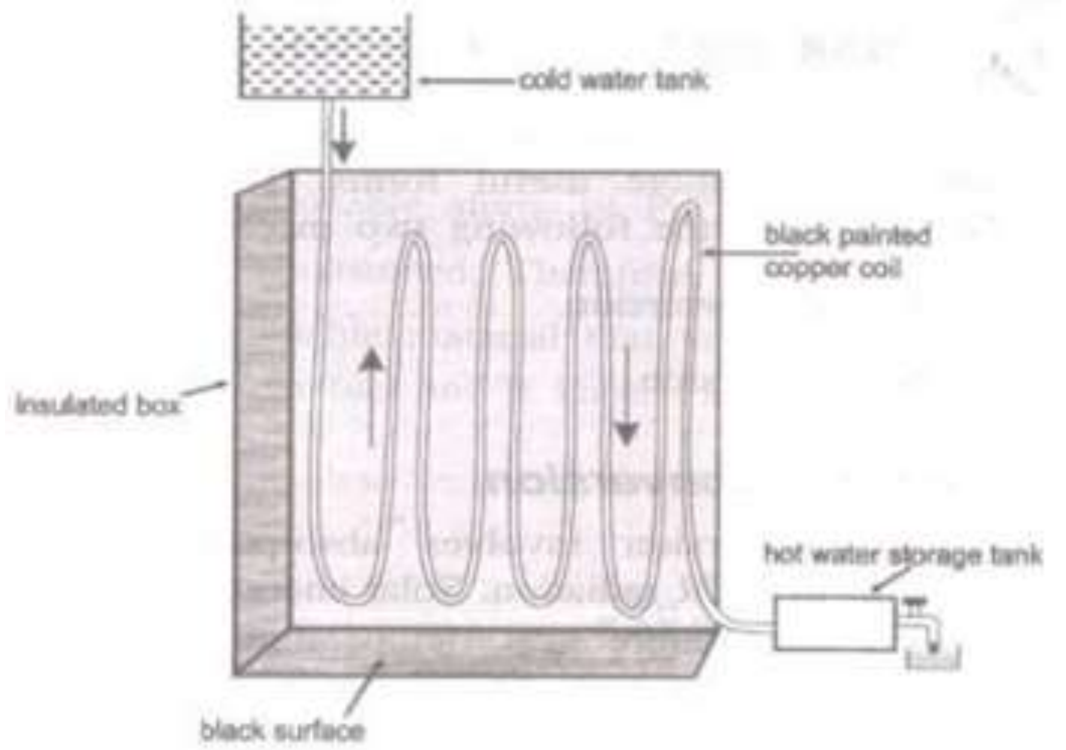
(i) Solar heat collectors:

It is made of natural elements such as stones, bricks, or glass, which may absorb heat during the day and slowly release it at night.

Uses: It is utilized in cold climates where heat collectors are employed to keep houses warm.

(ii) Solar water heater:

It consists of an insulated box inside of which is painted with black paint. It is also provided with a glass lid to receive and store solar heat. The black painted copper coil allows the cold water in and heats it up and flows out into a storage tank.



Solar water heater

B. Photo conversion:

It involves conversion of light energy directly in to electrical energy.

Example: Photo galvanic cell or solar cell

Photo galvanic cell or solar cell. It is the one which converts the solar energy directly into electrical energy.

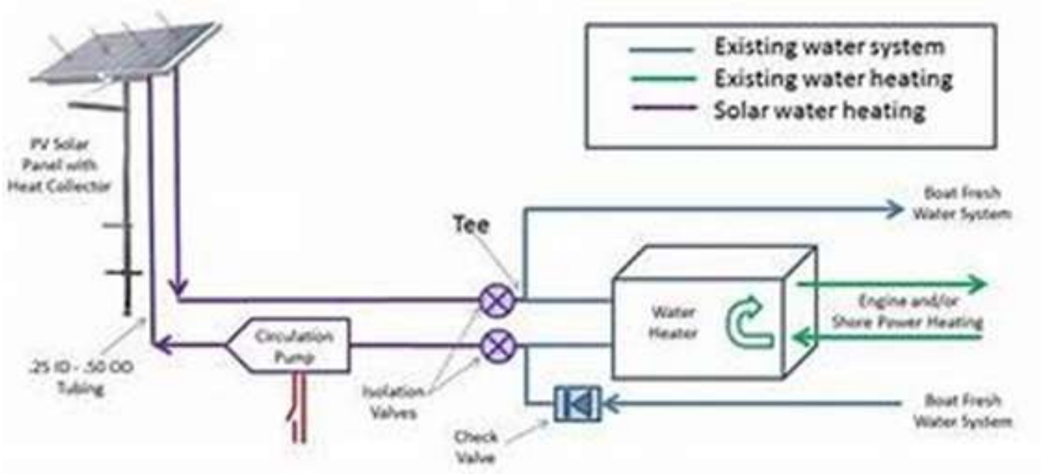
- **Principle:**

The photovoltaic effect is at the heart of the concept. A potential difference between the two layers is created when sun rays fall on two-layer semiconductor devices.

The movement of electrons is caused by the potential difference, which results in the production of electricity.

- **Construction:**

A p-type semiconductor (Si doped with B) and an n-type semiconductor make up the solar cell (Si doped with P). They are in constant communication with one another.



- **Working:**

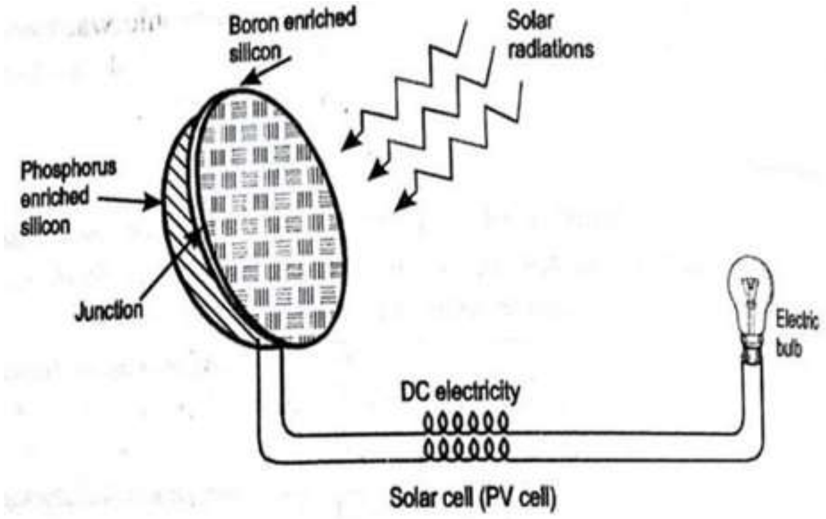
When sunlight strikes an n-type semiconductor, electrons in the valence band are promoted to the conduction band and bridge the p-n junction into the p-type semiconductor.

As a result, a potential difference is created, causing electrons to flow and hence current to be generated.

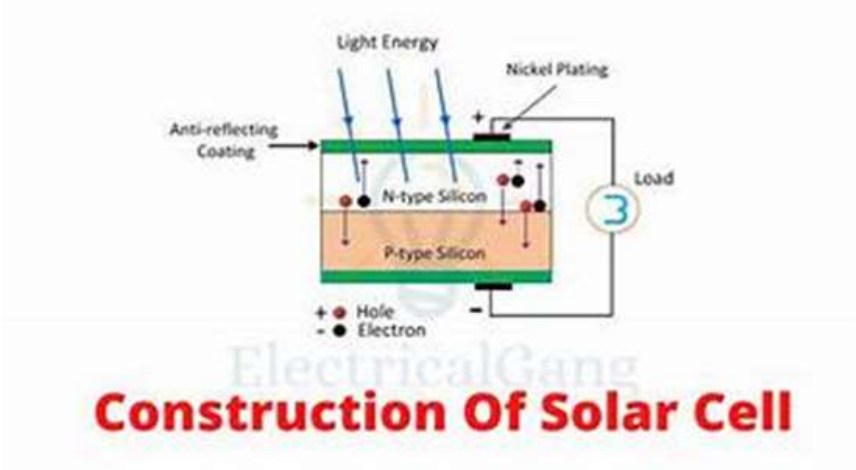
When these p and n layers are coupled to an external circuit, electrons flow from the n-layer to the player, resulting in the generation of current.

- **Applications of solar cells:**

Lighting purpose.



Solar pumps can be run by solar batteries.



Solar pump run by solar cells

- Used in calculators, electronic watches, radios and TV.
- Used to drive vehicles.
- Used in space craft and satellites.

Advantages:

- Solar cells may be employed in remote areas and steep terrain and they have a low maintenance cost.
- Solar cells are non-polluting and environmentally beneficial, with a long lifespan.
- They are not required to be charged.

Disadvantages:

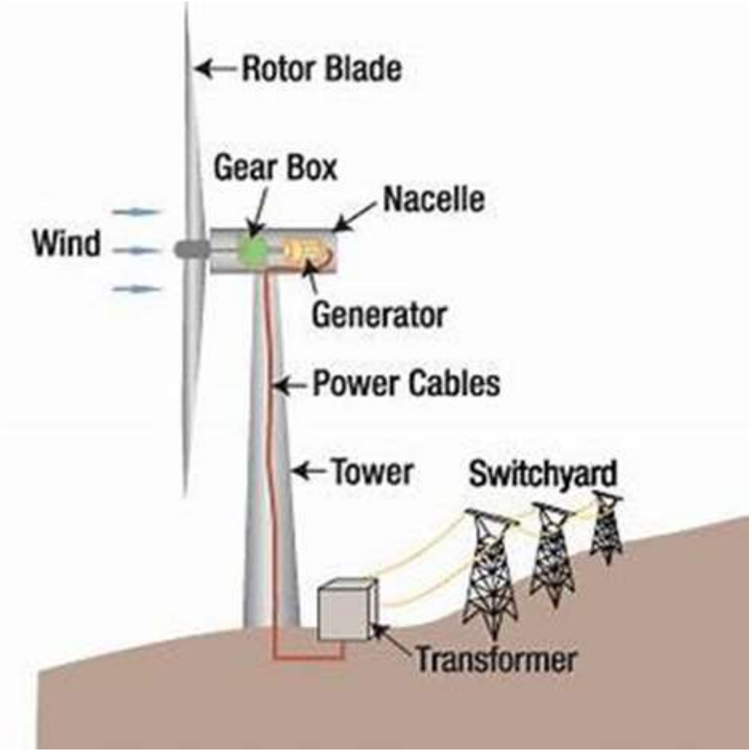
- The initial investment is considerable.
- It is not possible to store solar energy.
- It solely generates DC.
- At night, solar energy is unavailable.

5.6.2 Wind Energy (Part-B):

- Wind is the term for moving air.
- Wind energy is energy recovered from the force of the wind.
- Windmills are used to harness the wind's energy.

A. Wind mills:

The windmill rotates continually due to the impact of the wind on the blades. The blade's circular motion powers a variety of equipment, including water pumps, flour mills, and electric generators.



Wind Energy

Windmills nowadays have enormous propeller blades and are connected to a generator through a shaft. Windmills can generate approximately 100 kW of electricity.

- **Wind farms:**

A wind farm is formed when a large number of windmills are erected and connected in a specific configuration. A substantial amount of electricity is generated by the wind farm.

- **Condition:**

The lowest speed required for a wind generator to function properly is 15 kilometers per hour.

- **Advantages:**

(i) It does not pollute the environment.

(ii) It is quite inexpensive.

(iii) It is a renewable resource.

- **Disadvantages:**

- Because of the noise caused by the machines, the public opposes placing the wind forms near populated areas.
- Wind formations along migratory bird pathways will pose a threat to birds.
- Electromagnetic signals are disrupted by windmills.

5.7 Batteries:

A. Definition:

A battery is a collection of electrochemical cells that are connected in series and can be utilized as a source of direct current.

There is only one anode and one cathode in the cell.

There are numerous anodes and cathodes in the battery.

B. Requirements of a battery:

- It should be light and compact for simple transportation, and it should last a long time both when in use and when not. During use, the battery's voltage should not change significantly.

5.7.1 Types of Battery:

- Primary battery or Primary cell or Non – reversible battery

- Secondary battery or Secondary cell or reversible battery
- Fuel cell or Flow battery

A. Primary battery:

It's a device with a non-reversible cell reaction that can't be recharged. For instance, a dry cell or a mercury cell.

B. Secondary battery or storage cells:

These batteries can be recharged and reused. Its electrode reaction can go in either direction. During charging, the cell undergoes electrical work to produce the free energy required to cause the non-spontaneous reaction.

Example: Lead acid cell, Nickel cadmium cell

5.8 Fuel Cell:

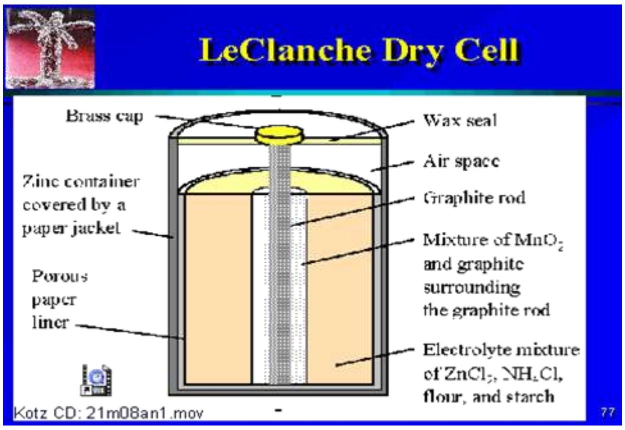
It is similar to a battery and produce electricity using chemicals. They do not run down like batteries.

Example: Hydrogen-oxygen cell, methanol fuel cell.

A. Dry cell or Leclanche's cell (Part-B):

It is a primary cell which works **without fluid** component.

Description:



- A dry cell is made up of an anode, which is a zinc cylinder.
- Ammonium chloride, zinc chloride, and MnO2 are mixed in a paste with flour and water to fill this zinc cylinder.
- A cathode is a graphite (carbon) rod.

- The cathode is immersed in the cell's middle, and the zinc cylinder is insulated by a cardboard casing.

B. Working:

- As the cell works, zinc loses electrons and dissolves in the electrolyte as Zn_2+.ion.
- The electrons are consumed at the cathode after passing through the circuit.
- The electrolyte releases NH_4+.ions as a result of this.
- Manganese is reduced from a +4 oxidation state to a +3 oxidation state in the cathode reaction.
- The release of ammonia gas causes the current flow to be disrupted.
- The presence of $ZnCl_2$ prevents this.

$$ZnCl_2 + 2NH_3 \rightarrow [Zn(NH_3)_2]\ Cl_{2\ (s)}$$

- Anode – Zinc powder
- Cathode – Carbon rod
- Electrolyte – NH_4Cl, $ZnCl_2$ and MnO_2
- Cell representation- $Zn_{(s)}$ /NH_4Cl/$MnO2_{(s)}$
- Anode reaction (oxidation) (loss of electron):

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

Cathode reaction (reduction) (gain of electron):

$$NH^{4(aq)+} \quad + MnO_{2(s)} + 2e^{-} \rightarrow MnO(OH)^{-} + NH_3$$

The net reaction is

$$Zn + NH^{+} \quad + MnO_{2(s)} \rightarrow Zn^{2+} + MnO(OH)^{-} + NH_3$$

The cell develops an e. m. f of 1.5 volt.

Disadvantages:

- Its lifetime is less. Since NH4Cl corrodes the zinc container easily.
- Voltage drop occurs.

Uses:

It is used in radios, tape recorders, torches and electronic photographic flash units.

C. Lead acid battery or Lead storage accumulator (Part-B):

- Gaston Planet created it in 1859, and it works as both a voltaic and electrolytic cell.

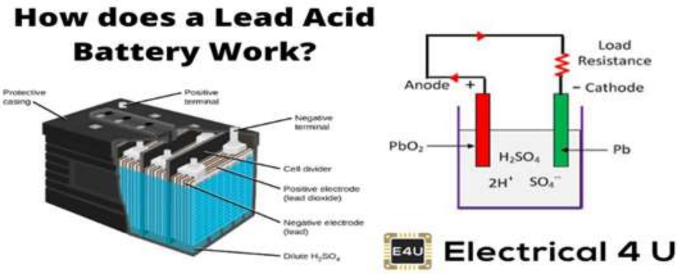
- When electrical energy is supplied, the cell functions as a voltaic cell; when the cell is recharged, it functions as an electrolytic cell.

$$Pb_{(s)} + So_4^{2-} \rightarrow PbSo_4(s) + 2e^-$$

$$Pbo_2(s) + 4H^+ + So_4^{2-} + 2e^- \rightarrow PbSo_4(s) + H_2o$$

Description:

- It is made up of three to six voltaic cells connected in series.
- Lead serves as anode in each cell, whereas PbO_2 serves as a cathode.
- Rubber insulators separate the anode and cathode electrodes.
- The entire arrangement is submerged in a dilute sulphuric acid solution containing 38 percent sulphuric acid by mass and a density of 1.30 g/ml.



Lead storage cell

- Anode – Lead
- Cathode – PbO_2
- Electrolyte - dil. H_2SO_4 (density- 1.38 g/ml)
- Insulator- rubber or glass fiber.
- Cell representation- Pb /$PbSO_4$ // H_2SO_4(aq) // $PbSO_4$/ PbO_2
- Anode reaction (oxidation) (loss of electron):

$$_{(s)} + \boldsymbol{SO^{2-}} \rightarrow \boldsymbol{PbSO_4} + \boldsymbol{2e^-}\ \mathbf{E^0_{anode}=\text{-}0.36V}$$

Cathode reaction (reduction) (gain of electron):

$$\boldsymbol{PbO_2}_{(s)} + \boldsymbol{4H^+} + \boldsymbol{SO^{2-}_4} + \boldsymbol{2e^-} \rightarrow \boldsymbol{PbSO_4}_{(s)} + \boldsymbol{H_2O} \qquad \mathbf{E^0_{cathode}=+1.69V}$$

The net reaction:

$$Pb_{(s)} + Pbo_2(s) + 2H_2So_4 \rightarrow 2PbSo_4 + H_2o$$

$$\left(4H^{+} + So^{2-}_{4}\right)$$

$E^0cell = E^0cathode - E^0 anode$

$E^0cell = 1.69 - (-0.36) = 2.05V$

The cell develops an e. m. f of 2 volts.

Uses:

It is mostly used to supply current in autos such as cars, buses, lorries, and other vehicles. It is also utilized in the ignition of gas engines, telephone exchanges, hospitals, and power plants.

Advantages:

- It is simple to make.
- It generates a lot of currents.
- The rate of self-discharging is low.
- It works well at low temperatures.

Disadvantages:

- Battery recycling is hazardous to the environment.
- Mechanical strain affects the capacity of the battery.

D. Lithium ion batteries (LIB) (Part –B)

Lithium ion battery is a **secondary** battery. It has three components

- Cathode – positive electrode – Layers of lithium cobalt oxide
- Anode – negative electrode – Layers of porous carbon (graphite)
- Electrolyte – Polymer gel

E. Construction:

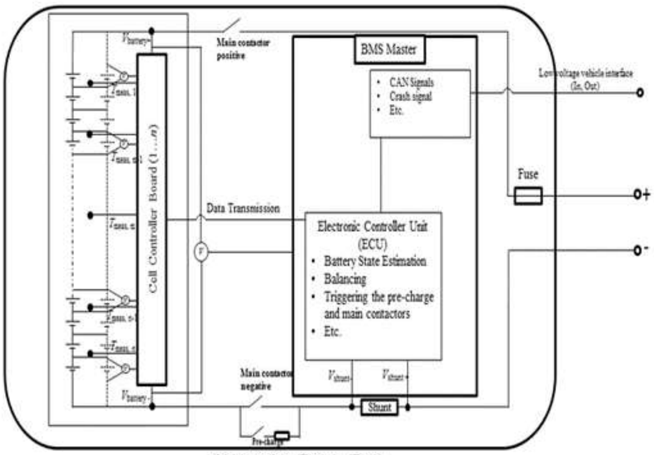
The anode and cathode are separated by a perforated plastic separator after being dipped in a polymer gel.

Working:

During charging, Li+ ions travel through the polymer electrolyte from the positive electrode (cathode) to the negative electrode (anode). Through the wire, electrons move from the positive electrode to the negative electrode. At the negative electrode, electrons and Li+ ions mix and deposit as Li.

- **Charging reaction:**

$$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + CLi_x$$



Lithium-Ion Battery Pack

- **Discharging reaction:**

$$Li_{1-x}CoO_2 + CLi_x \rightarrow LiCoO_2 + C$$

The reverse reaction occurs during the discharge reaction. That is, Li+ ions pass through the electrolyte from the negative electrode to the positive electrode. Similarly, electrons pass through a wire from the negative electrode to the positive electrode. As a result, Li forms at the positive electrode.

Uses:

It can be found in cell phones, laptop computers, portable LCD televisions, power equipment, and electric vehicles.

Lithium battery is the cell of future, why?

- Its cell voltage is high, 3.0V
- Since Li is a light weight metal, only 7g (1mole) material is required to produce 1 mole of electrons
- Since it has the most negative E0 value, it generates a higher voltage than the other types of cells.
- Since all the constituents of the battery are solids, there is no risk of leakage from the battery.
- This battery can be made in variety of sizes and shapes.

Fuel cells (Part –B)

A fuel cell is a type of photovoltaic cell that turns the chemical energy of fuels directly into electricity without the need for burning.

$$\boldsymbol{Fuel + Oxygen \rightarrow Oxidation\, products + Electricity}$$

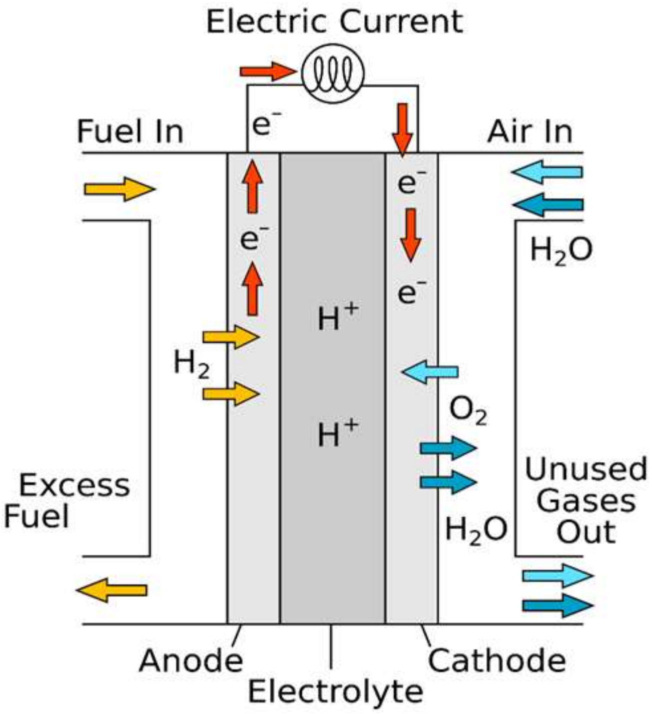
Example: 1. Hydrogen – Oxygen fuel cell

2. Methyl alcohol –Oxygen fuel cell

Description:

- Electricity can be created in a fuel cell as long as the cell is supplied with fuel and oxygen.
- It is made up of an anode, a cathode, and an electrolyte.
- Fuel is delivered through the anode and oxygen is delivered through the cathode in a fuel cell.
- The electrolyte transports charged particles from the anode to the cathode and back.

F. Hydrogen – Oxygen fuel cell:



- Anode- Hydrogen gas
- Cathode- Oxygen gas
- Electrolyte- 25-40% KOH

- Electrode- Two porous carbon electrode impregnated with a finely platinum or nickel as catalyst.
- Cell representation: H_2, C, Pt or Ni /KOH/ C, Pt or Ni, O_2
- Anode reaction:

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

- Cathode reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

- Net reaction:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

- The cell generates a 1.23V emf.
- The hydrogen-oxygen fuel cell has a 70% efficiency.
- The operating temperature is 60-70 degrees Celsius.

G. Advantages:

- It is quite dependable.
- It does not pollute the environment.
- It generates water that may be taken with you.
- It's employed in spacecraft and submarines.

Disadvantages:

- Hydrogen gas is costly.
- Because hydrogen is a gas, compressing it into a liquid requires a lot of pressure, which is why it's utilized in automobiles.

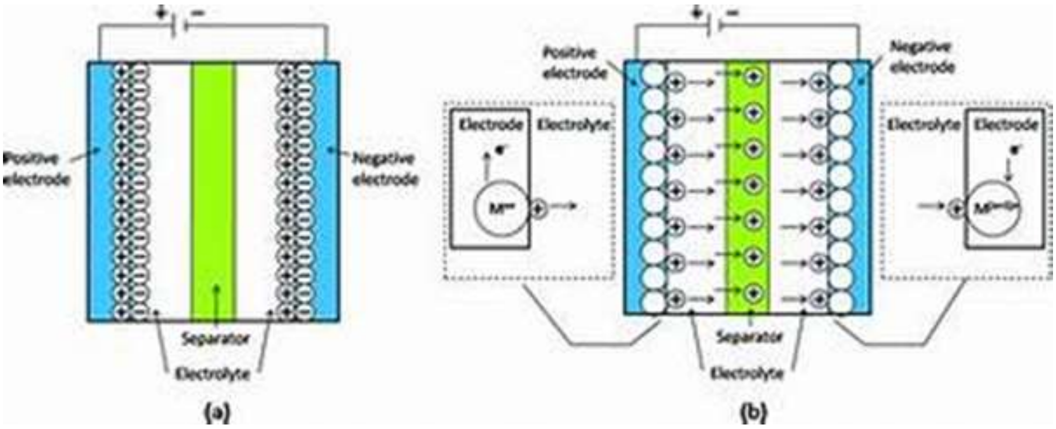
H. Applications:

- It is used in military and commercial vehicles of various types, as well as in the Apollo spacecraft to produce energy and water.

A super capacitor (Electrochemical capacitor) (Part –B)

- High-capacity capacitors store 10 to 100 times more energy per unit space than batteries and give charge considerably faster.

- Instead of using a traditional solid dielectric, super capacitors use electrostatic double-layer capacitance.



Design of the super capacitor

- It consists of two electrodes that are separated by an ion-permeable membrane and dipped in the electrolyte.
- The electrodes are constructed of a metal-coated porous substance such as powdered activated carbon.
- The electrolyte connects the electrodes and contains both positive and negative ions.

I. Working:

- When the electrodes are linked to the power source, the ions in the electrolyte form an electrical double layer, which creates an electric field between the electrodes and the electrolyte. At the electrode/electrolyte contact, electrical energy is thus stored.
- For example, at the electrode/electrolyte interface, positive electrodes have a layer of negative ions and vice versa.

J. Advantages:

- It is extremely safe.
- It has a long lifespan.
- It may be charged in seconds and lasts for 10 to 20 years.
- It has a high power density and high efficiency. It has a high power density and high load currents, and it works well at low temperatures.

Disadvantages:

- It is expensive, and it cannot be utilized as a source of continuous power.
- If higher voltage is required, the cells must be connected in series.
- Self-discharge is high.

K. Applications:

- Start/stop system voltage stability
- Energy harvesting
- Kitchen appliances
- Consumer electronics
- Wind energy
- Utility meters
- Remote power sensors, LEDs, switches.

6. References

BOOKS:

1. Engineering chemistry by K. SUBRAMANIAN, V. PUSHPANATHAN., REVISED EDITION 2018
2. Engineering Chemistry by A. SHEIK MIDEEN REVISED 2017-APRIL.
3. Engineering Chemistry by A. RAVIKRISHNAN
4. https://sites.google.com/a/perthgrammar.co.uk/physics/_/
5. http://3.bp.blogspot.com/
6. https://image.slidesharecdn.com/powerreactors.
7. https://www.custommarineproducts.com
8. https://tse1.mm.bing.net
9. http://www.public.asu.edu
10. https://tse2.mm.bing.net
11. https://www.learningengineering.com

ABOUT THE BOOK:

The book is written in simple language and covers the engineering chemistry topics. This book has consistently been used by students studying the first year course in engineering. The book is intended to be an ideal text book encompassing the following aspects:

- *Water treatment methods*
- *Adsorption and Catalytic concepts*
- *Phase rule and alloys*
- *Fuel and Combustion*
- *Energy storage Devices*

Each chapter is presented in a clear style with an understandable approach.

ABOUT THE AUTHORS:

Rajabhuvaneswari Ariyamuthu *received her M.Sc (Chemistry) from Madurai Kamarajar University and Ph.D (Polymer Chemistry) from Anna university, College of Engineering , Guindy, Chennai.*

She has been as an academician for 14 years in various Anna university affiliated Engineering and Arts and Science colleges. She is a board of study member for Anna university affiliated colleges and also Editorial board member for science journal of chemistry and society of polymer science India. She has published Research papers , books and book chapters.

Dr.Valentine Rupa *received her M.Sc., Chemistry from Salem, Periyar University and stood as a rank holder during her studies. She received her Ph.D (Catalysis) from Anna University , A.C Tech Campus, Guindy Chennai.*

She has been teaching chemistry for students under UG and PG level.she has teaching experience for more than 12 years. She has published her research findings in various international journals and presented her finding in national and international conferences. She is also author of books and book chapters.

KRIPA DRISHTI
PUBLICATIONS

Kripa-Drishti Publications
A-503 Poorva Heights, Pashan-Sus Road, Near Sai Chowk,
Pune – 411021, Maharashtra, India.
Mob: +91 8007068686
Email: editor@kdpublications.in
Web: https://www.kdpublications.in

ISBN: 978-93-90847-88-4
9 789390 847884