

# **GUDLAVALLERU ENGINEERING COLLEGE**

(An Autonomous Institute with Permanent Affiliation to JNTUK, Kakinada)

Seshadri Rao Knowledge Village, Gudlavalleru – 521 356.

## **Department of Mechanical Engineering**



## **HANDOUT**

**on**

## **INDUSTRIAL CHEMISTRY**

## **Vision**

- ❖ To become a competent centre in moulding students as professional mechanical engineers having ethical standards and social consciousness.

## **Mission**

- ❖ To impart value based education and to enhance competencies of students through effective design and delivery of the curriculum that fulfils the needs of the industry.
- ❖ To instill desire and confidence in the students to cater the needs of the society through their activities of excellence.
- ❖ To impart technical skills and nurture values, and mould the students as professionals to offer solutions to the technological challenges.

## **Program Educational Objectives**

- PEO-1 Graduates of the program will have bright careers in Mechanical Engineering domain and allied areas.
- PEO-2 Graduates of the program will have life skills, sense of ethical conduct and social responsibility.
- PEO-3 Graduates of the program will continue to learn and update their competencies to face dynamically changing technological environment.

# INDUSTRIAL CHEMISTRY

## I Year – II Semester

Lecture: 4

Internal Marks: 40M

Credits: 3

External Marks: 60M

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### 1. Brief History and Scope of the Subject

Chemistry is the study of matter, its properties and the changes that it may undergo and how these properties and changes are affected by its composition. It is important for engineers to have knowledge of chemistry, since they can expect to find problems in fields as diverse as the design and development of new materials, quality control and environmental engineering that are basically chemical in nature. Chemistry is the back bone in designing and understanding the nature of various engineering materials. Many advances in engineering either produce a new chemical demand as in the case of polymers or wait upon chemical developments for their application as in the case of implants and alloys. Currently, the mechanical engineers are on look out for micro fluids and the civil engineers are also looking for materials that are environment friendly, economical but long lasting.

the electronics and computers engineers are waiting for suitable biopolymers and nano-molecules for use in miniature super computers; the electrical engineers are in search of proper conducting polymers;

### 2. Pre-Requisites

Intermediate Chemistry

### 3. Course objectives:

- To impart knowledge of corrosion prevention methods and water treatment technologies.
- To enable the students to obtain the knowledge on various types of electro chemical energy systems, polymers, fuels, lubricants and their applications in engineering.

### 4. Course outcomes:

Students will be able to

- explain the working of lead acid battery, nickel - cadmium battery, lithium ion battery and fuel cells.
- apply a suitable method of corrosion prevention for a given problem.
- apply a suitable method of water treatment depending on the quality requirement.
- explain the analysis of fuels, to calculate the calorific value and air requirement for combustion of a given fuel and to explain the synthesis and extraction methods of different liquid fuels.
- explain the preparation, properties and applications of polymers and composite materials.
- explain the characteristic features of a lubricant and their applications

### 5. Program Outcomes:

Graduates of the Mechanical Engineering Program will have

- a) Apply knowledge of Mathematics, Science and Engineering to solve complex Mechanical Engineering problems.
- b) Identify, formulate and analyze problems related to Mechanical Engineering.
- c) Design Mechanical engineering systems, to meet the desired needs with the economic, environmental, social, ethical, health and safety constraints.
- d) Investigate the technological challenges through the use of research based knowledge to design experiments, critical analysis and interpretation of data, synthesis of the data to arrive at valid conclusions.
- e) Model and simulate Mechanical engineering systems, to conduct experiments and analyze the performance using modern software tools.
- f) Assesses issues pertaining to societal, health, safety, legal, cultural and accordingly engage in professional engineering practices.
- g) Demonstrate knowledge for sustainable development with an understanding on the impact of professional engineering on society and environment.
- h) Follow professional ethics, norms and standards of engineering practices.
- i) Work as an effective member of the team and also as an individual in diverse and multi disciplinary streams.
- j) Prepare reports and present effectively and also orally communicate fluently with the society and engineering community.

- k) Apply knowledge of Management and Finance for effective project management.  
 l) Engage in life-long learning independently to stay with the changes in technology.

6. **Mapping of Course Outcomes with Program Outcomes:**

|     | a | b | c | d | e | f | g | h | i | j | k | l |
|-----|---|---|---|---|---|---|---|---|---|---|---|---|
| CO1 | H | M | H |   |   |   |   |   |   |   |   |   |
| CO2 | H | M | M |   |   |   |   |   |   |   |   |   |
| CO3 | H | L |   |   |   |   |   |   |   |   |   |   |
| CO4 | H | M |   |   |   |   |   |   |   |   |   |   |
| CO5 | H | H | H |   |   |   |   |   |   |   |   |   |
| CO6 | H | M | L |   |   |   |   |   |   |   |   |   |

7. **Prescribed Text Books**

- Text book of Engineering Chemistry by Jain & Jain. Dhanpat Rai Publishing Company, 16<sup>th</sup> Edn., 2015.
- A Text book of Engineering Chemistry by Shashi Chawla. Dhanpat Rai Publications, 3<sup>rd</sup> Edn., 2013.

8. **Reference Text Books**

- A Text book of Engineering Chemistry by S.S.Dara. S.Chand&Company Ltd., 12<sup>th</sup> Edn.,2010.
- Engineering Chemistry by J.C.Kurisasose and J.Rajaram. volumes 1 & 2, Tata Mc Graw-Hill Publishing.

9. **URLs and Other E-Learning Resource**

- <http://www.hunterwater.com.au/Water-and-Sewer/WaterSupply/WaterTreatmentProcesses.aspx>  
<http://www.mpoweruk.com/chemistries.htm>  
[http://chemwiki.ucdavis.edu/Core/Analytical\\_Chemistry/Electrochemistry/Case\\_Studies/Corrosion/Corrosion\\_Basics\\_II](http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Electrochemistry/Case_Studies/Corrosion/Corrosion_Basics_II)  
<http://www.open.edu/openlearn/science-maths-technology/science/chemistry/introduction-polymers/content-section-0>

10. Digital Learning Materials:

- <http://www.faadoengineers.com/threads/7899-Engineering-Chemistry-Ebook-pdf-free-download>

11. **Lecture Schedule / Lesson Plan**

| Topic  | No. of Periods |          |
|--|----------------|----------|
|  | Theory         | Tutorial |
| <b>UNIT –1: Electro Chemical Energy Systems</b>  |                |          |
| Differences between primary cells and secondary cells  | 2              | 2        |
| Construction, electro chemical reactions and applications of secondary cells – Ni-Cd battery                       | 1              |          |
| Lithium ion battery  | 1              |          |
| Pb-acid storage battery and maintenance free lead acid battery   | 2              | 2        |
| Construction, electro chemical reactions and applications of Fuel cells – H <sub>2</sub> -O <sub>2</sub> fuel cell | 1              |          |
| Methanol-oxygen fuel cell, Phosphoric acid fuel cell   | 2              |          |
| <b>UNIT-II : Corrosion and its prevention</b>  |                |          |
| Dry corrosion mechanism and Pilling - Bedworth Rule  | 1              | 2        |
| Wet corrosion mechanism  | 1              |          |
| Types of Corrosion – galvanic corrosion, concentration cell corrosion, pitting corrosion and stress corrosion      | 1              |          |
| Factors influencing the rate of corrosion –Temperature, pH and dissolved oxygen                                    | 1              |          |
| Corrosion Prevention methods – Cathodic protection-Sacrificial Anodic method and Impressed current method          | 1              | 2        |
| Metallic coatings –galvanization and tinning methods   | 1              |          |
| Corrosion problems in boilers and preventive measures.   | 1              |          |
| Corrosion problems in heat exchangers and preventive measures.   | 1              |          |

|   |           |           |
|---|-----------|-----------|
| <b>UNIT-III: Water and its treatment</b>  |           |           |
| Hardness of water   | 1         | 2         |
| Calculation of hardness   | 1         |           |
| Disadvantages of using hard water in Boilers – priming and foaming<br>sludge and scale formation  | 1         |           |
| caustic embrittlement – Boiler corrosion  | 1         |           |
| Treatment of boiler feed water – Zeolite process  | 1         |           |
| Ion exchange process  | 1         | 2         |
| Internal treatment – Calgon conditioning and Colloidal conditioning   | 1         |           |
| Desalination of Brackish water by RO method   | 1         |           |
| <b>UNIT-IV: Fuels</b>   |           |           |
| Definition and classification of fuels  | 1         | 2         |
| Calorific value of a fuel – Characteristics of a good fuel  | 1         |           |
| Coal – Types of Coal.   | 1         |           |
| Analysis of Coal – Proximate Analysis   | 1         |           |
| Ultimate analysis   | 1         |           |
| Bomb Calorimeter  | 1         |           |
| Junker’s gas Calorimeter  | 1         | 2         |
| Problems on calculation of calorific value  | 1         |           |
| Liquid fuels – Petroleum Extraction – Fractional distillation   | 1         |           |
| Synthetic Petrol – Bergius process and Fisher Tropsch process   | 1         |           |
| Problems on air requirement for combustion.   | 1         |           |
| <b>UNIT-V: Polymers and Composites</b>  |           |           |
| Definition of a polymer and polymerization – Degree of polymerization – Functionality – Types of polymerization – addition, condensation and co-polymerization with examples. | 2         | 2         |
| Plastics – thermo plastics and thermo setting plastics  | 1         |           |
| Compounding of plastics   | 1         |           |
| Moulding techniques – Compression, Injection and Blow film moulding   | 2         | 2         |
| Preparation, properties and applications of PVC, Polystyrene, Teflon  | 1         |           |
| Preparation, properties and applications of Bakelite.   | 1         |           |
| Composites – Definition of matrix and reinforcement   | 1         |           |
| Fibre reinforced plastics – Glass fibre, preparations, properties and applications  | 1         |           |
| Carbon fibre reinforced plastics- preparations, properties and applications   | 1         |           |
| Preparation methods – hand layup method, matched metal die moulding method  | 1         |           |
| <b>UNIT-VI: Lubricants</b>  |           |           |
| Definition and functions of a good lubricant  | 1         | 2         |
| classification of lubricants  | 2         |           |
| Mechanism of lubrication  | 1         |           |
| Experimental determination of properties of a liquid lubricant – Viscosity, Aniline point   | 2         | 2         |
| Flash and Fire point, Pour and Cloud point  | 1         |           |
| Additives to lubricants. Lubrication by nano films. Applications of lubricants  | 1         |           |
| <b>Total No. of Periods:</b>  | <b>57</b> | <b>24</b> |

## 12. Seminar Topics

- Modern fabrication techniques of plastics.
- Corrosion problems in boilers and heat exchangers, preventive measures.

**UNIT-I**  
**Electrochemical energy systems**

**Objective:**

- To familiarize the students in electrical energy generation and storage by batteries used in electrical and electronic equipment.
- To familiarize the students in electrochemistry of different fuel cells.

**Syllabus:**

(a) Differences between primary cells and secondary cells, Construction, electro chemical reactions and applications of secondary cells- Ni-Cd battery, Lithium ion battery, Pb-acid storage battery, maintenance free lead acid battery. Construction, electro chemical reactions and applications of Fuel cells - H<sub>2</sub>-O<sub>2</sub> fuel cell, Methanol-oxygen fuel cell, phosphoric acid fuel cell

**Outcomes:** After learning the subject of this unit, the student will be able to

1. Understand that potential difference is generated during redox reactions and these electrochemical reactions are basic for electrical energy generation and storage.
2. Understand the characteristics of primary cells.
3. Understand the working and applications of secondary cells (rechargeable batteries)
4. Understand the working and applications of Fuel cells (continuous replenishment of energy via external fuel).

**Primary cell or Dry cell:**

The cell in which the cell reaction is not reversible is called a Primary cell. Thus when the reactants have been converted to products, no electricity is produced and the cell becomes dead and cannot be used after that. These batteries are used as a source of DC power. The dry cells are convenient to use and cost of discharge is not much. These are generally used in torchlights, transistor radios and calculators etc.

Eg: Dry cell(Leclanche cell), alkaline batteries and Lithium cells etc.

**Secondary cells or Storage cells:**The cell in which the cell reaction is reversible is called a Secondary cell. A secondary cell works like an electrochemical cell(Galvanic cell) as well as an electrolytic cell. During working as galvanic cell, secondary cell supplies the electrical energy and forms the products from reactants. If electrical energy is supplied in reverse direction to the secondary cell, then it works as electrolytic cell and the reactants are generated at the electrodes from the products i.e. the cell is again ready for supply of electrical energy. Hence these cells are used for storing electrical energy and named as Storage cells. This advantage of secondary cells finds many applications in automobile industry, as inverter battery and to store electricity produced by photovoltaic systems.

Eg:Ni-Cd batteries, Pb-Acid batteries and Lithium ion batteries etc.

**Differences between Primary cell and Secondary cell:**

| S.No. | Primary cell  | Secondary cell  |
|-------|---|---|
| 1     | Cell reaction is not reversible.                                      | Cell reaction can be reversed.                                    |
| 2     | Cannot be recharged.  | Can be recharged.   |
| 3     | Can be used as long as the materials are active in their composition. | Can be used again and again by recharging the cell.               |
| 4     | Example: Leclanche cell or Dry cell, Alkaline cells etc.              | Lead acid storage cell, Ni-Cd batteries and Li-ion batteries etc. |

**Secondary cells or Storage cells:** The cell in which the cell reaction is reversible is called a Secondary cell. A secondary cell works like an electrochemical cell (Galvanic cell) as well as an electrolytic cell. During working as galvanic cell, secondary cell supplies the electrical energy and forms the products from reactants. If electrical energy is supplied in reverse direction to the secondary cell, then it works as electrolytic cell and the reactants are generated at the electrodes from the products i.e. the cell is again ready for supply of electrical energy. Hence these cells are used for storing electrical energy and named as Storage cells. This advantage of secondary cells finds many applications in automobile industry, as inverter battery and to store electricity produced by photovoltaic systems.

**Ni-Cd Battery:**

Ni-Cd battery is a rechargeable battery of 1.2 V which has longer life than lead acid storage cell.

Anode: Cadmium electrode

Cathode: Nickel(III) oxide-hydroxide [NiO(OH)]

Electrolyte: KOH

Electrochemical reactions at electrodes during discharge:

At Anode:  $\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2 + 2\text{e}^-$

At Cathode:  $2\text{NiO}(\text{OH}) + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ni}(\text{OH})_2 + 2\text{OH}^-$

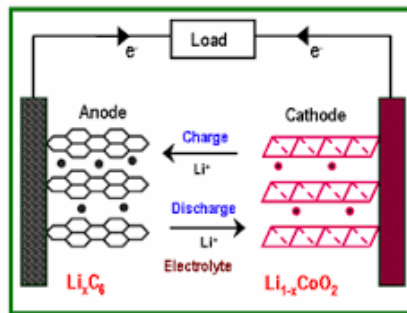
Overall reactions:  $\text{Cd} + 2\text{NiO}(\text{OH}) + 2\text{H}_2\text{O} \rightarrow \text{Cd}(\text{OH})_2 + 2\text{Ni}(\text{OH})_2$

Applications: Ni-Cd cells are used in calculators, cordless and wireless telephones, emergency lightning and remote controlled electric model airplanes etc.

**Lithium ion battery:**

Lithium ion batteries (Li-ion batteries) can be rechargeable hence they are used as storage batteries. In this battery, lithium is taken in a state of intercalation compound both in anode and cathode.  $\text{LiCoO}_2$  acts as cathode and porous carbon acts as anode. Lithium salts such as

$\text{LiPF}_6$  or  $\text{LiBF}_4$  is taken in an organic solvent such as ethylene carbonate. Anode and cathode are separated by a membrane.



During discharge, the current flows within the battery from the anode to cathode and  $\text{Li}^+$  ions move from graphite to cobalt oxide through the non-aqueous electrolyte.

During charging, by an external power source, negative terminal is connected to anode of the cell and positive terminal is connected to cathode and  $\text{Li}^+$  ions move from cobalt oxide to graphite through the non-aqueous electrolyte.

The cathode half-cell reaction:  $\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$

The anode half-cell reaction is:  $x\text{Li}^+ + xe^- + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6$

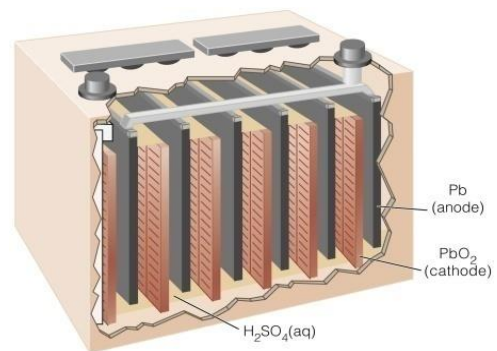
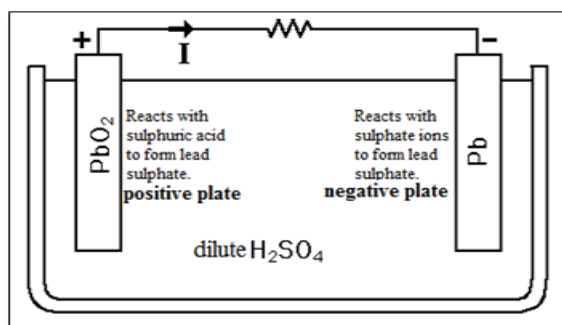
Overall reaction is:  $\text{LiCoO}_2 + 6\text{C} \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6$

Advantages:

- 1) Li-ion batteries have high energy-to-weight ratio, hence they are portable.
- 2) Li-ion batteries have high slow-discharge when not in use.

Application: Li-ion cells are used in mobile phones, laptops and other electronic equipment.

**Lead acid storage cell:**



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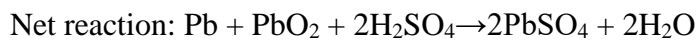
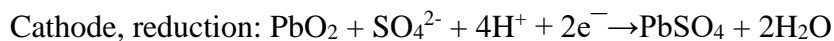
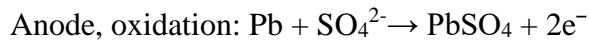
Secondary cells can be recharged. An automobile battery—the lead storage battery—is a rechargeable battery. The 12V version of this battery contains six voltaic cells, each generating about 2 V. The lead storage battery can produce a large initial current, an essential feature when starting an automobile engine.



The anode of a lead storage battery is metallic lead. The cathode is also made of lead, but it is covered with a layer of compressed, insoluble lead(IV) oxide,  $\text{PbO}_2$ . The electrodes are arranged alternately and separated by thin fiberglass sheets in aqueous sulfuric acid.

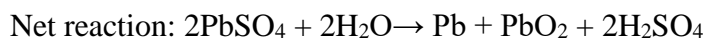
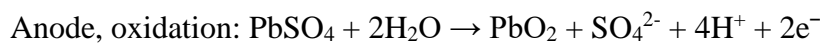
*During cell discharge (When cell supplies energy):*

When the cell supplies electrical energy, the lead anode is oxidized to lead(II) sulfate. This lead(II) sulphate is an insoluble substance that adheres to the anode electrode surface. The two electrons produced per lead atom move through the external circuit to the cathode, where  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  ions that, in the presence of  $\text{H}_2\text{SO}_4$ , also form lead(II) sulfate.



*During cell recharge:*

A lead storage battery is recharged by supplying electrical energy. The  $\text{PbSO}_4$  coating on the surfaces of the electrodes is converted back to metallic lead and  $\text{PbO}_2$  and sulfuric acid is regenerated. Recharging this battery is possible because the reactants and products remain attached to the electrode surface.



**Advantages:**

1. When the automobile (say car) starts running, it can be easily recharged.
2. It has constant potential 12V
3. It is portable and inexpensive.
4. Low maintenance requirements — no electrolyte to fill.
5. Capable of high discharge rates.

**Disadvantages:**

1. Environmentally unfriendly — the electrolyte and the lead content can cause environmental damage.
2. Lead storage batteries have the disadvantage of being large and heavy.

**Maintenance free Lead-acid battery:**

Introduction: In lead-acid battery the water levels decreases during utilization hence by checking the water levels in the battery, distilled water is added by opening the valves that are present in the battery. This type of lead acid batteries is called flooded batteries and which requires maintenance.

Maintenance free lead acid batteries are generally called by valve-regulated lead-acid battery (VRLA battery) or sealed lead-acid (SLA) or gel cell.

Construction:

VRLA cells have the same chemistry as that of flooded battery consists of lead as anode and lead oxide as cathode and which are suspended in dilute sulfuric acid.

There are two types of VRLA batteries, AGM and Gel.

Gel cells add silica dust to the electrolyte, forming a thick putty-like gel. These are sometimes referred to as "silicone batteries". AGM (Absorbent Glass Mat) batteries feature fiberglass mesh between the battery plates which serves to contain the electrolyte.

### Mechanism:

In all lead-acid battery designs, charging current must be adjusted to match the ability of the battery to absorb the energy.

If the charging current is too high, electrolysis will occur, decomposing water into hydrogen and oxygen, in addition to the intended conversion of lead sulfate and water into lead dioxide, lead, and sulfuric acid (the reverse of the discharge process.)

In VRLA they retain in the battery as long as pressure maintained in the safe levels. Usually the hydrogen and oxygen recombine with in the battery itself to form water sometimes with the help of a catalyst.

However, if the pressure exceeds safety limits, safety valves open to allow the excess gases to escape, and in doing so regulate the pressure back to safe levels (hence "Valve-Regulated" in "VRLA").

But in flooded battery these gases are allowed to escape, hence the battery will need to have water added from time to time.

**Applications of VRLA batteries:** VRLA's are mostly useful where discharging and charging cycles takes place at slower rate such as power storage applications.

1. These are used in Standby and Emergency Backup applications such UPS, emergency lightning and telephone switching etc.
2. These are used in Sail boats, electronics and electrical vehicles etc.

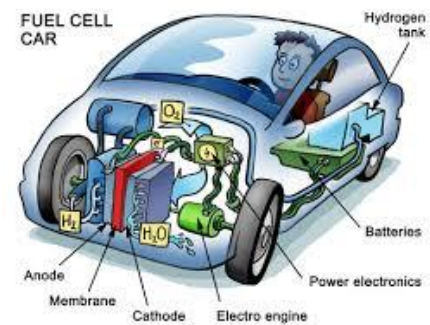
### Limitation:

The main limitation of the VRLA design is that the immobilizing electrolyte also impedes the chemical reactions that generate current. For this reason, VRLAs have lower peak power ratings than conventional designs. This makes them less useful for applications like car starting batteries where usage patterns are brief high-current pulses (during starting) followed by long slow recharging cycles.

## Fuel cells:

A fuel cell is an electrochemical “device” that continuously converts chemical energy into electric energy for as long as fuel and oxidant are supplied. The characteristics of fuel cells are a) high efficiency, ii) low noise levels and iii) free from thermal pollution

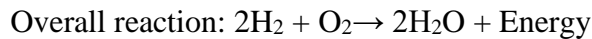
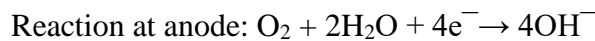
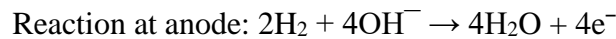
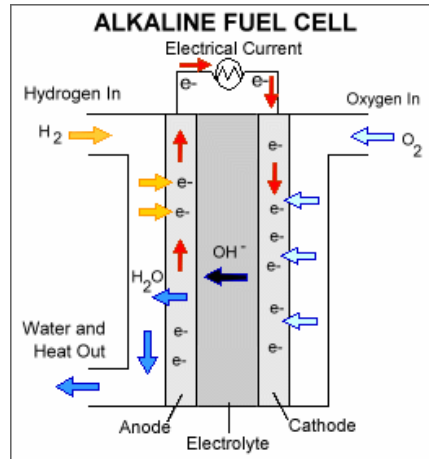
The efficiency of the fuel cell is higher in producing useful work than the electrical power plant using the same fuel. The energy produced by the fuel cell is also considered as green energy because usually the byproduct is water used for drinking purpose. Hence these are used in space vehicles for power supply and the water produced is useful for astronauts for drinking. It finds application in automobile industries by replacing the fossil fuels.



## Hydrogen-Oxygen fuel cell:

Hydrogen-Oxygen fuel cell has two electrodes made of graphite impregnated with finely divided Pt.

1. At anode hydrogen gas is passed and at cathode oxygen from air is supplied.
2. Anode and cathode are separated by proton exchange membrane which allows the flow of hydrogen ions.
3. The hydrogen enters the fuel cell at the anode. It is oxidized to hydrogen ions in presence of hydroxyl ions to form H<sub>2</sub>O and the electrons travel through wires to cathode.
4. The oxygen enters at the cathode, usually from the air. The oxygen picks up the electrons that have completed their circuit.
5. The oxygen then combines with the H<sub>2</sub>O and Hydroxyl ions are formed.
6. In the overall reaction hydrogen combines with oxygen in presence of KOH to produce water as byproduct.
7. Cells currently in use run at temperatures of 70–140 °C and produce about 1.24 V.



#### Advantages of Fuel cells:

1. Noise and thermal pollution are low.
2. Maintenance cost is low.
3. The product  $\text{H}_2\text{O}$  is a drinking water source for astronauts.
4. The energy conversion is very high (75–82%).

#### Applications of hydrogen oxygen fuel cell:

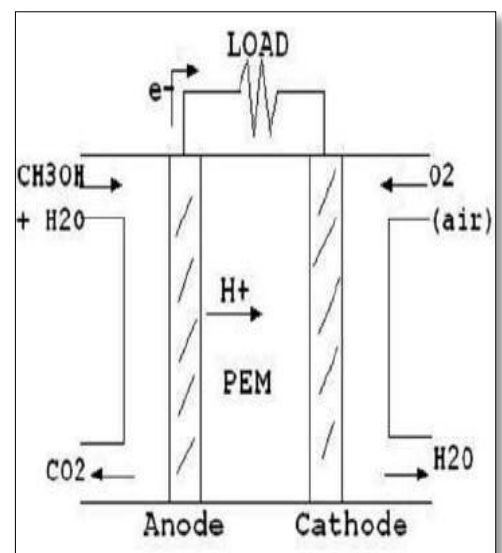
1. These are used as one of the energy sources in space vehicles.
2. These are also used in submarines, military vehicles etc.
3. Because of their light weight, these fuel cells are used in space crafts. And the exhausted  $\text{H}_2\text{O}$  is used as drinking water for astronauts.

#### Limitations:

1. The lifetime is not accurately known.
2. Platinum is used as catalyst. So the initial cost is high.
3. The distribution of hydrogen is not same all the time.
4. To use in automobiles, storage of hydrogen is the limiting factor. Not only has that, since hydrogen is the light weight gas, less hydrogen occupied more volume. So we cannot store enough fuel for to travel long distances.
5. If hydrogen gas contains carbon monoxide (if  $\text{H}_2$  is derived from hydrocarbons, methanol, it generally contain  $\text{CO}$ ), it will poison the Pt catalyst. So efficiency of the fuel cell decreases.

#### Direct Methanol-oxygen fuel cell (DMFC):

1. In this fuel cell,  $\text{H}^+$  ions are generated at anode using a mixture of methyl alcohol and  $\text{H}_2\text{O}$ .
2. Following reactions take place  
 $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$  (at anode)  
 $3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3 \text{H}_2\text{O}$  (at cathode)  
 $\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  (Overall reaction)
3. The product of the reaction is carbon dioxide which is non-toxic.



4. It gives a voltage of 1.2V.
5. It is used in spacecrafts to have continuous power supply. It is also used in military in large scale for power production.

**Advantages:**

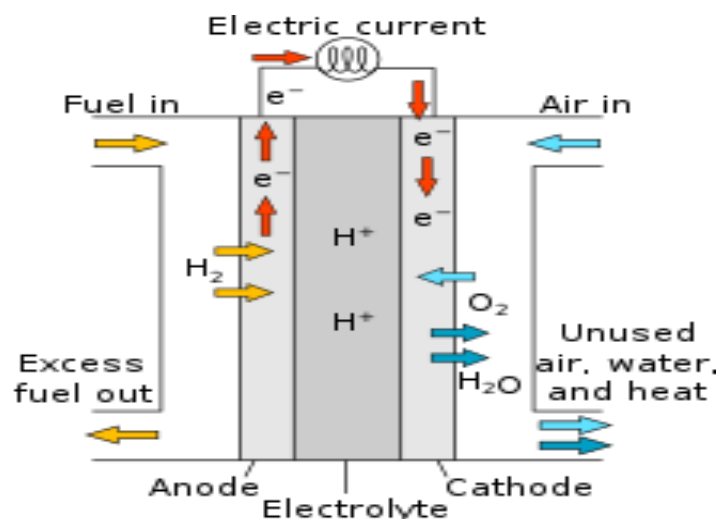
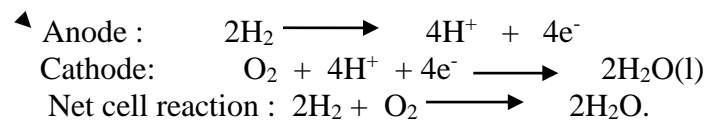
1. To overcome hydrogen storage problem, methyl alcohol mixed with steam is used as fuel source at anode. Since methyl alcohol is a liquid, we can transport and store it easily (where as it is not possible for hydrogen).
2. In the reaction between CH<sub>3</sub>OH and H<sub>2</sub>O, more H<sup>+</sup> ions (six) are produced. So we can load enough fuel for to travel long distances.

**Limitation:**

1. The waste product is CO<sub>2</sub> which is a greenhouse gas.
2. Some amount of methyl alcohol will pass through proton exchange membrane. This is called methanol crossover. This penetrated methanol will be oxidized at cathode without producing any electrons. As a result
  - (a) Quantity of methyl alcohol stored will be reduced without producing electricity.
  - (b) Efficiency of oxygen cathode will be reduced.

**Phosphoric acid fuel cell:**

The electrodes are made up of porous carbon. The liquid phosphoric acid is used as electrolyte. Phosphoric acid gives hydrogen ions from anode to cathode. The hydrogen migrates through electrolyte and combines with oxygen at cathode to form water. The production of hydrogen ions is increased by the use of platinum catalyst and operating the cell at high temperature (150-200°C). The cell reactions are as follows



**Advantages:**

- The efficiency of fuel cell is 40- 70%
- PAFCs are CO<sub>2</sub> tolerant and even can tolerate a CO concentration of about 1.5%.

**Disadvantages:**

- At lower temperatures phosphoric acid is a poor ionic conductor, and CO damage the platinum catalyst.
- The cost of fuel cell is high.

ASSIGNMENT CUM TUTORIAL QUESTIONS

**(A) Questions Testing the Understanding/Remembering Level Of Students**

**I. Objective questions:**

1. The catalyst used in phosphoric acid fuel cell [     ]  
(a) Pt     (b) Cu     (c) Zn     (d) Na
2. The electrode used in PAFC is \_\_\_\_\_
3. The potential of a single electrode or half-cell is called \_\_\_\_\_ [     ]  
(a) Single electrode potential (b) oxidation potential  
(c) Cell potential                      (d) Reduction potential
4. The electrolyte used in H<sub>2</sub>-O<sub>2</sub> fuel cell is \_\_\_\_\_
5. Which of the following is electrolyte in Ni-Cd battery? [     ]  
(a) H<sub>2</sub>SO<sub>4</sub>     (b) HCl  
(c) Alkali     (d) Cadmium hydroxide
6. The solvent used in Li-ion cells is \_\_\_\_\_ [     ]  
(a) HCl                      (b) Distilled water  
(c) Organic solvent     (d) Alkali
7. The anode used in Pb-Acid battery is \_\_\_\_\_ [     ]  
(a) Pb (b) PbSO<sub>4</sub>     (c) PbO<sub>2</sub>     (d) H<sub>2</sub>SO<sub>4</sub>
8. The cathode in Li-ioncell is an intercalation compound of \_\_\_\_\_ [     ]  
(a) Graphite (b) H<sub>2</sub>SO<sub>4</sub>     (C) PbSO<sub>4</sub>     (d) LiCoO<sub>2</sub>
9. Electrochemical sensors work on principle of \_\_\_\_\_ [     ]  
(a) Precipitation titration                      (b) Redox reaction  
(C) Complexometric reaction                      (d) Neutralization reaction
10. VRLA battery means \_\_\_\_\_
11. \_\_\_\_\_ is the electrolyte in phosphoric acid fuel cell.
- 12.. Match the following [     ]
 

| List I                            | List II   |
|-----------------------------------|---|
| (Electrolytes)                    | (Storage batteries)   |
| 1) H <sub>2</sub> SO <sub>4</sub> | A) Lithium ion cell   |
| 2) LiBF <sub>4</sub>              | B) H <sub>2</sub> -O <sub>2</sub> alkaline fuel cell          |
| 3) KOH                            | C) Lead-Acid accumulator                                      |
| (a) 1-C, 2-A, 3-B                 | (b) 1-A, 2-C, 3-B     (c) 1-B, 2-A, 3-C     (d) 1-C, 2-B, 3-A |

- 13.. Which of the following statement is true? [      ]
- At cathode always oxidation takes place.
  - At anode always oxidation takes place.
  - At both the electrodes always first reduction takes place and then oxidation takes place.
14. A galvanic cell converts \_\_\_\_\_ energy to \_\_\_\_\_ energy.

## **II. Descriptive questions**

- What is a primary cell? Give an example of it.
- What do you mean by storage battery? Give an example of it.
- What is an electrochemical cell?
- What is a secondary cell? Give examples.
- What is a fuel cell? Write it's advantages.
- What are batteries? On which principle they work?

## **B) Questions testing the ability of students in applying the concepts**

### **I. Level one questions:**

1. The negative pole of a lead acid battery is made of \_\_\_\_\_ [      ]
- (a) Carbon    (b)  $\text{PbO}_2$     (c)  $\text{PbSO}_4$     (d) Pb
2. During discharge of lead acid storage cell, the active material of both the positive and negative plates is changed to \_\_\_\_\_ [      ]
- (a) Pb    (b)  $\text{PbO}_2$     (C) PbO    (d)  $\text{PbSO}_4$
3. Which of following battery can you suggest for space shuttle? [      ]
- (a)  $\text{H}_2\text{-O}_2$  fuel cell (b) VRLA (C) Lead -acid accumulator (d) Lithium ion batteries
4. Where would you most likely find a lead-acid battery? [      ]
- (a) In a mobile (b) In an inverter (c) In a digital wall clock (d) In a torch light.
5. Usually mobile phones run by the following electrochemical cells \_\_\_\_\_ [      ]
- (a) Primary cells (b) Lithium ion batteries    (c) VRLA    (d) Fuel cell
6. In nickel-cadmium, the anode is \_\_\_\_\_ [      ]
- (a) Cadmium (b) Ni    (c) KOH    (d) Pb
7. Which of the following statement is correct [      ]
- a) Pb-Acid accumulator used in inverter is an example of secondary cell.

- b) Leclanche cell used in electronic equipment works as a storage cell also.  
 c) Fuel cells used in space vehicles can be charged.

8. Which of the following statement is false. [       ]

- a) The concentration of  $\text{H}_2\text{SO}_4$  decreases while the lead-acid cell is discharging.  
 b) The concentration of  $\text{H}_2\text{SO}_4$  increases while the lead-acid cell is charging.  
 c) The concentration of  $\text{H}_2\text{SO}_4$  is not constant during overall cycle of charging and discharging.

9. Which of these statements about a galvanic cell are not true? [       ]

- i. The cathode carries a positive sign  
 ii. Oxidation occurs at the cathode  
 iii. The electrons are released through the anode  
 iv. Reduction occurs at the anode  
 a) i and iii      b) i and ii      c) ii and iii      d) ii and iv

II. Level two questions:

- Discuss the characteristics of primary cell.
- Describe the construction of lead acid storage cell and explain how it works as a storage battery?
- Define fuel cell. Explain the construction and working of  $\text{H}_2\text{-O}_2$  fuel cell. What are advantages and limitations of the cell?
- Explain the working principle of methanol-oxygen fuel cell with reactions. Discuss its applications and limitations.
- How VRLA batteries working as maintenance free batteries? Explain the construction and working of the battery.
- Explain the working principle of phosphoric acid fuel cell and discuss its advantages and disadvantages.

### C. Questions testing the analysing / evaluating ability of students

Level three questions:

- Give a comparative account of primary, secondary and fuel cells.
- Differentiate between the characteristics of an electrolytic cell and a galvanic cell.
- Which types of cells are rechargeable?
- Can you evaluate the difference in electrochemistry of primary cell than in secondary cell?
- Identify the reason, why fuel cell can't be used as a storage battery?
- Why do electrochemical cells stop working after some time?
- Identify primary cells, secondary cells and fuel cells among the following and explain them.  
 (i) Leclanche cell    (ii) Li-Ion cell    (ii) Methanol-Oxygen fuel cell.  
 (iv) Standard Hydrogen Electrode.



# INDUSTRIAL CHEMISTRY

## Unit – II

### CORROSION AND ITS PREVENTION

#### Objectives:

- To introduce the students to basic concept of corrosion, factors influencing the rate of corrosion, types of corrosion and the application of various chemical methods to prevent corrosion of metals.
- To identify the corrosion related problems in boilers and heat exchangers and use a suitable method to prevent corrosion.

#### Syllabus

Dry and wet corrosion and their mechanisms. Pilling - Bedworth Rule. Types of Corrosion – galvanic corrosion, concentration cell corrosion, pitting corrosion and stress corrosion – Factors influencing the rate of corrosion – Temperature, pH and dissolved oxygen – Corrosion Prevention methods – Cathodic protection-Sacrificial Anodic method and Impressed current method – Metallic coatings –galvanization and tinning methods. Corrosion problems in boilers and heat exchangers and preventive measures.

#### Course outcomes:

##### Students will be able to

- explain various types of corrosion
- explain the factors influencing the rate of corrosion
- apply various chemical methods to prevent corrosion of metals in the various engineering fields.

#### Introduction:

- Corrosion is defined as the slow and gradual degradation or deterioration of metal due to its reaction with the environment.

#### Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ] on the surface of copper.

- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it

**Reason for corrosion:**

- All the metals exist in nature in combined forms as oxides, carbonates, sulphides etc.
- High amount of energy is required to extract the metal from ore.
- Thus, the metal is in thermodynamically unstable state.
- It is the natural tendency of metal to revert back to thermodynamically stable state when it comes in contact with the elements in the environment.

**Disadvantages of corrosion:**

- Enormous waste of machineries and different types of metallic materials.
- It leads to sudden failure of machines.
- Metals lose metallic lustre and other important metallic properties.
- It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is expensive.
- It may result leakage of inflammable gas from the corroded pipe lines resulting to fire accidents etc.
- It causes contamination of potable water.
- It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

**Theories (or) Mechanism of corrosion:**

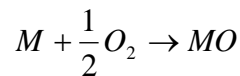
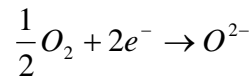
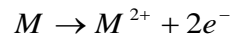
- \* Dry or Chemical theory
- \* Wet or Electrochemical theory

**Direct chemical attack theory (or) Mechanism of dry corrosion:**

- ◆ The direct chemical action of atmosphere gases like oxygen, halogen, H<sub>2</sub>S etc in a dry environment on metals is called dry corrosion. A solid film of the corrosion product is formed on the surface of the metal.
- ◆ This is known as chemical corrosion.

**1. Oxidation corrosion (Reaction with oxygen):**

- Some of the metals directly react with oxygen in the absence of moisture.
- Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- The metal ion and oxide ion combine to form metal oxide on the metal surface.



- The nature of metal oxide layer formed plays an important role in determining further corrosion.

**a) Protective (stable) and non porous oxide film:** Metals such as Al, Cr, Cu and W develop nonporous and stable oxide film on the surface. This film prevents further corrosion of the metal.

**b) Unstable oxide film:** Au & Pt develop unstable oxide film which instantaneously decomposes to form metal and oxygen and thereby no corrosion occurs.

**c) Volatile oxide film:** Molybdenum develops an oxide which immediately vaporizes. As a result, metal surface easily undergoes rapid and continuous corrosion.

**d) Porous and non protective film:** Alkali and alkaline earth metals form porous oxide layer which further increases the rate of corrosion of the metal due to porous nature of the film.

**Pilling Bedworth rule:** The ratio of volume of oxide film to the volume of metal consumed is known as Pilling-Bedworth rule (or ratio).

**Significance:**

The protective or non protective nature of oxide film is determined by this rule.

- If the ratio is <1, the metal oxide layer is porous and non protective. Ex. Oxide layer on alkaline metals.
- If the ratio is ≥1, the metal oxide layer is non porous protective layer. It

stops further corrosion of metal. Ex. Oxide layer on Al, Cr, Cu, W.

$$\text{Pilling Bedworth rule} = \frac{\text{Vol. of metal oxide layer}}{\text{Vol of metal consumed}}$$

## 2. Corrosion by other gases:

- This type of corrosion is due to the attack of other gases like  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_x$  in dry atmosphere on the metal.
- The corrosion products may be protective or non-protective.
- Dry  $\text{Cl}_2$  reacts with Ag and forms AgCl which is protective layer, where as  $\text{SnCl}_4$  is volatile.

## 3. Liquid metal corrosion:

This type of corrosion takes place, when molten metal passes through metallic pipes due to dissolution of solid metal by liquid molten metal or due to internal penetration of solid metal into liquid metal.

Ex.1 Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

Ex.2 Coolant (sodium metal) leads to corrosion of cadmium (moderator) in nuclear reactors.

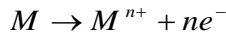
## Electrochemical Corrosion (or) Wet Corrosion (Mechanism of Wet corrosion by Electrochemical theory):

- This type of corrosion occurs when a metal is exposed to moisture (electrolytic medium).
- This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting medium.
- These anodic and cathodic regions are formed due to several factors like
  - on a metal surface if the concentration of oxygen is different.
  - due to contact of two different metals.
  - when a metal surface is subjected to stress.
- **At anodic area, oxidation reaction occurs**, thereby destroying the anodic metal due to dissolution. Hence, corrosion always occurs at anodic parts.

➤ **At cathodic area, reduction reaction occurs.**

**Anodic reaction:**

- At anode, oxidation takes place so that metal is converted into metal ions with the liberation of electrons.
- These electrons migrate towards cathode.



**Cathodic reaction:**

At cathode, reduction takes place. Depending upon the nature of the corrosive environment, cathodic reaction takes place in the following way:

- a) Evolution of hydrogen.
- b) Absorption of oxygen depending upon the nature of corrosion environment.

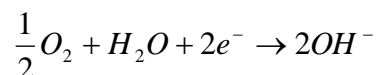
**a) Evolution of Hydrogen type:**

In acidic medium and in the absence of oxygen, H<sup>+</sup> ions are reduced to H<sub>2</sub> gas.



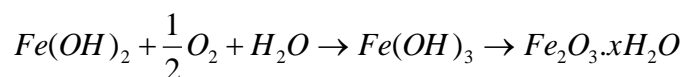
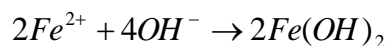
**b) Absorption of oxygen:**

In neutral and aerated or basic medium: If the solution is neutral and aerated, hydroxyl ions are formed as follows.



**Formation of corrosion product:**

- The hydroxyl ions react with metal ions and forms corrosion product.
- In case of iron, hydroxide ions react with ferrous ions and forms insoluble hydrated ferric oxide called brown rust.



**Differences between dry corrosion and wet corrosion:**

|                      |                      |
|----------------------|----------------------|
| <b>Dry corrosion</b> | <b>Wet corrosion</b> |
|----------------------|----------------------|

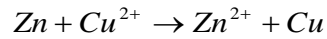
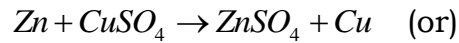
|   |  |
|---|--|
| 1.It occurs in dry condition.   | 1.It occurs in wet condition.  |
| 2.If the corrosion takes place due to direct chemical attack (in the absence of moisture), the corrosion is known as dry corrosion. | 2.If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium, the corrosion is known as wet corrosion |
| 3.Explained by absorption mechanism   | 3.Explained by electrochemical mechanism   |
| 4.It occurs on both heterogeneous and homogeneous surfaces.   | 4.It occurs only on heterogeneous metal surfaces.  |
| 5.Corrosion is uniform.   | 5.Corrosion is not uniform.  |
| 6.It is a slow process.   | 6.It is a fast process.  |
| 7.Corrosion products accumulate at the place where corrosion occurs.  | 7.Corrosion take place at anode but products accumulate near the cathode   |

### **Galvanic series**

- Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e., sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble character. The series is given below:

**Mg,Mg alloys,Zn,Al, cast iron, stainless steel(active),Pb-Sn alloys, Pb, Sn, brass, Cu, bronze, Ag, stainless steel(passive), Monel, Graphite, Ti, Gold, Pt**

- A metal having higher position can replace (reduce) other metals that have lower position in the series.
- For example:

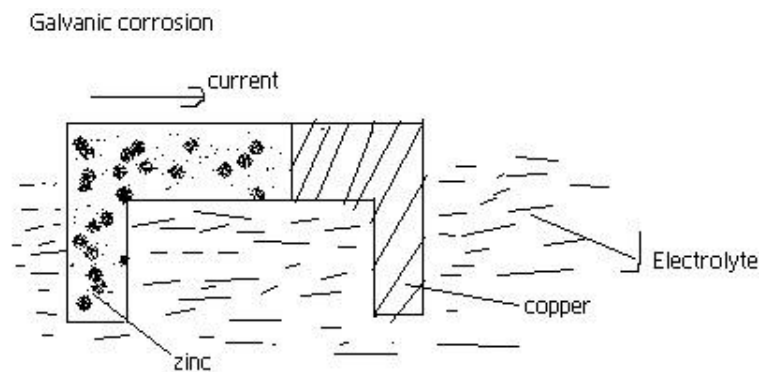


- Or in other words, zinc will corrode faster than copper.
- More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni-Mo-Fe alloys.
- Brasses, Cu, Ni, Cr-alloy, Ag, Ti, Au, Pt towards noble nature.
- **From left to right of the series, anodic nature decreases, corrosion tendency decreases.**

## Types of Corrosion

### Galvanic corrosion:

- When two dissimilar metals are connected and exposed to an electrolyte, then the metal higher in electrochemical series undergoes corrosion. This type of corrosion is also called galvanic corrosion or bimetallic corrosion.
- For example, zinc and copper are connected and exposed to an electrolytic medium, the **more reactive zinc acts as anode and undergoes corrosion.**



- **The less reactive copper behaves as cathode and gets protected from corrosion.**
- The extent of corrosion depends on the potential difference between the two metals.
- This galvanic corrosion can be minimized by
  - Avoiding galvanic couple

- Selecting metals closely placed in electrochemical series as galvanic couple
- Providing an insulating material between the two metals

## Corrosion due to Differential Aeration (Or) Concentration Cell

### Corrosion:

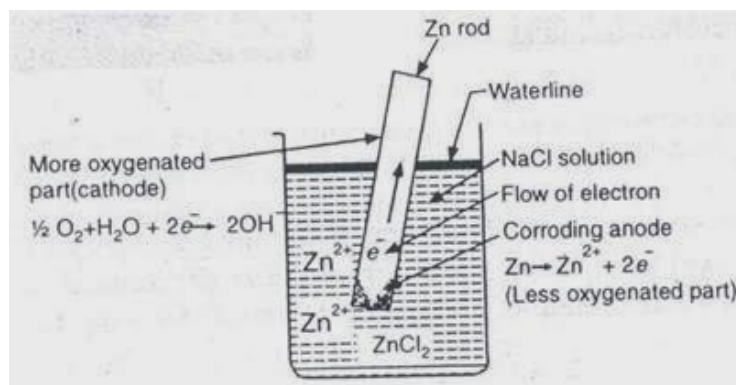
- This type of corrosion arises due to **exposure of metal to different concentrations of electrolyte or of varying aeration.**
- When metal is exposed to different concentrations of oxygen(air), part of the metal exposed to **less concentration of oxygen(air) acts as anode** and other parts exposed to **high concentration of oxygen(air) acts as cathode.**
- Anodic part undergoes corrosion.

### Example:

- If a metal is partially immersed in a dilute solution of a neutral salt solution, then the **parts above the solution are more strongly aerated hence, become cathodic.**
- The **metal part immersed in solution is less aerated and thus become anodic.**

**Examples:** Water line corrosion, water drop corrosion

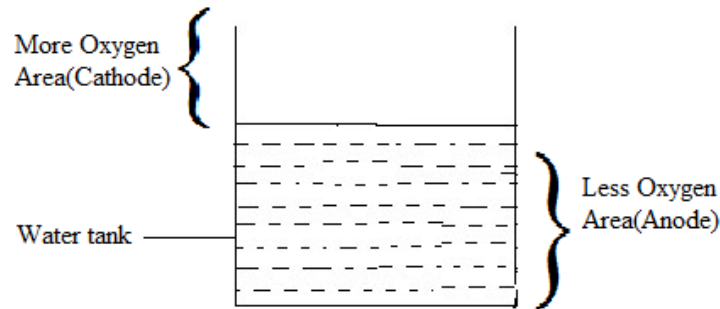
### ◆ Water line corrosion:



- The rusting of an iron tank partially filled with water takes place along the line just beneath the level of water in it.

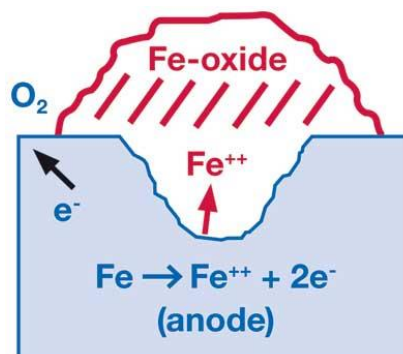


- It is due to differential aeration.
- The **area above the waterline (well aerated) acts as cathode** whereas the **area below the waterline (less aerated) acts as anode and is corroded.**



### Pitting corrosion:

- Pitting of metal occurs where there is a break in the protective layer.
- Pitting corrosion is a non uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin holes in the metal.
- This gives rise to the formation of small anodic and large cathodic areas.
- The presence of the impurities (like sand, dust, scale etc) on the surfaces of metals also leads to pitting.
- A part below the impurity become the anodic area and undergoes corrosion and the surrounding part become the cathodic area.
- Once a small pit is formed, the rate of corrosion will be increased.



### Stress corrosion:

- Stress corrosion is observed in metals which undergo mechanical operations such as welding, bending, pressing etc.
- When a metal is subjected to uneven stress and exposed to corrosion environment, it undergoes stress corrosion.
- The stressed portion is in thermodynamically unstable state that's why **areas under stress act as the anode and unstressed areas act as the cathode.**
- Anode part undergoes corrosion.

### **Factors influencing (effecting) the rate of corrosion:**

- **Temperature:**
  - As temperature increases, the rate of almost every chemical reaction increases.
  - Thus, **the rate of corrosion also increases with increase in temperature.**
- **Effect of pH:**
  - Corrosion occurs at a **faster rate in acidic medium.**
  - Low pH accelerates corrosion by providing more hydrogen ions.
- **Effect of Dissolved Oxygen:**
  - **Dissolved oxygen (DO) refers to the volume of oxygen that is contained in water.**
  - Dissolved oxygen can destroy the protective hydrogen film that is formed on many metals.
  - As the amount of DO increases, the rate of corrosion also increases.

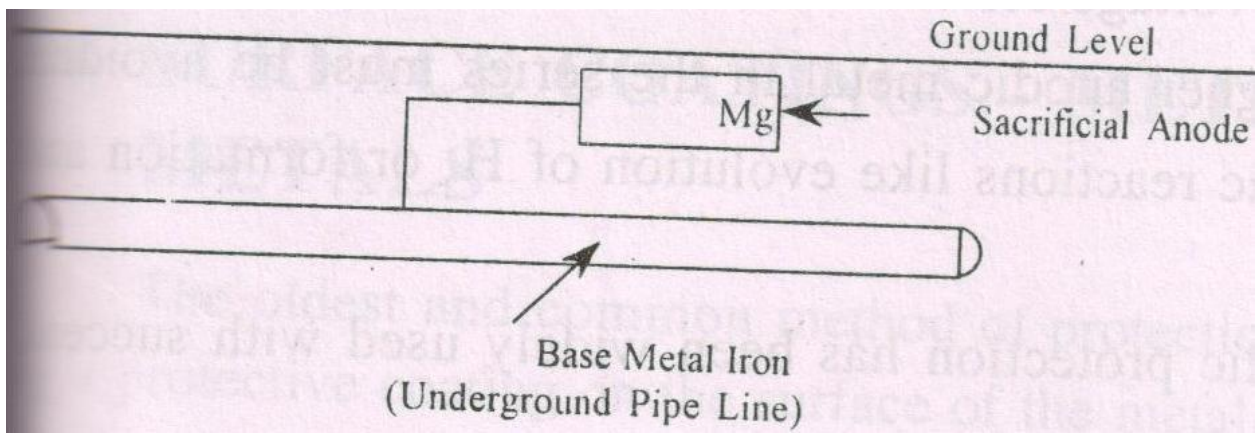
### **Methods for prevention of corrosion:**

- 1. Cathodic Protection**
- 2. Coating methods (metallic coating)**

- **Cathodic Protection:**
  - The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.
  - There are two types of cathodic protection.

#### **a) Sacrificial anodic protection method:**

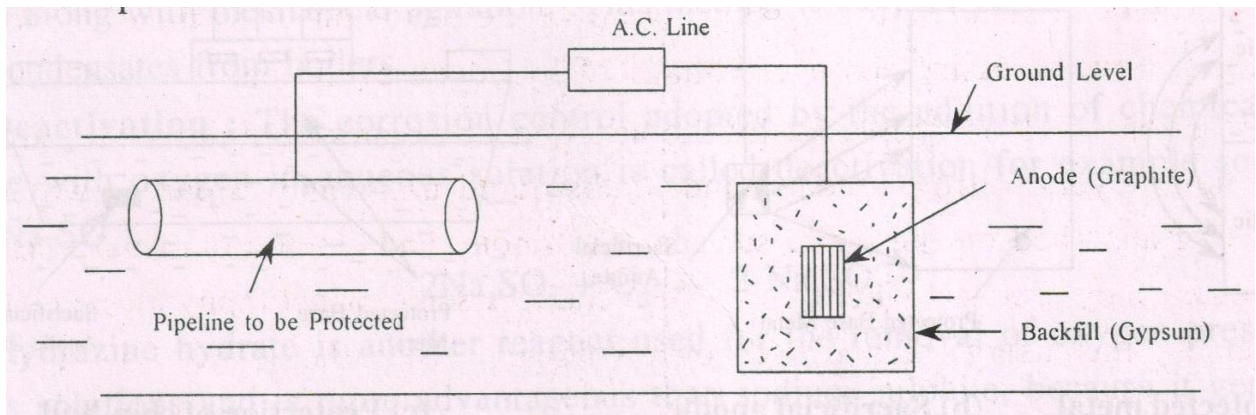
- In this method, the metallic structure to be protected is connected by a wire to a more anodic metal (more reactive metal).
- Thus during corrosion more anodic metal gets corroded. The **base metal becomes cathode and is protected.**
- The more **active metal used is known as sacrificial anode** which is to be replaced from time to time by fresh one.
- Metals commonly used as sacrificial anode are magnesium and zinc.
- This method is used for the protection of buried pipelines, ships and boat hulls, iron water tanks, etc.



Sacrificial anodic protection

### b) Impressed current cathodic protection:

- In this method, the metallic object to be protected is made cathode by connecting it with the negative terminal of the DC source.
- The positive terminal is connected to an insoluble anode like graphite, scrap iron or platinum.
- The impressed current nullifies the corrosion current and converts the base metal from anode to cathode.
- The electrons flow to the metallic object. As a result, it acts as cathode and is protected.



- This method is used for the protection of buried pipelines, underground cables, transmission line towers, water tanks etc.

#### **Advantages of impressed voltage method:**

- Useful for long term operations.

#### **Limitations of impressed voltage method:**

- Capital investment and maintenance costs are high.
- Stray currents produced may corrode the neighbouring metallic structure.

#### ➤ **Surface coatings(or) protective coatings:**

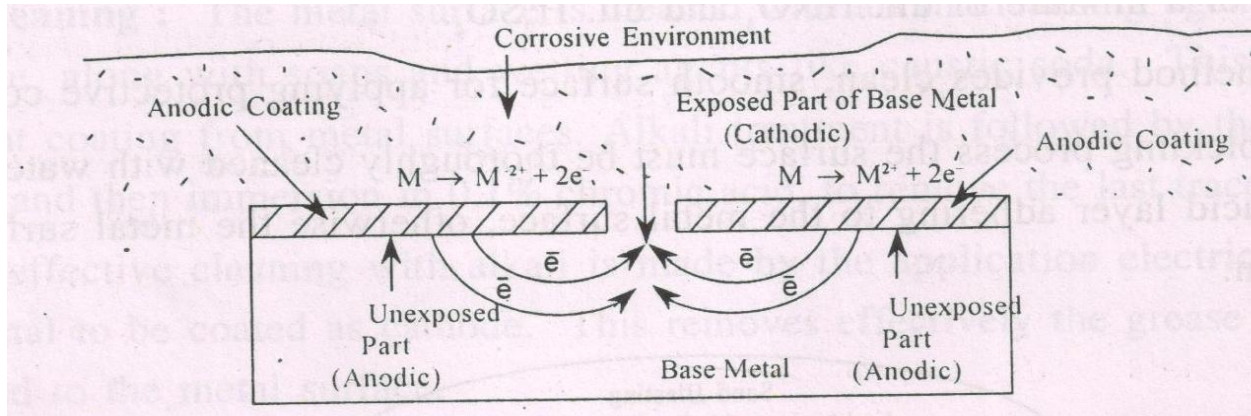
- Coating the surface of the metal with continuous non porous material to protect the metal from corrosion is known as surface coating.

#### ➤ **Metallic coatings:**

- In metallic coatings, the base metal to be protected from corrosion is coated with another metal which is either anodic or cathodic to the base metal.
- The metallic coatings often used are of Zn, Sn, Ni, Cu etc.
- Metallic coatings are of two types.

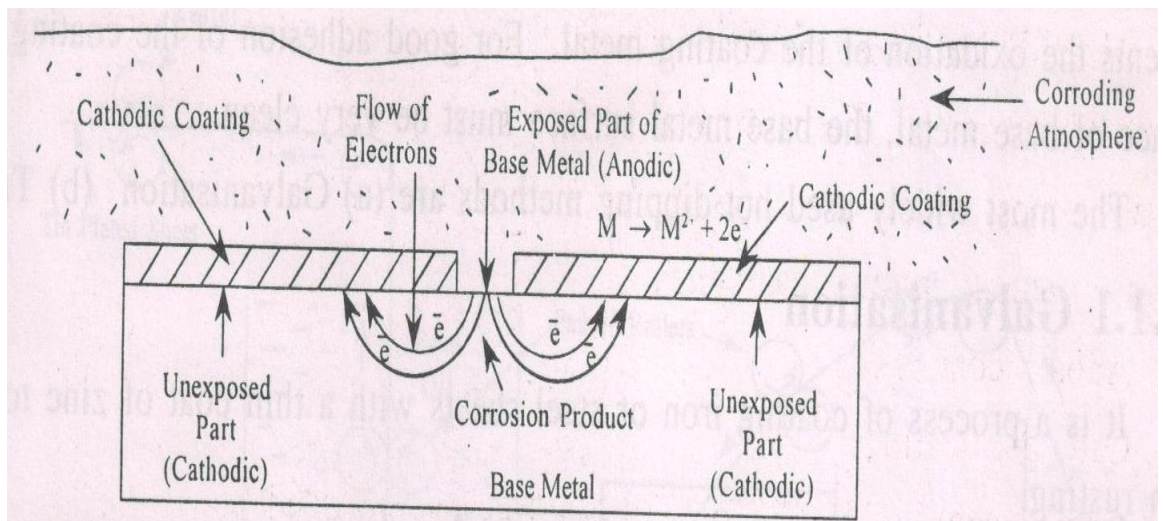
#### ➤ **Anodic coating (Sacrificial coating):**

- Anodic coating is a method of coating a more anodic metal on to the base metal.
- If the protective layer develops any cracks or pores, the base metal becomes cathode and it does not undergo corrosion.
- Ex: The coating of Zinc on to iron is known as galvanizing.



➤ **Cathodic coating (Noble coating):**

- Cathodic coating is a method of coating a more cathodic metal on to the base metal.
- If the protective layer develops any cracks or pores, the base metal becomes anode and undergoes corrosion.
- Ex: The coating of tin on to iron is known as tinning.

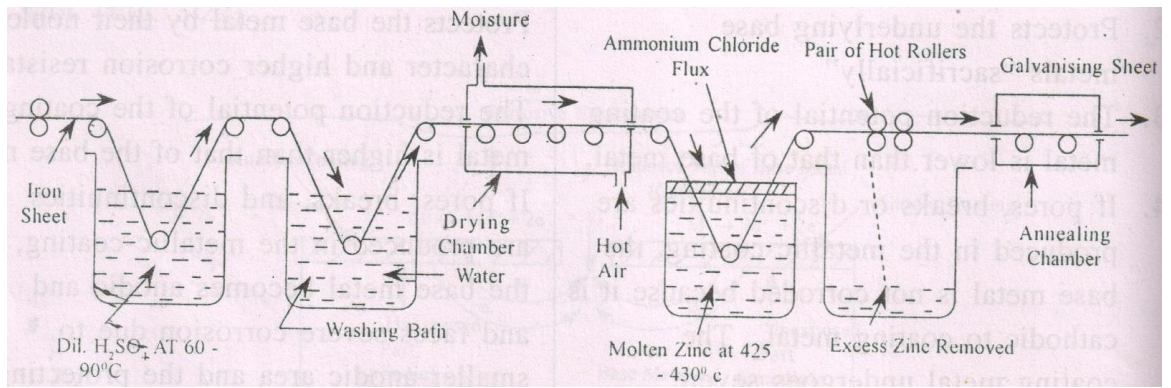


### Differences between anodic and cathodic coating:

| Anodic coating   | Cathodic coating   |
|--|--|
| 1. Protects the underlying base metal sacrificially.   | 1. Protects underlying base metal due to noble character and higher corrosion resistant.             |
| 2. Electrode potential of coating metal is lower than the base metal.  | 2. Electrode potential of coating metal is higher than the base metal.                               |
| 3. If pores or breaks or discontinuity appear on the coating, base metal does not undergo corrosion until all the coating is consumed. | 3. If pores or breaks or discontinuity appears on the coating metal, base metal undergoes corrosion. |
| 4. Coating of Zn on Iron is an example.  | 4. Coating of Sn on Iron is an example.  |

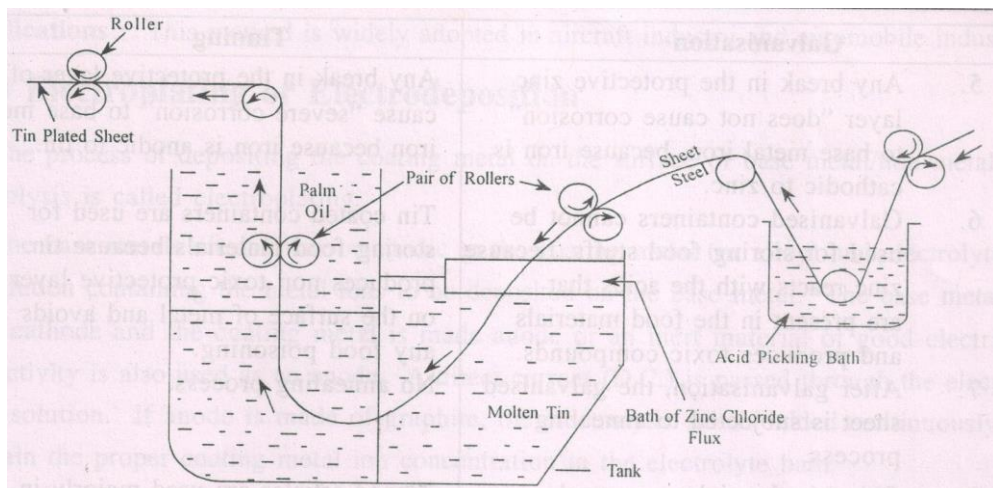
#### ➤ Galvanizing:

- Iron article is treated with dil.  $H_2SO_4$  to remove the traces of rust and dust etc. at  $60-90^\circ C$  for about 15-20 minutes.
- It is then washed and dried.
- Then it is passed through molten bath of zinc at  $430^\circ C$  which is covered with an ammonium chloride flux to prevent oxide formation.
- The coated base metal is then passed through the rollers to correct the thickness of the film.
- Then the sheet is subjected to the annealing process and cooled slowly.
- It is used to protect iron used for roofing sheets, wires, pipes, tubes etc.



### ➤ Tinning:

- Iron article is treated with dil.  $H_2SO_4$  to remove the traces of rust and dust etc. at  $60-90^\circ C$  for about 15-20 minutes.
- Then it is passed through molten bath of tin maintained at a temperature of  $240^\circ C$  which is covered with a zinc chloride flux to prevent oxide formation.
- The coated base metal is then passed through the rollers immersed in palm oil bath. Palm oil helps to protect the tin coated surface against oxidation.
- The rollers remove excess of tin.
- The containers coated with tin are used for storing food stuff, pickles, oils etc.



### Differences between Galvanizing & Tinning:

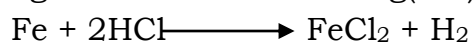
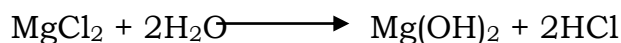
| Galvanizing  | Tinning   |
|--|---|
| 1.Coating of iron with zinc to prevent corrosion   | 1.Coating of iron with tin  |
| 2.Zinc protects the iron sacrificially   | 2.Tin protects iron due to its noble nature.  |
| 3.Protection continues even if cracks and pores develop on the surface of coating.   | 3.Protection is provided only when coating is perfect. Any break in the protective layer of tin, cause severe corrosion of base metal iron because iron is anodic to tin. |
| 4.Food materials cannot be stored in zinc coated containers as zinc reacts with food items and produce compounds that are toxic. | 4.Tin coating is non toxic and so food items can be stored.   |

### Corrosion problems in boiler:

The decay of boiler material by chemical or electrochemical attack by its environment is called boiler corrosion. Boiler corrosion generally occurs due to three reasons.

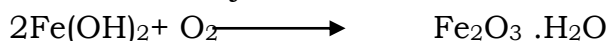
#### **(a) Acid formation by dissolved salts:**

Magnesium chloride present in the boiler water undergoes hydrolysis producing hydrochloric acid. This acid reacts with boiler material (iron) to form rust.



The HCl formed in above reaction again attacks boiler. A chain reaction is set up which causes extensive corrosion.

The ferrous hydroxide is further form rust.



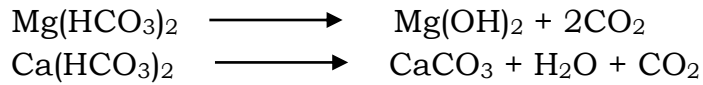
#### Prevention:

The acid formation can be prevented by adding calculated amount of alkali to neutralize the acid.

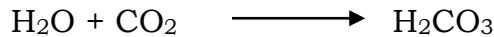


**(b) Dissolved carbon dioxide:**

The main source of CO<sub>2</sub> is the decomposition of bicarbonates of calcium and magnesium.



Carbon dioxide reacts with water forming carbonic acid, which will increase the rate of corrosion.

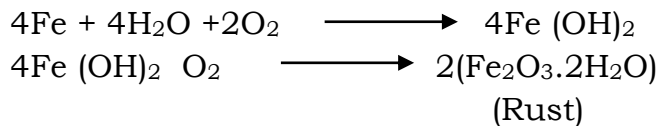


Prevention:

Carbon dioxide can be removed by adding ammonium hydroxide or mechanical deaeration.

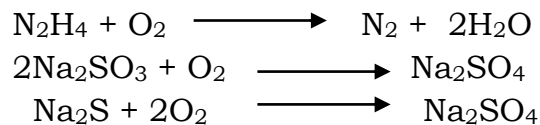
**(c) Dissolved Oxygen:**

Water normally contains 8 ppm of oxygen at room temperature. But during heating in boiler oxygen decomposes and reacts with boiler material to form rust.



Prevention:

The hydrazine, sodium sulphite or sodium sulphide can be used to remove dissolved oxygen.



Excess hydrazine gives NH<sub>3</sub> gas, which causes corrosion. Excess sodium sulphite at high temperature produces SO<sub>2</sub>, which forms corrosive sulphurous acid. So use only 5-10M sodium sulphite solution. The dissolved oxygen will also be removed by using mechanical deaeration at high temperature under vacuum.

**Disadvantages of boiler corrosion:**

1. The maintenance cost increases.
2. The efficiency of boiler decreases.
3. Leakage takes place at joints of boiler.

**Corrosion problems in Heat exchanger:**

- A heat exchanger is a device designed to efficiently transfer or exchange heat from one matter to another. When a fluid is used to transfer heat, the fluid could be a liquid, such as water or oil, or could be moving air.
- Materials used in the construction of heat exchanger are copper, stainless steel, and copper/nickel alloy, bronze, brass and various alloys.

- The stainless steel undergoes pitting corrosion and in acidic environment its corrosion is high.
- The brass (alloy of Cu and Zn) undergoes galvanic corrosion; so the alloy of copper and nickel can use which can reduce corrosion.
- The corrosion of metal can form by fast moving of fluid in the heat exchanger under high temperature is called erosion-corrosion.
- It can damages the protective oxide layer on the metal surface and increase rate of corrosion. The bends and joints of metal undergo corrosion rapidly.
- To prevent erosion-corrosion the speed of fluid could be reduce, the bends should be smooth, the pH of fluid should be neutral and remove dissolved oxygen from fluid.
- The epoxy coating on metal surface will also reduce effect of erosion-corrosion.

## Assignment-Cum-Tutorial Questions

### Section-A

#### I) Objective Questions

- From the following, which is inert to oxidation?  
A. Cu                      B. Fe                      C. Steel                      D. Pt
- Chemical formula of Rust is,  
A.  $\text{Fe}_2\text{O}_3$               B.  $\text{FeO}$               C.  $\text{Fe}_3\text{O}_4$               D.  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
- Corrosion process is nothing but -----.  
A. Reduction    B. Oxidation    C. Protection    D. Both oxidation and reduction
- Electrochemical corrosion takes place on,  
A. Anodic area    B. Cathodic area    C. Near cathode    D. Near anode
- Volatile oxidation corrosion product of a metal is,  
A.  $\text{Fe}_2\text{O}_3$               B.  $\text{MoO}_3$               C.  $\text{Fe}_3\text{O}_4$               D.  $\text{FeO}$
- Lower the pH, corrosion is,  
A. Greater              B. Lower              C. Constant              D. None of above
- Process of corrosion is enhanced by,  
A. Air & Moisture                      B. Electrolytes in water  
C. Gases like  $\text{CO}_2$  &  $\text{SO}_2$                       D. All of these
- In differential aeration corrosion, poor oxygenated parts are,  
A. Anodic              B. Cathodic              C. Corroded              D. None of above
- In waterline corrosion, highly oxygenated parts acts as,  
A. Cathodic              B. Anodic              C. Corroded              D. None of above
- In galvanic series, a metal high in series is more -----.  
A. Anodic              B. Cathodic              C. Corroded              D. None of the above
- The metal at the top of Galvanic series is  
A. most stable    B. best protective    C. most stable    D. most active

12. Identify the metal which is not employed as Sacrificial anode.  
A. Mg                      B. Zn                      C. Al                      D. Na
13. Which of the following metals could provide cathodic protection to Fe?  
A. Al & Cu      B. Al & Zn      C. Zn & Cu      D. Al & Ni
14. The formation of ----- type of metal oxide film causes rapid and continuous corrosion.
15. -----is the process of coating Fe or steel with a zinc coating.  
A. Tinning                      B. Hot dipping  
C. Galvanizing                      D. None of above
16. The buried pipeline is protected from corrosion by connecting to Mg block. It is called  
A. impressed voltage protection    B. Sacrificial cathodic protection  
C. sacrificial anodic protection      D. any of these
17. Ratio of volumes of metal oxides to metal is known as -----
18. More active metal used in sacrificial anodic protection method is known as -----
19. ----- is the process of coating of tin over Fe or steel.
20. Anodic metal protects the underlying metal -----
21. During galvanic corrosion, the more noble metal acts as -----
22. During the electrochemical corrosion in acidic environment, evolution of ----- occurs.
23. The buried pipe line is protected from corrosion by connecting it to Mg block. It is called -----

### **Section-B**

1. Define corrosion. Write the formula for rust.
2. Define Pilling Bedworth rule.
3. Explain the factors affecting the rate of corrosion.
4. Explain the mechanism of electro chemical corrosion.
5. Write a brief note on dry corrosion.
6. Define galvanic corrosion.
7. Define concentration cell corrosion. Give an example.
8. Discuss different methods of corrosion control.

9. Write short note on cathodic protection for the prevention of corrosion.
10. Explain with an example, the prevention of corrosion by sacrificial anode process.
11. Explain with an example, the prevention of corrosion by impressed current method.
12. Define galvanic series. Give its significance.
13. Describe the following metallic coatings (i) Tinning (ii) Galvanizing
14. Give the significance of Pilling Bedworth rule.
15. Differentiate galvanic and concentration cell corrosion.
16. Explain the differences between wet and dry corrosion.
17. Of the zinc coating on iron and tin coating on iron, which type of coating protects iron even after the development of cracks on the surface of coating? Why?
18. Explain the process of corrosion occurring when:
  - (i) an iron pipe is connected to the copper plumbing.
  - (ii) iron tank is partially filled with water.
  - (iii) ship hull connected to a zinc plate.
19. Write the advantages and limitations of impressed voltage method.
20. Differentiate anodic coating and cathodic coating.
21. Write the differences between tinning and galvanizing.

### **Section-C**

1. Corrosion of half-filled iron water tank occurs from below the water line. Why?
2. How do you protect the buried pipelines from corrosion?
3. Why food items should not be stored in galvanized containers?

# Industrial Chemistry

## Unit-III

### Water and its treatment

#### **Objective:**

- To understand the troubles with hardness of boiler feed water.
- To learn internal and external treatment of hard water for boiler applications.

#### **Unit-V: Water and its treatment**

Hardness of water – Calculation of hardness- Disadvantages of using hard water in Boilers – priming and foaming, sludge and scale formation – caustic embrittlement – Boiler corrosion.

Treatment of boiler feed water – Zeolite process, Ion exchange process. Internal treatment – Calgon conditioning and Colloidal conditioning. Desalination of Brackish water by RO method.

#### **Course outcomes:**

*The students will be able to*

After completion of the course the students will be able to

- explain how the hardness of water effects boiler.
- calculate hardness of water.
- apply internal treatment for softening of hard water.
- explain use of Zeolite process, Ion exchange process and RO method in the treatment of water.

#### **Introduction:**

- Water is the most abundant and most useful natural component for the existence of all living beings.
- It also occupies a vital position in industries.
- It is important for the steam generation and thereby used to produce electricity.

#### **Sources of Water:**

The chief sources of water classified in to two groups

1. Surface water
2. Ground water

## **Surface water:**

The water present on the earth surface is known as surface water. It is available in many types

1. **Rain water:** The rain water is obtained by the evaporation of the surface water, it is considered as the purest form of the natural water. But Rain water during its downward path to the earth dissolves considerable amount of gases (e.g.; CO<sub>2</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>...,) and also suspended solid particles present in the atmosphere.
2. **River water:** The source of the river water is ultimately the rain water and spring water. Rain water contains dissolved impurities and also contains the organic products (From the decomposition of the plants and animals bodies) and small particles of sand and rock in suspension.
3. **Lake water:** Lake Water is static water. In this type of the water, the main impurities observed is the organic matter (bacteria etc.).
4. **Sea water:** Sea water is the most impure form of natural water. Sea water is found to have about 3.5% of dissolved salts, out of which 2.6% is NaCl and hence sea water is always saltish in taste.

**Ground Water:** A part of rain water which falls on earth surface percolates into the earth and continues its journey till it meets a hard rock where it may be stored or come in the form of the spring. During its downward journey, it dissolves a number of salts.

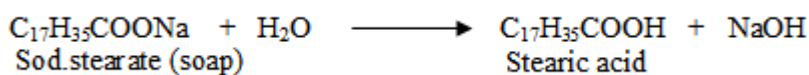
## **Impurities in water:**

The common impurities present in natural water may be classified as follows.

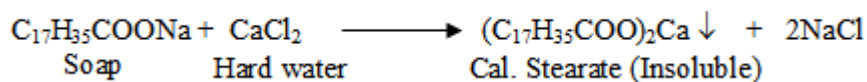
- **Dissolved minerals:** Mostly comprise of carbonates, bicarbonates, chlorides and sulphates of calcium, Magnesium, sodium and potassium.
- **Dissolved gases:** Mostly O<sub>2</sub> and CO<sub>2</sub>.
- **Suspended matter:** Mostly comprise of mineral matter, giving turbidity to the water. Organic matter may also be present. They impart turbidity, colour and odour to the water.
- **Microscopic matter:** Consists of plants and bacterial life giving colour, taste and odour.

## **Hard Water:-**

- The water which does not produce lather easily with soap is called hard water. Hard water contains salts like Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub> etc.
- Water which produces lather easily with soap is called soft water.
- Soap is a sodium salt of higher fatty acid i.e., Sodium or Potassium salts of stearic or palmitic or oleic acid. Soap is highly soluble in soft water and forms lather immediately.



- Soap forms insoluble salts with hard water and does not form lather.



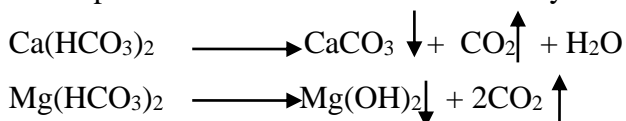
### Types of hardness:

The hardness of water may be of two types

1. Temporary hardness (carbonate hardness)
2. Permanent hardness (non-carbonate hardness)

### Temporary hardness:

Temporary hardness is due to the presence of soluble bicarbonates of calcium and magnesium in water. It can be removed easily by boiling of water. In this process bicarbonates are decomposed to insoluble carbonates and hydroxides that can be removed by filtration.



### Permanent hardness:

Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium in water. Permanent hardness cannot be removed by boiling. It can be removed only by special methods like Zeolite process, Ion-exchange process etc.

### Degree of hardness (or) Expression of hardness:

The total hardness of water is caused by different dissolved salts of calcium and magnesium. [Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub>].

The concentration of Hardness causing salts in water is expressed in terms of CaCO<sub>3</sub> equivalents.

#### **Reason:**

- Because CaCO<sub>3</sub> molecular weight is 100, it is easy for calculation.

Hardness of hardness causing salts in terms of CaCO<sub>3</sub> equivalents is

$$= \left[ \frac{\text{Amount of the hardness causing salt in mg/l}}{\text{Molecular weight of hardness causing salt}} \right] \times 100 \text{ ppm}$$

### Units of hardness:

There are four different units in which the hardness of water is expressed as given below:

- **Parts per million (ppm):** The number of parts by weight of CaCO<sub>3</sub> equivalents of hardness causing salts present in one million parts of water (10<sup>6</sup> parts).



- **Milligrams per litre (mg/l):** The number of parts by weight of CaCO<sub>3</sub> equivalents of hardness causing salts in milligrams present in one litre of water.  
1mg/L=1ppm
- **Degree Clark (°Cl):** It is expressed as the number parts of CaCO<sub>3</sub> equivalents of hardness causing salt in 70,000 parts of water.
- **Degree French (°Fr):** It is expressed as the number of parts of CaCO<sub>3</sub> equivalents of hardness causing salt in 10<sup>5</sup>parts of water.
- The relationship between different units of hardness is

$$1\text{ppm}=1\text{mg/L}=0.07(^{\circ}\text{Cl})=0.1(^{\circ}\text{Fr})$$

$$1^{\circ}\text{Cl}=1.43^{\circ}\text{Fr}=1.43\text{ppm}=14.3\text{mg/L}$$

**Example:**

A sample of hard water contains 120 mg/L of hardness. Express the hardness in ppm, degree French, degree Clark.

Sol:

Hardness of water sample = 120mg/l

Conversion = 1 ppm =1mg/l = 0.07°Cl = 0.1 °Fr

Hardness of water in degree Clark = 120x0.07=8.4°Cl

Hardness of water in degree French = 120x0.1=12°Fr

Hardness of water in ppm = 120ppm

**Disadvantages of using hard water in domestic use :**

**Washing :**When hard water is used for washing purpose, it does not produce lather freely with soap and it produces sticky precipitates of calcium and magnesium soaps. This cause wastage of lot of soap.

**Cooking:** Due to presence of dissolved hardness the boiling point of water is elevated. Therefore, more fuel and time are required for cooking.

**Drinking:** Hard water causes bad effect on our digestive system and also possibility of forming calcium oxalate crystals in urinary tracks is increased.

**Disadvantages of using hard water in Industries: -**

**Disadvantages of hard water in steam generation in boilers:**

If hard water directly fed into the boilers it may cause many troubles as follows :

- Scale and sludge formation
- Corrosion
- Priming and foaming
- Caustic embrittlement

**Textile industry:**The precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics when dyed do not produce exact shades of colour.

**Sugar industry:**If hard water is used in sugar refining, it causes difficulties in the crystallization of sugar and the produced sugar may be deliquescent.

**Dyeing industry:**Hard water if used in dyeing yield impure shades and give spots on the fabrics being dyed.

**Laundry:** Hard water if used in laundry causes much wasting of the soap used in washing and may even cause coloration of clothes.

**Concrete making:** It affects the hydration of cement and the final strength of the hardened concrete.

**Pharmaceutical industry:** If hard water is used for preparing pharmaceutical products like drugs or injection may produce certain undesirable products in them.

### **Boiler problems with Hard Water:-**

**Priming and Foaming:** Due to the presence of oily impurities (or due to rapid heating), boiler feed water faces two problems, viz., priming and foaming. The salts carried out due to priming and foaming will be deposited on turbine blades and on other machine parts. As a result the efficiency and life of boiler and machines decreases.

**Priming:** “The process of wet steam formation in the boiler due to excess of dissolved solids and uneven or sudden heating of water” is called priming.

**Foaming:** “the production of foam or bubbles in the boiler due to presence of impurities in water” is called foaming.

**Causes of priming and foaming:** Priming & Foaming occurs mainly due to

1. Presence of dissolved impurities
2. Presence of oily, soapy impurities for foaming in boiler feed water.
3. Formation of sludge and scale in the boiler.
4. Sudden and uneven heating of water.
5. Defective boiler design and excess water feeding (more than its level) in boiler.

**Minimization of priming and foaming:** Priming & foaming can be minimized by,

1. Feeding soft water and feeding the water free from oily, soapy impurities for foaming.
2. Using properly designed boilers which maintain uniform heating.
3. Maintaining uniform heat supply.
4. By removing scale and sludge from time to time.
5. Adding the anti-foaming agents like castor oil, polyamide, etc.
6. Connecting steam purifiers to the boiler.

### **Sludge and Scale formation:-**

**Sludge:** “Sludge is a soft, loose and slimy precipitate formed within the boiler.” It forms at comparatively colder portion of the boiler and deposits in the bent area of boiler where the flow rate is slow. Sludge is formed by substances which have greater solubility in hot water than in cold water. The formation of sludge may be due to the presence of salts like  $MgCO_3$ ,  $MgCl_2$ ,  $CaCl_2$ ,  $MgSO_4$  etc., in water

**Scale:** “Scale is hard adhering deposit which sticks firmly to the inner surfaces of the boiler.” Scale is difficult to remove. The formation of scale may be due to the presence of salts like  $CaCO_3$ ,  $Ca(OH)_2$ ,  $CaSO_4$ ,  $CaSiO_3$ ,  $Mg(OH)_2$ ,  $MgSiO_3$  etc., in water.

**Disadvantages of sludge & scale formation:**

1. Sludge and Scale are poor conductors of heat. So heat used to boil water will be wasted.
2. It blocks openings like valves and tubes of boiler. So troubles the operation of boiler.
3. It causes corrosion of boiler material.

4. If sludge is formed along with scale, sludge will be entrapped in scale. So thick layer of scale will be formed.
5. Distortion of boiler tubes due to its uneven expansion.

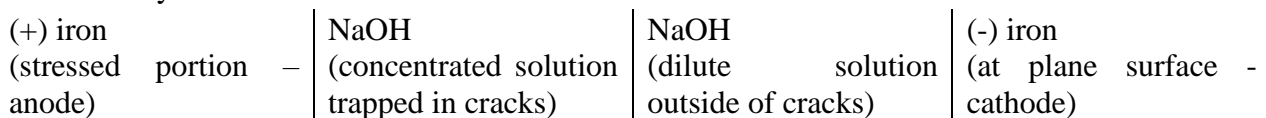
**Removal of sludge and scale:**

1. By giving thermal shocks, i.e., strong heating and sudden cooling.
2. By blow down operation.
3. By spraying chemicals in which the scale is soluble.  
Ex: Calcium carbonate scale is soluble in 10% HCl. Calcium phosphate scale can be removed by EDTA solution.
4. By scrapping with wire brush.

**Caustic embrittlement:-**

Caustic embrittlement is one type of boiler corrosion which is caused due to the feeding highly alkaline water into the boiler. In soda-lime softening technique, some amount of sodium carbonate left unreacted in water. This  $\text{Na}_2\text{CO}_3$  dissolves in water to give NaOH which makes the water alkaline.

When this NaOH entrapped in small cracks and pits of boiler, it reacts with iron to form sodium ferrate. This type of corrosion is called Caustic embrittlement. This type of corrosion occurs mainly at stressed areas in boiler.



The iron at concentrated NaOH becomes anodic and gets corroded. The caustic embrittlement can be prevented by adding sodium sulphate or lignin to boiler water. Or by using sodium phosphate as softening agent in place of  $\text{Na}_2\text{CO}_3$ .

**Boiler corrosion:-**

“Decay of boiler material due to chemical or electrochemical attack of its environment is called Boiler corrosion.”

**Causes for boiler corrosion:** Boiler corrosion is mainly due to

1. The presence of alkalinity.
2. Presence of free mineral acids
3. Presence of dissolved gases like oxygen, carbon dioxide, hydrogen sulphide etc. in water.
4. Formation of sludge and scale in the boiler.
5. Formation of series of galvanic cells.

**Control of boiler corrosion:**

Boiler corrosion can be minimized by

- Removing dissolved gases from the boiler feed water
- Feeding soft and salt free water.
- Preventing the formation of sludge and scale in the boiler.
- Neutralizing free acids and bases present in water before feeding it to boiler.

**Treatment of boiler feed water:**

**Softening Methods:**

Water required for industrial purposes (such as for steam generation) should be very soft. The process of removing hardness – producing salts from water, is known as softening of water. In industry, main three methods employed for softening of water are,

- (i) Zeolite process    (ii) Ion-exchange process.

**(i) Permutit or Zeolite Process:**

- Hydrated sodium aluminosilicates with the general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$  (where  $x=2-10$  and  $y=2-6$ ) are known as zeolite.

**Types of zeolite:**

(i) Natural zeolites

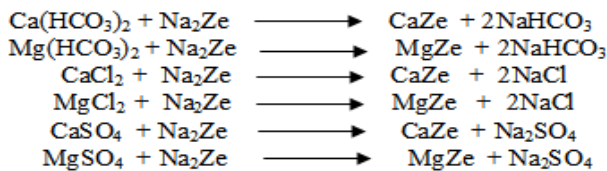
- Ex: Natrolite -  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- It is non porous in nature.

(ii) Synthetic Zeolites

- Synthetic form of zeolite is known as **permutit**.
- It can be synthesized by heating together solutions of sodium silicate, sodium aluminate and aluminium sulphate.
- It is porous in nature.

**Principle:**

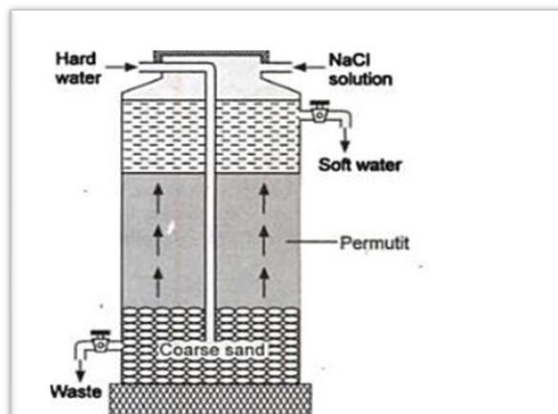
- Zeolites are represented as  $\text{Na}_2\text{Ze}$ .
- These are capable of replacing its sodium ions with cations in water, thereby reducing hardness of water.
- When hard water is passed through zeolite bed,  $\text{Na}^+$  ions are replaced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to form  $\text{CaZe}$  and  $\text{MgZe}$ .



- Sodium salts formed in the above reactions remain dissolved in the softened water and do not impart any hardness to the treated water.

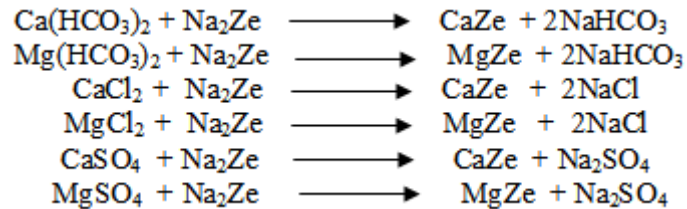
**Process:**

- When hard Zeolite bed,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to form  $\text{CaZe}$  and  $\text{MgZe}$ .



**Fig. 9.9 : Permutit method for softening of hard water**

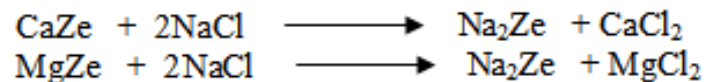
water is passed through  $\text{Na}^+$  ions are replaced by  $\text{Mg}^{2+}$  ions to form  $\text{CaZe}$  and



- After the process continues, the bed gets exhausted. Exhausted bed cannot further soften the water; hence it needs to be regenerated.

**Regeneration of exhausted zeolite:**

- The exhausted zeolite bed can be regenerated into sodium zeolite bed by passing brine solution (10% NaCl) through the bed.



✦ **Advantages:**

- ✓ Residual water hardness of about 15 ppm can be obtained.
- ✓ The equipment occupies less space.
- ✓ Softening time is less.
- ✓ No sludge is formed.

✦ **Disadvantages:**

- ✓ Only cations are removed.
- ✓ As sodium ions are replaced, treated water contains more sodium salts leading to the boiler troubles like caustic embrittlement and boiler corrosion.
- ✓ Mineral acids destroy the zeolite bed.
- ✓ Turbid water is not suitable to treat by this method.

**Ion exchange process or Demineralization process:**

- ✦ In this method ion exchange resins are used for softening of water.
- ✦ Ion exchange resins are high molecular weight, insoluble, cross linked long chain organic polymers.
- ✦ Types of ion exchange resins are

**(i)Cation exchange resins:**

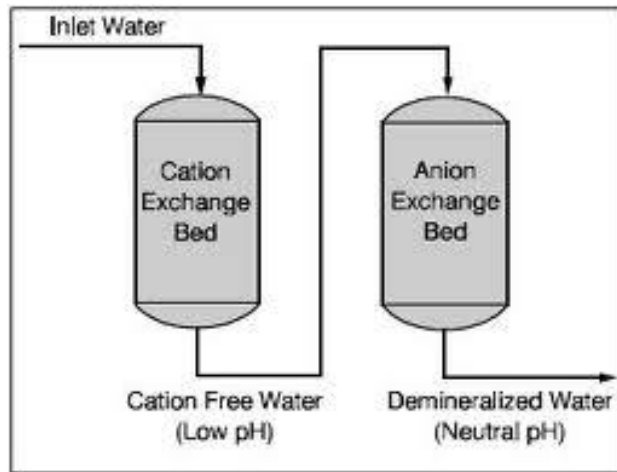
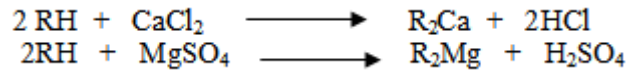
Resins containing acidic groups like –COOH, –SO<sub>3</sub>H, are capable of exchanging their H<sup>+</sup> ions with other cations in water. These resins are denoted as RH.

**(ii)Anion exchange resins:**

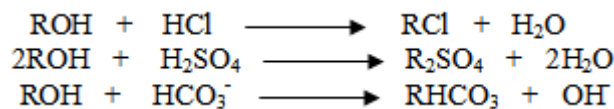
Resins containing basic groups like  $\text{-OH}$ , are capable of exchanging their  $\text{OH}^-$  ions with other anions present in water. These resins are denoted as  $\text{ROH}$ .

**Principle and Process:**

The apparatus used for deionization of water is shown in the following figure. It consists of two types of cylinders. Cation exchange cylinder and anion exchange cylinder. The hard water is passed first through cation exchange cylinder, where all the cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  etc., are removed off by exchanging with  $\text{H}^+$  ions of resin and equivalent number of  $\text{H}^+$  ions are released to the water.



Water coming from cation exchange resin, is passed through anion exchange resin. The anions like  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc. present in the water are removed off by exchanging with  $\text{OH}^-$  ions of resin and equivalent amount of  $\text{OH}^-$  ions are released to water.



$\text{H}^+$  and  $\text{OH}^-$  ions released from cation and anion exchange column, respectively combine to produce water molecule.

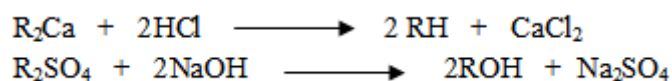


Thus, the water obtained in this process is free from ions. This water is called **deionized** or **demineralized** water.

- When all the  $\text{H}^+$  ions of cation exchange resin and  $\text{OH}^-$  ions of anion exchange resin are replaced, the resins are said to be exhausted.

**Regeneration of exhausted ion-exchange resins :**

- Regeneration of exhausted cation exchange resin and anion exchange resin are carried out by passing dil.HCl and dil.NaOH solution respectively into the bed and washing with distilled water.



✦ **Advantages:**

- Water softened by this method is completely free from cations and anions.
- Highly acidic or alkaline water samples can be purified by this method.
- Residual hardness of water softened by this method is less than 2 ppm.
- Water obtained by this method is suitable for high pressure boilers.

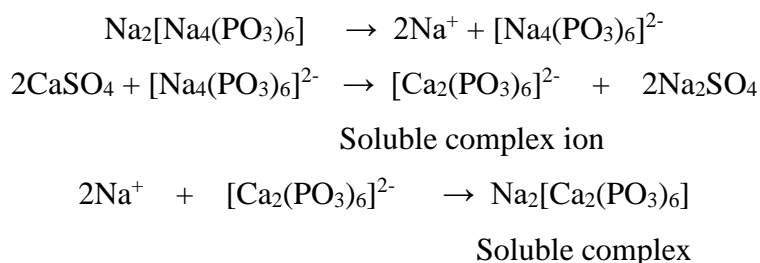
✦ **Disadvantages:**

- The cost of equipment and chemicals used for regeneration are very expensive.
- Turbid water is not suitable for this process because these particles block the pores present in the resin.

**Internal treatment methods:**

***Calgon conditioning:***

It involves adding sodium hexametaphosphate (also called calgon) to boiler water to prevent scale and sludge formation. Calgon converts the scale forming impurities into highly soluble complexes.



***Colloidal conditioning:***

Colloids like tannin, agar-agar gel, kerosene are added to the boiler. They form a coating around scale forming particles and thus prevent them from aggregating together to form scale. This method is effective in case of low pressure boilers.

**Desalination of Brackish Water by Reverse Osmosis:**

- The water containing dissolved salts with a particular salty or brackish taste is called brackish water.
- The process of removal of dissolved salts from brackish water (sea water or saline water) is known as desalination of brackish water.

**Desalination:**

- The process of removal of dissolved salt from the water is known as desalination.

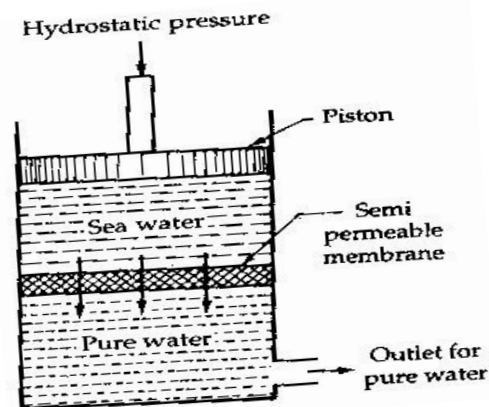
Desalination can be done by **Reverse Osmosis**

## REVERSE OSMOSIS

- The flow of solvent molecules from a dilute solution to the concentrated solution when these two are separated by a semi permeable membrane is called osmosis.
- The external pressure is applied to stop away the osmosis is called Osmotic Pressure.
- If a pressure higher than the osmotic pressure is applied on the concentrated solution side, solvent flows in reverse direction i.e. from high concentration solution to lower concentration solution. This process is known as reverse osmosis.
- This membrane filtration is also called super filtration or hyper filtration.

### Process:

- The reverse osmosis chamber consists of semi permeable membrane fitted in the middle, above which the sea water is taken and pressure of about 15 to 40kg/cm<sup>2</sup> is applied on sea water side. The pure water is forced through the semi-permeable membrane by using piston.
- The pure water is collected at the bottom of the tank.
- The membranes are made of poly methacrylate, poly amide polymers.



### ❖ Advantages:

- Maintenance cost is low.
- Life time of membrane is high.
- It removes ionic, non ionic, colloidal and organic matter from water.
- The water used in high pressure boilers is produced by reverse osmosis.



## Assignment-Cum-Tutorial Questions

### A. Questions testing the remembering / understanding level of students

#### I) Objective Questions:

- Temporary hardness in water is removed by [ ]  
(a) Filtration (b) Sedimentation (c) Boiling (d) Coagulation.
- Hard water is unfit for use in boilers for generating steam because [ ]  
(a) Its boiling point is higher.  
(b) Hard water does not produce lather inside the boiler.  
(c) Water decomposes in to  $O_2$  and  $H_2$ .  
(d) It produces scales inside the boiler.
- Hardness in water is caused due to the presence of [ ]  
(a) Un-dissolved salts of calcium and magnesium.  
(b) Dissolved sulphates of potassium.  
(c) Dissolved salts of calcium and magnesium.  
(d) Un-dissolved calcium carbonate.
- The purest form of the naturally occurring water is [ ]  
(a) Rain water (b) Lake water (c) Pond water (d) Well water.
- One part of  $CaCO_3$  equivalent hardness per  $10^5$  parts of water is called [ ]  
(a) Degree Clark (b) PPM (c) Degree French (d) mgs/L
- Hard water can be softened by passing it through [ ]  
(a) Lime stone. (b) Sodium aluminate.  
(c) Ion exchange resin. (d) Sodium silicate.
- The Purification of brackish water by reverse osmosis is also called as [ ]  
(a) Super – Filtration (b) Supra – Filtration (c) Hypo – filtration (d) Filtration
- The compound used in recharging of permutit is [ ]  
(a) NaCl (b) HCl (c) NaOH (d)  $CaCl_2$
- Rain water picks up gases like  $CO_2$ ,  $O_2$  etc. from \_\_\_\_\_.
- Anion exchange resin is regenerated by using \_\_\_\_\_.
- The chemical formula of Zeolite is \_\_\_\_\_.
- The solvent molecules move from low concentration region to high concentration region through the semi permeable membrane is called \_\_\_\_\_.
- Which of the following statement is correct? [ ]  
(I) Temporary hardness in water cannot be removed by boiling.  
(II) Temporary hardness in water can be removed by boiling.  
(III) Hard water gives lather easily with soap solution.  
(IV) Temporary hardness is also called as bi carbonate hardness.  
(a) only II (b) both I & IV (c) only IV (d) both I & III
- Which of the following statement is correct for ion exchange bed? [ ]  
(I) Cross linked polymers with micro porous structure.  
(II) Branched polymers with porous structure.  
(III) Cross linked polymers with non-porous structure.  
(IV) Branched polymers with non-porous structure.  
(a) only I (b) both I & III (c) only II (d) both II & IV
- Match the list-I and list-II of the following. [ ]  

| List-I        | List-II                     |
|---------------|-----------------------------|
| (1) Natrolite | (A) Sodium Chloride         |
| (2) Calgon    | (B) Natural Zeolite         |
| (3) Sea Water | (C) Styrene divinyl benzene |

- (4) Ion exchange resin (D) sodium hexametaphosphate  
 (a) 1-B,2-D,3-A,4-C (b) 1-A,2-C,3-D,4-B (c) 1-C,2-A,3-D,4-B (d) 1-A,2-B,3-C,4-D

## II) *Descriptive Questions*

1. Define carbonate and non carbonate hardness of water; list out the various disadvantages of hard water for domestic use?
2. What is hard water? Give the action of hard water on soap.
3. How many types of hardness are there in hard water? Define it.
4. What happens when temporary hard water is boiled? (give equations)
5. Why hardness of water is expressed in terms of  $\text{CaCO}_3$  equivalents?
6. Explain the softening of hard water by Zeolite process?
7. How can you apply the Ion –exchange process for the softening of hard water? Explain in detail.
8. What are the chemicals used for regeneration of ion exchange resins?
9. What is principle of reverse osmosis? How it is used for the conversion of sea water to pure water.
10. Distinguish between zeolite and Ion – Exchange processes.
11. What is the main advantage of Reverse osmosis over Ion exchange process?
12. Explain internal treatment of water.
13. Write an essay on boiler troubles with hard water.
14. Why a soft water need not be demineralised water but a demineralised water is always soft water?
15. Explain the following a) priming and foaming b) Caustic embrittlement C) Calgon conditioning.

## Problems

1. Determine the hardness of water in terms of ppm, °Fr, if the hardness of water sample is 14 degree Clark
2. A sample of water contains 100ppm of total hardness and 25ppm of temporary hardness. Calculate the permanent hardness of water in degree Clark and degree French.
3. Determine the  $\text{CaCO}_3$  equivalents of 83 mg of  $\text{Mg}(\text{HCO}_3)_2$  (Molecular weight 146)
4. Calculate the  $\text{CaCO}_3$  equivalents of the following dissolved salts present in 1000 liters of a sample of water Containing in ppm,  
 $\text{Ca}(\text{HCO}_3)_2=16.2, \text{CaCl}_2=11.1, \text{MgSO}_4=60, \text{MgCl}_2=19.$
5. Calculate the temporary, permanent and total hardness of a water sample having the following analysis.  
 $\text{Ca}(\text{HCO}_3)_2 = 16.2\text{mgs}, \text{CaCl}_2=11.1\text{mgs}, \text{MgSO}_4=60\text{mgs}, \text{MgCl}_2=19\text{mgs}.$
6. Calculate the temporary hardness of a water sample having the following analysis.  
 $\text{Ca}(\text{HCO}_3)_2=162\text{mgs/L}, \text{Mg}(\text{HCO}_3)_2=7.3\text{mgs/L}, \text{CaCl}_2= 22.2\text{mgs/L}$  and  $\text{MgCl}_2=95\text{mgs/L}.$
7. A sample of hard water contains the following dissolved salts per litre.  
 $\text{CaCl}_2=111\text{mgs},$   
 $\text{CaSO}_4=1.36\text{mgs}, \text{Ca}(\text{HCO}_3)_2=16.2\text{mgs}, \text{Mg}(\text{HCO}_3)_2=14.6\text{mgs}, \text{Silica}=40\text{mgs},$   
 $\text{Turbidity}=10\text{mgs}.$  Calculate the temporary, Permanent and total hardness of water in ppm, degree Clark and degree French.
6. A sample of water on analysis has been found to contain following in ppm.  
 $\text{Ca}(\text{HCO}_3)_2=4.86; \text{Mg}(\text{HCO}_3)_2=5.84; \text{CaSO}_4=6.80; \text{MgSO}_4=8.40;$  Calculate the temporary and permanent hardness of water.  
 (Atomic weights: Ca=40; Mg=24; C=12; S=32; O=16, H=1).



# Unit-4

## Fuels

### Objective:

- ❖ To impart knowledge of analysis of coal and determine Calorific value of fuel by bomb calorimeter and Junker's calorimeter.
- ❖ To impart knowledge of preparation of synthetic petrol by Bergius process and Fisher Tropsch process and air requirements for combustion of fuel.

### **Syllabus**

#### **FUELS:**

Definition and classification of fuels. Calorific value of a fuel – Characteristics of a good fuel. Coal – Types of Coal. Analysis of Coal – Proximate and Ultimate analysis. Bomb Calorimeter and Junker's gas Calorimeter. Problems on calculation of calorific value. Liquid fuels – Petroleum Extraction – Fractional distillation. Synthetic Petrol – Bergius process and Fisher Tropsch process. Problems on air requirement for combustion.

#### **Learning out comes:**

On completion of this chapter a student will be able to explain:

- Definition of fuel.
- Classification of fuels.
- Characteristics of good fuel
- Coal – Types of Coal
- Analysis of Coal – Proximate and Ultimate analysis
- Determination calorific value of fuel by bomb calorimeter and Junker's gas Calorimeter
- Extraction of petroleum by fractional distillation
- Procedure for the preparation of synthetic petrol by Bergius process, Fischer-Tropsch process.
- Air requirement for combustion.

## **Fuels:**

The combustible substance which gives large amount of heat during combustion is known as fuel.

### **Classification of Fuels:**

Fuels can be classified as follows:

#### **A) On the basis of their occurrence:**

##### **(i) Natural (or) Primary fuels:**

Fuels which are found in nature as such are called natural fuels.

Ex: Wood, coal, petroleum and natural gas

##### **(ii) Artificial (or) Secondary fuels:**

Fuels which are prepared artificially from primary fuels are called artificial fuels.

Ex: Coke, Kerosene oil, Petrol, Coal gas

#### **B) On the basis of physical state of aggregation:**

(i) Solid fuels: Wood, peat, coal, charcoal, coke

(ii) Liquid fuels: Petroleum oil, petrol, diesel

(iii) Gaseous fuels: Natural gas, coal gas, bio gas, water gas.

### **Characteristics of a good fuel:**

- It should have high calorific value.
- Its moisture content should be low.
- It should not produce harmful gases during combustion.
- It should have low content of non-combustible matter in the form of ash.
- It should have moderate ignition temperature.
- It should be available easily.

## **Coal:**

Coal is produced when the plant and animal debris are decomposed under high temperature and pressure conditions over millions of years. It contains C, H, N and O and non combustible matter.

## Types of coal:

The coal can be classified into different types depending upon percentage of Carbon content.

- a) The 57% of carbon content of coal is called **peat**.
- b) The peat is subjected to heat and pressure converted to **lignite**. It contains 67% of carbon.
- c) The lignite becomes **bituminous coal** under high temperature and pressure. It has 83-90% of carbon.
- d) Finally the bituminous coal converted into **Anthracite**. It contains 93% of carbon.

## Analysis of coal:

The quality of coal can be determined by two types of analysis. Those are

- ✓ Proximate analysis
- ✓ Ultimate analysis

### Proximate analysis:

The determination of moisture content, volatile matter, ash content and fixed carbon of coal is called proximate analysis.

#### 1. Moisture content:

A known weight of coal sample is heated in the oven at about 105°C- 110°C for one hour.

$$\% \text{ of moisture} = \frac{\text{loss in weight of sample}}{\text{Weight of coalsample taken}} \times 100$$

#### Significance:

The good quality of coal should have low moisture content.

#### 2. Volatile matter:

A known weight of moisture free coal is heated in oven with a lid at 950°C for 7-10 minutes.

After that taken out from oven and weighed again.

$$\% \text{ of volatile matter} = \frac{\text{loss in weight of sample}}{\text{Weight of coalsample taken}} \times 100$$

#### Significance:

- ✓ Coal containing high percentage of volatile matter burns with a long flame, high smoke and produces low heat.

### **3. Ash content:**

A known weight of coal sample is heated for half an hour at 750°C without lid in muffle furnace to remove moisture and volatile matter from sample. The residue left is cooled in a dessicator and weighed.

$$\% \text{ of Ash} = \frac{\text{weight of residue obtained}}{\text{Weight of coal sample taken}} \times 100$$

#### **Significance:**

- ✓ High percentage of ash in coal reduces the calorific value of the fuel.
- ✓ Presence of ash will increase the transporting, handling and storage cost.

### **4. Fixed Carbon:**

It is the quantity of carbon that burnt during combustion.

$$\% \text{ of fixed carbon} = 100 - [\% \text{ of moisture} + \% \text{ of ash} + \% \text{ of volatile matter}]$$

#### **Significance:**

- ✓ Higher % of fixed carbon, greater the calorific value of coal.

## **Ultimate analysis**

Ultimate analysis is also known as elemental analysis, it is the method to determine the Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen content present in solid fuel.

### **a) Determination of carbon & hydrogen**

About 0.2g of accurately weighed coal is burnt in oxygen in apparatus shown above. The carbon and hydrogen in the sample are converted into CO<sub>2</sub> and H<sub>2</sub>O respectively. The CO<sub>2</sub> absorbs by KOH and H<sub>2</sub>O absorbs by anhydrous CaCl<sub>2</sub>. Increases in weights of the tubes are noted.

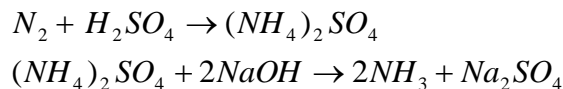
$$\% \text{ of C: } \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{weight of the coal sample taken} \times 44}$$

$$\% \text{ of H: } \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{weight of the coal sample taken} \times 18}$$

### **b) Determination of Nitrogen**

1g of accurately weighed powdered coal is heated with conc.H<sub>2</sub>SO<sub>4</sub> in kjeldahl flask. The nitrogen converted into ammonium sulphate.

- It is treated with excess NaOH to liberate ammonia. The ammonia is distilled and absorbed in a known volume of standard solution of acid.
- Unused acid is determined by back titration with standard NaOH solution.



$$\% \text{ of N: } \frac{\text{volume of acid used} \times \text{Normality of acid} \times 1.4}{\text{weight of the coal sample taken}}$$

### **c) Determination of sulphur**

- ✓ A known weight of coal is burnt completely in the presence of oxygen.
- ✓ The Sulphur is converted into sulphate.
- ✓ The washings are treated with BaCl<sub>2</sub>.
- ✓ The formed BaSO<sub>4</sub> is precipitated.
- ✓ The Precipitate is filtered, washed and heated to constant weight.

$$\% \text{ of S} = \frac{\text{weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{weight of coal sample taken} \times 233}$$

### **d) Determination of oxygen**

$$\% \text{ of Oxygen} = 100 - [\% \text{ of C} + \% \text{ of H} + \% \text{ of N} + \% \text{ of S}]$$

## **Calorific value:**

The total quantity of heat liberated from combustion of an unit mass (or) unit volume of fuel is called calorific value.

**Units:** Calorie, kilo calorie, British thermal unit (B.Th.U), Centigrade heat unit (C.H.U.)

## **Calorie:**

The amount of heat required to increase the temperature of 1g of water through one degree centigrade.

## **Kilo calorie:**

The quantity of heat required to increase the temperature of one kilogram of water through one degree centigrade.

$$1 \text{ k.cal} = 1000 \text{ Cal.}$$



### **British thermal unit:**

The quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit.

$$1 \text{ B.Th.U} = 252 \text{ Cal} = 0.252 \text{ k.cal}$$

$$1 \text{ k.cal} = 3.968 \text{ B.Th.U.}$$

### **Centigrade heat unit:**

The quantity of heat required to increase the temperature of one pound of water through one degree centigrade.

**Inter conversion formula among different units of calorific value:**

$$1 \text{ k.cal} = 1000 \text{ cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

### **Higher (or) gross calorific value (H.C.V.) or (G.C.V.):**

The amount of heat liberated, when an unit mass of fuel is burnt completely and the products of combustion are cooled to room temperature.

### **Lower (or) net calorific value (L.C.V.) or (N.C.V.):**

The net heat produced, when an unit mass of the fuel is burnt completely and the combustion products are allowed to escape.

$$\text{LCV} = \text{HCV} - 0.09 \times H \times 587 \text{ Cal/g}$$

Where H= Percentage of hydrogen in fuel.

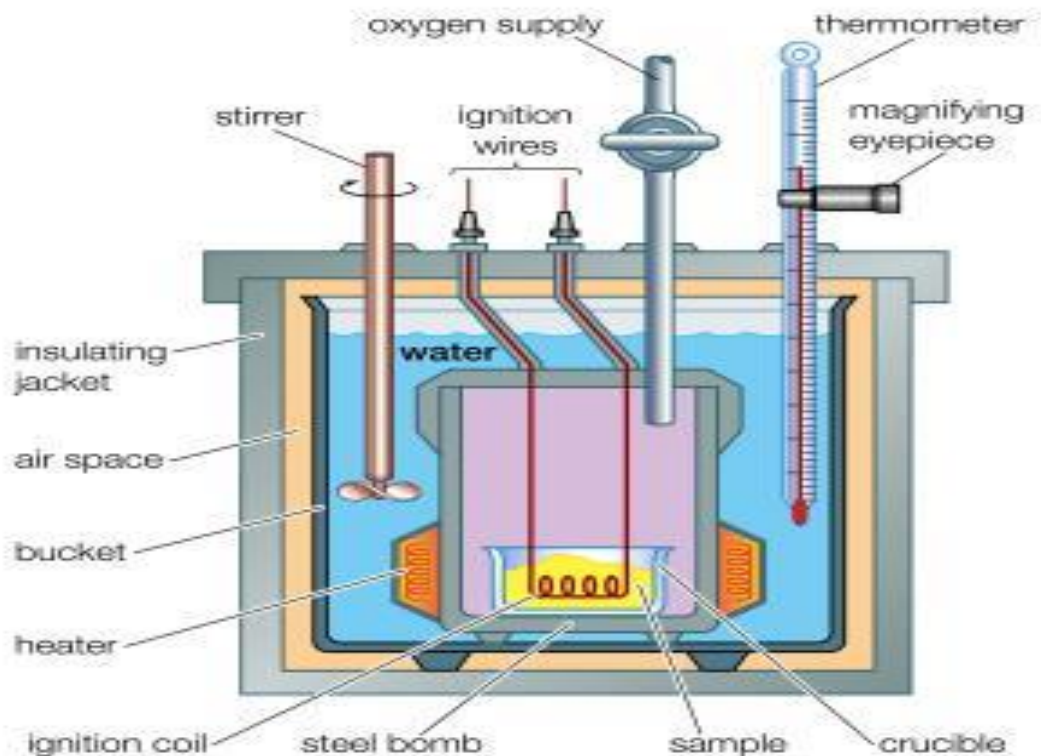
587 is amount latent heat of steam.

### **Determination of calorific value of a fuel by bomb calorimeter:**

Bomb calorimeter is an apparatus used to find calorific value of both solid and liquid fuels.

#### **Principle:**

A known mass of fuel is burnt and the quantity of heat produced is absorbed in water and measured. Then the quantity of heat produced by burning an unit mass of fuel is calculated.



## Bomb calorimeter

### Construction and working:

- Bomb calorimeter consists of a cylindrical stainless steel vessel known as bomb,
- The bomb contains crucible for the combustion of fuel.
- Bomb is provided with a lid, which contains two electrodes and oxygen inlet valve.
- The wire touching the crucible was stretched across electrodes.
- The bomb is placed in a copper calorimeter having a known weight of water
- Calorimeter is surrounded by an air jacket and water jacket to prevent heat loss
- Calorimeter is provided with a stirrer and Beckmann's thermometer.
- The electrodes are connected with a battery
- The fuel burns and the heat liberated, is transferred to water.

### Calculations:

Let  $X$  = weight of fuel sample in grams

$W_1$  = weight of water in grams

$W_2$  = weight of water equivalent (apparatus, stirrer) in grams

$T_1^\circ\text{C}$  = Initial temperature of water

$T_2^\circ\text{C}$  = Final temperature of water

L = Higher (or) gross calorific value of fuel

Heat liberated by fuel = X. L Cal

Heat gained by water =  $W_1 \times S \times (T_2 - T_1)$

Where S = specific heat of water = 1 Cal

Heat gained by apparatus =  $W_2 \times (T_2 - T_1)$  cal

$$\begin{aligned} \text{Total gain of heat by water and apparatus} &= W_1 (T_2 - T_1) + W_2 (T_2 - T_1) \\ &= (W_1 + W_2) (T_2 - T_1) \end{aligned}$$

But heat liberated from fuel = heat absorbed by water and apparatus

So  $X.L = (W_1 + W_2)(T_2 - T_1)$  cal

$$L = (W_1 + W_2)(T_2 - T_1) \div X \text{ Cal/g.}$$

### **Corrections:**

To get accurate results, the following corrections must be considered while calculating the calorific value of fuel.

#### **Fuse wire correction:**

The GCV calculated in this method includes heat liberated by the ignition of fuse wire. Hence this amount to be subtracted from total value.

#### **Acid correction:**

During combustion, sulphur and nitrogen present in the fuel get oxidized to sulphuric acid, Nitric acid respectively. It is exothermic reaction, so this value subtracted from obtained GCV.

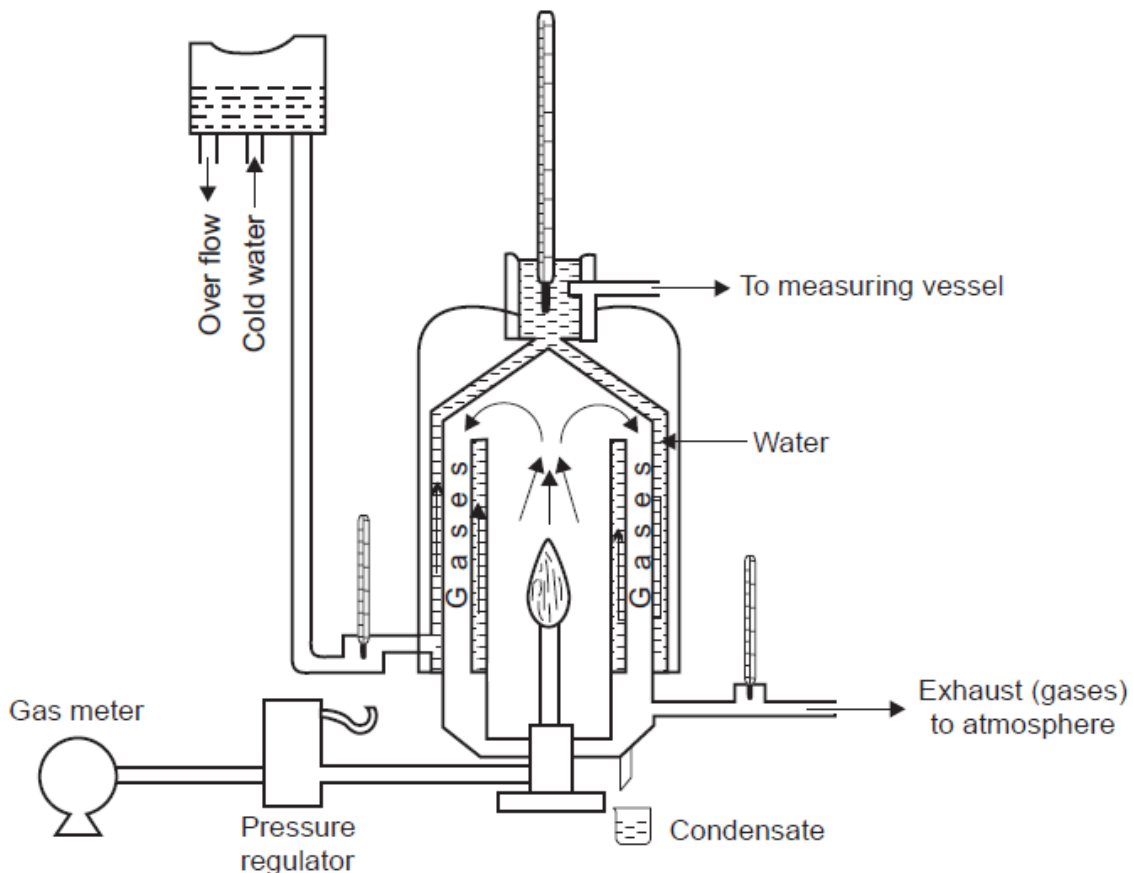
#### **Cooling correction:**

The loss of heat due to radiation is to be added to the calorific value.

Then the overall equation is

$$HCV = \frac{[(w_1 + w_2)(T_2 - T_1) + \text{cooling correction} - (\text{acid} + \text{fuse wire correction})]}{\text{mass of fuel}(x)}$$

## Junker's gas Calorimeter



### Working principle

This Gas Calorimeter works on the Junker's principle of burning of a known volume of gas and imparting the heat with maximum efficiency to steadily flowing water and finding out of the rise in temperature of a measured volume of water.

The apparatus mainly consists of

- ✓ Cylindrical shell with copper coil
- ✓ Water inlet and outlet to circulate through the copper coil,
- ✓ Pressure regulator,
- ✓ Wet type gas flow meter
- ✓ Gas Bunsen burner
- ✓ Temperature sensors for measuring inlet, outlet water temperature, and for flue gas temperature
- ✓ measuring jar.

## Procedure

- The gas whose calorific value is to be measured is supplied through a pipeline to the gas burner where it is burnt.
- The flow rate of gas is measured by a flow meter.
- The pressure of gas is measured by a manometer attached to the pressure regulator.
- The heat produced by combustion of gas is absorbed by the cold water.
- The gases are cooled upto room temperature,so that entire heat released from the combustion may be absorbed by circulating water.
- The temperature of cooling water at inlet and outlet and exit gas temperature are measured.
- Weight and flow rate of cooling water is also measured.
- Volume of gas measured in litres.

## Formula

Calorific value of gas =  $(V_w \times \rho_w \times C_{Pw} \times \Delta T) / V_g \times \rho_g$

where

$\rho_w$  is the density of water

$V_w$  is the volume of water collected in litres

$C_{Pw}$  is the specific heat of water

$\Delta T$  is the change in temp. of water

$V_g$  is the volume of gas burnt in litres

$\rho_g$  is the density of the gas burnt

## Petroleum

The term petroleum is taken from Greek language, “Petra” means rock and “oleum” means oil. The petroleum is available at deep of the earth. Petroleum is formed when large quantities of dead organisms are buried under earth and subjected to both intense heat and pressure.

It consists mixture of hydrocarbons of various molecular weights and some optically active compounds having S and N. The composition of petroleum is

C=80-87%

H=12-15%

S=0.1-4%

N and O=0.1-0.5%

## Refining of petroleum

The petroleum is made free of impurities and separation of petroleum into different fractions having different boiling ranges is called refining of petroleum. This process involves the following steps

### 1. Separation of water

The crude oil is allowed to flow between two electrodes where colloidal water droplets are separate out from the oil.

### 2. Removal of harmful impurities

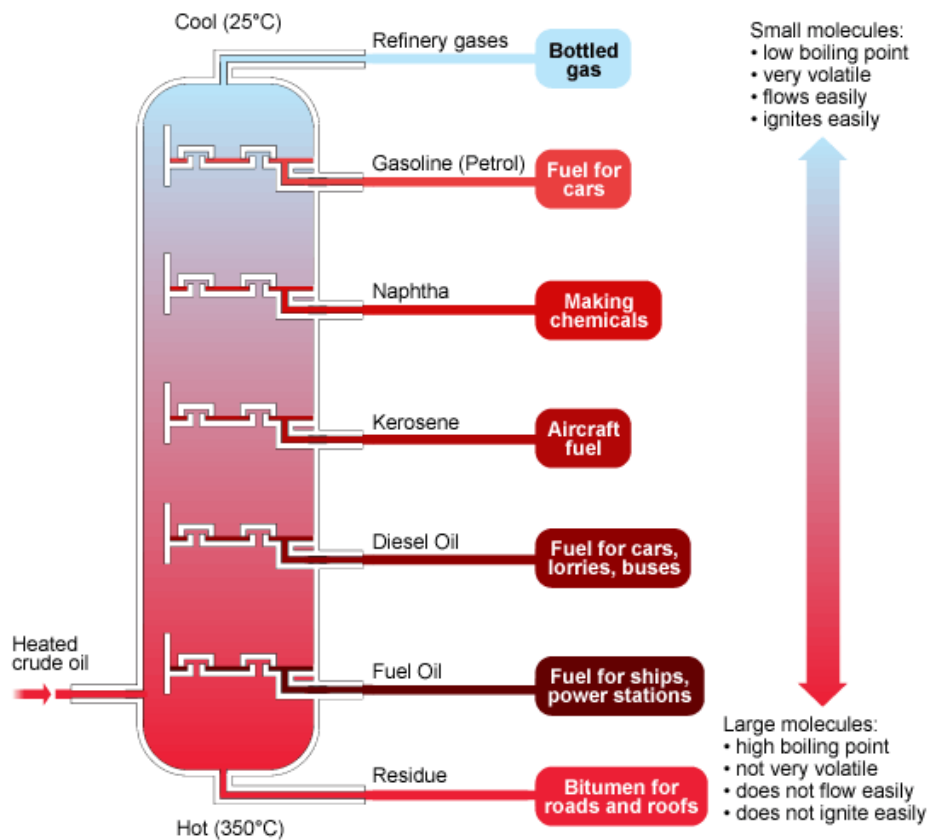
The sulphur compounds are removed by treating crude oil with copper oxide to form copper sulphide. This can be removed by filtration.

### 3. Fractional distillation

Fractional distillation separates a mixture into a number of different parts, called fractions. A tall column is fitted above the mixture, with several condensers coming off at different heights. The column is hot at the bottom and cool at the top. Substances with high boiling points condense at the bottom and substances with low boiling points condense at the top.

## **Oil fractions**

The diagram below summarises the main fractions from crude oil and their uses, and the trends in properties. Note that the gases condense at the top of the column, the liquids in the middle and the solids stay at the bottom.

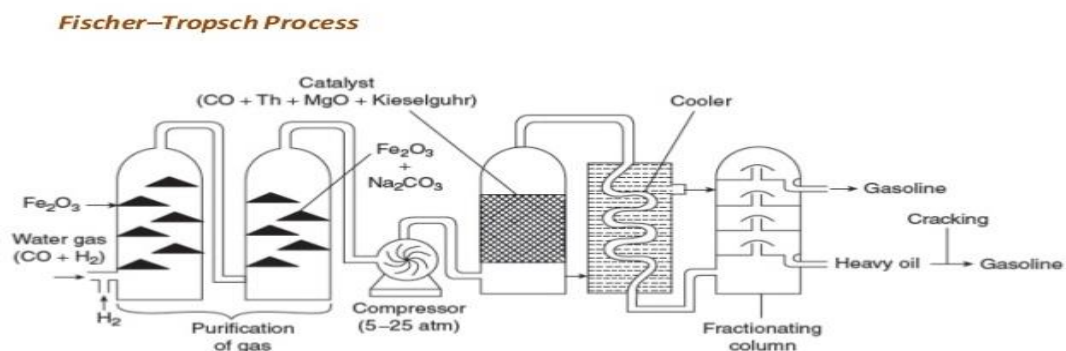


## Synthetic petrol:

The increasing demand of gasoline (or) petrol, the synthetic methods is used for the synthesis of petrol from coal. The petrol can synthesis by two processes.

- (i) Fischer Tropsch process
- (ii) Bergius process.

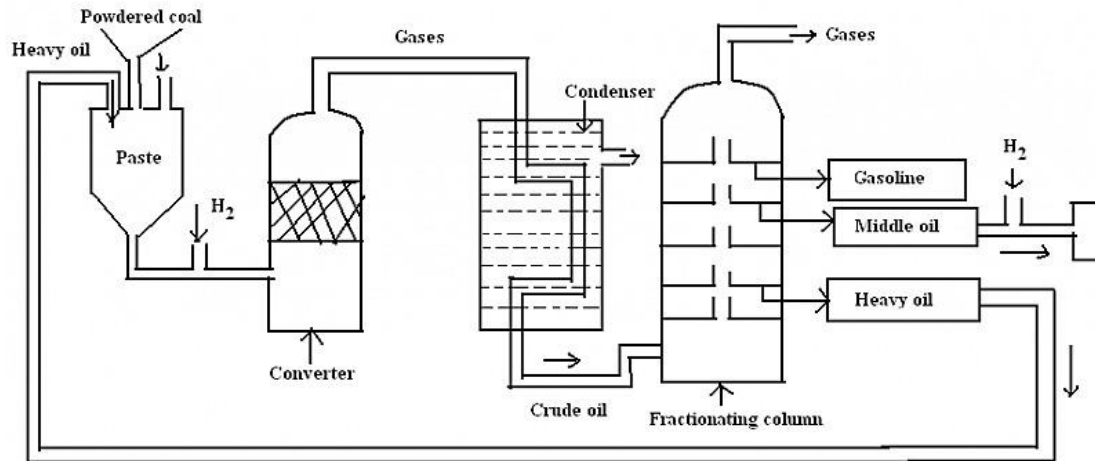
## Fischer-Tropsch process:



- This method was developed by two German scientists Franz Fischer and Hans Tropsch.
- The raw material is coke which is converted into water gas by passing steam
- $$\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$$
- The water gas is passing through  $\text{Fe}_2\text{O}_3$  to remove  $\text{H}_2\text{S}$ .
- Then passing through  $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$  to remove organic sulphur compounds.
- The purified gas is compressed to 5-25atm and then passed through a converter maintained at about 200-300°C.
- The converter is packed with catalyst , consists of mixture of Cobalt(100 parts),Thoria(5 parts), Magnesia(8 parts),Keiselguhr earth(200 parts)
- Then mixtures of saturated and unsaturated hydrocarbons are formed.
- $$n \text{ CO} + 2n \text{ H}_2 \longrightarrow \text{C}_n\text{H}_{2n} + n \text{ H}_2\text{O}$$
- $$n \text{ CO} + (2n+1) \text{ H}_2 \longrightarrow \text{C}_n\text{H}_{2n+2} + n \text{ H}_2\text{O}$$
- The out coming hot gaseous mixture from the exothermic reaction is led to cooler, where a liquid crude oil is obtained.
- The crude oil then fractionated to get gasoline.



## Bergius process:



- This method was devised by German scientist Bergius.
- The low ash coal is powdered well and made into a paste with heavy oil and mixed with catalyst (Tin, Nickel oleate).
- The paste is heated with hydrogen at 450°C under the pressure of 200—250 atm.
- The coal undergoes hydrogenation to form saturated hydrocarbons, which on cracking yield lower hydrocarbons.
- The out coming gases from vessel are led to condenser, where liquid crude oil is obtained.
- The crude oil is then fractionated to get (i) gasoline (ii) middle oil (iii) heavy oil.
- Heavy oil is used again for making paste with fresh coal.

## Assignment cum Tutorial questions

### A. Questions testing the remembering / understanding level of students

#### I) *Objective Questions.*

1. A good fuel should possess
  - a) High ignition temperature
  - b) High calorific value
  - c) Moderate ignition temperature
  - d) Both high calorific value and moderate ignition temperature.
2. Which of the following statement is true?
  - a) Ash is a desirable constituent of coal.
  - b) Ash produces clinkers.
  - c) Clinkers are good conductors of heat.
  - d) Coal with high ash content is selected for production of heat.
3. Pick up odd pair among the following.
  - a) Wood, coal
  - b) petroleum oil, natural gas
  - c) coal, natural gas
  - d) petrol, petroleum oil
4. Calorific value of a fuel is expressed as
  - a) K.cal/kg
  - b) k.cal/cm
  - c) k.cal/m<sup>3</sup>
  - d) k.cal/mm
5. Petrol is synthesized from water gas by
  - a) Fischer Tropsch process
  - b) Bergius process
  - c) thermal cracking
  - d) Fractional distillation.
6. Bomb calorimeter is used for determining the calorific value of
  - a) Solid fuels
  - b) Liquid fuels
  - c) Gaseous fuels
  - d) both solid and liquid fuels.
7. Define HCV.
8. Discuss the relationship between HCV and LCV.
9. Junkers calorimeter is used to determine the calorific value of a
  - (a) Gaseous fuel
  - (b) solid fuel
  - (c) Liquid fuel
  - (d) all of the above
10. On the basis of carbon content the best quality coal is
  - (a) Peat
  - (b) Lignite
  - (c) Bituminous
  - (d) Anthracite

#### II) **Descriptive questions**

1. Classify the following fuels into primary and secondary fuels.
  - a) LPG
  - b) coal
  - c) crude oil
  - d) petrol
  - e) heavy oil
  - f) natural gas
  - g) coke
  - h) water gas.
2. Explain the following terms.
  - a) Calorie
  - b) kilo calorie
  - c) B.Th.U.
  - d) C.H.U.
3. Define fuel along with examples.
4. Discuss about the characteristics of a good fuel.

5. Explain the determination of calorific value of solid fuel using bomb calorimeter.
  6. Express in own words about working of junker's calorimeter with neat diagram.
  7. Give a short note on proximate analysis.
  8. How does Ultimate analysis use to determine quality of fuel.
  9. Write about Fischer-Tropsch process.
  10. Examine the Bergius process with neat diagram.
- 11.** Calculate the volume of air required for the complete combustion of 1L of CO.(volume pure oxygen in air is 21%).

**B. Question testing the ability of students in applying the concepts.**

**Level one questions:**

1. Why LCV is lesser than HCV?
2. 2500calories is equal to \_\_\_\_\_ B.Th.U..
3. The removal of impurities like methane, ethane, propane from gasoline is called
  - a) Cracking
  - b) Hydrogenation
  - c) Stabilization
  - d) pyrolysis.
4. Bergius process of synthetic petrol involves mainly
  - a) Catalytic hydrogenation of coal
  - b) Cracking of heavy oil
  - c) Heating coal alone under pressure
  - d) Passing water gas over hot powdered coal under pressure.
5. How the impurities can be removed from water gas in Fischer Tropsch method.
6. Calculate LCV of the fuel in C.H.U., if HCV is 8500cal. and latent heat of steam is 587 k.cal/kg.(% Hydrogen is 5.)

**Level two questions:**

1. Interpret the important processes used for the preparation of synthetic petrol.
2. A liquid fuel weighing 0.98grams kept in bomb calorimeter. calculate the H.C.V and L.C.V of fuel with following data  
 Amount of water taken in calorimeter = 1450grams.  
 Water equivalent of calorimeter = 450grams.  
 Rise in temperature = 1.8°C.  
 Latent heat of steam = 587cal/gm. coal contains 8% of hydrogen.
3. A sample of coal containing 92%C, 5%H, 3%ash. Calculate calorific value with bomb calorimeter using following data.  
 Wt. of coal burnt = 0.95g, Wt. of water taken = 700g, Wt. of water equivalent of bomb calorimeter = 2000g, Rise in temperature = 2.48°C, Fuse wire correction = 10cal. Cooling correction = 0.02°C, Acid correction = 60cal.(Assume latent heat of steam as 580cal/g).
4. A coal sample contains C = 92%, H = 4%, S = 2%. O = 2%. Calculate the G.C.V. and L.C.V. of fuel, if latent heat of steam is 587cal/g.
5. A gas used in internal combustion engine had the following composition by volume:  
 H<sub>2</sub>= 45%, CH<sub>4</sub>= 36%, CO= 15%. Find the volume of air required for the combustion of 1m<sup>3</sup> of the gas.

## Unit-5

### **Polymers and Composites**

#### **Objectives:**

- To introduce the students to basic concept of polymer, polymerization and applications of various polymers in different fields.
- To impart knowledge of fibre reinforced plastics and their applications in the different areas.

#### **Syllabus**

Polymers – Definition of a polymer and polymerization – Degree of polymerization – Functionality – Types of polymerization – addition, condensation and co-polymerization with examples.

Plastics – thermo plastics and thermo setting plastics. Compounding of plastics. Moulding techniques – Compression, Injection and Blow film moulding. Preparation, properties and applications of PVC, Polystyrene, Teflon and Bakelite.

Composites – Definition of matrix and reinforcement. Fibre reinforced plastics – Glass fibre, Carbon fibre reinforced plastics. Preparation methods – hand layup method, matched metal die moulding method, Properties – applications

#### **After learning this Unit, the student will be able to**

- ❖ Explain the terms - monomer, polymer and polymerization and their importance.
- ❖ Distinguish between thermo plastics and thermosetting plastics.
- ❖ Describe the preparation of some important synthetic polymers and their properties, applications in different areas.
- ❖ Make use of various composites in different areas and their preparation by hand layup method, matched metal die moulding method.

#### **Learning material**

##### **Introduction**

Do you think that daily life would have been easier and colorful without the discovery and varied applications of polymers? The use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tyres, gears and seals, electrical insulating materials and machine parts has completely revolutionized the daily life as well as the industrial scenario. Indeed, the polymers are the backbone of four major industries viz. plastics, elastomers, fibres and paints and varnishes.

- **The word 'polymer' is coined from two Greek words: poly means many and mero means unit or part.**
- The term polymer is defined as very large molecules having high molecular mass ( $10^3$ - $10^7$ u) formed by repeating joining of large number of monomers by covalent chemical bond.



## **PLASTICS**

### **Definition:-**

“Plastics are high molecular weight organic polymers which can be moulded into desired stable shape by the application of heat and pressure.”

- Plastics Greek word and it derived from plastikos i.e. being able to mould or shaped.
- All plastics are polymers but all polymers are not plastics.

### **5.1.5 Types of Plastics**

Plastics are classified into two types:

1. Thermoplastics and
2. Thermosetting plastics.

#### **Thermoplastics:**

They are the resins which soften on heating and set on cooling. Therefore, they can be remoulded any number of times and used.

Example: Polythene, PVC, Nylon, etc.

#### **Thermosetting plastics:**

They are the resins which set on heating and cannot be resoftened. Hence, their scrap cannot be reused.

Examples: Phenol-formaldehyde resin (Bakelite), urea-formaldehyde resin, etc.

### **Differences between thermoplastics and thermosetting plastics:-**

| <b>Thermoplastics</b>   | <b>Thermosetting plastics</b>   |
|---|---|
| They soften on heating and set on cooling every time  | They set on heating and cannot be resoftened.                             |
| The polymer chains are held together by weak force called Van der Waal's force of attraction. | The polymers chains are linked by strong chemical bonds. (covalent bonds) |
| They are soluble in organic solvents.   | They are insoluble in organic solvents.                                   |
| They expand very much on heating.   | Their expansion is only marginal due to heat.                             |
| They are formed by addition polymerization  | They are formed by condensation polymerization                            |
| They are processed by injection moulding.   | They are processed by compression moulding.                               |
| Scarp can be reused.  | Scarp cannot be reused.   |
| Polythene, PVC, Nylon   | Bakelite, Plaskon   |

## Compounding of plastics

The plastic is mixed with different ingredients to impart useful properties is called compounding.

The following are the ingredients

### 1. Resin:

The major portion of the body of plastics, which can act as binder and holds different constituents together.

Ex: thermo plastics and thermo setting plastics

### 2. Plasticizers:

Plasticizers increase plasticity and flexibility of the plastics by reduce the intermolecular attraction forces among monomers, which imparts freedom of movement the plastic molecules.

Ex: Camphor, vegetable oils, tricresylphosphate etc.

### 3. Fillers:

Fillers give better hardness, tensile strength to the plastics.

These are reduce the cost of the polymer

Fillers decrease the shrinkage of the plastics during weather changing.

Fillers are used to reduce brittleness of the plastics.

Ex: wood flour, gypsum, saw dust, paper pulp, metallic oxides, and carbon black

### 4. Lubricants:

Lubricants impart glossy finish to the plastics and make easy in moulding of plastics.

Ex: waxes, oils, oleates, soaps

## Individual Polymers:-

### A) Polyvinyl Chloride :- (PVC)

Polyvinyl chloride is prepared by polymerization of vinyl chloride in presence of benzoyl peroxide as catalyst.



### Properties:-

- PVC is colorless, odorless, non-inflammable powder.
- Resistance to sun light, atmospheric oxygen.
- Resistance to chemicals (acids & bases).
- High stiffness and rigid.
- It has specific gravity=1.38 & M.P=148<sup>0</sup>c

**Uses:-**

Safety helmets ,tank lining ,tyres and cycle mudguard, refrigerator components ,toys , toilet goods ,radio-components.

**B) Poly Styrene:-(PS)**

Polystyrene is prepared by polymerization of styrene in presence of benzoyl peroxide as catalyst.

**Properties:-**

- Polystyrene is a transparent material.
- Excellent moisture resistant.
- High electrical insulator.
- Good chemical resistant.

**Uses:-**

In molding of articles like toys ,combs ,buttons ,radio and television parts, refrigerator parts ,battery cases.

**C) Poly Tetra Fluoro Ethylene:-(PTFE)**

PTFE is obtained by polymerization of tetra fluoro ethylene under the presence of benzoyl peroxide as catalyst.

**Properties:-**

- Due to the presence of highly electronegative fluorine , it give extreme toughness ,high softening point.
- High chemical resistance .
- Good electrical and mechanical properties.

**Uses:-**

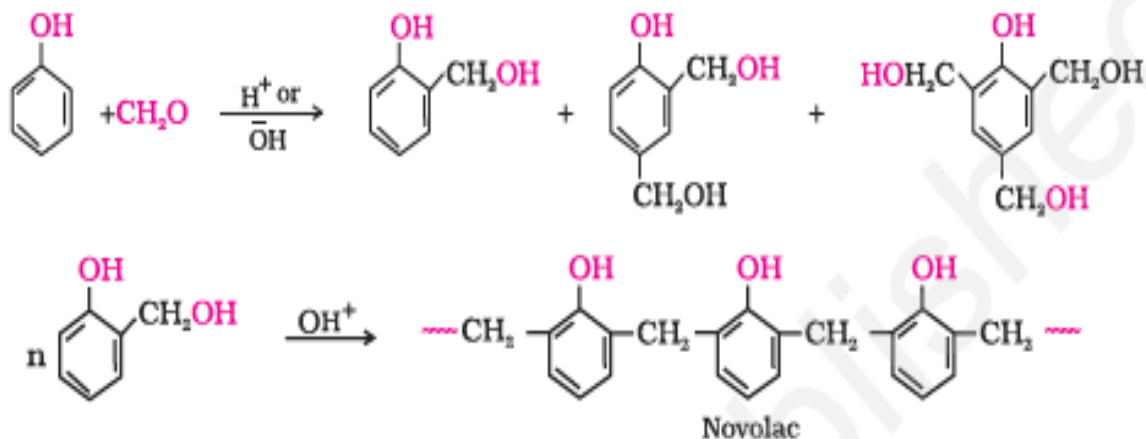
- For making insulating material like cables ,wires .
- For making gaskets ,packings ,pump parts ,tank lining ,tanks.



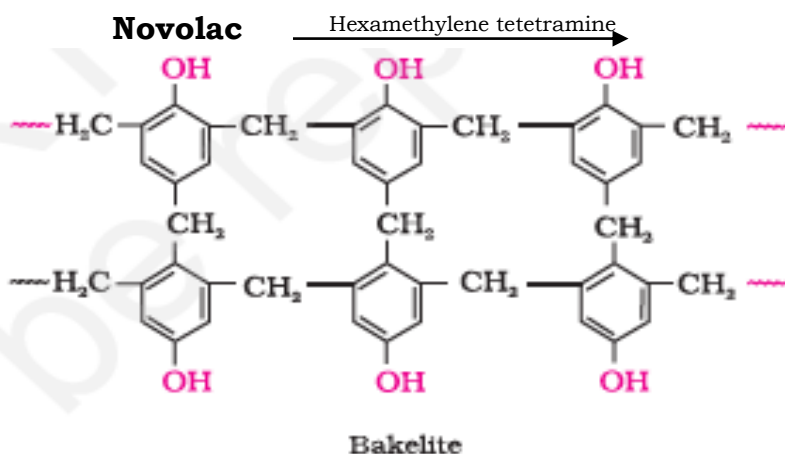
### D) Bakelite:-(Phenol-Formaldehyde Resin)

It is a thermosetting plastic and it is the world's first synthetic plastic developed by Dr. Leo Baekeland in year of 1909.

#### Step1:-



#### Step2:-



#### Properties:-

- Bakelite is pinkish brown substance.
- It has excellent heat and moisture resistance.
- It has good chemical resistant.
- It has good electrical insulator.
- It has good abrasion resistance.
- It is hard ,rigid and strong material with respect to heat and pressure.

#### Uses:-

- Used for production of ion-exchange resins.
- Making of electric insulator like switches, plugs, switch-boards, heater-handles etc.
- For making moulding articles like telephone parts, cabinets of radio and television.
- In paints and varnishes.

Fibre reinforced plastics:

- Fibre reinforced plastic [FRP] is a composite material.

- Composite material consists of physically distinct and mechanically separable two (or) more materials that retain their properties when combined together.
- FRP composites are anisotropic; therefore FRP composites properties are directional.
- Mechanical properties are in the direction of the fibre placement.
- FRP contains two components.

Components of composite (FRP):

Fibre (reinforcement):

- Fibre (reinforcement) is the substance that is used to strengthen plastic compounds.
- The properties of FRP are mainly influenced by the choice of fibres.
- There are three main types of fibres carbon, glass & Aramid fibres
- All fibres have generally high stress capacity than the ordinary steel.

Matrix:

- The plastic material used in FRP is called matrix.
- Matrix is a relatively weak plastic that is reinforced by stronger fibres.
- It transfers the forces b/w the fibres and protects the fibre from the environment.
- Generally thermosetting plastics are used as matrix.
- Vinyl esters and epoxy resins are most commonly used matrixes.

Demand for FRP's is increasing because they replace metals and they do have good performance than metals.

FRP's have thermal stability, high tensile strength, dimensional stability etc.

Along with good mechanical properties, they possess design free reduced weight and corrosion resistance.

FRPs are commonly used in aerospace, automotive, marine and construction industries.

Glass fibre reinforced plastics:

Preparation:

- Glass fibre is made up of sand, limestone, folic acid and other minor ingredients.
- The mixture is heated till it melts at about 1260°C.
- The molten glass is then allowed to flow through fine holes in a platinum plate.
- The glass strands are cooled, gathered & wound.
- The fibres are woven into various forms for use in composites.

- Another glass fibre prepared from aluminium + lime + borosilicate has high insulating properties, low susceptibility to moisture and high mechanical strength.

Properties:

- They have high surface area to weight.
- Glass fibre has good thermal insulation due to the presence of air gaps.
- Glass fibre absorbs moisture.
- Glass fibre undergoes more elongation before it breaks.
- Glass fibre is drawn at moderately low viscosity. If it is too high, fibre will break during drawing. If it is too low, the glass will form droplets.

Uses:

- Bridges
- Airplane wings
- Boat hulls
- Corrosion resistant equipment
- Circuit boards
- Automobile industry

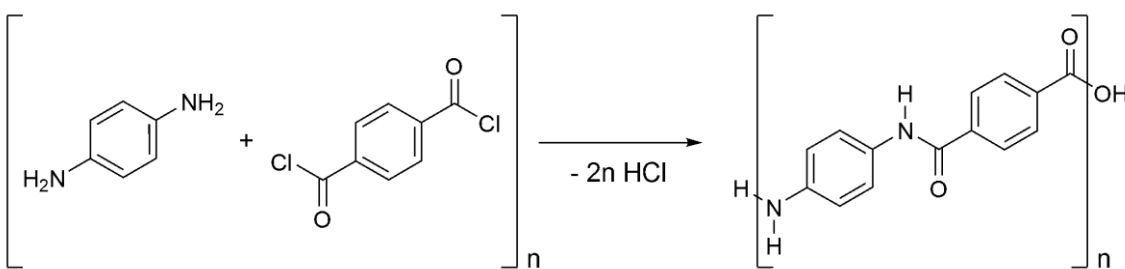
Aramid fibre reinforced plastics [bullet proof plastic]:

- Aramid is a short form of aromatic polyamide.
- Ex: Kevlar.

Kevlar:

Preparation:

- It is prepared by condensation polymerization of 1,4-diamino benzene and Isophthaloyl Chloride. In Kevlar, the repeating groups between the amide links are benzene rings



Properties:

- This is five times as strong as steel.
- Usually yellow in appearance
- Low density
- High strength
- Thermal resistance
- Good impact resistance
- Good abrasion resistance.
- Good chemical resistance.
- Compressive strength

Uses:

These are used in the manufacture of

- Bullet proof vests
- Boat hulls
- Aircraft body parts.
- Clutch plates, brake pads.
- Gaskets
- Adhesives & sealants

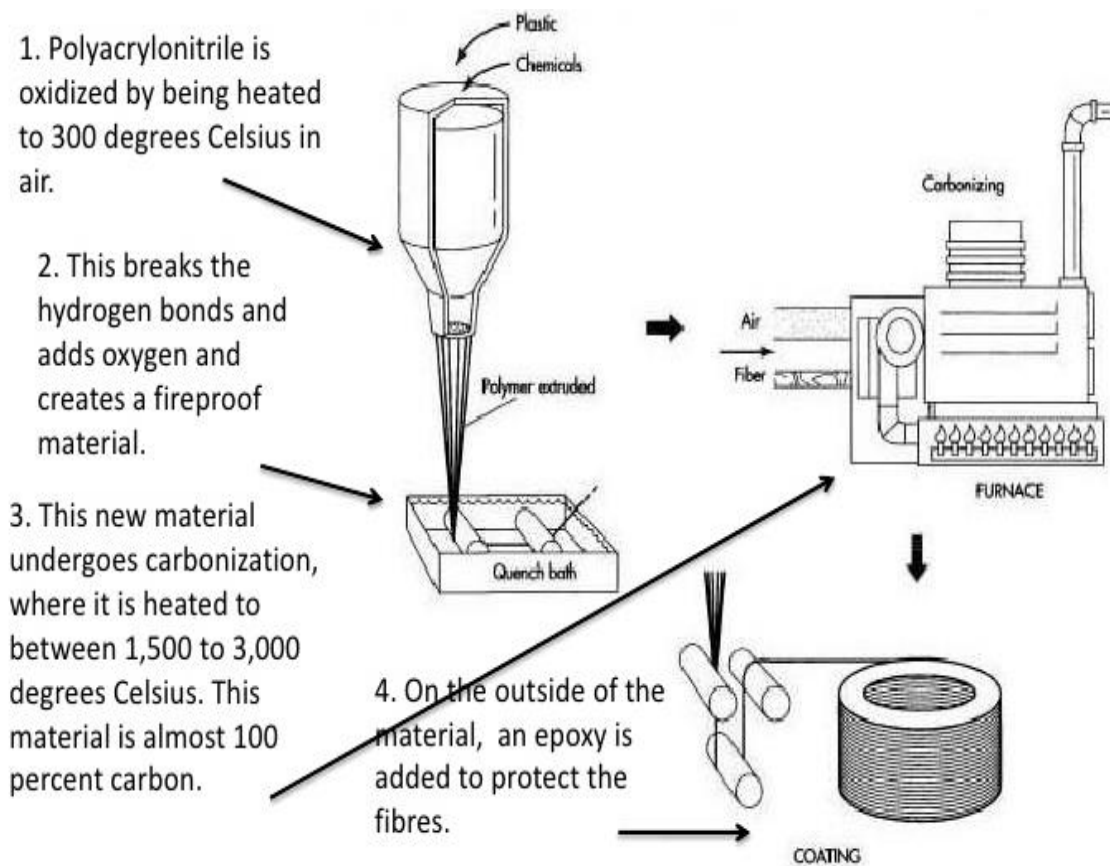
Carbon fibre reinforced plastic (CFRP or CRP):

The raw material used to make carbon fibre is called the precursor.

About 90% of the carbon fibres produced are made from polyacrylonitrile (PAN)

The remaining 10% are made from rayon or petroleum pitch.

Preparation of CFRP:



Properties:

- High strength
- High rigidity
- Corrosion resistance
- non poisonous
- not flammable
- good tensile strength

Disadvantages:

- Relatively expensive

Uses:

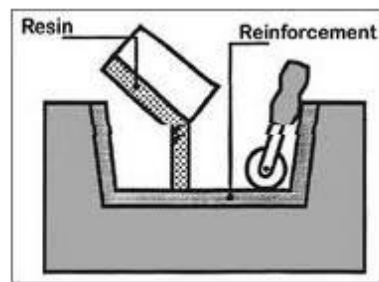
- Airspace and aircraft industries
- Automotive body parts
- Mobile cases
- Musical instruments
- Badminton racket
- Golf stick

- construction industry
- Wind mill and turbine blades
- Helmets

Methods for producing FRP's:

Hand lay up method:

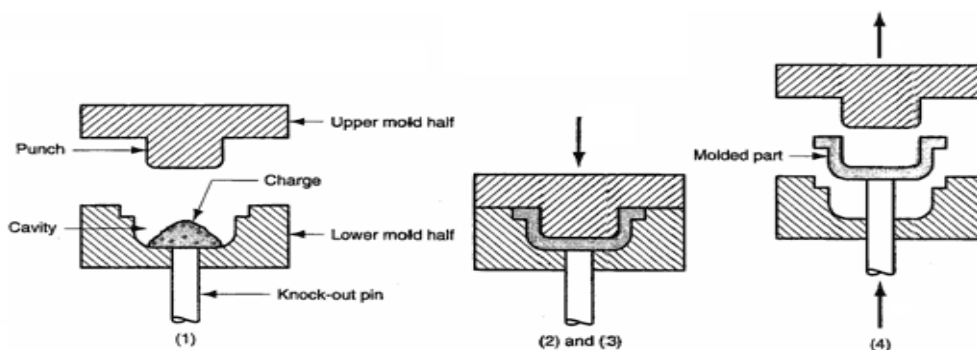
- This is a simple method for forming thermosetting plastics.
- The mould can be made of low cost wood (or) plaster.
- The reinforcing mat (or) fabric is cut to fit, laid in the mould and resin is applied by hand using a brush (or) roller (or) spray gun.
- Layers are built up to desired thickness and laminate is cured to render it hard.



Hand lay up

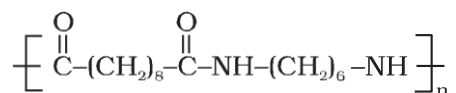
Matched metal die moulding:

- ♦ It is the most common method used.
- ♦ With this process, the plastic and reinforcement are squeezed into its desired shape with the help of pressure and heat.
- ♦ The plastic and reinforcement are pressed in matched upper and lower moulds.
- ♦ This is heated to required temperature and required time.





12. Explain the term co-polymerization and give two examples.
13. Define thermo plastics and thermosetting plastics with two examples of each.
14. Write the monomers used for getting the following polymers.  
i) Polyvinyl chloride (ii) Teflon (iii) Bakelite
15. What are the monomeric repeating units of Nylon-6,6?
16. Identify the monomer in the following polymeric structure.







# **INDUSTRIAL CHEMISTRY**

## **Unit-6** **Lubricants**

### **Learning Objectives:**

- To impart knowledge of different types of lubricants and mechanism of lubrication
- To impart knowledge on experimental determination of properties of liquid lubricants and additives to lubricants.

### **Syllabus:**

Definition and classification of lubricants. Functions of a good lubricant. Mechanism of lubrication. Experimental determination of properties of a liquid lubricant – Viscosity, Aniline point, Flash and Fire point, Pour and Cloud point. Additives to lubricants. Lubrication by nano films. Applications of lubricants

### **Learning out comes:**

On completion of this chapter a student will be able to know:

- definition and classification of lubricants.
- characteristics of good lubricant.
- mechanism of lubrication.
- experimental determination of Properties of liquid lubricants.
- the additives used to improve quality of lubricants.
- lubrication of nano films
- applications of lubricants in different areas.

### **Learning material**

### **Lubricants:**

#### **Definition of lubricant:**

The substance which reduces the friction between two metal surfaces is called lubricant and the phenomenon is known as lubrication.

#### **Functions of lubricants:**

- The lubricant is to reduce friction.
- It reduces wear and tear and surface deformation.
- It acts as coolant to carry away heat.
- It keeps away dirt.
- It prevents corrosion.

## **Mechanism of lubrication:**

Depending upon the operating conditions and lubricant characteristics lubrication is classified by following types.

1. Fluid film (or) thick film (or) hydrodynamic lubrication
2. Thin film (or) boundary lubrication.
3. Extreme pressure lubrication

### **1. Fluid film (or) thick film lubrication:**

- This lubrication can use in low load and high speed machines.
- The two sliding metal surfaces are separated by a thick, continuous unbroken film of the lubricant.
- The thickness of the fluid film is at least  $1000 \text{ \AA}$ .
- The two metal surfaces do not come in contact with each other, so friction reduces between them.
- The lubricant should have minimum viscosity at the same time separate the sliding surfaces.
- Hydrocarbon oils are considered to be satisfactory lubricants for fluid film lubrication.
- But viscosity of these lubricant decreases with rise in temperature, so to maintain viscosity, lubricants are blended with long chain polymer.
- The unsaturated hydrocarbons undergo oxidation easily, to prevent this antioxidants such as aminophenol is added to lubricant.

#### Applications:

- ✓ Delicate instruments like watches, clocks;
- ✓ light machines like sewing machines, scientific instruments.

### **2. Thin film (or) boundary lubrication:**

- This lubrication occurs in high load and slow speed machines.
- In this the lubrication film is thin. So the effectiveness of lubricant depends on its oiliness.
- The thickness of boundary film is  $20\text{-}30 \text{ \AA}$
- The thin film of lubricant is adsorbed on the metal surface.
- The coefficient of friction is generally  $0.05 - 0.15$ .

#### Requirements of thin film lubrication:

- The lubricant must have high viscosity index.
- The lubricant must have long hydrocarbons, which increases lateral attraction forces.
- Lubricant must have high resistance to heat and oxidation.
- It must have low pour and cloud point.
- Oil should have active functional groups to adsorb on metal surface easily.
- The polar groups in oil to promote wetting and spreading over metal surface.

Examples: vegetable oils, animal oils, colloidal solution of graphite are used.

### **3. Extreme pressure lubrication:**

If the sliding metal surfaces are subjected to high pressure and speed, then heat is generated causing the following effects.

- The liquid lubricants fail to stick and may decompose (or) vapourized.
- Metal surface deformation takes place.

To overcome the above difficulties, the extreme pressure additives are added to the lubricant.

Ex: Chlorinated esters, sulphurized oils and tri cresyl phosphate.

These additives react with metallic surfaces at high temperature to form metallic chlorides, sulphides, phosphates in form of durable films.

The films will withstand at very high loads and high temperature due to their high melting point.

### **Classification of lubricants:**

On the basis of their physical state lubricants are classified as

(i) Lubricating oils (ii) Greases (iii) solid lubricants

#### **(1) Lubricating oils:**

- Lubricating oils also known as liquid lubricants.
- These are provided continuous fluid film in between moving surface of machines to reduce friction.
- They also act as cooling and sealing agent.

Lubricating oils are further classified into following types

- (i) Animal and vegetable oils
- (ii) Mineral oils
- (iii) Blended oil
- (iv) Synthetic oil

#### **(i) Animal and vegetable oils:**

- Animal oils are extracted from the crude fat of animals.
- Vegetable oils are obtained by crushing the seeds.
- Both animal and vegetable oils possess good oiliness and undergo oxidation easily in presence of moist air.
- Ex: Animal oils: whale oil, lard oil, Tallow oil.  
Vegetable oils: Olive oil, palm oil, castor oil, rape seed oil.

#### **(ii) Mineral oils:**

These are obtained by fractional distillation of petroleum oil.

- These oils are cheap, stable under operating conditions, hence they are widely used.
- These oils possess low oiliness than animal oil.

#### **(iii) Blended oils (or) compounded oils:**

Desirable characteristics of lubricating oils can be improved by adding small quantities of various additives.

**Ex:** (i) To improve viscosity index of lubricants, hexanol is added.

(ii) Organic compounds of phosphorus (or) antimony are added as corrosion protective.

(iii) Tri cresyl phosphate is added as an abrasive Inhibitor.

(iv) **Synthetic oils:**

These are work under the conditions of high speed machinery, wide variations in temperature conditions, fire risk and heavy load bearing machines.

Ex: Dibasic acid esters, poly glycol ethers, silicones and silicate esters.

## **(2).Greases (or) Semi—solid lubricants:**

A semi solid lubricant obtained by combining lubricating oil with thickening agent is called grease. These are classified on the basis of soap used in it.

- (i) Soda based greases
- (ii) Calcium based greases
- (iii) Aluminum based greases.

## **(3).Solid lubricants:**

These are used either as a dry powder (or) mixed with oil, water in colloidal forms.

Ex: Graphite, Molybdenum di sulphide.

- Graphite as oil dag (Graphite dispersed in oil) is used for lubricating, in the internal combustion engines, air compressors and lathes.
- Molybdenum di sulphide used in air-frame lubrication.

## **Properties of lubricants:**

### **1. Viscosity of lubricating oil :**

- Viscosity is the property of a liquid that determines its resistance to flow.
- It indicates flow ability of oil, lower the viscosity greater the flow ability.

### **Effect of temperature on viscosity:**

Viscosity of the lubricating oil is inversely proportional to temperature because due to decreasing of inter molecular attraction forces among molecules.

### **Viscosity index:**

The rate at which the viscosity of oil changes with temperature is known as viscosity index.

- A relatively small change in viscosity index with temperature is indicated by high viscosity index.  
Ex: The Pennsylvanian oils are arbitrarily assigned a V.I. value of 100.
- The low viscosity index shows a relatively large change in viscosity with temperature.  
Ex: oils of gulf coast origin are arbitrarily assigned a V.I. of 0.
- V.I. of test oil  $V.I. = [(L-u) \div (L - H) ] \times 100.$

L = viscosity of standard oil at 38°C having the V.I of zero.

U= viscosity of test oil at 38°C

H=viscosity of standard oil at 38°C having a V.I. of 100.

**Note:**

The viscosity index depends on the molecular structure of the compound. Linear molecules have high viscosity index than Branched molecules, because branches prevent the alignment of neighbouring molecules.

**2. Flash and Fire point :**

**FLASH POINT:**

The lowest temperature at which it gives off vapours that will ignite for a moment when a small flame is brought near it.

**FIRE POINT:**

The lowest temperature at which the vapours of the oil continuously burnt for at least 5 seconds when a small flame is brought near it.

Flash and Fire point is determined with the help of Pensky-Martin apparatus.

**SIGNIFICANCE:**

Good lubricating oil should have the flash point at least above the temperature at which it is to be used, to prevent fire accidents.

**3. Cloud and pour point:**

**CLOUD POINT:**

The temperature at which the solidifiable compounds (paraffin wax) present in the oil begin to crystallized, when oil is cooled under specified conditions.

**POUR POINT:**

The temperature at which the oil ceases flow (or) pour.

**SIGNIFICANCE:**

Lubricants used in a machine working at low temperature should possess low pour point. Otherwise solidification of lubricant will cause jamming of machine.

**4. Aniline point:**

The minimum equilibrium solution temperature for equal volume of aniline and oil sample is called aniline point.

**PROCEDURE:**

- The equal volumes of oil sample and aniline are mixing in a test tube and heating the mixture until a homogeneous solution is obtained.
- Then, the tube is allowed to cool at constant temperature.
- The temperature at which the oil and aniline phases are separate out is recorded as aniline point.

**SIGNIFICANCE:**

A lower aniline point of an oil have higher percentage of aromatic hydrocarbons which is damage the rubber sealing, packing of container. So higher aniline point of oil contains lower percentage of aromatic hydrocarbons is desirable.

## Additives to lubricants

- **Boundary Lubricity Additives** enhance fluid lubricity by adsorbing on the metal surface to form a film, limiting metal-to-metal contact. Examples include lard and canola oil. Solid lubricants can also be used for boundary lubrication.
- **Extreme Pressure Additives** are a special type of boundary lubricity additive that form a metal salt layer between mating surfaces that limit friction, wear and damage. Examples include:
  - Zinc dialkyl dithiophosphate (ZDDP)
  - Chlorinated paraffins
  - Sulfurized lard oils
  - Phosphate esters
  - Overbased calcium sulfonates
- **Corrosion Inhibitors** prevent the fluid from corroding machine surfaces, metal work piece, cutting tool and machine tool. Examples include:
  - Overbased sulfonates
  - Alkanolamides
  - Aminoborates
  - Aminocarboxylates
- **Reserve Alkalinity Additives** essentially serve as a buffer, neutralizing acidic contaminants to preserve the fluid's corrosion protection and maintain the pH in a suitable range. Examples include alkanolamines like:
  - Monoethanolamine (MEA)
  - Triethanolamine (TEA)
  - Aminomethylpropanol (AMP)
  - 2-(2-aminoethoxy) ethanol
- **Metal Deactivators** prevent the staining of nonferrous alloys (such as copper and brass) and reduce corrosion when dissimilar metals contact each other. They act by forming a protective coating on the metal surface. Examples include:
  - Mercaptobenzothiazole
  - Tolyltriazole
  - Benzotriazole
- **Detergents** stabilize dirt and wear debris in oil formulations.
- **Emulsifiers** reducing interfacial tension between incompatible components by forming micelles, thereby stabilizing oil-soluble additives in water. These micelles droplets in a colloidal system then can remain suspended in the fluid.  
Examples: sodium petroleum sulfonate and alkanolamine salts of fatty acids.
- **Chelating Agents** (also known as water softeners or conditioners) reduce the destabilizing effect of hard water (calcium and magnesium ions).  
Example: ethylenediaminetetracetic acid (EDTA).
- **Antimist Additives** minimize the amount of lubricant that disperses into the air during machining. They are typically polymers and/or wetting agents. For oil-based systems, ethylene, propylene copolymers and polyisobutenes are used. For water-based systems, polyethylene oxides are common.
- **Dyes** change the color of the lubricant usually as requested by the customer. In water-diluted fluids, their main value is to indicate that product is present, since some of these can be clear and water-like in appearance. However, dyes carry some negatives:
  - They can stain skin and paint
  - Some water-soluble dyes are unstable and can change color
  - Some dyes can pass through waste treatment systems, resulting in pollution downstream.

## Nano lubricants

- The tungsten di sulphide( $WS_2$ ) can used as nano lubricants. It shows following properties.

- ✓ Better impact resistance under extreme conditions.
- ✓ User safe and environmentally friendly substance.
- ✓ Good energy efficiency.
- ✓ Superior quality to extend life of machinery parts.
- ✓ It has good anti wear and anti friction properties.
- ✓ It reduced operating noise of machinery parts.

The Nano Lubricants having layer like structure and possess no friction on the metal surface. This phenomenon is known as super lubrication.

Ex: Graphene, Carbon black,  $MoS_2$  used as nano lubricants.



## Assignment cum Tutorial questions

### **A. Questions testing the remembering / understanding level of students**

#### ***I) Objective Questions.***

1. Define Lubricant.
2. Write the examples of solid lubricants.
3. A good lubricant has
  - a) Low freezing point
  - b) Low vapour pressure
  - c) High boiling point
  - d) All of the above.
4. Oiliness is least in case of
  - a) Greases
  - b) Mineral oils
  - c) Animal oils
  - d) vegetable oils
5. Define flash point and fire point.
6. \_\_\_\_\_ are adding to mineral oils to increase oiliness.
7. The examples of semi-solid lubricants are\_\_\_\_\_.
8. Write the significance of aniline point.
9. What is cloud and pour point?
10. Write two applications of lubricants.

#### ***II) Descriptive questions***

1. Explain the classification of solid lubricants, semi –solid lubricants.
2. Determine the classification of liquid lubricants with examples.
3. Explain the aniline point of lubricant and its significance.
4. Discuss the functions of lubricant.
5. Explain the pour and cloud point of lubricant.
6. Give a short note on viscosity index of lubricant.
7. Write a note on solid lubricants.
8. Why are lubricants used? Discuss synthetic lubricating oils, giving their utility.
9. Explain the additives to lubricants.