BATU-EXAM

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at MET Bhujbal Knowledege City

Engg Chemistry Department

Unit 1

Q.1) Explain in detail Zeolite Process of Softening of Water with its Advantages & Disadvantages

Ans.) Zeolite process of water softening involves the use of a zeolite material, which is a natural or synthetic material with a highly porous structure that can selectively absorb certain ions. It has the formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$.

Process: The process involves passing hard water through a bed of zeolite material, which contains sodium ions that exchange with the calcium and magnesium ions in the water. As a result, the hardness-causing ions are removed from the water, and the sodium ions are released into the water.

Regeneration: The zeolite material used in the process has a limited capacity for removing hardness-causing ions from water. Once the capacity is reached, the material needs to be regenerated to maintain its effectiveness. Regeneration involves the addition of sodium ions to the zeolite bed, which displaces the calcium and magnesium ions that have been adsorbed by the zeolite. This is typically done by flushing the bed with a sodium chloride solution, which replaces the calcium and magnesium ions with sodium ions.
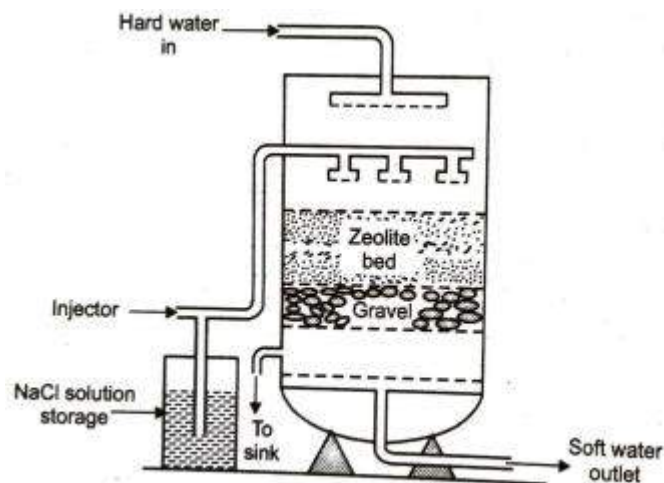

Fig. 1.1: Zeolite process

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Advantages:

1. Effective: Zeolite process is an effective method for softening hard water. It can remove a significant amount of calcium and magnesium ions from water, which can improve the quality of the water.
2. Low cost: Zeolite is an inexpensive material, making the zeolite process a cost-effective method for softening water.
3. Low maintenance: Zeolite beds are easy to maintain and require little maintenance compared to other methods of water softening.

Disadvantages:

1. Regeneration: The zeolite material used in the process needs to be regenerated periodically to maintain its effectiveness. This requires the addition of sodium ions to the zeolite bed, which can be a time-consuming process.
2. Limited capacity: Zeolite beds have a limited capacity for removing hardness-causing ions from water. Once the capacity is reached, the bed needs to be regenerated, which can cause a temporary interruption in the water supply.
3. Salt discharge: The process results in the discharge of salt into the environment, which can have a negative impact on the environment if not properly managed.

Q.2) Explain in detail Ion exchange process of softening of water with its advantages and disadvantages

Ans.) Process: The ion exchange process of water softening involves the use of ion exchange resins, which are synthetic materials with a high affinity for hardness-causing ions. The process involves passing hard water through a bed of ion exchange resin, which contains sodium ions that exchange with the calcium and magnesium ions in the water. As a result, the hardness-causing ions are removed from the water, and the sodium ions are released into the water.

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<u>Regeneration</u>: **The ion exchange resin used in the process has a limited capacity for removing hardness-causing ions from water. Once the capacity is reached, the resin needs to be regenerated to maintain its effectiveness. Regeneration involves the addition of sodium ions to the resin bed, which displaces the calcium and magnesium ions that have been adsorbed by the resin. This is typically done by flushing the bed with a sodium chloride solution, which replaces the calcium and magnesium ions with sodium ions.**
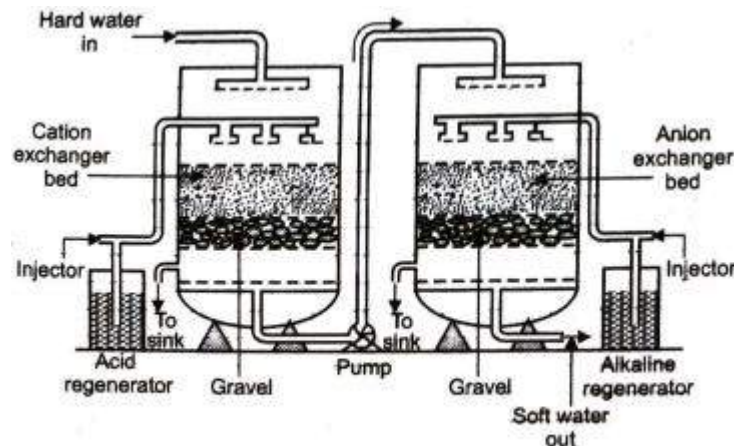

Fig. 1.2: Ion exchange process

<u>Advantages</u>:

1. **Effective: Ion exchange process is an effective method for softening hard water. It can remove a significant amount of calcium and magnesium ions from water, which can improve the quality of the water.**
2. **High capacity: Ion exchange resins have a high capacity for removing hardness-causing ions from water. This means that they can be used for a longer time without requiring regeneration.**
3. **Fast process: Ion exchange process is a fast process, and the water can be softened quickly.**
4. **Easy maintenance: Ion exchange resins are easy to maintain and require little maintenance compared to other methods of water softening**

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Disadvantages:

1. **Regeneration:** The ion exchange resin used in the process needs to be regenerated periodically to maintain its effectiveness. This requires the addition of sodium ions to the resin bed, which can be a time-consuming process.
2. **High cost:** Ion exchange resins are relatively expensive compared to other materials used for water softening. This can make the process a costly method for water softening.
3. **Environmental impact:** The regeneration process involves the discharge of saltwater into the environment, which can have a negative impact on the environment if not properly managed.

Q.3) Explain in detail Hot – lime soda process of softening of water with its advantages and disadvantages

Ans.) Process: Hot-lime soda process of water softening involves the use of lime (calcium hydroxide) and soda ash (sodium carbonate) to remove hardness-causing ions from water. The process involves adding lime to the water to raise the pH and cause the calcium and magnesium ions to precipitate as calcium carbonate and magnesium hydroxide. Then, soda ash is added to the water to neutralize the excess lime and raise the pH to the desired level. The precipitated calcium carbonate and magnesium hydroxide are then removed by settling or filtration.
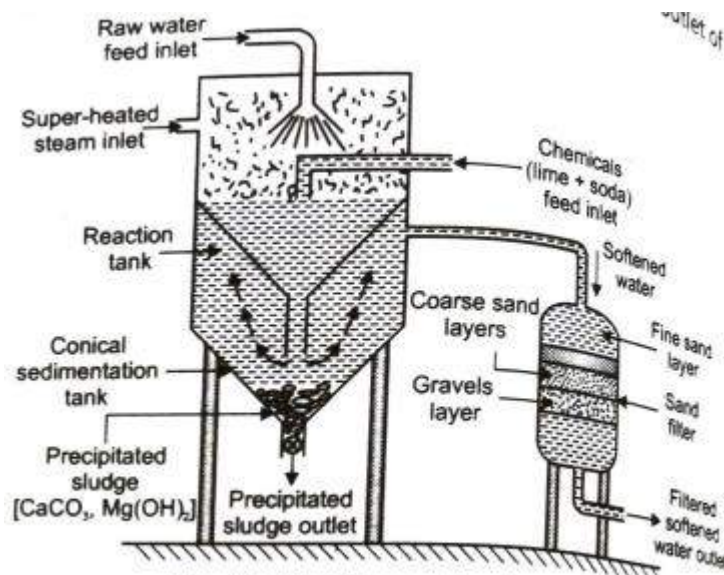

Fig. 1.3: Hot lime and soda process

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Advantages:

1. **Cost-effective: Hot-lime soda process is a cost-effective method for water softening. The materials used in the process are relatively inexpensive, and the process can be performed using simple equipment.**
2. **Effective: Hot-lime soda process is an effective method for removing hardness-causing ions from water. It can remove a significant amount of calcium and magnesium ions from water, which can improve the quality of the water.**
3. **Minimal maintenance: Hot-lime soda process requires minimal maintenance compared to other methods of water softening.**

Disadvantages:

1. **Wastewater disposal: The wastewater generated during the process contains high levels of calcium and magnesium ions and can be difficult to dispose of properly.**
2. **Scaling: The process can lead to scaling or buildup of calcium carbonate on the surfaces of pipes, fixtures, and appliances, which can lead to reduced efficiency and damage.**
3. **High chemical usage: The process requires the use of large amounts of chemicals, including lime and soda ash, which can be a disadvantage if chemicals are expensive or difficult to obtain.**

Q.4) Explain the determination of Dissolved Oxygen in water by Winkler's method

Ans.) Winkler's method is a widely used method for the determination of dissolved oxygen in water. Here's a detailed explanation of the method:

1. **Sample Collection: Collect a water sample in a clean, clear, and airtight container. Ensure that the container is filled to the brim to minimize the contact of air with the water.**
2. **Addition of Reagents: Add 1 mL of manganese sulfate solution ($MnSO_4$) and 1 mL of alkaline iodide azide solution ($KI-NaN_3$) to the sample. The manganese sulfate oxidizes the dissolved oxygen to form MnO_2, while the alkaline iodide azide solution converts the formed MnO_2 to MnO_4^-.**
3. **Acidification: Add 1 mL of concentrated sulfuric acid (H_2SO_4) slowly to the sample. The sulfuric acid liberates iodine from the iodide-manganese complex**

formed in the previous step. The liberated iodine is then titrated with standardized sodium thiosulfate (Na2S2O3) solution.

4. **Titrating:** Titrate the liberated iodine with standardized sodium thiosulfate solution until a pale yellow color is observed. The pale yellow color indicates the endpoint of the titration.

5. **Calculation:** Calculate the amount of dissolved oxygen present in the water sample using the following formula:

$$N_a V_a = N_b V_b$$

Where,

N_a = Normality of Sample Solution

V_a = Volume of Sample Solution

N_b = Normality of $Na_2S_2O_3$

V_b = Volume of $Na_2S_2O_3$

Thus, Weight of Dissolved Oxygen = V_b x N_b x 8 x 1000 / V_a mg of O_2

Advantages:

1. **Accurate:** Winkler's method is a highly accurate method for the determination of dissolved oxygen in water.
2. **Sensitive:** The method is sensitive and can detect low levels of dissolved oxygen in water.
3. **Simple:** The method is simple to perform and requires only basic laboratory equipment.

Disadvantages:

1. **Time-consuming:** The method is time-consuming and requires multiple steps for the determination of dissolved oxygen.
2. **Reagents:** The method requires the use of several reagents, including manganese sulfate, alkaline iodide azide, and sulfuric acid, which can be expensive and require careful handling.

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3. **Interference:** The method can be interfered by the presence of oxidizing agents or other substances that react with the reagents used in the method.

Q.5) Define Hard and Soft water. How does the hardness of water determined by using EDTA method?

Ans.)

Hard Water:

Water which does not give lather with soap but forms curdy precipitate is called as Hard Water. Hard Water contains Chloride and Sulphates of Calcium and Magnesium. Example: Pond Water, River Water, Sea Water etc.

Soft Water:

Water that gives good lather with soap is called as soft water. Example: Rain Water, Distilled Water, De-Ionized Water etc.

The hardness of water can be determined by using EDTA (ethylene-diamine-tetra-acetic acid) titration method. EDTA is a chelating agent that forms a complex with metal ions, particularly calcium and magnesium ions, which are responsible for water hardness. The following steps are involved in determining the hardness of water using EDTA titration method:

1. **Sample Collection and Preparation:** Collect a water sample in a clean, clear, and airtight container. If the sample contains any suspended particles or debris, filter it to obtain clear water.
2. **Standardization of EDTA Solution:** Prepare a standard solution of EDTA by dissolving a known amount of EDTA in distilled water. Standardize the solution by titrating a known volume of the solution against a standard solution of calcium ions.
3. **Water Sample Titration:** Pipette a known volume of the water sample into a conical flask and add a few drops of indicator (Eriochrome black T). The indicator forms a complex with calcium and magnesium ions, giving a wine-red

color to the solution. Titrate the solution with standardized EDTA solution until the wine-red color changes to blue.

4. **Calculation: Calculate the amount of calcium and magnesium ions present in the water sample using the following formula:**

Hardness (mg/L) = [(Volume of EDTA × Normality of EDTA × 1000) / Volume of Water Sample] × 50

Advantages:

1. **Accurate: The EDTA method is a highly accurate method for the determination of water hardness.**
2. **Selective: The method is selective for the determination of calcium and magnesium ions, which are the major contributors to water hardness.**
3. **Simple: The method is simple to perform and requires only basic laboratory equipment.**

Disadvantages:

1. **Interference: The method can be interfered by the presence of other metal ions that can form a complex with EDTA.**
2. **Sensitivity: The method is sensitive to the pH of the water sample, which can affect the accuracy of the results.**
3. **Reagents: The method requires the use of several reagents, including EDTA and indicator, which can be expensive and require careful handling.**

Q.6) Discuss the Disadvantages of Hard Water in Domestic & Industrial Use

Ans.) Hard water is water that contains high levels of dissolved minerals, mainly calcium and magnesium ions. While it is not harmful to health, hard water can cause several problems in both domestic and industrial use. Here are some of the disadvantages of hard water

Domestic Use:

1. **Soap Scum:** Hard water reacts with soap to form soap scum, which leaves an unsightly residue on surfaces, making cleaning more difficult and time-consuming. This can lead to increased use of cleaning products.
2. **Clogged Pipes:** The minerals in hard water can build up in pipes, leading to clogs and blockages. This can reduce water flow and increase the risk of damage to appliances and plumbing.
3. **Poor Water Quality:** Hard water can also affect the taste and odor of drinking water, making it less appealing to drink.
4. **Reduced Efficiency of Water-Using Appliances:** Hard water can cause a buildup of minerals in water-using appliances such as dishwashers, washing machines, and water heaters, leading to reduced efficiency and increased energy consumption.

<u>**Industrial Use**</u>:

1. **Increased Energy Consumption:** Hard water can cause scale buildup in industrial machinery, leading to reduced efficiency and increased energy consumption.
2. **Reduced Equipment Lifespan:** The buildup of scale in industrial equipment can also lead to corrosion and premature equipment failure.
3. **Increased Maintenance Costs:** The scale buildup in industrial machinery requires regular maintenance and cleaning, which can be costly and time-consuming.
4. **Reduced Product Quality:** Hard water can affect the quality of products produced in industries such as food and beverage manufacturing, paper and pulp production, and pharmaceutical manufacturing.

Unit 2:

Q.1) What is Phase Rule. Explain the terms Phase, Component & Degree of Freedom with suitable examples

Ans.)

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The phase rule, also known as the Gibbs phase rule, is a fundamental principle in thermodynamics that relates the number of phases, components, and degrees of freedom in a system at equilibrium. It was first proposed by the American scientist J. Willard Gibbs in the 19th century.

The phase rule states that the number of degrees of freedom in a system at equilibrium is equal to the number of independent variables that can be changed without altering the number of phases in the system.

The Phase Rule Equation is given as: $F = C - P + 2$

Where, F = Degree of Freedom

C = Component

P = Phase

Phase:

A phase is a physically distinct and homogeneous portion of a system that is separated from other portions of the system by a boundary. A phase is characterized by its physical state (solid, liquid, or gas), composition, and properties. For example, water and ice are two different phases of the same substance.

Component:

A component is a chemically distinct substance that can be present in a system. The number of components in a system determines the number of chemical species that can be varied independently. For example, water and ethanol are two components of a solution of water and ethanol.

Degree of Freedom:

The degree of freedom is a measure of the number of independent variables that can be changed without altering the number of phases in the system.

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Q.2) Explain in Detail Phase Diagram of Water System

Ans.)

Water System:

Water System under normal conditions is of 3 Phases and 1 Component. The 3 Phases are Solid – Ice, Liquid – Water and Gas – Water Vapor. All these phases can be represented by one chemical entity (i.e. H_2O). Hence it is One Component System.

Applying Phase Rule to Water System we get,

$$F = C - P + 2 \qquad F = 1 - P + 2 \qquad F = 3 - P$$

From the above value of degree of freedom (F), we can say that, the degree of freedom (F) depends on the number of phases present at the equilibrium. Therefore, the following three different cases are possible,

P = 1, then F = 2: System is Bivariant

P = 2, then F = 1: System is Monovariant

P = 3, then F = 0: System is Zero Variant

Phase Diagram:

Fig. 2.5.1 : Phase diagram of water system
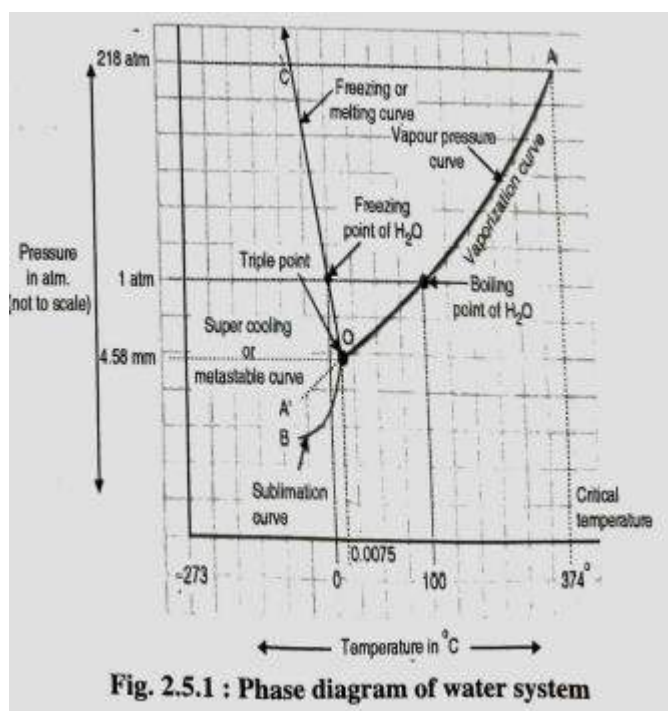
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Curve OA:

The curve OA terminates at A, the critical point 218 atm. and 374° temperature. It represents the vapor pressure of liquid water at different temperatures.

The two phases water and water vapor coexist in equilibrium along this curve. Here, are two phases (P = 2) and one component (C = 1), therefore

$$F = 1 - 2 + 2 = 1$$

Hence, system is monovariant or univariant or having one degree of freedom

Curve OB:

The curve OB terminates at B, the absolute zero, i.e. -273° temperature. It shows the vapour pressure of solid ice at different temperature.

The two phases solid-ice and water-vapour coexist in equilibrium along this curve. Therefore, degree of freedom for this system is also one and system is monovarient.

Curve OC:

The curve OC terminates at C, the critical pressure. The two phases solid-ice and liquid-water coexist in equilibrium. This curve indicates that the melting point of ice decreases with increase of pressure.

Again, along the curve OC, there are two phases in equilibrium and system is of one component.

Areas AOB, AOC & BOC:

1. Area AOC represents conditions for liquid phase, i.e. water
2. Area AOB represents conditions for gaseous phase, i.e. water vapour
3. Area BOC represents conditions for solid phase, i.e. ice.

Triple Point:

All the three curves, OA, OB and OC meet at the point O called as tripple point, where all the three phases solid, liquid and vapour are simultaneously in equilibrium. This

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triple point occurs at 0.0075°C and 4.58 mm Hg pressure. Since, there are three phases and one component, therefore

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

The system at triple point is zero variant or nonvariant

Metastable Curve:

This curve is also known as super cooling (water/vapour) curve. This is the extension of curve OA, i.e. vapour pressure curve. That is water can be super cooled by eliminating solid particles carefully which includes crystallization.

The super cooled water system is unstable. It at once reverts back to stable system on the slightest of disturbance

Q.3) Explain Phase Diagram of Sulphur System

Ans.) Sulphur is a 1 Component System and it can exist in 2 forms: Rhombic & Monoclinic
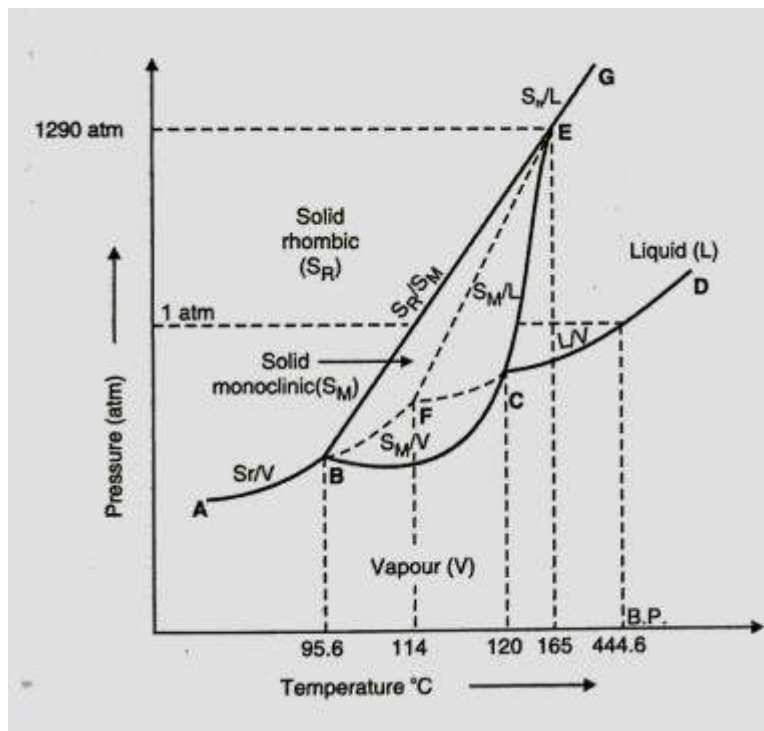
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Sulphur can exist in 4 possible phases:

- **Rhombic Sulphur**
- **Monoclinic Sulphur**
- **Sulphur Liquid**
- **Sulphur Vapour**

Thus in Sulphur 4 Triple Points exist for the 4 respective phases.

Components in Sulphur System:

All the four phases can be represented by the only chemical individual "SULPHUR" itself. Hence Sulphur is also a One Component System.

Phase Rule (F = C – P + 2) becomes,

$$F = 3 – P$$

Phase Diagram has 4 areas:

- **ABEG: Only Rhombic Sulphur**
- **BCE: Only Monoclinic Sulphur**
- **DCEG: Only Liquid Sulphur**
- **ABCD: Gaseous Sulphur**

Corresponding Curves are:

- **AB: Sublimation Curve of Rhombic Sulphur**
- **BC: Sublimation Curve of Monoclinic Sulphur**
- **CD: Vapor Pressure Curve**
- **AE: Transition Curve**
- **BE: Melting Point Curve**
- **EG: Melting Point Curve**

Three Triple Points:

- **B: Rhombic S is in Equilibrium with Monoclinic S**
- **C: Monoclinic S melts**
- **E: Rhombic, Monoclinic & Liquid S are in Equilibrium**
- **Critical Point: Here Liquid & Gaseous S have same density**

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Curves:

At any curve, Phase Rule becomes F = 3 – P = 3 – 2 = 1 (Monovariant)

Triple Points:

- **Triple Point B**
- **Triple Point C**
- **Triple Point E**
- **At any Triple Point, Phase Rule becomes F = 3 – P = 3 – 3 = 0 (Zero Variant)**

Areas:

- **Area ABEG (Rhombic S)**
- **Area BCEB (Monoclinic S)**
- **Area DCEG (Liquid S)**
- **Area ABCD (Vapor S)**
- **In an area Phase Rule becomes F = 3 – 1 = 2 (Bivariant)**

Q.3) Explain Phase Diagram of Ag-Pb Alloy System (Silver-Lead)

Ans.) This system has 2 Components and 4 Phases. The Phases are:

- **Solid Silver**
- **Solid Lead**
- **Solution of Molten Silver & Lead**
- **Vapour**

But the boiling points of silver and lead being considerably high, the vapour phase is practically absent. Since the pressure has nearly no effect on equilibrium so the system can be conveniently represented by a constant and one variable pressure which is neglected, Hence the condensed form of the phase rule,

$$F = C - P + 1 = 2 - P + 1 = 3 - P$$

will be applicable

Since, the degree of freedom in such case is reduced by one, therefore, it can be also termed as reduced phase rule and represented by the equation.

$$F = C - P + 1$$

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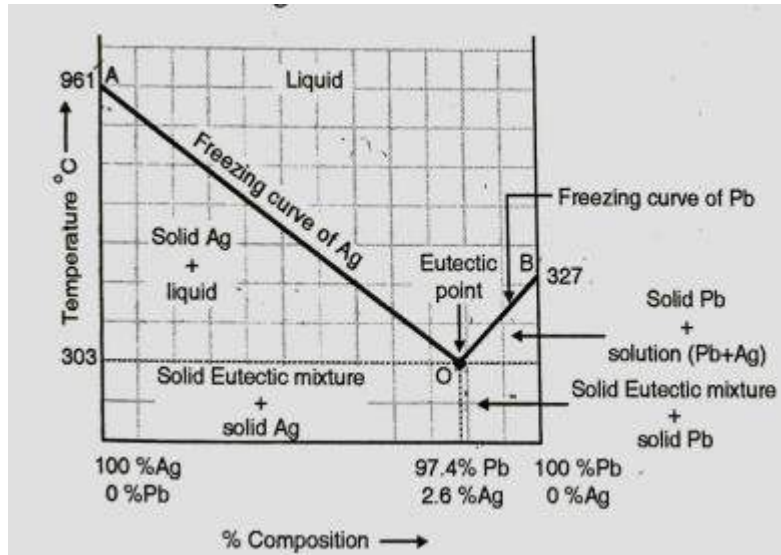
Curve AO:

The curve starts from A (961°C) the melting point of Ag, where pure Ag coexists as solid and liquid. This curve, indicates that the melting point of Ag gradually on adding Pb, along AO, till the lowest point O (303°C) is reached

Along this curve, solid Ag and solution (vapour being negligible) coexist and hence, according to reduced phase rule equation:

$$F = 3 - P = 3 - 2 = 1 \text{ (System is Univariant)}$$

Curve BO:

It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead (327°C). Along BO, the melting point gradually falls on the addition of Ag, till lowest point O is reached.

On cooling the whole mass (having eutectic composition) crystallizes out. The system is univariant like AO.

Point O:

The two curves AO and BO meet at O, where three phases-solid Ag, solid Pb and their solution coexist and according to condensed phase rule, the system will be invariant (F= 3-P=3-3=0).

The point O (303°C) represents a fixed composition of Ag = 2.6 % : Pb = 97.4 % and is

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called eutectic composition temperature. At the eutectic composition point, the temperature remain constant, until the whole of the melt solidifies in block to become solid of eutectic composition.

However, further cooling results in the simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O.

Area AOB:

It represents solution of Pb-Ag. If a sample of lead containing less than 2.6 % Ag is taken, at an arbitrary point on curve. On allowing the mass to cool, the temperature gradually falls without any change in composition till this point is reached on the curve BO

On lowering the temperature, lead begins to separate out and the composition varies along PO till point O is reached. On further cooling the whole mass solidifies in block to the eutectic composition

Unit 3:

Q.1) Write a Note on Electrochemical Corrosion (Wet Corrosion)

Ans.)

If metal is partially dipped in a salt solution, then a chemical potential/potential difference is developed between the rod surfaces and then solution, this potential difference depends upon concentration of solution, nature of metal and temperature.

If two such electrodes are electrically connected to complete the circuit, then it forms a galvanic cell which conducts an electric current. This phenomenon of electric current is strongly associated with electrochemical corrosion.

Thus, electrochemical corrosion occurs when –

a) Conducting liquid is in contact with metal

b) Two dissimilar metals are dipped in a solution

At anode, oxidation reaction takes place by loss of electron .Thus there is a tendency at anode to destroy the metal by forming metallic ions therefore corrosion always occurs at the anodic area.

On the other hand, at cathode reduction reaction takes place (gain of electrons), the dissolve constituents in the electrolyte gains this electron and forms ions such as OH^-, O_2^- etc.

Rate of Electrochemical Corrosion:

Rate of electrochemical corrosion depends upon the nature of corrosion product.

a) If the corrosion product dissolves into the solution or evolves as a gas, then corrosion reaction goes on changing.

b) If the corrosion product is insoluble compound, then it forms or covers the metal surface. Therefore, decrease the rate of corrosion.

Mechanism:

Corrosion of metal in an aqueous solution is an electrochemical phenomenon in which current flow between anode and cathode areas. The reaction occurring at anode involves liberation of free electrons forming metallic ions with dissolution of metal.

At cathode, it consumes these electron either by evolution of hydrogen or by absorption of O_2 depending upon the nature of corrosion product.

Evolution of Hydrogen:

The evolution of H_2 takes place in the acidic solution like industrial waste, non-oxidizing acid (HCL) etc.

In this type of corrosion, anodes are very large areas while cathodes are very small areas. Thus in hydrogen evolution mechanism, the displacement of hydrogen ions from acidic solution by metal ions.

Absorption of Oxygen:

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In this process, corrosion of metal occurs in the presence of aqueous neutral solution of electrolyte (NaCl)

Let us consider the iron metal on the surface of iron, thin oxide film is obtained, however if this oxide film develops some cracks, then if forms anode areas on the surface. While remaining part of the metal acts as cathode, thus it is clear that anode areas are very small while cathode areas are very large.

Q.2) Write a Note on Direct Chemical Corrosion (Dry Corrosion)

Ans.) This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O2, CO2, H2S, Cl2, and Br2, SO2 etc. with metal or alloy surfaces.

The extent of corrosion depends on:

(a) Chemical affinity between metal and corrosive environment.

(b) The ability of metal to form a protective film.

Thus, the surfaces of metals are directly attacked by the atmospheric gases and get coated with corresponding compounds like Oxides, Sulphides, Chlorides, and Carbonates etc. Such type of corrosion is called as Direct Chemical Corrosion or Dry Corrosion.

Generally Dry corrosion occurs due to oxygen. It has been found that, oxygen present in the medium directly attacked the metal surface at low or high temperature in the absence of moisture. It is represented by this equation

$$2M + O_2 \rightarrow 2\ MO$$
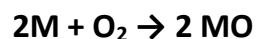
When oxidation starts, a thin oxide film is formed on the surface of the metal. The nature of oxide film plays an important role in oxidation process. This film decides the prevention or continuation of corrosion. The oxide film so produced can be classified into three categories:

Stable Film:

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1) Alkali and alkaline earth metals on oxidation produce oxide film of smaller volume than the respective metals from which they were formed. This results in the formation of porous film through which oxygen can diffuse to bring the further attack of the metal.

2) On the other hand, heavy metals like Al, Cr, Pb, Cu etc. form oxide film of greater volume than the metal from which they were formed. This non porous stable film prevents the diffusion of oxygen and hence the rate of further attack decreases.

<u>Unstable Film</u>:

When oxide film formed is unstable then it decomposes back into the metal and oxygen.

$$2MO \rightarrow 2M + O_2$$
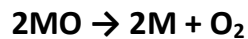
Therefore oxidation process or corrosion is not possible in case of noble metals like Ag, Au, Pt etc.

<u>Volatile Film</u>:

When the oxide film formed is volatile, it vaporizes as soon as it is formed. Therefore, the underlying metal surface is exposes for further attack of oxygen and thus causes continuous and excessive corrosion.

Example: Molybdenum oxide (MoO_3) is volatile

Q.3) Explain in detail various factors affecting the rate of corrosion

Ans.)

The rate extent of corrosion depends upon the following factors

- **Nature of the metal**
- **Nature of the corroding environment**

1) <u>Nature of the Metal:</u>

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a) **Position in the Galvanic Series:**

When two metals or alloys are electrically connected and exposed to an electrolyte, then metal which is higher in electrochemical series suffers from corrosion. The rate of corrosion depends upon relative difference in their electrochemical positions, Greater is the difference, and faster is the rate of corrosion.

b) **Relative Areas of Anodic & Cathodic part:**

When two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the ratios of areas of anodic and cathodic parts. The rate of corrosion is more rapid, if the anodic area is smaller because the current density at the smaller anodic area is much higher thus rapid destruction of anodic metal takes place

c) **Solubility of Corrosion Product:**

In electrochemical corrosion, if the corrosion product is soluble in the corroding medium the rate of corrosion increases. On the other hand, if the corrosion product is soluble then it covers the metal surface and thus the rate of corrosion decreases.

2) **Nature of the Corroding Environment:**

a) **Temperature:**

As temp. Increases the rate of corrosion as well as diffusion increases. But the rate of solubility of oxygen decreases. Thus corrosion generally increases with rise in environmental temperature

b) **Presence of Suspended Particles in Atmosphere:**

Atmospheric condition is influenced by the presence of solid particles in air.

If these particles are chemically active in nature, then they absorb moisture and acts as strong electrolytes and thus increases the rate of corrosion. If these particles are chemically inactive in nature, then they absorb both Sulphur gases and moisture and slowly enhance the rate of corrosion.

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c) **Effect of pH:**

Generally acidic media are more corrosive than alkaline or neutral media. The corrosion of iron in oxygen free water is slow. However the corresponding corrosion rate in the presence of oxygen is much higher.

Zn suffers minimum corrosion at pH =11, Al has minimum corrosion rate around pH =5.5. While Tin corrodes rapidly at pH greater than 8.5

**Q.4) Explain in detail Galvanic Corrosion**

Ans.)

When two dissimilar metals e.g. Zn and Cu are electrically connected and exposed to an electrolytes the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called as galvanic corrosion.

In the above example, Zn is higher in electrochemical series and thus forms the anode and gets dissolved in solution. Whereas, Cu which is lower in electrochemical series and thus acts as cathode. The nature of corrosive environment decides the type of cathodic reaction.

In acidic solution, the corrosion occurs by H2 evolution, oxygen absorption mechanism occurs. The electronic current flow from Zn metal to Cu metal. Thus it is clear that, corrosion occurs at the anodic metal while the cathodic area is protected from attack

Example:

 1) Lead –Antimony solder around the Cu wire.

 2) Steel pipe connected to Cu plumbing.

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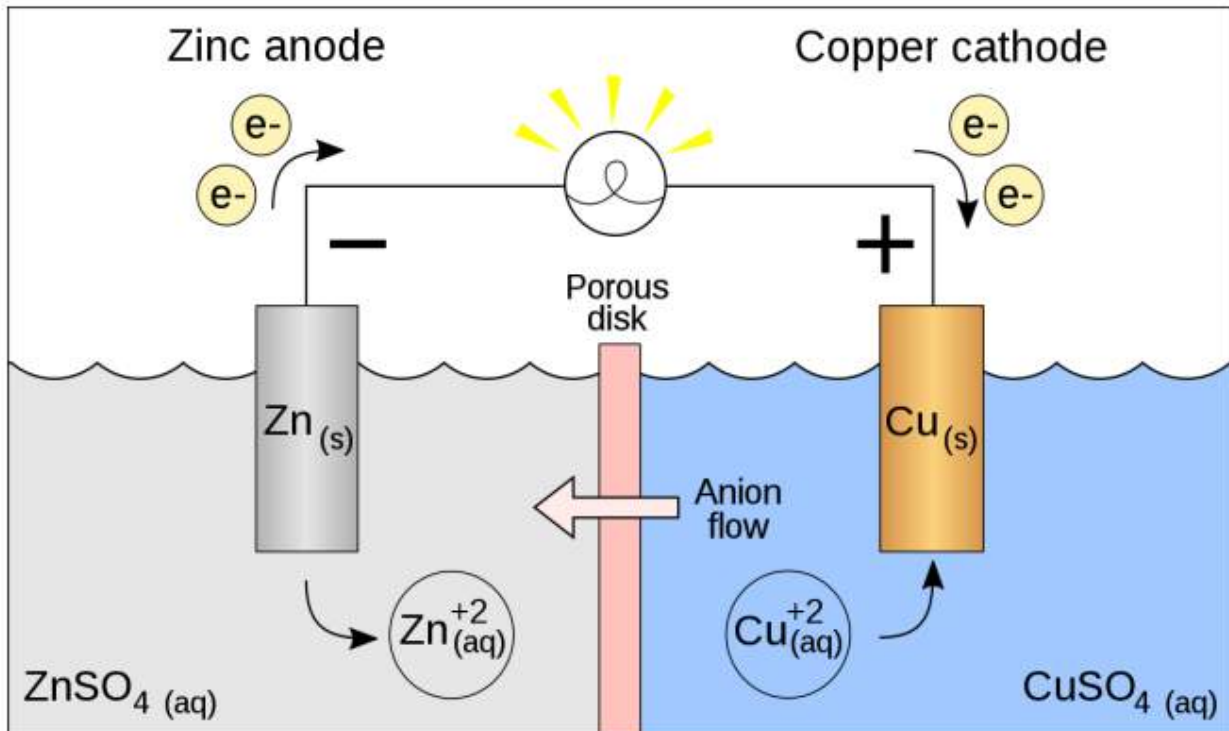
Q.5) Explain Methods to Minimize Rate of Corrosion

Ans.)

Only under ideal service conditions corrosion can be stopped completely. However ideal condition means uniform composition without heterogeneity and absolute uniform environment are impossible to attain. Thus it is possible only to minimize the rate corrosion considerably.

Since types of corrosion are so numerous and the conditions under which corrosion occurs are so different that diverse methods are used control corrosion. The choice of the method depends upon the environmental conditions to which metal is exposed. Some of corrosion control methods describe as following:

1) **Proper Designing:**

A proper selection of metallic material for any particular environment and proper design is the best way of controlling corrosion .The design of the material should be

such that corrosion even if it occurs,which is uniform does not result intense and localized corrosion. Important design principles are:

a) Avoid the contacts of dissimilar metals in the presence of a corroding solution. If this principle is not taken into the consideration then corrosion occurs on the more active metal while less active metal remains protected.

b) If two dissimilar metals in contact but they should be as close as possible to each other in the electrochemical series.

c) Whenever the direct joining of dissimilar metal is unavoidable, then insulating fitting may be applied between them to avoid metal-metal electrical contact
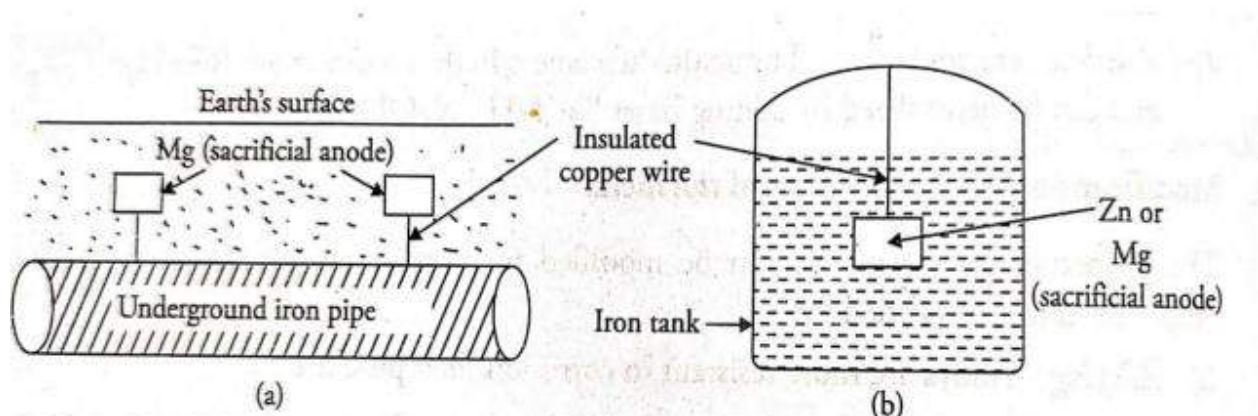
2) Cathodic Protection:

The main 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 protections.

a) Sacrificial anodic protection method:

In this method the metallic structure to be protected is connected by a wire to more so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly while the parent metallic structure (which becomes cathode) is protected.

The more active metal so used is called as 'sacrificial anode'. The corroded sacrificed anode can be replaced by a fresh anode when consumed completely

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b) Impressed current cathodic protection:

In this method an impressed current is passing in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Generally D.C. source is used to pass impressed current with an insoluble anodes like Graphite, Stainless steel, Platinum etc.
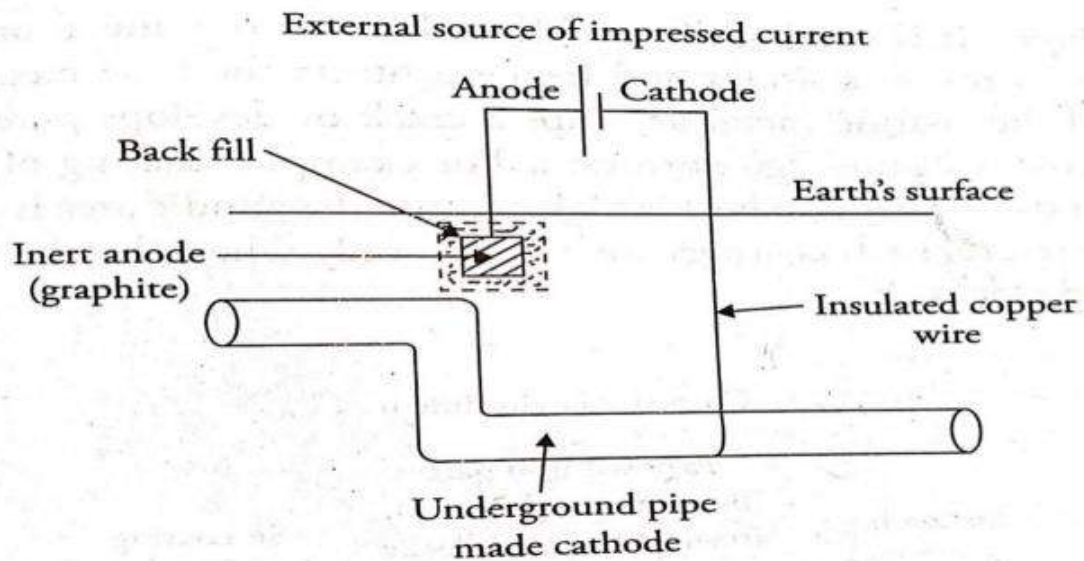
A sufficient direct current is applied to an insoluble anode immersed in the corroding medium, connected to the metallic structure which is to be protected. This type of cathodic protection can be used in water box coolers, water tanks, pipeline, condenser etc.

Unit 4:

Q.1) What are Fuels? How they classified? State characteristics of a good fuel?

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Fuel: A fuel is substance that produces useful energy either through combustion or through nuclear reaction. An important property of fuel is that the energy is released in a controlled manner and it can be used economically for domestic and industrial purpose

Example: Wood, Coal, Petrol, Diesel etc.

Fuels can be classified on the basis of their Occurrence & Physical Types

1) **On the basis of occurrence fuel are of two types.**

a) **Primary fuel or Natural fuel:** These are found to occur in nature and are used such without processing or after being processed to a certain extent, which does not alter the chemical constitution of the fuel.
These are also known as fossil fuels. For Example: Wood, Coal, Lignite, Peat, and Natural Gas

b) **Secondary fuel or Derived fuel or Artificial fuel:** These are fuels that are derived from primary fuel by further chemical processing. For Example: Coke, Charcoal, Kerosene, Producer Gas, and Water Gas.

2) **On the basis of their physical state fuels can be classified as:**

a) **Solid fuel**
b) **Liquid fuel**
c) **Gaseous fuel**

Characteristics of Good Fuels:

(i) **High calorific value: A good fuel should posses high calorific value because calorific value determines the efficiency of the fuel .Higher the calorific value greater is the heat liberated per unit mass or volume.**

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(ii) **Ignition Temperature: It is the lowest temperature to which a fuel must be preheated so that it starts burning smoothly. The fuel should have moderate ignition temperature. Low ignition temperature can cause fire hazards, making storage and transportation difficult. Fuel with low ignition temperature can burn spontaneously leading to explosion. High ignition temperature, on the other hand makes it difficult to ignite the fuel.**

(iii) **Moisture content – Moisture content should be low because the presence of moisture lowers the calorific value.**

(iv) **Velocity of combustion – If the velocity of combustion is low, the part of the liberated heat may get radiated instead of raising the temperature. Hence the required high temperature may not be attached. On the other hand if the velocity of combustion is very high then the rate of combustion might become uncontrollable. For a continuous supply of heat fuel must be burn with moderate rate.**

(v) **Cost of fuel – A good fuel should be readily available at a low cost.**

(vi) **Storage and Transportation – A good fuel should be easy to handle, store and transport at low cost.**

Q.2) What is Coal? Explain various types of coals

Ans.)

Coal is fossil fuel. It is naturally occurring black mineral and highly carbonaceous matter. It is composed of a mixture of C, H, O, N and S.

Coal is used as fuel reducing agent in metallurgy in the manufacturing of Coke, electricity in the manufacturing of Synthetic Petrol and Natural Gas.

Types of Coal:

1) **Peat** – **Peat is the brown and fibrous in texture. It is the first stage of transformation of wood into coal. Air dried peat contains 25% moisture. It contains C= 57%, H=6 %, O= 35%, ash = 2%.**

   Calorific value of peat is about 5400 kcal/ kg.

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Uses - i) It is used for soil conditioning.

ii) It is used for packing, gas purification and sometimes for power generation

2) <u>Lignite</u> – It is the second stage of transformation of wood into coal. It is brownish black and more compact than peat. Fresh lignite contains more percentage of moisture i.e. up to 60% which can be Air dried lignite contains 20% moisture. It contains C= 67%, N= 1.5%, H= 5.0%, O= 20%, ash= 8%.

Calorific value of is about 5500 kcal/ kg.

Uses – i) It is used for making producer gas.

ii) It can be used for power generation.

3) <u>Bituminous</u> – It is the third stage of transformation of wood into coal. Bituminous coal is divided into sub bituminous coal and semi bituminous coal on the basis of carbon content

Calorific value is about 8500- 8600 kcal/ kg.

Uses – i) Making of coke, coal gas for tar and chemical.

4) <u>Anthracite coal</u> – It is the final stage transformation of wood into coal. It is hard, black, and brittle and it contain C=92%, H=3.0%, O=2.0%, ash = 3.0%. Air dried contains 1.5 %moisture.

Calorific value is about 8600- 8700 kcal / kg.

Uses – i) It is used for making electrodes.

ii) It is used as metallurgical fuel

Q.3) Describe in brief types of lubricants

Ans.)

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A lubricant is a substance introduced between two moving parts surfaces to reduce friction. Friction is occurring in all types of machines. This is due to the mutual rubbing of one part against another part.

To minimize such effect a thin layer of lubricant is applied between two moving parts of the machine. The processes of reducing friction between the two moving parts by the introduction of lubricants are known as lubrication.

Lubricants are classified as:

A) **Liquid Lubricants**: Liquid lubricant or lubricating oils reduces the friction and wear and tear between metals surface by providing a continuous layer between them. They also acts as a cooling medium prevent corrosion and act as a sealing agent.

Liquid lubricant can be further subdivided into three types:

1. Animal Oil or Vegetable Oil
2. Mineral Oil or Petroleum Oil
3. Blended Oil

(i) **Animal or Vegetable Oil:**

These are extracted from animals and vegetables matter and contain glycerides of higher fatty acids. They are known for their oiliness. A property by which thy sticks to the metal surface even under high temperature and high load.

These possess oiliness due to which it gets adhered or sticks to machines surface and helps to reduce friction

(ii) **Mineral or Petroleum Oil:**

These oils are obtained by fractional distillation of crude petroleum. On being subjected to vacuum distillation, the heavy residual fraction yield lubricating oil. This oil normally has long hydrocarbon chain of 12 to 50 carbon atom.

These oils are most widely used as lubricating because they are cheap. They have low oiliness as compared to vegetable oils. Their oiliness is increased by blending them with vegetable oil and animal oil

(iii) **Blended Oil:**

Blended oils are termed as doped or compounded oils. No single oil can serve as satisfactory lubricants under all conditions. Hence their properties are improved by adding certain additives. This phenomenon is called as blending.

Oiliness carriers - They increases the oiliness of the lubricants. These carriers are added in lubricants used in boundary lubrication. For e.g. vegetable oil, castor oil, mustard oil, fatty acids like oleic acid, stearic acid.

B) Semi-Solid Lubricants:

Greases are the most common e.g. semi – solid lubricants. They are oils made semi – solid by adding a thickening agents. The thickeners dispersed in the lubricating oil produce a stable and colloidal structure of gel. Thickeners are mainly special soaps of Li, Ca, Ba, etc. None soaps thickeners like carbon, siloxane etc.

The petroleum product such as grease, Vaseline, and waxes. Which are neither solid nor liquid at ordinary temperature.

Preparation of Greases: Greases are prepared by the saponification of fat with alkali NaOH, Ca $(OH)_2$ followed by the addition of hot lubricating oil with constant stirring.

Fatty acids + Base → Soap + Hot Oil → Greases

C) Solid Lubricants:

Solid lubricants are used either in the form of powder or mixed with water or oil. The most common solid lubricants are graphite and molybdenum disulphate. Their lubrication properties are due to their layer structure. The layer is held together by weak van der Waal's forces and hence can easily slip over each other.

(i) Graphite:

Graphite is a soft, soapy, and non – inflammable and not gets oxidized in air below 3750C. It can be used as a suspension with oil called oildag. It is use in internal combustion engine. It can be used as a suspension with water called aquadag.

It is used where oil free lubricant is required. Graphite is commonly used in air compression food industry, railway track joint

(ii) Molybdenum disulphide (MoS_2):

It is stable in air up to 4000C MoS_2 has excellent adhesion, high load carrying capacity protection against corrosion. MoS_2 is an excellent lubricant in vacuum; hence it finds use in space vehicles. A solid lubricating surface vehicle is made from 70% MoS_2 and 71% graphite bonded with 237 silicates.

Other common solid lubricants are soapstone, talc, mica, polytetrafluroethylene (PTFE), hexagonal boron nitride (white graphite).

Q.4) Give Physical Properties of Lubricants

Ans.)

1) **Viscosity**: Viscosity is the property of the liquid or fluid by virtue of which it offers resistance to its own flow. Internal resistance of liquid is measured by knowing the viscosity of liquid is measured by using viscometer. It is the most important property of a lubricants oil since it determines the operating characteristics of the lubricants. It is expressed in centipoise or centistoke.

The viscosity of oil decrease with increases in temperature. For light load and speed machines like sealing machines, watches, scientific equipment, and liquid of low viscosity are used. For heavy load & low speed machines like track joints, lathes machines, liquid of high viscosity are used

2) <u>Viscosity Index</u>: A rate of change of viscosity with respect to temp. the viscosity index is defines as the average decrease of viscosity of oil per degree rise in temp between 100° F and 210° F

   If the viscosity of lubricant decreases rapidly with the rise in temp it is said to have low viscosity index. If the viscosity does not changed much with the increasing temp then the lubricant is said to have high viscosity index. A good lubricant in which viscosity does not change with temp.

3) <u>Surface Tension</u>: It is define as the force in acting along the surface of liquid at right angles to any line of unit length (1 meter). It has unit of (Nm-1). It is denoted by T. surface tension is due to intermolecular forces of attraction and therefore liquid with grater intermolecular forces of attraction have large value of surface tension.

   As the temp increase intermolecular forces of attraction diminished and hence surface tension decreases with temp. Surface tension tends to reduce the surface area of liquid to minimum. For these reason that drop of liquid and bubbles of gas in liquid becomes spherical. Surface tension of lubricants does not change much with temperature

4) <u>Flash Point and Fire Point</u>: Flash point is the minimum temp at which oil vapor air mixture ignites for a moment producing a spark when a small flame is brought near it. Fire point is the minimum temp at which oil is burn continuously for at least 5 seconds when a small flame is brought near it.

   Generally the fire point is the 5-40 higher than the flash point. A good lubricating oil should have flash and fire point at least 5-10oC above the working temp of machine. The flash and the fire point are very important properties of oil because this help in knowing the highest temp up to which an oil can be used as a lubricants.

Q.5) Explain in Detail Refining of Petroleum

Ans.)

Crude oil obtains form the oil wells or mines is not fit for use as it contains lots of impurities which must be removed. The process of removing unwanted impurities and dividing petroleum into useful fractions with different boiling ranges is called as refining of petroleum.
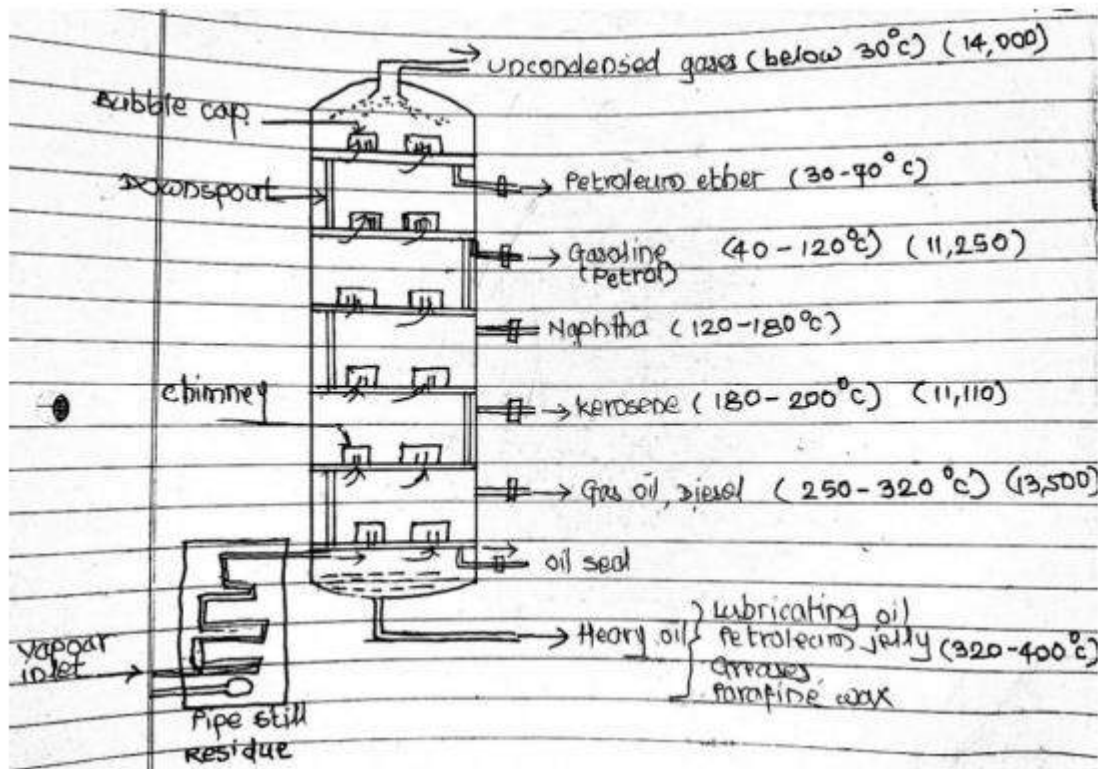
1] Separation of water: The crude oil from the well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets collapse to form large drop which separate out from the oil.

2] Removal of harmful impurities: NaCl and $MgCl_2$ corrode the refining equipment's. These are removed by modern techniques like electrical desalting and dehydration.

3] Fractional distillation: The crude oil is heated to 400° C where by all the volatile constituent except coke is evaporated. The vapor is then passed into fractionating Column which is tall cylindrical tower. The tower is hot towards the lower end and cooler at upper end.

It consists of number of horizontal stainless steel trays at shorts distance. This stays are provided with individual chimneys which are converted in loose caps. As the vapor goes up the fractional condensation occurs at different height of the column.

Higher boiling fractions condensed first while the lower boiling fraction condensed later. The residue form the bottom fractionating lower is vacuum distilled to recover various fractions.

Fractional distillation column showing: Uncondensed gases (below 30°C) (14,000); Petroleum ether (30-70°C); Gasoline (Petrol) (40-120°C) (11,250); Naphtha (120-180°C); Kerosene (180-200°C) (11,110); Gas oil, diesel (250-320°C) (13,500); oil seal; Heavy oil { Lubricating oil, Petroleum jelly (320-400°C), Greases, Paraffine wax }; Labels: Bubble cap, Downspout, Chimney, Vapour inlet, Pipe still, Residue.

Q.6) Explain Proximate Analysis of Coal

Ans.)

Proximate analysis of coal involves the determination of moisture, ash, volatile matter and fixed carbon. The proximate analysis gives the information of practical utility of coal.

1) **Determination of moisture: Weigh about 1 gm. of coal sample in a silica crucible fitted with lid. The crucible is placed in oven about 1 hrs. Which is maintained at 1100C. After 1 hrs. Crucible is taken out and weighed with lid. The process of heating, cooling, weighing is repeated till the constant weight is obtained and then cooled in dedicator.**

   % of moisture = Loss in weight of coal / weight of coal taken X 100

Significance – High moisture content is undesirable because it reduces calorific value and increases the transportation cost.

2) **Determination of volatile matter:** The dried sample of coal left in the crucible stage (1) is then covered with lid and placed in an electric furnace for 7 min. which is maintained at 9250C. The hot crucible is then taken out and cooled By knowing the weight of volatile matter removed from coal its can be calculated as :

% Volatile matter = weight of volatile matter removed / weight of moisture free from coal taken X 100

Significance – Coal containing high % of volatile matter burns with a long flame, high smoke have low calorific value .A high % of volatile matter indicates that a large proportion of fuel is burnt as gas.

3) **Ash:** Ash usually consist of silica , Al ,Fe, oxide and small quantities of lime magnesia .Ash content is determined by heating the residual obtained after removal of moisture and volatile matter at 7500C. For 1 Hrs. in muffle furnace. The residual left is cooled in a desiccators and weight. The process of heating, cooling, weighing is repeated till the constant weight is obtained.

% of Ash = weight of ash formed / weight of dry coal taken X 100

Significance – High % of ash is undesirable as it reduces the calorific value of fuel. Presence of ash increases the transporting, heating, handling and storage cost.

4) **Determination of fixed carbon:** Fixed carbon is the material remaining after determination of moisture, volatile matter, and ash content.

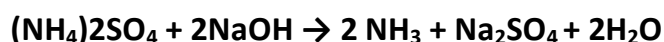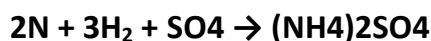**% of fixed carbon = 100 - % (moisture + ash + volatile matter)**

Significance – Higher the % of fixed carbon greater is the calorific value

Q.7) How analysis of N and S in coal can be determined?

Ans.)

Determination of % Nitrogen:

Nitrogen is present in coal sample is heated by Kjeldahl's method. Accurately weighed coal sample is heated with Conc. H2SO4 in the presence of K2SO4 in a long – necked flask. Nitrogen present in the coal gets converted to $(NH_4)_2SO_2$ quantitatively.

$$2N + 3H_2 + SO4 \rightarrow (NH4)2SO4$$

$$\text{Nitrogen from coal} + H_2SO4 + \text{heat} \rightarrow (NH_4)2SO_4$$

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

When a clear solution is obtained (i.e. whole nitrogen is converted into ammonium sulphate) the content is transferred into a round bottom flask and the solution is heated with excess of NaOH to liberated NH_3.The NH_3 liberated is absorbed in a known volume of standard H_2SO_4 solution.

The volume of unused H_2SO_4 is determined by titrating against standard NaOH solution. Difference gives the volume of acid used from the volume of acid used by the NH_3 the % of nitrogen can be calculated as follows:

% of Nitrogen = (14 × volume of acid × Normality of H_2SO_4 / 1000 × weight of coal sample) × 100

Determination of % Sulphur - A known amount of coal is burnt completely in a bomb colorimeter in a current of oxygen. Sulphur present in a coal gas oxidized to sulphates $(SO4)^{2-}$ which when treated with $BaCl_2$ solution to precipitate as BaSO4. The precipitate of $BaSO_4$ is filtered washed, dried, and weighed.

By knowing the weight of $BaSO_4$ formed, the amount of sulphur present in coal can be determined.

$$S + O_2 \rightarrow H_2SO_4{}^{2-} + BaCl_2 \rightarrow BaSO_4$$
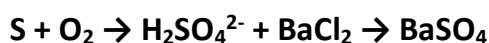
% of Sulphur = (weight of $BaSO_4$ formed × 32/ weight of coal taken × 233) ×100
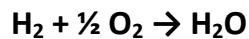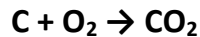
Q.8) Describe the process of determination of % Carbon, Hydrogen and Sulphur In the coal.

Ans.)

Determination of carbon and Hydrogen:

Accurately weighed coal sample is burnt in a combination tube in a presence of O_2, The carbon and hydrogen present in the fuel is converted to CO_2 and H_2O respectively. These are then absorbed by pre- weighted tube containing KOH and anhydrous $CaCl_2$

The increases in weight of these tube gives the amount of CO_2 and H_2O formed. CO_2 is absorbed in KOH tube and H_2O absorbed in $CaCl_2$ tube

$$C + O_2 \rightarrow CO_2$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

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

$$CaCl_2 + 7H_2O \rightarrow CaCl_2 . H_2$$

% Carbon = (increases in weight of KOH x 12 / weight of coal taken x 44) x 100

% Hydrogen = (increases in weight of $CaCl_2$ X 2 /weight of coal taken X 18) 100

Significance – Greater the % of carbon and hydrogen greater the calorific value. % of carbon forms is the basis of classification of coal. Hydrogen of coal is responsible for the production of many useful material such as gaseous hydrogen, methane etc.

BATU-EXAM