

Lecture notes:**UNIT 1 ELECTROCHEMISTRY AND BATTERIES:****1.1 .Concept of Electro Chemistry:**

The study of the processes involved in the inter conversion of electrical energy and chemical energy is known as electro chemistry.

Conductance-electrolyte in solution:

Ohm's law states that "the resistance of a conductor is directly proportional to its length and inversely proportional to its area of cross section.

$$R = \rho \cdot l / A$$

Where R = resistance (ohm)

ρ = specific resistance or resistivity

l = length (cm)

A = area of cross section (cm²)

Specific conductance, Equivalent conductance and molar conductance:

Specific conductivity (k) :

The reciprocal of specific resistance or resistivity of an electrolytic solution is known as specific conductivity.

Unit : ohm⁻¹cm⁻¹ or S cm⁻¹

Equivalent Conductivity (Λ_{eq}) :

The conductance of all the ions present in 1 equivalent of the electrolyte present in the given solution at a given dilution is known as equivalent conductivity.

Unit : ohm⁻¹ cm² eq⁻¹

Molar Conductivity (Λ_m):

The conductance of all the ions present in one mole of the electrolyte present in the given solution at a given dilution is known as molar conductivity.

Unit : ohm⁻¹ cm² mol⁻¹

Variation of specific conductivity with dilution:

Specific conductivity depends on the following factors:

- (1) the number of ions
- (2) the amount of water present.

As the dilution i.e., the amount of water increases, the conducting power of 1 cm³ of the electrolytic solution decreases.

Variation of Equivalent Conductivity with dilution:

The conducting power of an electrolyte is due to the ions present and this increases with increase in the dilution. The equivalent or molar conductivity increases as the number of ions present in a solution having one equivalent or one mole of electrolyte increases with dilution.

1.2 KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus,

$$\Lambda^\infty = \lambda_a + \lambda_c$$

The λ_c and λ_a are called the ionic conductance of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = k u_c \quad \text{and} \quad \lambda_a = k u_a$$

where u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

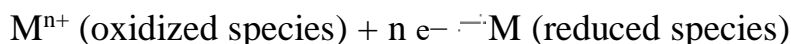
$$\text{Degree of dissociation, } \alpha = \Lambda / (\Lambda^\infty)$$

$$= (\text{Equivalent conductance at a given concentration}) / (\text{Equivalent conductance at infinite dilution})$$

1.3 Galvanic cells:

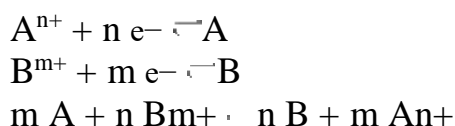
A Galvanic cell consists of two half-cells. In its simplest form, each half-cell consists of a metal and a solution of a salt of the metal. The salt solution contains a cation of the metal and an anion to balance the charge on the cation. In essence the half-cell contains the metal in two oxidation states and

the chemical reaction in the half-cell is an oxidation-reduction (redox) reaction, written symbolically in reduction direction as



In a galvanic cell one metal is able to reduce the cation of the other and, conversely, the other cation can oxidize the first metal. The two half-cells must be physically separated so that the solutions do not mix together. A salt bridge or porous plate is used to separate the two solutions.

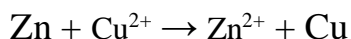
The number of electron transferred in both directions must be the same, so the two half-cells are combined to give the whole-cell electrochemical reaction. For two metals A and B:



This is not the whole story as anions must also be transferred from one half-cell to the other. When a metal in one half-cell is oxidized, anions must be transferred into that half-cell to balance the electrical charge of the cation produced. The anions are released from the other half-cell where a cation is reduced to the metallic state. Thus, the salt bridge or porous membrane serves both to keep the solutions apart and to allow the flow of anions in the direction opposite to the flow of electrons in the wire connecting the electrodes.

The voltage of the Galvanic cell is the sum of the voltages of the two half-cells. It is measured by connecting a voltmeter to the two electrodes. The voltmeter has very high resistance, so the current flow is effectively negligible. When a device such as an electric motor is attached to the electrodes, a current flows and redox reactions occur in both half-cells. This will continue until the concentration of the cations that are being reduced goes to zero.

For the Daniel cell, depicted in the figure, the two metals are zinc and copper and the two salts are sulfates of the respective metal. Zinc is the more reducing metal so when a device is connected to the electrodes, the electrochemical reaction is



The zinc electrode is dissolved and copper is deposited on the copper electrode. By definition, the cathode is the electrode where reduction (gain of electrons) takes place, so the copper electrode is the cathode. The cathode attracts cations, so has a negative charge. In this case copper is the cathode and zinc the anode.

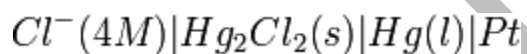
Galvanic cells are typically used as a source of electrical power. By their nature they produce direct current. For example, a lead-acid battery contains a number of galvanic cells. The two electrodes are effectively lead and lead oxide.

1.4 Reference electrode:

Saturated calomel electrode

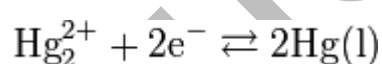
The Saturated calomel electrode (SCE) is a reference electrode based on the reaction between elemental mercury and mercury (I) chloride. The aqueous phase in contact with the mercury and the mercury (I) chloride (Hg_2Cl_2 , "calomel") is a saturated solution of potassium chloride in water. The electrode is normally linked via a porous frit to the solution in which the other electrode is immersed. This porous frit is a salt bridge.

In cell notation the electrode is written as:



Theory of operation

The electrode is based on the redox reaction

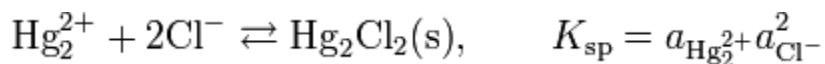


The Nernst equation for this reaction is

$$E = E^0_{\text{Hg}_2^{2+}/\text{Hg}} - \frac{RT}{2F} \ln \frac{1}{a_{\text{Hg}_2^{2+}}}$$

where E^0 is the standard electrode potential for the reaction and a_{Hg} is the activity for the mercury cation (the activity for a liquid is 1). This activity

can be found from the solubility product of the reaction



By replacing the activity in the Nernst equation with the value in the solubility equation, we get

$$E = E_{\text{Hg}_2^{2+}/\text{Hg}}^0 + \frac{RT}{2F} \ln K_{\text{sp}} - \frac{RT}{2F} \ln a_{\text{Cl}^-}^2$$

The only variable in this equation is the activity (or concentration) of the chloride anion. But since the inner solution is saturated with potassium chloride, this activity is fixed by the solubility of potassium chloride. When saturated the redox potential of the calomel electrode is +0.2444 V vs. SHE at 25 °C, but slightly higher when the chloride solution is less than saturated. For example, a 3.5M KCl electrolyte solution increases the reference potential to +0.250 V vs. SHE at 25 °C, and a 0.1 M solution to +0.3356 V at the same temperature.

Application

The SCE is used in pH measurement, cyclic voltammetry and general aqueous electrochemistry.

This electrode and the silver/silver chloride reference electrode work in the same way. In both electrodes, the activity of the metal ion is fixed by the solubility of the metal salt.

The calomel electrode contains mercury, which poses much greater health hazards than the silver metal used in the Ag/AgCl electrode.

Quinhydrone electrode:

The quinhydrone electrode is a type of redox electrode which can be used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH meter.

The electrode consists of an inert metal electrode (usually a platinum wire) in contact with quinhydrone crystals and a water-based solution. Quinhydrone is slightly soluble in water, dissolving to form a mixture of two substances, quinone and hydroquinone, with the two substances present at

equal concentration. Each one of the two substances can easily be oxidised or reduced to the other.

The potential at the inert electrode depends on the ratio of the activity of two substances (quinone-hydroquinone), and also the hydrogen ion concentration. The electrode half-reaction is:



Because the electrode half-reaction involves hydrogen ions, the electrode potential depends on the activity of hydrogen ions. From the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln a_{\text{H}^+}$$

For practical pH measurement, a second pH independent reference electrode (such as a silver chloride electrode) is also used. This reference electrode does not respond to the pH. The difference between the potential of the two electrodes depends (primarily) on the activity of H^+ in the solution. It is this potential difference which is measured and converted to a pH value.

The quinhydrone electrode is not reliable above pH 8. It is also unreliable in the presence of strong oxidising or reducing agents, which would disturb the equilibrium between hydroquinone and quinone. It is also subject to errors in solutions containing proteins or high concentrations of salts

Other electrodes commonly used for measuring pH are the antimony-antimony oxide electrode, the glass electrode and the hydrogen electrode.

1.5 Ion selective electrode:

An ion-selective electrode (ISE), also known as a specific ion electrode (SIE), is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode. Ion-selective electrodes are used in biochemical and biophysical research, where measurements of ionic concentration in an aqueous solution are required, usually on a real time basis.

Types of ion-selective membrane:

There are four main types of ion-selective membrane used in ion-selective electrodes: glass, solid state, liquid compound electrode.

Glass membranes:

Glass membranes are made from an ion-exchange type of glass (silicate or chalcogenide). This type of ISE has good selectivity, but only for several single-charged cations; mainly H^+ , Na^+ and Ag^+ . Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+} , and Cd^{2+} . The glass membrane has excellent chemical durability and can work in very aggressive media. A very common example of this type of electrode is the pH glass electrode.

Nernst equation:

In electrochemistry, the Nernst equation is an equation that can be used to determine the equilibrium reduction potential of a half-cell in an electrochemical cell. It can also be used to determine the total voltage (electromotive force) for a full electrochemical cell. It is named after the German physical chemist who first formulated it, Walther Nernst.

Expression:

The two (ultimately equivalent) equations for these two cases (half-cell, full cell) are as follows:

$$E_{\text{red}} = E_{\text{red}}^{\ominus} - \frac{RT}{zF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} \quad (\text{half-cell reduction potential})$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln Q \quad (\text{total cell potential})$$

where

- E_{red} is the half-cell reduction potential at the temperature of interest
- E_{Ored} is the standard half-cell reduction potential
- E_{cell} is the cell potential (electromotive force)
- E_{Ocell} is the standard cell potential at the temperature of interest
- R is the universal gas constant:
- T is the absolute temperature

- a is the chemical activity for the relevant species, where a_{Red} is the reductant and a_{Ox} is the oxidant. $a_X = \gamma_X c_X$, where γ_X is the activity coefficient of species X. (Since activity coefficients tend to unity at low concentrations, activities in the Nernst equation are frequently replaced by simple concentrations.)
- F is the Faraday constant, the number of coulombs per mole of electrons:
- z is the number of moles of electrons transferred in the cell reaction or half-reaction
- Q is the reaction quotient.

At room temperature (25 °C), RT/F may be treated like a constant and replaced by 25.693 mV for cells.

The Nernst equation is frequently expressed in terms of base 10 logarithms (i.e., common logarithms) rather than natural logarithms, in which case it is written, for a cell at 25 °C:

$$E = E^0 - \frac{0.05916 \text{ V}}{z} \log_{10} \frac{a_{\text{Red}}}{a_{\text{Ox}}}.$$

The Nernst equation is used in physiology for finding the electric potential of a cell membrane with respect to one type of ion.

1.7 Concentration cell

A Concentration cell is an electrochemical cell that has two equivalent half-cells of the same material differing only in concentrations. One can calculate the potential developed by such a cell using the Nernst Equation. A concentration cell produces a voltage as it attempts to reach equilibrium, which will occur when the concentration in both cells are equal.

Concentration cell methods of chemical analysis compare a solution of known concentration with an unknown, determining the concentration of the unknown via the Nernst Equation or comparison tables against a group of standards. Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cells:

Metal ion concentration cells

In the presence of water, a high concentration of metal ions will exist under faying surfaces and a low concentration of metal ions will exist adjacent to the crevice created by the faying surfaces. An electrical potential will exist between the two points. The area of the metal in contact with the high concentration of metal ions will be cathodic and will be protected, and the area of metal in contact with the low metal ion concentration will be anodic and corroded.

Oxygen concentration cells

Water in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Corrosion will occur at the area of low-oxygen concentration which are anodic.

Active-passive cells

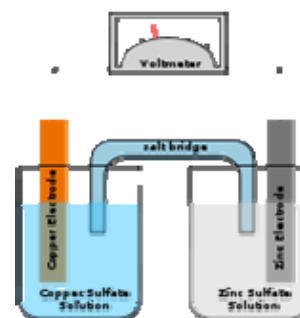
For metals that depend on a tightly adhering passive film (usually an oxide) for corrosion protection, salt that deposits on the metal surface in the presence of water, in areas where the passive film is broken, the active metal

beneath the film will be exposed to corrosive attack. An electrical potential will develop between the large area of the cathode (passive film) and the small area of the anode (active metal). Rapid pitting of the active metal will result.

Galvanic cells

Non-rechargeable:
primary cells

Alkaline battery · Aluminium battery ·
Bunsen cell · Chromic acid cell · Clark
cell · Daniell cell · Dry cell · Grove cell ·
Leclanché cell · Lithium battery ·
Mercury battery · Nickel oxyhydroxide
battery · Silver-oxide battery · Weston
cell · Zamboni pile · Zinc-air battery ·
Zinc-carbon battery



Rechargeable:
secondary Lead-acid battery · Lithium air battery ·
Lithium-ion battery · Lithium-ion

cells | polymer battery · Lithium iron phosphate battery · Lithium sulfur battery · Lithium-titanate battery · Nickel-cadmium battery · Nickel hydrogen battery · Nickel-iron battery · Nickel-metal hydride battery · Low self-discharge NiMH battery · Nickel-zinc battery · Rechargeable alkaline battery · Sodium-sulfur battery · Vanadium redox battery · Zinc-bromine battery

Kinds of cells | Battery · Concentration cell · Flow battery · Fuel cell · Trough battery · Voltaic pile

Parts of cells | Anode · Catalyst · Cathode · Electrolyte · Half cell · Ions · Salt bridge · Semipermeable membrane

1.8 Galvanic series:

The galvanic series (or electro potential series) determines the nobility of metals and semi-metals. When two metals are submerged in an electrolyte, while electrically connected, the less noble (base) will experience galvanic corrosion. The rate of corrosion is determined by the electrolyte and the difference in nobility. The difference can be measured as a difference in voltage potential. Galvanic reaction is the principle upon which batteries are based.

Galvanic series (most noble at top)

The following is the galvanic series for stagnant (that is, low oxygen content) seawater. The order may change in different environments.

- Graphite
- Palladium
- Platinum
- Gold
- Silver
- Titanium

- Stainless steel 316 (passive)
- Stainless Steel 304 (passive)
- Silicon bronze
- Stainless Steel 316 (active)
- Monel 400
- Phosphor bronze
- Admiralty brass
- Cupronickel
- Molybdenum
- Red brass
- Brass plating
- Yellow brass
- Naval brass 464
- Uranium 8% Mo
- Niobium 1% Zr
- Tungsten
- Stainless Steel 304 (active)
- Tantalum
- Chromium plating
- Nickel (passive)
- Copper
- Nickel (active)
- Cast iron
- Steel
- Lead
- Tin
- Indium
- Aluminum
- Uranium (pure)
- Cadmium
- Beryllium
- Zinc plating

1.9. Batteries:

Batteries are classified into two broad categories, each type with advantages and disadvantages.

Primary batteries irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is

exhausted, energy cannot be readily restored to the battery by electrical means.

Secondary batteries can be recharged; that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition.

Primary batteries

Primary batteries can produce current immediately on assembly. Disposable batteries are intended to be used once and discarded. These are most commonly used in portable devices that have low current drain, are only used intermittently, or are used well away from an alternative power source, such as in alarm and communication circuits where other electric power is only intermittently available. Disposable primary cells cannot be reliably recharged, since the chemical reactions are not easily reversible and active materials may not return to their original forms. Battery manufacturers recommend against attempting recharging primary cells.

Common types of disposable batteries include zinc-carbon batteries and alkaline batteries. Generally, these have higher energy densities than rechargeable batteries, but disposable batteries do not fare well under high-drain applications with loads under 75 ohms ($75\ \Omega$).

Secondary batteries:

Secondary batteries must be charged before use; they are usually assembled with active materials in the discharged state. Rechargeable batteries or secondary cells can be recharged by applying electrical current, which reverses the chemical reactions that occur during its use. Devices to supply the appropriate current are called chargers or rechargers.

The oldest form of rechargeable battery is the lead-acid battery. This battery is notable in that it contains a liquid in an unsealed container, requiring that the battery be kept upright and the area be well ventilated to ensure safe dispersal of the hydrogen gas produced by these batteries during overcharging. The lead-acid battery is also very heavy for the amount of electrical energy it can supply. Despite this, its low manufacturing cost and its high surge current levels make its use common where a large capacity (over approximately 10Ah) is required or where the weight and ease of handling are not concerns.

A common form of the lead-acid battery is the modern car battery, which can generally deliver a peak current of 450 amperes. An improved type of liquid electrolyte battery is the sealed valve regulated lead acid (VRLA) battery, popular in the automotive industry as a replacement for the lead-acid wet cell. The VRLA battery uses an immobilized sulfuric acid electrolyte, reducing the chance of leakage and extending shelf life. VRLA batteries have the electrolyte immobilized, usually by one of two means:

- Gel batteries (or "gel cell") contain a semi-solid electrolyte to prevent spillage.
- Absorbed Glass Mat (AGM) batteries absorb the electrolyte in a special fiberglass matting.

Other portable rechargeable batteries include several "dry cell" types, which are sealed units and are therefore useful in appliances such as mobile phones and laptop computers. Cells of this type (in order of increasing power density and cost) include nickel-cadmium (NiCd), nickel-zinc (NiZn), nickel metal hydride (NiMH) and lithium-ion (Li-ion) cells.[40] By far, Li-ion has the highest share of the dry cell rechargeable market. Meanwhile, NiMH has replaced NiCd in most applications due to its higher capacity, but NiCd remains in use in power tools, two-way radios, and medical equipment. NiZn is a new technology that is not yet well established commercially.

Recent developments include batteries with embedded functionality such as USBCELL, with a built-in charger and USB connector within the AA format, enabling the battery to be charged by plugging into a USB port without a charger, and low self-discharge (LSD) mix chemistries such as Hybrio, ReCyko, and Eneloop, where cells are precharged prior to shipping.

1.10 Lead-acid battery

Lead-acid batteries, invented in 1859 by French physicist Gaston Planté, are the oldest type of rechargeable battery. Despite having a very low energy-to-weight ratio and a low energy-to-volume ratio, their ability to supply high surge currents means that the cells maintain a relatively large power-to-weight ratio. These features, along with their low cost, make them attractive for use in motor vehicles to provide the high current required by automobile starter motors. In the charged state, each cell contains electrodes of elemental lead (Pb) and lead(IV) oxide (PbO_2) in an electrolyte of approximately 33.5% v/v (4.2 Molar) sulfuric acid (H_2SO_4).

In the discharged state both electrodes turn into lead(II) sulfate (PbSO_4) and the electrolyte loses its dissolved sulfuric acid and becomes primarily water. Due to the freezing-point depression of water, as the battery discharges and the concentration of sulfuric acid decreases, the electrolyte is more likely to freeze during winter weather.

The chemical reactions:

Anode (oxidation):



Cathode (reduction):



Because of the open cells with liquid electrolyte in most lead-acid batteries, overcharging with high charging voltages generates oxygen and hydrogen gas by electrolysis of water, forming an explosive mix. The acid electrolyte is also corrosive.

Practical cells are usually not made with pure lead but have small amounts of antimony, tin, calcium or selenium alloyed in the plate material to add strength and simplify manufacture.

Nickel-cadmium battery

The nickel-cadmium battery (commonly abbreviated NiCd or NiCad) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes.

The abbreviation NiCad is a registered trademark of SAFT Corporation, although this brand name is commonly used to describe all nickel-cadmium batteries. The abbreviation NiCd is derived from the chemical symbols of nickel (Ni) and cadmium (Cd).

There are two types of NiCd batteries: sealed and vented. This article mainly deals with sealed cells.

1.11 Applications

Sealed NiCd cells may be used individually, or assembled into battery packs containing two or more cells. Small NiCd dry cells are used for portable electronics and toys, often using cells manufactured in the same sizes as primary cells. When NiCds are substituted for primary cells, the lower terminal voltage and smaller ampere-hour capacity may reduce performance as compared to primary cells. Miniature button cells are sometimes used in photographic equipment, hand-held lamps (flashlight or torch), computer-memory standby, toys, and novelties.

Specialty NiCd batteries are used in cordless and wireless telephones, emergency lighting, and other applications. With a relatively low internal resistance, a NiCd battery can supply high surge currents. This makes them a favourable choice for remote-controlled electric model airplanes, boats, and cars, as well as cordless power tools and camera flash units. Larger flooded cells are used for aircraft starting batteries, electric vehicles, and standby power.

Nickel-cadmium cells have a nominal cell potential of 1.2 V. This is lower than the 1.5 V of alkaline and zinc-carbon primary cells, and consequently they are not appropriate as a replacement in all applications. However, the 1.5V of a primary alkaline cell refers to its initial, rather than average, voltage. Unlike alkaline and zinc-carbon primary cells, a NiCd cell's terminal voltage only changes a little as it discharges. Because many electronic devices are designed to work with primary cells that may discharge to as low as 0.90 to 1.0 V per cell, the relatively steady 1.2 V of a NiCd is enough to allow operation. Some would consider the near-constant voltage a drawback as it makes it difficult to detect when the battery charge is low.

NiCd batteries used to replace 9 V batteries usually only have six cells, for a terminal voltage of 7.2 volts. While most pocket radios will operate satisfactorily at this voltage, some manufacturers such as Varta made 8.4 volt batteries with seven cells for more critical applications. 12 V NiCd batteries are made up of 10 cells connected in series.

1.12 Advantages and disadvantages

Both advantages and disadvantages depend on the materials and design that make up the battery. This summary reflects older designs that use carbon

anode, metal oxide cathodes, and lithium salt in an organic solvent for the electrolyte.

A lithium-ion battery from a laptop computer

- Wide variety of shapes and sizes efficiently fitting the devices they power.
- Much lighter than other energy-equivalent secondary batteries.
- High open circuit voltage in comparison to aqueous batteries (such as lead acid, nickel-metal hydride and nickel-cadmium). This is beneficial because it increases the amount of power that can be transferred at a lower rate of current.
- No memory effect.
- Self-discharge rate of approximately 5-10% per month, compared to over 30% per month in common nickel metal hydride batteries, approximately 1.25% per month for Low Self-Discharge NiMH batteries and 10% per month in nickel-cadmium batteries. According to one manufacturer, lithium-ion cells (and, accordingly, "dumb" lithium-ion batteries) do not have any self-discharge in the usual meaning of this word. What looks like a self-discharge in these batteries is a permanent loss of capacity (see Disadvantages). On the other hand, "smart" lithium-ion batteries do self-discharge, due to the drain of the built-in voltage monitoring circuit.

Disadvantages

Shelf life

- Charging forms deposits inside the electrolyte that inhibit ion transport. Over time, the cell's capacity diminishes. The increase in internal resistance reduces the cell's ability to deliver current. This problem is more pronounced in high-current applications. The decrease means that older batteries do not charge as much as new ones (charging time required decreases proportionally).
- High charge levels and elevated temperatures (whether from charging or ambient air) hasten capacity loss. Charging heat is caused by the carbon anode (typically replaced with lithium titanate which drastically reduces damage from charging, including expansion and other factors).
- A unit that is full most of the time at 25 °C (77 °F) irreversibly loses approximately 20% capacity per year. Poor ventilation may increase

temperatures, further shortening battery life. Loss rates vary by temperature: 6% loss at 0 °C (32 °F), 20% at 25 °C (77 °F), and 35% at 40 °C (104 °F). When stored at 40%–60% charge level, the capacity loss is reduced to 2%, 4%, and 15%, respectively.

Internal resistance

- The internal resistance of lithium-ion batteries is high compared to other rechargeable chemistries such as nickel-metal hydride and nickel-cadmium. Internal resistance increases with both cycling and age. Rising internal resistance causes the voltage at the terminals to drop under load, which reduces the maximum current draw. Eventually increasing resistance means that the battery can no longer operate for an adequate period.
- To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more efficient than connecting a single large battery.

Safety requirements

Li-ion batteries are not as durable as nickel metal hydride or nickel-cadmium designs, and can be dangerous if mistreated. They may suffer thermal runaway and cell rupture if overheated or overcharged. In extreme cases, these effects may be described as "explosive." Furthermore, over discharge can irreversibly damage a battery. To reduce these risks, batteries generally contain a small circuit that shuts down when the battery moves outside the safe range of 3–4.2 V. When stored for long periods, however, the small current drawn by the protection circuitry itself may drain the battery; normal chargers are then ineffective. More sophisticated battery analyzers can recharge deeply discharged cells by slow-charging them to first reactivate the safety circuit and allow the battery to accept charge. Over discharge can short-circuit the cell, in which case recharging can be unsafe.

- shut-down separator (for overtemperature)
- tear-away tab (for internal pressure)
- vent (pressure relief)
- thermal interrupt (overcurrent/overcharging)

These devices occupy useful space inside the cells, reduce their reliability; ,and irreversibly disable the cell when activated. They are required because

the anode produces heat during use, while the cathode may produce oxygen. These devices and improved electrode designs reduce/eliminate the risk of fire or explosion.

These safety features increase costs compared to nickel metal hydride batteries, which require only a hydrogen/oxygen recombination device (preventing damage due to mild overcharging) and a back-up pressure valve.

Many types of lithium-ion cell cannot be charged safely below 0°C.

1.12 Fuel cell:

The actual fuel cell stack is the layered cube shape in the center of the image. A fuel cell is an electrochemical cell that converts a source fuel into an electrical current. It generates electricity inside a cell through reactions between a fuel and an oxidant, triggered in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate continuously as long as the necessary reactant and oxidant flows are maintained.

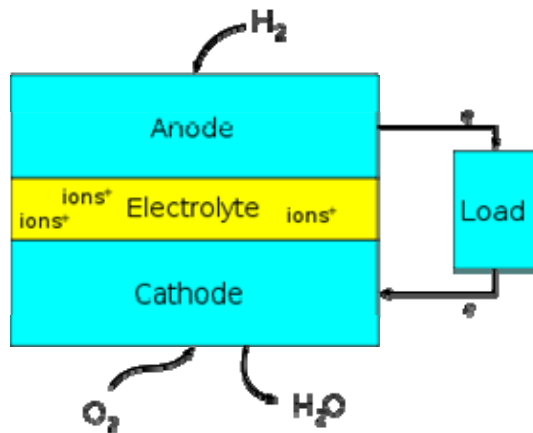
Fuel cells are different from conventional electrochemical cell batteries in that they consume reactant from an external source, which must be replenished thermodynamically open system. By contrast, batteries store electrical energy chemically and hence represent a thermodynamically closed system.

Many combinations of fuels and oxidants are possible. A hydrogen fuel cell uses hydrogen as its fuel and oxygen (usually from air) as its oxidant. Other fuels include hydrocarbons and alcohols. Other oxidants include chlorine and chlorine dioxide.

Fuel cells come in many varieties; however, they all work in the same general manner. They are made up of three segments which are sandwiched together: the anode, the electrolyte, and the cathode. Two chemical reactions occur at the interfaces of the three different segments. The net result of the two reactions is that fuel is consumed, water or carbon dioxide is created, and an electrical current is created, which can be used to power electrical devices, normally referred to as the load.

At the anode a catalyst oxidizes the fuel, usually hydrogen, turning the fuel into a positively charged ion and a negatively charged electron. The electrolyte is a substance specifically designed so ions can pass through it,

but the electrons cannot. The freed electrons travel through a wire creating the electrical current. The ions travel through the electrolyte to the cathode. Once reaching the cathode, the ions are reunited with the electrons and the two react with a third chemical, usually oxygen, to create water or carbon dioxide.



A block diagram of a fuel cell

The most important design features in a fuel cell are:

- The electrolyte substance. The electrolyte substance usually defines the type of fuel cell.
- The fuel that is used. The most common fuel is hydrogen.
- The anode catalyst, which breaks down the fuel into electrons and ions. The anode catalyst is usually made up of very fine platinum powder.
- The cathode catalyst, which turns the ions into the waste chemicals like water or carbon dioxide. The cathode catalyst is often made up of nickel.

A typical fuel cell produces a voltage from 0.6 V to 0.7 V at full rated load. Voltage decreases as current increases, due to several factors:

- Activation loss
- Ohmic loss (voltage drop due to resistance of the cell components and interconnects)
- Mass transport loss (depletion of reactants at catalyst sites under high loads, causing rapid loss of voltage).

To deliver the desired amount of energy, the fuel cells can be combined in series and parallel circuits, where series yields higher voltage, and parallel allows a higher current to be supplied. Such a design is called a fuel cell stack. Further, the cell surface area can be increased, to allow stronger current from each cell.

Proton exchange fuel cells:

In the archetypal hydrogen–oxygen proton exchange membrane fuel cell (PEMFC) design, a proton-conducting polymer membrane, (the electrolyte), separates the anode and cathode sides. This was called a "solid polymer electrolyte fuel cell" (SPEFC).

On the anode side, hydrogen diffuses to the anode catalyst where it later dissociates into protons and electrons. These protons often react with oxidants causing them to become what is commonly referred to as multi-facilitated proton membranes. The protons are conducted through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) because the membrane is electrically insulating. On the cathode catalyst, oxygen molecules react with the electrons (which have traveled through the external circuit) and protons to form water - in this example, the only waste product, either liquid or vapor.

The materials used in fuel cells differ by type. In a typical membrane electrode assembly (MEA), the electrode–bipolar plates are usually made of metal, nickel or carbon nanotubes, and are coated with a catalyst (like platinum, nano iron powders or palladium) for higher efficiency. Carbon paper separates them from the electrolyte. The electrolyte could be ceramic or a membrane.

UNIT 2 CORROSION AND ITS CONTROL

2.1 Corrosion:

Corrosion is the disintegration of material into its constituent atoms due to chemical reactions with its surroundings. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as rusting. This type of damage typically produces oxide(s) and/or salt(s) of the original metal. Corrosion can also refer to other materials than metals, such as ceramics or polymers, although in this context, the term degradation is more common.

In other words, corrosion is the wearing away of metals due to a chemical reaction.

Many structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances (see below). Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate-conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

Rust, is most familiar example of corrosion.

2.2 Types of corrosion:

Galvanic corrosion

Galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. In order for galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. This effects a galvanic couple where the more active metal corrodes at an accelerated rate and the more noble metal corrodes at a retarded rate. When immersed, neither metal would normally

corrode as quickly without the electrically conductive connection (usually via a wire or direct contact). Galvanic corrosion is often utilized in sacrificial anodes. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures, such as pipelines or docked naval ships. Galvanic corrosion is of major interest to the marine industry and also anywhere water can contact pipes or metal structures.

Factors such as relative size of anode (smaller is generally less desirable), types of metal, and operating conditions (temperature, humidity, salinity, etc.) will affect galvanic corrosion. The surface area ratio of the anode and cathode will directly affect the corrosion rates of the materials.

Pitting corrosion:

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which compete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause corrosion pits of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an auto-catalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated, but it can be prevented by control of the alloy's environment.

High temperature corrosion

High temperature corrosion is chemical deterioration of a material (typically a metal) under very high temperature conditions. This non-galvanic form of corrosion can occur when a metal is subject to a high temperature atmosphere containing oxygen, sulfur or other compounds capable of oxidising (or assisting the oxidation of) the material concerned. For

example, materials used in aerospace, power generation and even in car engines have to resist sustained periods at high temperature in which they may be exposed to an atmosphere containing potentially highly corrosive products of combustion.

The products of high temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperature in hostile conditions. Such high temperature corrosion products in the form of compacted oxide layer glazes have also been shown to prevent or reduce wear during high temperature sliding contact of metallic (or metallic and ceramic) surfaces.

2.3 Applied coatings

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the (often cheaper, tougher, and/or easier-to-process) structural material. Aside from cosmetic and manufacturing issues, there are tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with a more active metal such as zinc or cadmium.

Reactive coatings

If the environment is controlled, corrosion inhibitors can often be added to it. These form an electrically insulating and/or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods obviously make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially-designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

2.4 Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores several nanometers wide appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area.

Controlled permeability formwork

Controlled permeability formwork (CPF) is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete placement, . CPF has been used in environments to combat the effects of carbonation, chlorides, frost and abrasion.

Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell.

It is a method used to protect metal structures from corrosion. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

Examples of ALWC (accelerated low water corrosion) are in abundance in the north sea gas field off the Scottish coast. The steel structures used for oil and gas exploration and transport freely corrode when there is no CP (Cathodic protection) systems in place.

Sacrificial anode protection:

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

2.5 Impressed current cathodic protection

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires.

Corrosion in nonmetals

Most ceramic materials are almost entirely immune to corrosion. The strong ionic and/or covalent bonds that hold them together leave very little free chemical energy in the structure; they can be thought of as already corroded. When corrosion does occur, it is almost always a simple dissolution of the material or chemical reaction, rather than an electrochemical process. A common example of corrosion protection in ceramics is the lime added to soda-lime glass to reduce its solubility in water; though it is not nearly as soluble as pure sodium silicate, normal glass does form sub-microscopic flaws when exposed to moisture. Due to its brittleness, such flaws cause a dramatic reduction in the strength of a glass object during its first few hours at room temperature.

Polymer degradation is due to a wide array of complex and often poorly-understood physiochemical processes. These are strikingly different from the other processes discussed here, and so the term "corrosion" is only applied to them in a loose sense of the word. Because of their large molecular weight, very little entropy can be gained by mixing a given mass of polymer with another substance, making them generally quite difficult to dissolve. While dissolution is a problem in some polymer applications, it is relatively simple to design against. A more common and related problem is swelling, where small molecules infiltrate the structure, reducing strength and stiffness and causing a volume change. Conversely, many polymers (notably flexible vinyl) are intentionally swelled with plasticizers, which can be leached out of the structure, causing brittleness or other undesirable changes. The most common form of degradation, however, is a decrease in polymer chain length. Mechanisms which break polymer chains are familiar to biologists

because of their effect on DNA: ionizing radiation (most commonly ultraviolet light), free radicals, and oxidizers such as oxygen, ozone, and

chlorine. Additives can slow these processes very effectively, and can be as simple as a UV-absorbing pigment (i.e., titanium dioxide or carbon black). Plastic shopping bags often do not include these additives so that they break down more easily as litter.

2.6 Hot-dip galvanizing

Hot-dip galvanizing is a form of galvanization. It is the process of coating iron, steel, or aluminum with a thin zinc layer, by passing the metal through a molten bath of zinc at a temperature of around 860 °F (460 °C). When exposed to the atmosphere, the pure zinc (Zn) reacts with oxygen (O₂) to form zinc oxide (ZnO), which further reacts with carbon dioxide (CO₂) to form zinc carbonate (ZnCO₃), a usually dull grey, fairly strong material that stops further corrosion in many circumstances, protecting the steel below from the elements. Galvanized steel is widely used in applications where rust resistance is needed, and can be identified by the crystallization patterning on the surface (often called a “spangle”).

The process of hot-dip galvanizing results in a metallurgical bond between zinc and steel with a series of distinct iron-zinc alloys. The resulting coated steel can be used in much the same way as uncoated. Galvanized steel can be welded; however, one must exercise caution around the resulting zinc fumes. Galvanized steel is suitable for high-temperature applications of up to 392 °F (200 °C). The use of galvanized steel at temperatures above this will result in peeling of the zinc at the intermetallic layer. Galvanized sheet steel is often used in automotive manufacturing to enhance the corrosion performance of exterior body panels.

Lead is often added to the molten zinc bath to improve the fluidity of the bath (thus limiting excess zinc on the dipped product by improved drainage properties), helps prevent floating dross, makes dross recycling easier and protects the kettle from uneven heat distribution from the burners. Lead is either added to primary Z1 Grade Zinc or already contained in used secondary zinc. A third, declining method is to use low Z5 Grade Zinc.

Steel strip can be hot-dip galvanized in a continuous line. Hot-dip galvanized steel strip (also sometimes loosely referred to as galvanized iron) is extensively used for applications requiring the strength of steel and resistance to corrosion. Applications include: roofing and walling, safety

barriers, handrails, consumer appliances and automotive body parts. One common use is in metal pails. They are also used in most heating and cooling duct systems in buildings.

Individual metal articles, such as steel girders or wrought iron gates, can be hot-dip galvanized by a process called batch galvanizing. Other modern techniques have largely replaced hot-dip for these sorts of roles. This includes electrogalvanizing, which deposits the layer of zinc from an aqueous electrolyte by electroplating, forming a thinner and much stronger bond.

2.7 Tinning

Tinning is the process of thinly coating sheets of wrought iron or steel with tin, and the resulting product is known as tinplate. It is most often used to prevent rust.

While once more widely used, the primary use of tinplate now is the manufacture of tin cans. Formerly, tinplate was used for cheap pots, pans and other holloware. This kind of holloware was also known as tinware and the people who made it were tinplate workers.

The untinned sheets employed in the manufacture are known as black plates. They are now made of steel, either Bessemer steel or open-hearth. Formerly iron was used, and was of two grades, coke iron and charcoal iron; the latter, being the better, received a heavier coating of tin, and this circumstance is the origin of the terms coke plates and charcoal plates by which the quality of tinplate is still designated, although iron is no longer used. Tinplate was consumed in enormous quantities for the manufacture of the tin cans in which preserved meat, fish, fruit, biscuits, cigarettes and numerous other products are packed, and also for the household utensils of various kinds made by the tinsmith.

Tinning processes:

There are two processes for the tinning of the black plates: hot-dipping and electroplating.

Hot-dipping:

Tinplate made via hot-dipped tin plating is made by cold rolling steel or iron, pickling or remove any scale, annealing to remove any strain hardening, and then coating it with a thin layer of tin. Originally this was done by producing individual or small packs of plates, which became known as the pack mill process. In the late 1920s strip mills began to replace pack mills, because they could produce the raw plates in larger quantities and more economically.

Electroplating:

In electroplating, the item to be coated is placed into a container containing a solution of one or more tin salts. The item is connected to an electrical circuit, forming the cathode (negative) of the circuit while an electrode typically of the same metal to be plated forms the anode (positive). When an electrical current is passed through the circuit, metal ions in the solution are attracted to the item.

Alternatives:

- Terne-plate is a similar product to tinplate, but the bath is not of tin, but of tin and lead mixed, the latter metal constituting from 7.59% of the whole. The name derives from 'terne' - meaning dull or tarnish. Terne-plates began to be produced in England about the middle of the 19th century, and are widely employed in the United States for roofing purposes.
- For many purposes, tinplate has been replaced by galvanised (zinc-coated) vessels, though not for cooking as zinc is toxic. Zinc protects iron electrolytically, that is, the zinc will oxidize and turn to a white powder to preserve the iron, whereas tin will only protect the iron if the tin-surface remains unbroken.

Cladding is the covering of one material with another. It has different meanings depending on the context.

In metallurgy, cladding is the bonding together of dissimilar metals. It is distinct from welding or gluing as a method to fasten the metals together.

Cladding is often achieved by extruding two metals through a die as well as pressing or rolling sheets together under high pressure.

The United States Mint uses cladding to manufacture coins from different metals. This allows a cheaper metal to be used as a filler.

2.8 Paints

Paint is any liquid, liquefiable, or mastic composition which after application to a substrate in a thin layer is converted to an opaque solid film.

Cave paintings drawn with red and yellow ochre, hematite, manganese oxide, and charcoal may have been made by early Homo sapiens as long as 40,000 years ago.

Paint was made with the yolk of eggs and therefore, the substance would harden and stick onto the surface applied. Pigments were made from plants, sands, and different soil types.

Components:

Pigment

Pigments are granular solids incorporated into the paint to contribute color, toughness, texture or simply to reduce the cost of the paint. Alternatively, some paints contain dyes instead of or in combination with pigments.

Pigments can be classified as either natural or synthetic types. Natural pigments include various clays, calcium carbonate, mica, silicas, and talcs. Synthetics would include engineered molecules, calcined clays, blanc fix, precipitated calcium carbonate, and synthetic silicas.

Hiding pigments, in making paint opaque, also protect the substrate from the harmful effects of ultraviolet light. Hiding pigments include titanium dioxide, phthalo blue, red iron oxide, and many others.

Fillers are a special type of pigment that serve to thicken the film, support its structure and simply increase the volume of the paint. Fillers are usually made of cheap and inert materials, such as diatomaceous earth, talc, lime, baryte, clay, etc. Floor paints that will be subjected to abrasion may even contain fine quartz sand as a filler. Not all paints include fillers. On the other hand some paints contain very large proportions of pigment/filler and binder.

Some pigments are toxic, such as the lead pigments that are used in lead paint. Paint manufacturers began replacing white lead pigments with the less toxic substitute, titanium white (titanium dioxide), even before lead was functionally banned in paint for residential use in 1978 by the U.S. Consumer Product Safety Commission. The titanium dioxide used in most paints today is often coated with silicon or aluminum oxides for various reasons such as better exterior durability, or better hiding performance (opacity) via better efficiency promoted by more optimal spacing within the paint film.

Binder or vehicle:

The binder, commonly referred to as the vehicle, is the actual film forming component of paint. It is the only component that must be present; other components listed below are included optionally, depending on the desired properties of the cured film.

The binder imparts adhesion, binds the pigments together, and strongly influences such properties as gloss potential, exterior durability, flexibility, and toughness.

Binders include synthetic or natural resins such as acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, or oils.

Binders can be categorized according to drying, or curing mechanism. The four most common are simple solvent evaporation, oxidative crosslinking, catalyzed polymerization, and coalescence. There are others.

Note that drying and curing are two different processes. Drying generally refers to evaporation of the solvent or thinner whereas curing refers to polymerization of the binder.

Paints that cure by oxidative crosslinking are generally single package coatings that when applied, the exposure to oxygen in the air starts a process that crosslinks and polymerizes the binder component. Classic alkyd enamels would fall into this category. Oxidative cure coatings are catalyzed by metal complex driers such as cobalt naphthenate.

Paints that cure by catalyzed polymerization are generally two package coatings that polymerize by way of a chemical reaction initiated by mixing

resin and hardener, and which cure by forming a hard plastic structure. Depending on composition they may need to dry first, by evaporation of solvent. Classic two package epoxies or polyurethanes would fall into this category.

Solvent:

The main purposes of the solvent are to adjust the curing properties and viscosity of the paint. It is volatile and does not become part of the paint film. It also controls flow and application properties, and affects the stability of the paint while in liquid state. Its main function is as the carrier for the non volatile components. In order to spread heavier oils (i.e. linseed) as in oil-based interior housepaint, a thinner oil is required. These volatile substances impart their properties temporarily—once the solvent has evaporated or disintegrated, the remaining paint is fixed to the surface. This component is optional: some paints have no diluent. Water is the main diluent for water-borne paints.

Solvent-borne, also called oil-based, paints can have various combinations of solvents as the diluent, including aliphatics, aromatics, alcohols, ketones and white spirit. These include organic solvents such as petroleum distillate, esters, glycol ethers, and the like. Sometimes volatile low-molecular weight synthetic resins also serve as diluents. Such solvents are used when water resistance, grease resistance, or similar properties are desired.

Additives:

Besides the three main categories of ingredients, paint can have a wide variety of miscellaneous additives, which are usually added in very small amounts and yet give a very significant effect on the product. Some examples include additives to modify surface tension, improve flow properties, improve the finished appearance, increase wet edge, improve pigment stability, impart antifreeze properties, control foaming, control skinning, etc. Other types of additives include catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), biocides to fight bacterial growth, and the like.

Additives normally do not significantly alter the percentages of individual components in a formulation.

Color changing paint:

Various technologies exist for making paints that change color. Thermochromic paints and coatings contain materials that change conformation when heat is applied, and so they change color. Liquid crystals have been used in such paints, such as in the thermometer strips and tapes used in fishtanks. Photochromic paints and coatings contain dyes that change conformation when the film is exposed to UV light, and so they change color. These materials are used to make eyeglasses.

Electrochromic paints change color in response to an applied electric current. Car manufacturer Nissan has been reportedly working on an electrochromic paint for use in its vehicles, based on particles of paramagnetic iron oxide. When subjected to an electromagnetic field the paramagnetic particles change spacing, modifying their color and reflective properties. The electromagnetic field would be formed using the conductive metal of the car body. Electrochromic paints can be applied to plastic substrates as well, using a different coating chemistry. The technology involves using special dyes that change conformation when an electric current is applied across the film itself. Recently, this new technology has been used to achieve glare protection at the touch of a button in passenger airplane windows.

Application:

Paint can be applied as a solid, a gaseous suspension (aerosol) or a liquid. Techniques vary depending on the practical or artistic results desired.

As a solid (usually used in industrial and automotive applications), the paint is applied as a very fine powder, then baked at high temperature. This melts the powder and causes it to adhere (stick) to the surface. The reasons for doing this involve the chemistries of the paint, the surface itself, and perhaps even the chemistry of the substrate (the overall object being painted). This is commonly referred to as "powder coating" an object.

As a gas or as a gaseous suspension, the paint is suspended in solid or liquid form in a gas that is sprayed on an object. The paint sticks to the object. This is commonly referred to as "spray painting" an object. The reasons for doing this include:

- The application mechanism is air and thus no solid object ever touches the object being painted;
- The distribution of the paint is very uniform so there are no sharp lines;
- It is possible to deliver very small amounts of paint;
- A chemical (typically a solvent) can be sprayed along with the paint to dissolve together both the delivered paint and the chemicals on the surface of the object being painted;
- Some chemical reactions in paint involve the orientation of the paint molecules.

In the liquid application, paint can be applied by direct application using brushes, paint rollers, blades, other instruments, or body parts such as fingers.

UNIT 3 POLYMERS

3.1 Introduction

Polymer – Definition:

Polymers are the substances consisting of giant or macromolecules made by linking a large number of smaller molecules (monomers).

Polymer is a molecule formed by joining of thousands of smaller molecular units together by chemical bonds.

A chemical process that leads to the formation of polymer is known as polymerization.

Degree of polymerization: The number of repeat units (or) monomeric units available in the polymer is known as degree of polymerization.

Functionality:

Definition: The number of bonding sites (or) reactive sites or functional groups present in the molecule.

Ex: The double bond in vinyl monomers ($\text{CH}_2 = \text{CHX}$) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



1. When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.

Ex: (a)vinyl monomers (b)adipic acid (c)hexamethylene diamine (d)terephthalic acid(e)ethylene glycol (f)amino acid

Example for polymer: HDPE (high density polythene)

2. When the functionality of monomer is three (tri-functional), three-dimensional net work polymer is formed.

Ex: phenol, glycerol

Examples for polymers : Urea formaldehyde, phenol formaldehyde.

Examples for bifunctional monomers:

i) Vinyl monomers ($\text{HC}_2 = \text{P-CH}$) [where P = pendant group]

a)ethylene b)propylene c)vinyl chloride d)vinyl cyanide e)vinyl acetate

f)styrene g)acrylic acid h)methyl methacrylate

ii)Dicarboxylic acids having general formula ($\text{HOOC} - \text{R} - \text{COOH}$)

a)succinic acid b)adipic acid c)terephthalic acid

iii) Amino acids with the general formula $\text{H}_2\text{N} - \text{R} - \text{CH} - \text{COOH}$

a)glycine b)alanine c)valine d) ϵ - amino caproic acid

iv)Diols with the general formula $\text{HO} - \text{H}_2\text{C} - \text{R} - \text{CH}_2 - \text{OH}$

a)ethylene glycol

v)Diamines with the general formula $\text{H}_2\text{N} - \text{CH}_2 - \text{R} - \text{CH}_2 - \text{NH}_2$

a)hexamethylene diamine

when a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

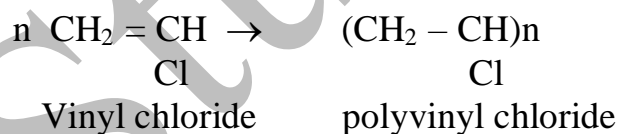
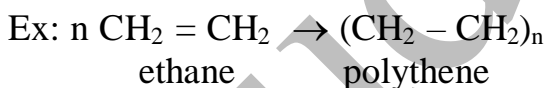
Ex: LDPE (LOW density polyethene)

Polymerisation:

Definition: “ The process in which the simpler molecules combine together to form very large molecule having high molecular weight is known as polymerization”. The molecule is known as polymer.

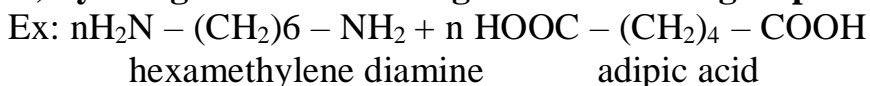
The different ways of doing polymerization are –

i)By opening a double bond



ii)By opening a ring

iii) By using molecules having two functional groups



3.2 Types of polymerization:

Polymers can be synthesized by the following polymerization processes.

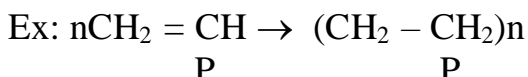
- I. Addition polymerization (or) chain polymerization
- II. Condensation or, step or, step growth polymerization
- III. Copolymerisation

I) Addition polymerization:

The addition polymerization is the process in which the linking together of monomer molecules by a chain reaction is observed.

Polymer synthesized by addition polymerization has the same empirical formula as that of monomer.

No molecule is evolved during polymerisation and the polymer is an exact multiple of the original monomeric molecule.



Where P = pendant group

P	-H	-CH ₃	-Cl	-C ₆ H ₅
Polymer	Polythene	Polypropene	Polyvinyl chloride	Polystyrene

* Addition polymerization is usually induced by light, heat or, a catalyst for opening the double bond of the monomer and creating the reactive sites.

II) Condensation polymerization:

An intermolecular reaction involving two different bifunctional reactants with affinity for each other and taking place through repeated condensation reaction is known as condensation polymerization.

* Monomers having – COOH and – OH or, –COOH and –NH₂ undergo condensation polymerization.

The reaction always accompanies the elimination of H₂O, HCl, CH₃OH, NH₃ molecules.

Examples:

1) Nylon 6.6 : [polymerization involving adipic acid and hexamethylene diamine]

2) Terelene: (polyethylene terephthalate)

[polymerization involving ethylene glycol and terephthalic acid]

3) Polyurethane: Polymerisation involving a diol

Ex: bisphenol A) and a diisocyanate (ex: toluene diisocyanate) to give polyurethane.

Condensation polymerization involving trifunctional reactants give rise to a cross – linked three-dimensional polymer.

Differences between addition and condensation polymerization:

Addition polymerization	Condensation polymerisation
1) It requires the presence of a double bond in the monomer	1) It requires two reactive functional groups to be present at both ends of the monomer. There should be at least two different bi-or, poly- functional monomers having functional groups with affinity for each other.
2. In this reaction, no by product is formed	2) generally a by product is formed in this reaction.
3. Homo-chain polymer is obtained. (generally thermoplastic)	3) Hetero-chain polymer is obtained (either thermoplastic or, thermostat)
4. The growth of chain is at one active centre.	4) The growth of chain occurs at minimum of two active centres.
5. Examples: a) polymerisation of ethylene to form polythene (PE) $n \text{ CH}_2 = \text{CH}_2 \rightarrow (\text{CH}_2 - \text{CH}_2)_n$ <div style="display: flex; justify-content: space-around; width: 100%;"> ethylene polythene </div>	5) Examples: a) condensation polymerisation of hexamethylene diamine and adipic acid to form Nylon 6.6 $n \text{ H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 + \text{hexamethylene diamine}$ $n \text{ HOOC} - (\text{CH}_2)_4 - \text{COOH} \text{ adipic acid}$
b) polymerisation of vinyl chloride to form poly-vinyl chloride (PVC) $n \text{ CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$ <div style="display: flex; justify-content: space-around; width: 100%;"> vinyl chloride polyvinyl chloride </div>	b) condensation polymerisation of terephthalic acid and ethylene glycol to give polyethylene terephthalate (terelene)

<p>c)polymerisation of styrene to form polystyrene. $n \text{CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$</p> <p>styrene polystyrene</p>	<p>c)condensation polymerisation of toluene diisocyanate and diol to form polyurethane</p>
<p>d)polymerisation of acrylonitrile (vinyl cyanide) to form polyacrylonitrile (orlon). $n \text{CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$</p> <p> CN CN Vinyl cyanide polyacrylonitrile (acrylonitrile) (orlon)</p>	<p>d)Nylon -6: $\text{NH}_2 - (\text{CH}_2)_5 - \text{COOH} \rightarrow \epsilon - \text{amino caproic acid}$ $(\text{NH} - (\text{CH}_2)_5 - \text{C})_n$ Nylon - 6</p>
<p>e)polymerisation of methyl methacrylate to form polymethyl methacrylate (plexiglas, Lucite) methyl methacrylate polymethyl methacrylate (Plexiglas, Lucite)</p>	<p>e)condensation polymerisation of hexamethylene diamine and sebaic acid to form nylon - 6, 10. $\text{NH}_2 - (\text{CH}_2)_6 - \text{NH}_2 + \text{hexamethylene diamine}$ $\text{HOOC} - (\text{CH}_2)_8 - \text{COOH} \rightarrow$ Sebaic acid $(\text{N} - (\text{CH}_2)_6 - \text{N} - \text{C} - (\text{CH}_2)_8 - \text{C})_n$ Nylon - 6, 10</p> <p>f)Nylon - 11: $\text{NH}_2 - (\text{CH}_2)_{10} - \text{COOH} \rightarrow$ amino decanoic acid $(\text{N} - (\text{CH}_2)_{10} - \text{C})_n$ Nylon - 11</p>

III) Copolymerisation:

Addition polymerisation involving a mixture of two (or) more suitable or compatible monomers gives a copolymer and the process is known as copolymerization.

(OR)

A reaction in which a mixture of two (or) more monomers is allowed to undergo polymerisation is known as copolymerization. The polymer is known as copolymer.

Examples:

1)Copolymerisation of styrene and methyl methacrylate

2) Copolymerisation of acrylonitrile and vinyl chloride

3) Copolymerisation of styrene and 1,3-butadiene.

$m\text{CH}_2 = \text{CH} + n\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ copolymerisation

Depending on the linkage, the following four types of monomers are possible.

S.No.	Copolymer	Structure	Description
1)	Alternate	$-\text{M}_1-\text{M}_2-\text{M}_1-\text{M}_2-\text{M}_1-\text{M}_2-$	Monomers are arranged in regular alternate fashion
2	Block	$-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_2-\text{M}_2-\text{M}_2-$	A block of repeating unit of one kind of monomer is followed by block of another kind of monomer
3	Random	$-\text{M}_1-\text{M}_2-\text{M}_2-\text{M}_1-\text{M}_2-\text{M}_1-$	Monomers randomly distributed along the polymer chain
4	Graft	$-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_1-$	Have branched structures in which the monomer segments on the back bone and branches differ

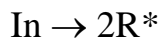
3.3 Chain growth mechanism : [Free radical mechanism]

The mechanism involves three steps.

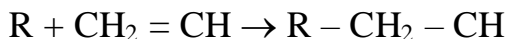
I. Chain initiation II. Chain propagation III Chain termination

I. Chain Initiation: This involves two steps.

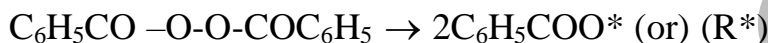
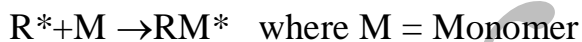
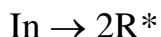
i) Decomposition of the initiator to form free radicals



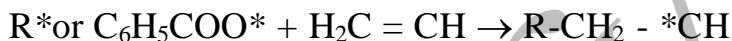
ii) Addition of the first vinyl monomer molecule to the free radical to form intermediate (I)



I) chain initiation : Initiator added to the monomer undergoes dissociation to form free radicals. Initiators commonly used are acetyl peroxide ($\text{CH}_3\text{CO} - \text{O} - \text{O} - \text{COCH}_3$), benzoyl peroxide ($\text{C}_6\text{H}_5\text{COO} - \text{O} - \text{COC}_6\text{H}_5$) and azobis – isobutyronitrile (AIBN).



Benzoyl peroxide free radical



II) Chain propagation: The intermediate (free radical) immediately reacts with a monomer molecule to form the reactive species which is responsible for the growth of the polymer chain.

III) Chain termination: Termination reaction may occur due to a coupling reaction or a disproportionation reaction.

- In coupling or combination reaction two reactive or, free radical polymer chains combine together to form a dead polymer.
- The disproportion reaction involves the transfer of a hydrogen atom from one of the free radical polymer chain to another free radical giving rise to one saturated and one unsaturated polymer molecules. Disproportionation also terminates the propagation or growth of the polymer chain resulting in a dead polymer
- The chain can be terminated by reaction with the solvent molecules like carbon tetrachloride.
- Chain can be terminated by the reaction of growing polymer chain with inhibitors like hydroquinone and trinitrobenzene.

3.4 Step – Growth polymerisation:

It proceeds by step – wise fashion

Monomer \rightarrow Dimer \rightarrow Trimer $\rightarrow \rightarrow$ oligomer \rightarrow n times polymer.

Monomer in step – growth polymerisation is capable of combining with itself or with any other species present with equal reactivity, hence it disappears early in the reaction.

The degree of polymerisation and hence the molecular weight of the polymer rises steadily throughout the reaction. The reactivity is governed by the functional groups.

It can be either addition or, condensation polymerisation.

Ex -1: As a diamide, urea is capable of forming polymers. It reacts with formaldehyde to form urea-formaldehyde resins. A space-network polymer is formed.

Condensation (Step-growth) Polymerisation:

Ex-1: Phenols and formaldehyde react to form phenol-formaldehyde resins (Bakelite and related polymers)

When phenol is treated with formaldehyde in the presence of acid or alkali, a high-molecular weight substance is obtained in which many phenol rings are held together by $-\text{CH}_2-$ groups

The stages involved in the formation of the polymer are –

a) phenol reacts with formaldehyde to form O – or P – hydroxyl methyl phenol.

b) Hydroxy methyl phenol reacts with another molecule of phenol to form a compound in which two rings are joined by a $-\text{CH}_2-$ link. During this reaction one water molecule is eliminated.

c) This process continues to yield a product of high molecular weight.

The final product contains many cross-links and hence has a rigid three-dimensional structure because three positions in each phenol molecule are susceptible to attack. Thus it is a space-network polymer.

Ex-2: A diol reacts with a dicarboxylic acid to form an ester. But each moiety of the simple ester still contains a group that can be react to generate another ester linkage and hence a large molecule, which itself can react further and so on.

If each monomer molecule contains just two functional groups, growth can occur in only two directions. A linear polymer is obtained.

Ex: Dacron

If the reaction occurs at more than two positions in a monomer, highly cross –linked space network polymer is obtained.

Ex: Glyptal

Carboxylic acids react with amines to yield amides, and with alcohols to form esters.

When an acid containing more than one-COOH group reacts with an amine that contains more than one –NH₂ group to form polyamides.

Ex: Nylon – 6, 6.

When an acid containing more than one-COOH group reacts with an alcohol that contains more than one – OH group to form polyesters.

Ex: Dacron, Glyptal

3.4 Plastics:

Plastics are the high polymers that can be molded by the application of heat and pressure. During molding process, there is no chemical change. The plastics have linear structure.

Examples: Polythene, polyvinyl chloride, polystyrene, nylons, polyesters.

Thermoplastics:

Thermo plastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times. They undergo reversible changes on heating.

Examples: Polythene (PE), polypropylene (PP), polyvinyl- chloride (PVC), polytetrafluoroethylene (PTFE or Teflon), polystyrene (PS), plexiglass, nylons, polyesters, PMMA, PVA, HIDS.

(Polymethyl methacrylate)

Thermoplastics –

- are formed by addition polymerisation
- consists of linear polymer chains with negligible cross-linking
- are soft and less brittle.
- are soluble in organic solvents.
- soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid and retains the moulded shape.
- can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.

Thermosetting polymers or, Thermosets:

Thermosets are the polymers that undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible. They will not soften on heating, Once they are set.

Examples: Phenol-formaldehyde resin, urea-formaldehyde resin, epoxy resins (araldite), melamine, bakelite

Thermosets (Thermosetting resins):

- are mostly formed by condensation polymerisation.
- are mostly branched polymer chains with potential to form a 3-dimensional structure.
- become hard and rigid on heating during moulding process.
- are not soluble in common organic solvents.
- exhibit their characteristic properties of non-softening and non-swelling nature, hardness and brittleness.
- cannot be softened, reformed, reshaped once they are set.
- cannot be reclaimed from wastes.

Differences between thermoplastics and thermosettings:

Thermoplastics	Thermosettings
1. Formed either by addition or by condensation polymerisation reactions	1. Formed by condensation polymerisation reactions.
2. They have either linear or branched	2. They have 3-dimensional, cross-linked network structure.

<p>structures.</p> <p>3. Adjacent polymer chains are held together by either vanderwaals forces, or by dipole-dipole forces or by hydrogen bonds.</p> <p>4. They soften on heating and stiffen on cooling</p> <p>5. Low molecular weight thermoplastics are soluble in their suitable solvents.</p> <p>6. They can be remoulded, re-shaped and re-used.</p> <p>7. They can be reclaimed from waste i.e., they can be recycled.</p> <p>8. There is no change in chemical composition and structure during moulding process.</p> <p>9. They undergo reversible changes, on the application of heat.</p> <p>10. They are soft and flexible.</p> <p>11. They swell or dissolve in organic solvents.</p> <p>12. They are tough materials</p> <p>13. The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.</p> <p>14. Curing can be done by cooling.</p>	<p>3. Adjacent polymer chains are held together by strong covalent bonds called crossed-links.</p> <p>4. They do not soften on heating.</p> <p>5. They are insoluble in any solvent.</p> <p>6. They cannot be remoulded and hence cannot be used.</p> <p>7. They cannot be reclaimed from waste. They cannot be recycled.</p> <p>8. They undergo chemical changes such as further polymerisation and cross-linking during moulding process.</p> <p>9. They undergo irreversible changes on the application of heat.</p> <p>10. They are hard, rigid and infusible.</p> <p>11. They neither dissolve nor swell in organic solvents.</p> <p>12. They are brittle materials.</p> <p>13. The moulded articles can be taken out of the moulds even when they are still hot without any deformations.</p> <p>14. Curing can be done by applying heat and pressure.</p> <p>15. Examples: Phenol-formaldehyde resin (PF), urea-formaldehyde resin (UF), Melamine – formaldehyde</p>
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15.Examples: Polyethylene(PE), Polypropylene(PP), Poly Vinyl Chloride(PVC), Polystyrene(PS), POLytetrafluoroethylene (PTFE or Teflon), Polymethyl methacrylate (PMMA – Lucite or plexiglass) nylons, Polyesters.	resin (MF), epoxy resins, XLPE, bakelite.
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3.5 Compounding of plastics:

Definition: “The process of mechanical mixing of various additives with polymers (without chemical reaction) to impart some special properties to the end product is known as compounding of plastics”.

The additives get incorporated into the polymer to give a homogeneous mixture.

The functions of additives are

- To modify the properties of the polymer
- To introduce new properties into the fabricated articles.
- To assist polymer processing
- To make the polymer products more pleasing and colourful.
- They should be cheap and sufficient in their functions.
- They should be stable under processing and service conditions.
- They should not impart taste or odour.
- They should be non-toxic for food grade application of final compound after processing.
- They should not adversely affect the properties of polymer.

The principal additives used in compounding are

- a) Fillers b) Plasticizers c) Lubricants d) Flame retarders
e) Colourants
f) Stabilisers g) Activators, accelerators and cross-linking agents
h) Nucleating agents i) Blowing agents.

3.6 Fabrication of plastics:

A variety of methods are used for fabricating plastic articles and products depending upon the nature of the resin used and the end use of the finished product. The methods are

- 1) Casting 2) Moulding 3) Extrusion 4) Blowing 5) Vacuum forming
6) Lamination 7) Surface coating

1) Casting: Casting is the simplest technique used for fabricating products of both thermoplastic and thermosetting resins. The molten compound mixture is poured into lead moulds and cured at about 70°C for several hours at atmospheric pressure to give finished products free from internal stress and amenable for polishing.

Ex: The curing time for phenolic resins is about 50 hours.

2) Moulding: Moulding is the most widely used method for fabricating plastic products. The different moulding methods used are –

- a) Injection moulding
- b) compression moulding
- c) cold moulding
- d) Transfer moulding

a) Injection moulding:

The method is mainly used for thermoplastic resins. The compounded mixture in the form of a powder/granules is fed into the heated cylinder (temperature range is 90-260°C) of the injection moulding machine. The softened plastic mass in the cylinder is injected at a controlled rate by a screw or, piston, plunger under high pressure into a cold mould. Curing of the softened plastic into rigid product occurs during cooling in the mould. The mould is opened after sufficient curing to remove the finished product.

b) Compression moulding:

The method is useful for fabricating thermoplastic and thermosetting resins. The required amount of a compounded mixture is placed in the mould and the mould is closed carefully. Then the mould is subjected simultaneously to high temperatures (in the range 100-200°C) as well as high pressures (100-500kg/cm²). Thermosetting resins undergo curing during heating while thermoplastic resins undergo curing during cooling of the mould.

c) Cold moulding:

In this method, the object is formed in the mould by the application of high pressure in the cold. Then it is taken out of the mould, heated (cured) to remove excess solvent and to promote further condensation and hardening.

d) Transfer moulding:

The method is a modification of injection moulding suitable for use with thermo setting plastics. The moulding composition is first plasticized by applying minimum heat and pressure in a chamber outside of the mould and

then it is injected into the mould where curing takes place under the influence of heat and pressure. The method is used for more complicated shapes and permits the use of delicate inserts.

3) Extrusion:

The method is also known as extrusion moulding. The method is used for fabricating thermoplastics having uniform cross-section such as sheets, rods, tubes, insulated electric cables etc., The compounded mixture is heated to a plastic condition and forced through a die of the required shape by a screw conveyor. The extruded product is cooled as it emerges out of the die on a conveyor by blowing air or spraying water.

4) Blowing:

In this method, the softened thermoplastic resin is blown by air or steam into a closed mould, just like industrial glass-blowing. The method is used for making bottles, toys etc.

5) Vacuum forming:

The method is useful for making boxes and complicated shapes from thermoplastic resins, it has 2 steps.

a) The thermoplastic material is made into a sheet by a process known as calendaring by passing the compound mixture between heated rollers and again between cooled rollers.

b) The sheet is held firmly in a frame and heated to soften it. The softened material is drawn into the mould by a vacuum pump and cured to form the finished product.

6) Lamination:

Lamination of sheets of cloth, paper or wood is carried out by impregnating them with a solution of the resin, piled one over the other to get a desired thickness and subjected to heat as well as pressure by pressing between polished sheets of steel to expel the solvent and heat to cure the resin. Usually thermosetting resins are used for lamination. The finished product has a high tensile and impact strength.

7) Surface coating:

Surface coating of a finished product made of metal and alloys or other materials by polymeric resins is adopted for protective or decorative purposes.

Ex: 1) Polyethylene is used to coat refrigerator parts, soap boxes and steering wheels.

2) Polytetrafluoroethylene (PTFE) or, Teflon, is coated on the surface of kitchen utensils for providing a non-sticky surface.

Surface coatings are carried out by coating the polymer powder on the hot degreased and cleaned surface of the article.

3.8. preparation, properties, engineering applications of polyethene and PVC:

I) Polyethylene:

Polyethylene is the simplest homo polymer and a thermoplastic. The structure of polyethylene is $(CH_2 - CH_2)_n$

There are two commercial grades of polyethylene. They are

i) Low density polyethylene (LDPE)

ii) High density polyethylene (HDPE)

i) Low density polyethylene (LDPE):

Preparation:

LDPE is prepared by polymerisation of ethylene under high pressure (1500 – 50,000 Psi) and high temperature (350°C) using a trace of oxygen or any peroxide such as benzoyl peroxide as initiator.

Properties:

- LDPE has a linear structure with extensive branching
- It has a low degree of crystallinity (40%)
- It has a low density (0.912 – 0.935)
- It has a low melting point (110°C)
- It has lower tensile strength, stiffness and hardness
- Its chemical resistance is also poor

ii) High Density polyethylene (HDPE):

Preparation:

HDPE is prepared by coordination polymerisation of ethylene using Ziegler natta catalyst $[TiCl_4 + Al(C_2H_5)_3]$ in hydrocarbon solvent]

Properties:

- HDPE is a linear polymer with no branching.

- It has relatively high degree of crystallinity (90%)
- It has high density (0.96)
- It has high melting point (140°C)
- It has high tensile strength, stiffness and hardness.
- It is not attacked by chemicals.

Distinguishing properties of LDPE and HDPE

LDPE	HDPE
1) Produced by chain polymerisation using oxygen (or) peroxides like benzoyl peroxide.	1) Produced by coordination polymerisation using Ziegler-Natta Catalyst $[\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3]$
2) Linear polymer with extensive branching.	2) Linear polymer with practically no branching.
3) Relatively lower degree of crystallinity (40%).	3) Relatively higher degree of crystallinity (90%)
4) Lower density (0.912 – 0.935)	4) Higher density (0.96)
5) Lower melting point (110°C)	5) Higher melting point (140°C)
6) Lower tensile strength, stiffness, hardness	6) Higher tensile strength, stiffness and hardness.
7) Chemical resistance is low	7) Chemical resistance is high
8) It is a white, waxy, translucent material.	
9) It does not dissolve in any solvent at room temperature.	

Applications:

- 1) Films and sheets: A large amount of polyethylene produced is used as packing materials for food and textile.
- 2) Molded articles: It is used for the manufacture of molded articles such as bottles, cans, buckets, toys, tubs, pipes, squeeze bottles etc.,
- 3) Insulating material: It is used for wire and cable coating because of its excellent electrical insulation properties.

II) Poly vinyl chloride (PVC):

Preparation:

Polyvinyl chloride is obtained by heating a water emulsion of the vinyl chloride in an autoclave under pressure in the presence of benzoyl peroxide or hydrogen peroxide.

Properties:

- 1) PVC is a colourless and odourless powder.
- 2) It is chemically inert and non-inflammable and exhibits high resistance to light, atmospheric oxygen, acids and alkalis.
- 3) It is soluble in chlorinated hydrocarbons, tetrahydrofuran (THF) and cyclohexanone.
- 4) Pure resin possesses a high softening point (148°C) and a greater stiffness and rigidity compared to polyethylene, but is brittle.
- 5) It is the most widely used synthetic plastic.

Applications:

1) Rigid PVC unplasticized PVC have superior chemical resistance and high rigidity but is brittle. It is used for making sheets, that are employed for tank – linings, light-fittings, safety, helmets, refrigerator components, tyres, cycle and motor cycle mudguards. It is also extruded in strip and tube form for use in the place of non-ferrous metals.

2) Plasticized PVC is used for making continuous sheets of different thicknesses from 0.1mm to 8mm. It is employed for packing rain coats, table-clothes and curtains, electrical insulation like coverings of electric cables, injection moulding of articles like toys, tool-handles, toiled-goods, radio-components, plastic-coated cloth, chemical containers, thermal insulating foam, conveyor belts etc.,

Plasticized PVC is obtained by adding plasticizers like dibutyl phthalate, dioctyl phthalate, tricresyl phosphate etc.

II) Polyvinyl chloride (PVC):

PVC is made by addition polymerization. It is of two types.

i) Rigid PVC : (Unplasticized PVC):

Preparation: Rigid PVC is made by heating vinyl chloride (in the form of emulsion of it in water) in the presence of small amount of benzoyl peroxide or H_2O_2 as catalyst under pressure in an autoclave.

Properties:

- a) Presence of chlorine atoms on the alternate carbon atoms of PVC causes an increase in the interchange attraction. This increases the hardness and stiffness of polymer. Its softening point is also high (148°C)
- b) The Cl-Cl dipole makes PVC a polymeric polar molecule, but because of the immobility of the dipole at room temperature, power factor of PVC is comparatively low.
- c) PVC is colourless, odourless and non-inflammable.
- d) It has superior chemical resistance but is soluble in ethyl chloride and tetrahydrofuran (THF).
- e) It has excellent oil resistance and resistance to weathering.

Applications:

- a) It is used in acid recovery plants and in plants for handling hydrocarbons, many of which adversely affect the polyolefins. This is due to its very good resistance to chemicals.
- b) Rigid PVC has great potential importance to building industry since it has excellent resistance to weathering. When considered regarding initial cost, installation and maintenance cost, it is found to be very economical. Hence, it is used for making pipes for drainage and guttering. It is also replacing wood for making window frames that neither corrodes or not.
- c) Rigid PVC is also used for making bottles –

i) For consumable liquids (like edible oils, fruit squashes, table wine and vinegar).

ii) For liquids of household use (like bisleri mineral water, cosmetics and detergents).

ii) Plasticized PVC:

Preparation: plasticized PVC is obtained by adding plasticizers such as DOP (dioctyl phthalate), dibutyl phthalate, tricresyl phosphate etc., to rigid PVC.

Properties:

Plasticized PVC is a very good insulator for direct current and low frequency AC current.

Applications:

a) Plasticized PVC is completely replaced rubber insulated wire for domestic flex and is used widely industrially.

b) It is used for sheathing in cables where polyethylene is employed as insulators.

c) Plasticized PVC is used for making leather cloth which is used in

i) Car applications in upholstery and trim,

ii) Kitchen upholstery

iii) Bathroom curtaining

iv) Ladies handbags.

Compared to leather, PVC-leather cloth has greater abrasion resistance, flex resistance and washability. Its cost is very low.

d) It is also used for making

i) Plastic rain wear ii) Baby pants iii) All PVC-shoes for beach wear &

iv) Garden hose.

These applications are due to flexibility and water-proof nature of plasticized PVC. It is also more economical and better aesthetically.

3.9 preparation, properties and engineering applications of PS and Teflon:

Polystyrene (PS):

Polystyrene (PS) is an addition polymer of styrene. It is a thermoplastic and has the following structure.

The monomer styrene is obtained by the alkylation of benzene followed by catalytic dehydrogenation.

Preparation: Polystyrene is prepared by free radical addition polymerization of styrene in the presence of benzoyl peroxide as catalyst.

Properties:

Polystyrene is a white, amorphous, linear thermoplastic.

It is chemically inert.

Because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient and hence it is amorphous polymer. Its specific gravity (1.054) is also low.

Polystyrene can be nitrated by fuming nitric acid

- It can be sulphonated by conc. H_2SO_4 .
- It yields water- soluble emulsion at about 100°C .
- It is highly electric insulating, highly resistant to acids.
- It has relatively low softening range ($90 - 100^\circ\text{C}$) and is brittle.
- It has the unique property of transmitting light through curved sections.
- It is readily attacked by a number of solvents.
- Its optical properties are excellent and its refractive index (1.60) is quite high.
- Its tensile strength is about 8000Psi.

Applications:

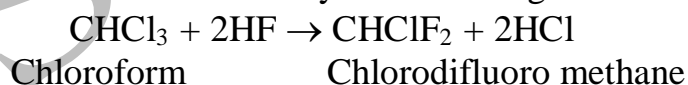
- 1) Moulded articles: A large amount of polystyrene is used for the manufacture of household articles such as containers, jars, lids, bottles, cabinets for TV, radio and washing machines, combs, toys, brush handles etc.
- 2) Optical objects: Because of its refractive index and clarity, it is used for the manufacture of lenses, fluorescent light diffuser etc.,
- 3) Insulating material: Because of its excellent electrical resistant properties, it is used for wire and cable coatings.
- 4) It is used for the production of a variety of foamed products.
- 5) The sulfonated polystyrene is used as an ion-exchange resin.

Polytetrafluoro ethylene (PTFE) : (Teflon):

Teflon is the trade name for polytetrafluoro ethylene. The linear structure of Teflon is $(\text{CF}_2 - \text{CF}_2)_n$

The monomer used is tetrafluoro ethylene which is a non-toxic gas.

The monomer is obtained by the following reactions:



Pyrolysis



Preparation:

Teflon is usually prepared by emulsion polymerisation of tetrafluoroethylene, under pressure in the presence of benzoyl peroxide as catalyst.

Properties:

- Teflon is essentially a linear polymer with no branching
- It is a thermoplastic
- Teflon has the following unique properties:
 - High degree of crystallinity (93-98%)
 - High melting point (327°C)
 - High density (2.30g/cm³)
 - Chemical inertness over a wide range of temperature
 - Excellent electrical insulation properties.
 - Non-adhesive characteristics
 - Very-low coefficient of friction
 - Excellent toughness and heat resistant.

Applications: Teflon is used for

- Wire and cable insulation
- Laminates for printed circuitry
- Coatings of frying pans.
- Non-lubricating bearings.
- Variety of seals, gaskets, packings valve and pump parts and stop-cocks for burettes.
- Insulators for motors, generators, coil transformers and capacitors.

Bakelite:

Properties:

- Phenolic resins are hard, rigid and strong materials
- They have excellent heat and moisture resistance.
- They have good chemical resistance.
- They have good abrasion resistance.
- They have electrical insulation characteristics
- They are usually dark coloured.
- Lower molecular weight grades have excellent bonding strength and adhesive properties.

Applications: Phenol formaldehyde resins are used for

- Domestic plugs and switches
- Handles for cooker and saucepans.
- Distributor heads for cars

- Adhesives for grinding wheels and brake linings.
- Varnishes, electrical insulation and protective coatings.
- The production of ion exchange resins.
- Impregnated paper, wood and other fillers, for producing decorative laminates and wall coverings and industrial laminates for electrical parts including printed circuits.

Nylon:

Synthetic fiber forming polyamides are termed as 'Nylons'.

Preparation:

- Nylon – 6 can be prepared by self-condensation of ϵ - amino caproic acid.
- Nylon-6 can be prepared by ring opening polymerisation of caprolactam.
- Nylon-6 can be synthesized from cyclohexane.

The steps involved are –

- Conversion of cyclohexane to cyclohexanone by oxidation.
- Treatment of cyclohexanone with hydroxyl amine to form an oxime.
- Conversion of cyclohexanone oxime into caprolactam by Beckmann rearrangement in the presence of H_2SO_4 .

Nylon 6.10:

- Nylon 6.10 is prepared by the condensation polymerisation of hexamethylene diamine and sebacic acid.

Properties:

- The structure of nylons are linear that permits side-by-side alignment. The molecular chains are held together by hydrogen bonds. Thus nylons have high crystallinity that imparts high strength, high melting point, elasticity,
- toughness, abrasion resistance and retention of good mechanical properties upto 125°C.
- They are also sterilisable.
- They have good hydrocarbon resistance since nylons are polar polymers. Larger the number of carbon atoms, greater will be ease of processing and hydrocarbon and moisture resistance.

Applications:

- Nylon 6.6 is primarily used for fibers that find use in making socks, undergarments, carpets etc.,

- Nylon 6.6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cans etc.,
- Nylon 11 and Nylon 12 are used for making flexible tubing for conveying petrol.
- Mouldings have application in medicine and pharmacy because of sterilisability.
- Durable but costly hair combs.
- Nylon 6.6 is also used for facketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.
- Nylon 6 is mainly used for making tyre cords.
- Nylon 6.10 is suitable for monofilaments that are used for bristles, brushes etc.,
- Glass reinforced Nylon plastics are used in housings and cosings of domestic appliances, radiator parts of car and for relay coil formers.

Nylon – 11:

Nylon -11 can be prepared by the self-condensation of ω -amino undecanoic acid.

Nylon 6,6:

i)Nylon 6.6 is prepared by the condensation polymerisation of hexamethylene diamine and adipic acid in 1:1 molor ratio without an external strong acid.

ii)Nylon 6.6 can be prepared starting form 1,3-butadiene

3.10 Conducting polymers:

Definition: A polymer that can conduct electricity is known as conducting polymer.

Classification: Conducting polymers can be classified as follows.

I) Intrinsically conducting polymers:

The polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two types.

1)Conducting polymers having conjugated π - electrons in the backbone:
Such polymers contain conjugated π -electrons in the back bone which increases their conductivity to a large extent.

Explanation: Overlapping of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

All the three forms of polyanilines have conductivities of the order of 10^{-10} Scm⁻¹. conductivity of these polymers having conjugated π -electrons in the backbone is not sufficient for their use in different applications.

2) Doped conducting polymers:

In comparison to conventional polymers, the conducting polymers having conjugated π -electrons in the backbone can be easily oxidized for reduced as they have low ionization potentials and high electron affinities. The conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. It is referred to as doping.

This is of two types.

- a) P-doping or oxidative doping
- b) n-doping or, reductive doping

a) p-doping:

It is done by oxidation process. P-doping involves treatment of an intrinsically conducting polymer with a lew's acid, thereby oxidation takes place and positive charges on the polymer backbone are created. The oxidation process leads to the formation of delocalized radical ion called 'Polaron'. A second oxidation of this polaron, followed by radical recombination yields two positive charge carriers on each chain which are mobile. These delocalized positive charges are current carriers for conduction.

The common p-dopants used are I_2 , Br_2 , ASF_5 , PF_6 , naphthyl amine.

b) n-doping: n-doping is done by reduction process. N-doping involves the treatment of an intrinsically conducting polymer with a lewis base like sodium naphthalide.

n-doping leads to the formation of polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.

II) Extrinsicly conducting polymers:

These are the polymers whose conductivities due to the presence of externally added ingredients in them. These are of two types.

1) Conductive element filled polymer: In this type, the polymer acts as the binder to hold the conducting element such as carbon black, metallic fibres, metallic oxides together in the solid entity.

Minimum concentration of conductive filler which should be added so that the polymer starts conducting is known as 'percolation threshold'. Because at this concentration of filler, a conducting path is formed in polymeric material. Generally special conducting grade C-black is used as filler which has very high surface area, more porosity and more filamentous properties.

These polymers possess reasonably good bulk conductivity. They are generally low in cost, light in weight, mechanically durable and strong and are easily processable in different forms, shapes and sizes.

2) Blended conducting polymers: These polymers are obtained by blending a conventional polymer with a conducting polymer. These polymers possess better physical, chemical, electrical and mechanical process and they can be easily processed.

Ex: upto 40% polypyrrole will have a little effect on tensile strength and also give a much higher impact strength than obtained with a carbon-black filled compounds at only 10% loading.

Applications of Conducting Polymers:-

In rechargeable Light weight batteries based on perchlorate doped Polyacetylene-lithium Systems: These are about 10 times lighter than conventional lead storage batteries. These can produce current density up to 50mA/cm^2 .

- In electrochromic displays and optical filters: ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters. Thus the conducting polymers can be used as electro chromic materials i.e., the

materials that change colour reversibly during the electrochemical processes of charge and discharge.

- In wiring in aircrafts and aerospace components.
- Conducting polymers are also used for making sensors for pH, O₂, NO_x, SO₂, NH₃ and glucose.
- In telecommunication systems.
- In electromagnetic screening materials.
- In electronic devices such as transistors and diodes.
- IN solar cells, drug delivery system for human body etc.,
- In photovoltaic devices.
- In non-linear optical materials.
- In molecular wires and molecular switches.
- Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion-exchangers and controlled release of drugs.

3.11 Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries of these *Hevea brasiliensis* is the most important source of natural rubber and the rubber obtained from this is known as “Hevea” rubber. Rubber is stored in the form of white fluid called ‘latex’ behind the bark of the rubber tree.

Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene). It is a hydrocarbon polymer having molecular formula (C₅H₈)_n.

Polyisopren eexists in two geometric isomers cis and transforms. Natural rubber is soft and has cis-configuration while ‘Guttapercha’ or, ‘Ballata’ has trans configuration.

Deficiencies of natural rubber:

- Natural rubber as such has no practical utility value. It is because of many inherent deficiencies. They are –
- It is hard and brittle at low temperature and soft and sticky at high temperature.
- It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS₂).
- It has high water absorption power.
- It is a sticky substance, rather difficult to handle
- It is readily attacked by acids and alkalies.
- It has low tensile strength.

- It has poor abrasion resistance.
- It is sensitive to oxidative degradation

Vulcanization:

Vulcanization is a process of heating the raw rubber at 100 – 140°C with sulfur for

1 – 4 hours. The sulfur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains.

The degree of vulcanization depends on the amount of sulfur used. Tyre industry uses 3 – 5% sulfur. If the amount of sulfur is increased to 30%, a hard and rigid rubber called “ebonite” is produced.

Advantages of vulcanization:

- The tensile strength of vulcanized rubber is very good. It is 10 times the tensile strength of raw rubber.
- It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
- It has better resistance to moisture, oxidation, abrasion.
- It has much higher resistance to wear and tear compared to raw rubber.
- It has broader useful temperature range (-40 to 100°C) compared to raw rubber's useful temperature range (10 – 60°C).
- It is a better electrical insulator Ex: Ebonite
- It is resistant to i) Organic solvents like petrol, benzene, CCl₄, ii) Fats and oils, but it swells in them.
- It has only slight tackiness.
- It has low elasticity. Their property depends on the extent of vulcanization. Ebonite has practically no elasticity.
- It is very easy to manipulate the vulcanized rubber to produce the desired shapes.

3.12 Elastomers:

Definition: Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.

Characteristics of Elastomers:

- Elastomers have linear but highly coiled structure.

- Inter chain cohesive forces are negligible because these are hydrocarbons.
- They have high degree of elasticity.
- They can retract rapidly.

BuNa – S : [Styrene rubber or, SBR (Styrene – butadiene rubber) or GRS (Government controlled styrene rubber)]

Preparation:

Buna – S is prepared by the copolymerization of butadiene (75%) and styrene (25%) in an emulsion system at 50°C in the presence of cumene hydroperoxide as catalyst.

If the emulsion polymerisation is carried out at low temperatures (-18° to 5°C) in the presence of redox catalyst like cumene hydroperoxide + dextrose in the presence of iron salt, the resultant SBR is known as cold SBR.

Vulcanization can be done either by sulfur or sulfur monochloride (S_2Cl_2). Less sulfur and more accelerators are required for vulcanization.

Properties:

- High abrasion resistance
- High load-bearing capacity
- Resilience (regaining original shape after removal of applied force)
- It swells in oils and solvents.
- Low oxidation resistance, as it gets readily oxidized, especially in the presence of traces of ozone present in the atmosphere.
- Vulcanized and compounded cold rubber has a greater tensile strength and greater abrasion resistance than the SBR or natural rubbers.

Applications:

SBR is used in the following applications.

- | | | |
|----------------------------------|----------------|-------------------------|
| 1) Motor tyres | 2) Shoes soles | 3) Foot wear components |
| 4) Insulation of wire and cables | | 5) Carpet backing |
| 6) Gaskets | 7) Adhesives | 8) Tank-lining |

Butyl rubber:

Preparation:

Butyl rubber is prepared by the aluminum chloride initiated cationic copolymerisation of isobutene with small amount (1-5%) of isoprene.

Properties:

- Under normal conditions, it is amorphous but it crystallizes on stretching.
- It is quite resistant to oxidation due to low degree of unsaturation.
- Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
- It can be degraded by heat or light to sticky low-molecular weight products so stabilization is must.
- Being non-polar, it has good electrical insulation properties.
- Compared to natural rubber it possesses outstanding low permeability to air and other gases.
- It does not crystallize on cooling and hence remains flexible down to -50°C .
- Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (ex: HCl , HF , HNO_3 , H_2SO_4 etc.)

Applications: It is used for

- Insulation of high voltage wires and cables
- Inner tubes of automobile tyres.
- Conveyor belts for food and other materials.
- Lining of tanks
- Hoses

Thiokol rubbers:**Preparation:**

Thiokol is prepared by the condensation polymerisation of sodium polysulfide (Na_2S_x) and ethylene dichloride ($\text{ClCH}_2\text{CH}_2\text{Cl}$). In these elastomers, sulfur forms a part of the polymer chain.

Properties:

- They have excellent resistance to swelling and disintegration by organic solvents and gasoline, kerosene, lubricating oils.
- Outstanding resistance to oxygen ozone, sun light.
- It undergo swelling by benzene and derivatives of benzene.
- It has lower tensile strength and modulus than natural rubber. It tends to lose shape under continuous pressure.
- It has offensive-mercaptan-like odour, that restricts its use.

Applications:

- Manufacture of oil hoses, chemically resistant tubing and engine gaskets.
- Diaphragms and seals in contact with solvents.
- Printing rolls
- Containers for transporting solvents and
- Solid propellant fuels for rockets.

3.13 Fibers:

Fibers are a class of materials that are continuous filaments or discrete elongated pieces. They are highly crystalline form of polymers.

The requisite properties for a natural or synthetic polymer molecule to function as a fiber for use in textile are –

- 1) High tensile strength
- 2) Flexibility
- 3) Abrasion resistance
- 4) Amenability of dyeing
- 5) Chemical stability in terms of resistance to hydrolysis under washing conditions.
- 6) Resistance to degradation on exposure to light

Classification:

Fibers are classified into two types. They are

- 1) Natural fibers
- 2) Artificial fibers (Synthetic fibers)

1) Natural fibers: Natural fibers include the fibers produced by plants, animals and geological material. They are environment friendly and biodegradable. They are –

i) Vegetable fibers: They are cellulosic material like cotton, jute, plant fibers are used for making textiles, ropes, mats, paper bags etc.,

ii) Wood fibers: The strength of a plant is due to the presence of wood fiber. Wood pulp is used in making paper. Wood fibers like jute are used for making bags.

iii) Animal fibers: They are made of protein. Pure silk, wool, hair are animal fibers.

iv) Mineral fibers: Ex: Asbestos, Mica etc.,

2) Synthetic fibers:

Synthetic fibers can be produced in large quantities and cheaper than some of the natural fibers. Fiber forming synthetic polymers include polyamides (nylon6 and nylon – 6,6), polyesters (ex.polyethylene terephthalate, terylene or, Dacron), Polyolefins (Polyacrylo nitrile). Polyethylene, polypropylene are also produced in the form of fibers which are hydrophobic, chemically resistant and difficult to dye and hence used for making ropes.

Polyester:

Synthesis of polyester is achieved by poly condensation of purified terephthalic acid (1,4 – benzene carboxylic acid) and monoethylene glycol.

The esterification is catalysed by the presence of mineral acid like HCl.

Fiber reinforced plastics: (FRP):

The fiber polymers impregnated with solids / fillers to impart mechanical strength and hardness without losing elasticity are known as fiber reinforced plastics (FRP).

Various fillers are known to impart characteristic property to the plastic material.

Ex – 1: Fillers like carborundum, quartz and mica are added to impart hardness and strength.

2) Barium salt fillers are impervious to X-rays.

3) Asbestos fillers added to plastic provide heat and corrosion resistant.

Nature of polymers used for FRP: Both thermoplastics and thermoset plastics are used such as polyethylene, polypropylene, Nylon-6, polyester, melamine.

Applications:

- For making door handles, battery cases, exhaust fans engine cooling fans etc., in automobiles using the base polymers like polyethene, polypropylene, nylon – 6.
- For making nose cones, pistol grips and rifle bullets in defense industries using the base polymers nylon-6 and polystyrene.

- For making shuttle and textiles using nylon-6 as base polymer in textile industries.
- For making the consumer goods like doors, windows, tables, chairs, almyrahs, cameras, housings etc., using polypropylene and acrylobutadiene styrene blended plastics.
- For making computer tape, insulators, wires and cable insulation, switch, gear parts exhaust fans as electrical appliances using the base polymers like polypropylene nylon and styrene acrylonitrile copolymer.
- For making the items like water meters and chemical pump housings, tubings, seat coverings etc., using the base polymers like polypropylene, m PVC and nylon – 6.

UNIT 4 WATER

4.1 Hardness of Water :-

Hard Water : The water which does not produce lather with soap.

Soft Water :- The water which produces lather with soap.

- Hardness of water is due to presence of soluble salts of calcium, magnesium and other heavier metals in water.
- Hard water does not give lather easily with soap, but produces a white scum or precipitate with soap.
- The scum or precipitate is due to the formation of insoluble soaps of calcium and magnesium ions react with soap.
- Hardness of water can be classified as temporary hardness and permanent hardness.

Types of hardness:

Temporary hardness : Temporary hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium. This can be removed by boiling.

Permanent hardness : Permanent hardness is due to presence of chlorides & sulfates of dissolved calcium , magnesium , iron & other heavy metals. The salts responsible for permanent hardening are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$. Permanent hardness cannot be removed by boiling. This is also known as non –carbonate or non – alkaline hardness. The sum of temporary and permanent hardness is referred as total hardness of water.

Although hardness of water is never presence in the form of CaCO_3 as it is insoluble in water hardness of water is conveniently expressed in terms of equivalents of CaCO_3 .

The hardness is expressed in terms of equivalent calcium carbonate.

The reason for choosing CaCO_3 as standard for report in hardness is ease in calculations on its molecular weight is exactly 100.

Units of Hardness :

1. **Parts Per Million :** Parts of CaCO_3 equivalent hardness per 10^6 parts of water.
1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

2. Milligrams per litre :- Number of milli grams of Calcium Carbonate equivalent hardness present in 1 litre of water.
 $1 \text{ mg / L} = 1 \text{ mg of CaCO}_3 \text{ equivalent hardness present in 1 liter of water.}$
 $1 \text{ L} = 1 \text{ Kg} = 1000 \text{ g} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg.}$
 $1 \text{ mg / L} = 1 \text{ mg of CaCO}_3 \text{ eq per } 10^6 \text{ mg of H}_2\text{O}$
 $= \text{ppm}$
3. Clarke's degree : ($^{\circ}\text{cl}$) No of grains (1/700 16) of CaCO_3 equivalent hardness per 70,000 parts of water.
 $1^{\circ}\text{Clarke} = 1 \text{ grain of CaCO}_3 \text{ eq hardness per gallon of water.}$
 $= 1 \text{ part of CaCO}_3 \text{ of hardness per 70,000 parts of water.}$
4. Degree French ($^{\circ}\text{Fr}$) : It is in the parts of CaCO_3 eq hardness per 10^5 parts of water.
5. Milliequivalents per litre : - No of milli equivalents of hardness present per litre.
 $1 \text{ meq/L} = 1 \text{ meg of CaCO}_3 \text{ per / litre of water.}$
 $= 10^{-3} \times 50 \text{ g of CaCO}_3 / \text{litre}$
 $= 50 \text{ mg /L of CaCO}_3 \text{ eq} = 50 \text{ ppm}$

Relation between various units of hardness:

$$1 \text{ ppm} = 1 \text{ mg /L} = 0.1^{\circ} \text{Fr} = 0.07^{\circ}\text{CL} = 0.02 \text{ meq / L}$$

$$1 \text{ mg /L} = 1 \text{ ppm} = 0.1^{\circ} \text{Fr} = 0.07^{\circ}\text{CL} = 0.02 \text{ meq /L}$$

$$1^{\circ} \text{cL} = 1.433^{\circ}\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg /L} = 0.286 \text{ meq /L}$$

$$1^{\circ}\text{Fr} = 10 \text{ ppm} = 10 \text{ mg /L} = 0.7^{\circ}\text{cL} = 0.2 \text{ meq /L}$$

$$1 \text{ meq /L} = 50 \text{ mg /L} = 50 \text{ ppm} = 5^{\circ}\text{Fr} = 0.35^{\circ}\text{CL}.$$

4.2 Estimation of hardness of water:

Hardness of water can be estimated by the following methods:

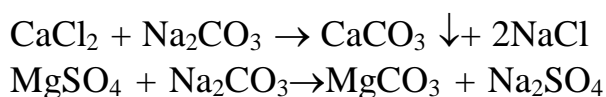
I –O.Hehner's method:

A) Temporary hardness is determined by finding the alkalinity of water before boiling and that left after boiling (temporary hardness is removed by boiling)

Procedure: Pipette out 50ml of water sample in a conical flask, 2-3 drops of methyl orange indicator is added and titrated against N/50 HCl. The volume of acid used is 'V₁ml. 100ml of water sample is taken in a pyrex beaker and evaporated to dryness. About 50ml of distilled water is added, warned,

stirred to dissolve the soluble portions left. The solution is filtered, washed the residue with distilled water. The solution is made up to 100mL. 50mL of this solution is taken in a conical flask and titrated against N/50HCl using methyl orange as indicator. The volume of acid used is 'V₂'mL.

B) Estimation of permanent hardness is based on the fact that it can be removed by boiling with a known excess of standard Na₂CO₃. The chloride and sulphates of calcium and magnesium form insoluble carbonates. The residual sodium carbonate is determined by titrating against a standard acid. The decrease in the amount of soda added is equivalent to permanent hardness.



Procedure: 50ml of the given water sample is taken in the beaker and 50ml of N/50 Na₂CO₃ solution is added. Boiled the solution for 15minutes. Cooled the solution, filtered the precipitate and the filtrate is collected in a conical flask. Titrated the unused Na₂CO₃ present in the flask against N/50 HCL. Using methyl orange as an indicator. The titre value is 'V'

II – Soap Titration Method: (or) Clarks Method:

Principle:

When soap solution is added to hard water, the hardness causing ions (Ca²⁺, Mg²⁺ and other heavy metal ions) are first to react to form a precipitate of insoluble calcium and magnesium soap is obtained.

The process takes place continuously until there is hardness in the sample of water. When all the hardness causing ions have been precipitated, further addition of soap solution gives lather.

Procedure:

Step – 1: Standardisation of sample solution:

The burette is first rinsed and filled with soap solution. In a narrow mouth 250mL glass-stoppered bottle, 50mL of standard water is taken (The hardness of standard hard water is 1g/L). Soap solution is added 0.2mL at a time to this standard hard water solution. After each addition, the contents

of the stoppered bottle are shaken vigorously until lather formation starts. Then the addition of soap solution is made at the rate of 0.1mL at a time till a lather is formed that persists for 2 minutes. Let the volume of the soap solution used is ' V_1 'mL.

Step- 2: Determination of total hardness of water:

The above procedure is repeated by taking 50mL of given water sample (Sample to be analysed.). The volume of the soap solution used in this is ' V_2 'mL.

Step -3: Determination of permanent hardness of water:

250mL of the water sample is taken in 500mL beaker. It is then boiled till the volume reduces to 50mL. (Boiling causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and Mg(OH)_2). The precipitate is filtered and washed with distilled water. Simultaneously, the filtrate and washings are quantitatively collected in a 250mL conical flask. The volume is then made 250mL by adding distilled water. 50mL of this sample is taken and procedure of Step – 1 is repeated titre value of the soap solution be ' V_3 'mL.

Step -4: Determination of lather factor:

50mL of distilled water of zero hardness is titrated with soap solution. The titration is continued till lather is obtained which lasts for 2 minutes. Let the titre value be V_4 mL. This volume must be subtracted from all the litre values.

Calculations:

Step – 1: Standardisation of soap solution:

50mL of standard hard water $\equiv (V_1 - V_4)$ mL of soap solution

50mL of standard hard water contains 50mg of CaCO_3

(Standard hard water contains 1g/L or

1mg/mL CaCO_3)

Thus, $(V_1 - V_4)$ mL of soap solution = 50mg of CaCO_3 eq.

$$1 \text{ mL of soap solution} = \frac{50}{(V_1 - V_4)} \text{ mg of } \text{CaCO}_3 \text{ eq.}$$

Step – 2: Determination of total hardness of water:

50mL of hard water $\equiv (V_2 - V_4)$ mL of soap solution

$$\equiv (V_2 - V_4) \times \frac{50}{(V_1 - V_4)} \text{ mg of CaCO}_3 \text{ eq.}$$

1000mL or 1L of hard water

Determination of hardness of water:

1) Soap solution method (or) soap titration method clark's method:

Soluble soaps consist of sodium (or) potassium salts of higher fatty acids. When soap solution is added to hard water, the hardness causing ions first react to form precipitate of calcium and magnesium soaps which are insoluble in water.

Thus, after all the hardness causing metal ions present in the hard water sample are precipitated, the further addition of soap gives lather.

The total hardness of water sample can be determined by titrating an aliquot of the sample against a standard soap solution in alcohol. The appearance of a stable lather persisting even after shaking for about 2 min marks end point.

The water sample is boiled for 30min to remove temporary hardness and then it is titrated with standard soap solution, the titre value corresponds to permanent hardness of sample.

The difference between the two measurements corresponds to the temporary hardness.

4.3 Estimation of hardness of water by EDTA Method:

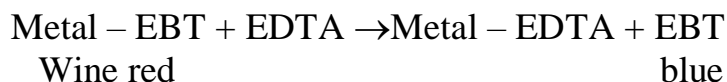
This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

Principle of EDTA titrations:

The quick, complete and 1:1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis for complexometric titrations.

Theory: The hard water is buffer to a p^H value of ~ 10 using $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer and few drops of EBT indicator solution are added. EBT forms a weak complex with metal ions that has a wine-red colour.

During the course of titration of water sample against EDTA, first EDTA combines with free Ca^{2+} or Mg^{2+} ions to give very stable and colour less metal-EDTA Complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator to form Metal-EBT complex.



At the equivalence point, there is change in colour from wine-red to blue.

Procedure:

Step – 1: Standardisation of EDTA solution:

The burette is filled with EDTA solution after washing and rinsing. Pipette out 50mL of standard hard water (1mL of it must contain 1mg of CaCO_3) into a 250mL conical flask, 10mL of buffer solution and 2-3 drops of EBT indicator are added and titrated against EDTA solution until the wine-red colour changes to blue. Let the volume of EDTA solution consumed be V_1 mL.

Step – 2: Determination of total hardness of water:

As per the same procedure (Step-1), 50mL of the unknown water sample is titrated against EDTA. Let the volume of EDTA solution consumed be V_2 mL.

Step -3: Determination of permanent hardness of water:

250mL of the water sample is taken in a 500mL beaker and boiled it till the volume is reduced to about 50mL. [The step causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$]. Filter and wash the precipitate with distilled water and quantitatively collect the filtrate and washings in a 250mL conical flask and made up the volume to 250mL with distilled water. 50mL of this water sample is titrated against EDTA solution as in Step-1. Let the volume of EDTA solution consumed be V_3 mL.

Calculations:

Step – 1: Standardisation of EDTA Solution:

V_1 mL of EDTA = 50mL of standard hard water

= 50mg of CaCO_3 (1mL contains 1mg of CaCO_3)

1mL of EDTA = $50 / V_1$ mg of CaCO_3 equivalent hardness.

Step -2: Determination of total hardness of water:

$$50\text{mL of unknown hard water sample} = V_2\text{mL of EDTA} \\ = V_2 \times 50 / V_1\text{mg of CaCO}_3 \text{ eq.}$$

Step-3: Determination of permanent hardness of water:

$$50\text{mL of boiled water} = V_3\text{mL of EDTA} \\ = V_3 \times 50 / V_1\text{mg of CaCO}_3 \text{ eq.}$$

Step-4: Determination of temporary hardness:

4.4 Scale and sludge formation:

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively.

When the concentration of the dissolved salts reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose/slimy precipitate, it is known as sludge.

If the precipitation takes place in the form of a hard, adhering crust/coating on the inner walls of the boiler, it is known as scale.

Sludge:

It is a soft, loose and slimy precipitate formed within the boiler. It is formed at colder portions of the boiler and collects in the system where the flow rate is slow or at bends. It can be removed very easily by a wire brush. It is formed by the substances that have greater solubility values in hot water than in cold water.

Ex: MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 etc.,

Disadvantages:

- 1) Sludges are poor conductors of heat, hence there is wastage of portion of the heat generated.
- 2) If sludges are formed along with scales, then sludge gets entrapped in the scales and both get deposited as scales.
- 3) Excessive sludge formation disturbs the working of the boiler.

Preventive measures:

- 1) By using softened water
- 2) By frequently 'blow-down operation' (drawing off a portion of the concentrated water).

Scales:

Definition: Scales are hard deposits firmly sticking to the inner surfaces of the boiler.

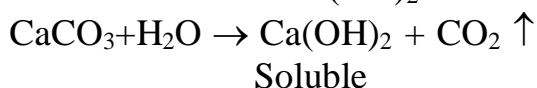
The scales are difficult to remove, even with the help of hammer and chisel and are the main source of boiler troubles.

Formation: The scales may be formed inside the boiler due to –

1) Decomposition of calcium bicarbonate:



The scale consisting of mainly CaCO_3 is soft and is the main cause of scale formation in low-pressure boilers. Whereas in high-pressure boilers, CaCO_3 is soluble due to the formation of Ca(OH)_2 .



2) Deposition of calcium sulphate:

The solubility of CaSO_4 in water decreases with increase in temperature. CaSO_4 is soluble in cold water and almost insoluble in hot water [may be due to increased ionization at high temperature so $K_{sp} < K_{ionic}$ product & less availability of water molecules for solvation at high temperature.]

CaSO_4 gets precipitated as hard scale on the hotter parts of the boiler. This type of scale causes troubles mainly in high-pressure boilers. CaSO_4 scale is quite adherent and difficult to remove even with the help of hammer and chisel.

3) Hydrolysis of magnesium salts:

Dissolved magnesium salts get hydrolysed forming magnesium hydroxide precipitate that forms a soft type of scale.



4) Presence of silica:

Even if a small quantity of SiO_2 (silica) is present. It may deposit as calcium or magnesium silicate (CaSiO_3 and / or MgSiO_3). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages:

1) Wastage of Fuel: Scales have low thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or, over heating is done and this causes increase in the consumption of fuel.

The wastage of fuel depends on the thickness and the nature of scale.

Ex:

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

2) Lowering of boiler safety: Over-heating of boiler is done in order to maintain a steady supply of steam due to the formation of scales. This makes the boiler material softer and weaker. This causes the distortion of the boiler tube and also makes the boiler unsafe.

3) Decrease in efficiency: Scales may deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in the efficiency of the boiler.

4) Danger of explosion: When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in the development of sudden high-pressure that may cause explosion of the boiler.

Removal of scales:

If the scales are loosely adhering, they can be removed by scraper or piece of wood or wire brush.

- If the scales are brittle, they can be removed by thermal shocks i.e, heating the boiler and then suddenly cooling with cold water.
- If the scales are loosely adhering, they can be removed by frequent blow-down operation.
- If the scales are adherent and hard, they can be removed by adding chemicals.

Ex: a) CaCO_3 scales can be removed by dissolving in 5-10% HCl.

b) CaSO_4 scales can be removed by adding EDTA, since the Ca-EDTA complex is highly soluble in water.

Prevention of scale formation:

1) External treatment: The treatment includes efficient 'softening of water' (removing hardness-producing constituents of water)

2) Internal treatment: In this process, an ion is prohibited to exhibit its original character by 'Complexing' or converting into other more stable salt by adding appropriate reagent.

- a) Colloidal conditioning b) Phosphate conditioning
- c) Carbonate conditioning d) Calgon conditioning
- e) Treatment with sodium aluminate (NaAlO_2)
- f) Electrical conditioning g) Radioactive conditioning
- h) Complexometric method.

4.5 Differences between sludges and scales:

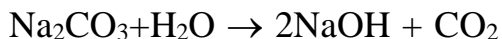
Sludges	Scales
<ol style="list-style-type: none"> 1. Sludges are soft, loose and slimy precipitate 2. Sludges are non-adherent deposits and can be removed easily. 3. Sludges are formed by substances like CaCl_2, MgCl_2, MgSO_4, MgCO_3, etc, 4. Formed at comparatively colder portions of the boiler 5. Decrease the efficiency of boiler but are less dangerous 6. Can be removed by blow-down operation. 	<ol style="list-style-type: none"> 1. Scales are hard deposits 2. Scales stick firmly to the inner surface of boiler and are very difficult to remove. 3. Scales are formed by substances like CaSO_4, Mg(OH)_2 etc., 4. Generally formed at heated portions of the boiler. 5. Decrease the efficiency of boiler and chances of explosions are also there. 6. Cannot be removed by blow-down operation.

Caustic Embrittlement:

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, free Na_2CO_3 is usually present in small portion in the softened water.

In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 . The NaOH produced makes the boiler water “Caustic”.



This caustic water flows into the minute hair-cracks, present in the inner side of the boiler, by capillary action. On evaporation of water, the concentration of dissolved caustic soda increases progressively that attacks the surrounding area, thereby dissolving iron of boiler as sodium ferrate. This causes embrittlement of boiler walls causing even failure of the boiler.

Embrittlement arises due to the setting up of a concentration cell.

With the iron surrounded by dilute NaOH is acting as the cathode whereas the iron surrounded by conc. NaOH is acting as anode. The anode in the anodic part gets dissolved or corroded.

Prevention:

Caustic embrittlement can be prevented

- i) by using sodium phosphate as softening reagent instead of Na_2CO_3 in external treatment of boiled water.
- ii) by adding lignin or tannin to boiler water that blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution in these areas.
- iii) by adding Na_2SO_4 to boiler water:
 Na_2SO_4 blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio.

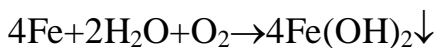
$[\text{Na}_2\text{SO}_4] / [\text{NaOH}]$ is kept as 1:1, 2:1 and 3:1 in boilers working respectively at pressures upto 10, 20 and > 20 atmospheres.

Boiler corrosion:

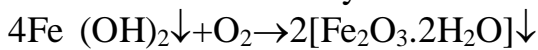
Boiler corrosion is ‘decay’ or ‘disintegration’ of boiler body material by either chemical or, electrochemical reaction with its environment.

Reasons for boiler corrosion:

1) Dissolved oxygen: This is the most usual corrosion causing factor., water usually contains about 8ppm of dissolved oxygen at room temperature. Dissolved oxygen reacts with iron of boiler in the presence of water and under prevailing high temperature to form ferric oxide (rust).



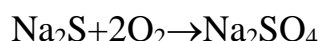
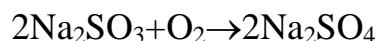
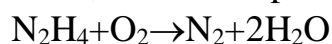
Ferrous hydroxide



Rust

Removal of dissolved oxygen:

- i) By adding calculated quantity of hydrazine or, sodium sulphite or, sodium sulphide

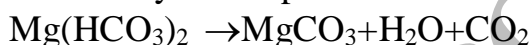


- ii) By mechanical deaeration: The process consists of spraying water over preheated perforated plates stacked in a tower. Removal of dissolved oxygen is ensured by applying high temperature and vacuum.

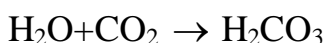
2) Carbon dioxide: Two sources of CO_2 in boiler water are –

a) dissolved CO_2 in raw water and

b) CO_2 formed by decomposition of bicarbonates.

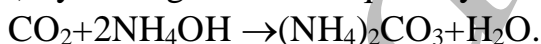


In the presence of water., CO_2 forms carbonic acid that has a corrosive effect on the boiler material like any other acid.



Removal of CO_2 :

- i) By adding calculated quantity of ammonium hydroxide



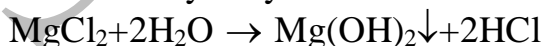
- ii) Mechanical de-aeration along with oxygen'

- iii) by filtering water through line stone

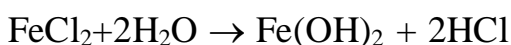
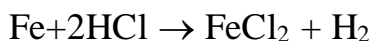


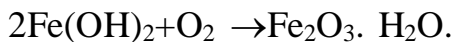
But this method increases hardness.

3) Mineral acids: Water containing dissolved magnesium salts (MgCl_2) liberate acids on hydrolysis.



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust.





Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Presence of even a small amount of MgCl_2 cause corrosion of iron to a large extent.

Disadvantages of corrosion:

- 1) Shortening of boiler life.
- 2) Leakage of the joints and revents.
- 3) Increased cost of repairs and maintenance.

4.6 Priming and foaming:

Priming:

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along with steam. The process of 'wet-steam' formation is known as 'priming'

Priming is caused by –

- 1) the presence of large amount of dissolved salts
- 2) high steam velocities.
- 3) sudden boiling
- 4) improper boiler design
- 5) sudden increase in steam-production rate.

Priming can be avoided by-

- 1) controlling rapid change in steaming velocities.
- 2) proper design of boilers.
- 3) ensuring efficient softening
- 4) filtration of the boiler-water carried over to the boiler
- 5) by blowing off sludges or, scales from time to time.
- 6) by maintaining low water levels in boilers.

Foaming:

The formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily.

Foaming is caused by the presence of an oil and alkalis in boiler-feed water

Foaming can be avoided by

- 1) the addition of anti-foaming agents like castor oil.
- 2) the removal of foaming agent (oil) from boiler water

Reverse osmosis:

Osmosis is the phenomenon by which flow of solvent takes place from a region of low concentration when two solutions of different concentrations are separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is osmotic pressure.

However, if a hydrostatic pressure in addition to osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis for reverse osmosis.

For practical purposes, semi-permeable membrane based on thin films of cellulose acetate, polymethyl acrylate and polyamide polymers are used, a pressure of the order of $15\text{--}40\text{ kg/cm}^2$ is applied for separating the water (pure solvent) from its contaminants. The process is also known as super filtration or hyper filtration.

Advantages:

- 1) Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
- 2) Colloidal SiO_2 can be removed by reverse osmosis which even cannot be removed by demineralization.
- 3) It is a simple and reliable process.
- 4) Capital and operating expenses are low.
- 5) The life of semi-permeable membrane is about 2 years and it can be easily replaced within few minutes, thereby nearly uninterrupted water supply can be provided.

Electrodialysis:

Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes, through ion-selective membranes under the influence of applied EMF.

The unit consists of electrodes (cathode and anode) and thin, rigid ion-selective membranes which are permeable to either cation or anion. The anode is placed near the anion-selective membrane while the cathode is placed near the cation-selective membrane.

Under the influence of an applied emf across the electrodes, the cations (Na^+) move towards the cathodes through cation selective membrane and anions (Cl^-) move towards the anode through anion selective membrane. The net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water is replaced by fresh samples.

For practical purposes, an electrodialysis cell is used.

It consists of large number of paired sets of ion-selective membranes. Under a pressure of about $5\text{-}6\text{kg/m}^2$, saline water is passed in and we get alternate streams of pure water and concentrated brackish water.

Advantages of desalination of electrodialysis:

- 1) The process is economical as per the capital cost and operational expenses are concerned.
- 2) The unit is compact and the method is best suited.

4.7. Softening of water:

Definition: The process of removing hardness-causing salts from water is known as “Softening of water”.

Internal treatment:

Internal treatment means treating the raw water inside the boiler. In this process (sequestration), an ion is prohibited to exhibit its original character by ‘complexing’ or converting it into other more soluble salt by adding appropriate reagent. This can be done by two processes.

- A) Appropriate chemicals are added to the boiler water to precipitate the scale-forming impurities in the form of ‘sludges’ which can be removed by blow-down operation.
- B) Problem causing cations are converted into compounds that will stay in “dissolved form” in water and thus do not cause any harm.

Internal treatment methods are –

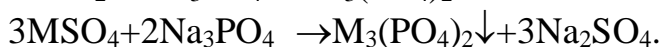
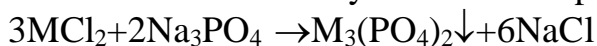
1) Colloidal conditioning:

Scale formation can be avoided in low-pressure boilers by adding organic substances like kerosene, tannin, agar-agar etc., that get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, these can be removed easily by blow-down operation.

2) Phosphate conditioning:

It is applicable to high-pressure boilers. Formation of scales is avoided by adding sodium phosphate, that reacts with magnesium and calcium salts to form non-adherent and easily removable, soft sludge of calcium and magnesium phosphate.

This can be removed by blow-down operation.



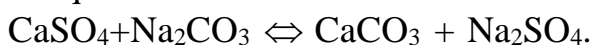
Where M = Mg^{2+} or Ca^{2+}

The main phosphates employed are –

- NaH_2PO_4 – sodium dihydrogen phosphate (acidic)
- Na_2HPO_4 – disodium hydrogen phosphate (weakly alkaline)
- Na_3PO_4 – trisodium phosphate (alkaline)

3) Carbonate conditioning:

In low-pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, when salts like CaSO_4 are converted into CaCO_3 in equilibrium.



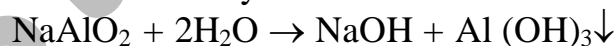
Deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 that can be removed by blow-down operation.

4) Calgon conditioning:

The method involves the addition of sodium hexameta phosphate (Calgon) to boiler water to prevent the formation of scale and sludge. Calgon converts the scale forming impurity like CaSO_4 into soluble complex compound.

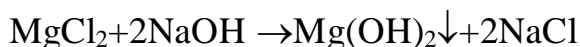
5) Treatment with sodium aluminate (NaAlO_2):

Sodium aluminate gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminium hydroxide.



Sodium aluminate gelatinous precipitate

The sodium hydroxide formed precipitates some of the magnesium as $\text{Mg}(\text{OH})_2$.



The flocculent precipitate of $\text{Mg}(\text{OH})_2 + \text{Al}(\text{OH})_3$ produced inside the boiler, entraps finely suspended and colloidal impurities. The loose precipitate can be removed by blow-down operation.

6)Electrical conditioning:

Sealed glass bulbs having mercury connected to a battery are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, that prevents scale forming particles to adhere/stick together to form scale.

7)Radioactive conditioning:

Tablets having radioactive salts are placed inside the boiler water at a few minutes. The energy radiations emitted by these salts prevent formation of scales.

8)Complexometric method:

The method involves 1.5% alkaline(pH8.5) solution of EDTA to feed water. The EDTA binds the scale forming cations to form stable and soluble complex. As a result, the sludge and scale formation.

The treatment

- a)Prevents the deposition of iron oxides in the boiler,
- b)Reduces the carry over of oxides with steam,
- c)Protects the boiler units from corrosion by wet steam.

4.8 Methods used for softening of water:

- 1)Lime-soda process
- 2)Zeolite or, permutit process
- 3)Ion exchange process

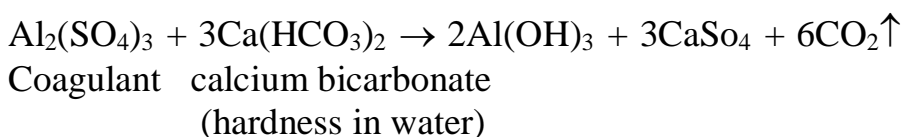
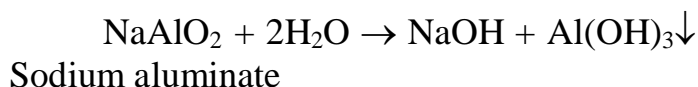
1)Lime-soda process:

In this method, the soluble calcium and magnesium salts in water are converted chemically into insoluble compounds by adding calculated amounts of lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$. Precipitates of calcium carbonate $[\text{CaCO}_3]$ and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ formed are filtered off.

i)Cold lime-soda process:

In this method, calculated quantity of lime and soda are mixed with water at room temperature. At room temperature, the precipitates formed

are finely divided so they do not settle down easily and cannot be filtered easily. Hence, small amounts of coagulants like alum, aluminium sulphate, sodium aluminate etc, that hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide and entraps the fine precipitates. Sodium aluminate as a coagulant helps the removal of silica as well as oil. Cold Lime-soda process provides water having a residual hardness of 50-60ppm.



Method:

Raw water and calculated quantities of chemicals (lime+soda+coagulant) are fed from the top into the inner vertical circular chamber fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, thereby softening of water takes place. As the softened water comes into the outer co-ocial chamber, it rises upwards, the heavy sludge settles down in the outer chamber. Then the softened water passes through a filtering media to ensure the complete removal of sludge. Finally filtered soft water flows out continuously through the outlet at the top. Sludge settled at the bottom of the outer chamber is drawn off.

ii) Hot Lime-soda process:

The process involves in treating water with softening chemicals at a temperature of 94-100°C, since hot process is operated at a temperature close to the boiling point of the solution. So-

- The reaction proceeds faster.
- The softening capacity of hot process is increased to many fold.
- No coagulants are needed as the precipitate and sludge formed settle down rapidly.
- Most of the dissolved gases are driven out of the water.
- Filtration of water becomes much easier as the viscosity of softened water is lower. This in turn increases the filtering capacity of filters.

Hot lime-soda process produces water of comparatively lower residual hardness of 15-30ppm.

Hot lime-soda plant consists of mainly 3 parts.

- a) a “reaction tank” in which raw water, chemicals and steam are thoroughly mixed.
- b) a “Conical sedimentation vessel” in which the sludge settles down.
- c) a “ sand filter” that ensures complete removal of sludge from the softened water.

Differences between Hot and Cold lime-soda process:

S.No	Cold Lime-Soda Process	Hot Lime-Soda Process
1	It is done at room temperature (25-30°C)	1. It is done at elevated temperature (94-100°C).
2	It is a slow process	2. It is a rapid process.
3	Use of coagulants is must.	3. Coagulants are not needed.
4	Filtration is not easy.	4. Filtration is easy as the viscosity of water becomes low at elevated temperatures.
5	Softened water has residual hardness around 60ppm	5. Softened water has residual hardness of 15-30ppm.
6	Dissolved gases are not removed	6. Dissolved gases like CO ₂ are removed to some extent.
7	Low softening capacity	7. High softening capacity

Advantages of Lime-soda process:

- Lime-soda process is economical.
- Treated water is alkaline and hence has less corrosion tendencies.
- Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.

- It removes not only hardness causing salts but also minerals.
- Iron and manganese are also removed from the water to some extent.
- If the process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.

Disadvantages:

- The process requires careful operation and skilled supervision for economical and efficient softening.
- Sludge disposal is a problem.
- The process can remove hardness only upto 15ppm, which is not good for high pressure boilers.

4.9 Zeolite or, permutit process:

Zeolites are naturally occurring hydrated sodium aluminosilicate minerals (like Na_2O , Al_2O_3 , $x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2-10$ and $y=2-6$) capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Zeolites are known as permutits and in greek it means “boiling stone”.

Zeolites are of two types.

i) Natural zeolites:

These are non-porous, amorphous and durable

Ex: natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

ii) Synthetic zeolites: These are porous and possess a gel structure. Prepared by heating together sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2)

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

Process:

For softening of hard water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite.

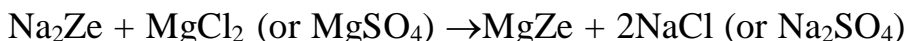
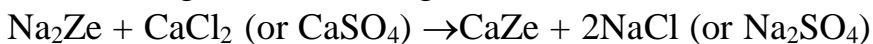
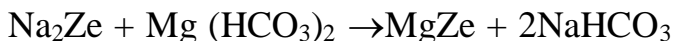
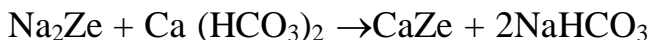
Zeolite holds sodium ions loosely and can be represented as Na_2Ze .

Where Ze =insoluble radical frame work.

The hardness causing ions (Ca^{2+} , Mg^{2+}) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts.

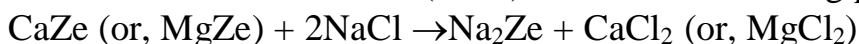
During this process, the water becomes free from Ca^{2+} and Mg^{2+} ions.

Reactions taking place during the softening process –



Regeneration:

After some time, the zeolite is completely converted into calcium and magnesium zeolites. Hence the bed ceases to soften water i.e, it gets exhausted, at this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated solution of sodium chloride(brine). The reaction taking place is



Exhausted zeolite brine reclaimed zeolite washings

The washings are led to drain and thus the regenerated zeolite bed is used again for softening purpose.

The working of zeolite softeners involve alternate cycles of softening run and the regeneration run. The scheme for softening and regeneration processes are represented as below.

Limitations of zeolite process:

- If the supplied water is turbid, the suspended matter must be removed before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.
- If water contains large quantities of coloured ions like Mn^{2+} and Fe^{2+} , they must be removed because these ions produce manganese and iron zeolites that cannot be regenerated easily.
- If mineral acids are present in water, they destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.
- The water to be softened should not be hot as the zeolite tends to dissolve in it.
- Anions are not removed by this process. The bicarbonates present in hard water get converted to NaHCO_3 that goes into soft water effluent. If it is used as boiler feed, under the boiler conditions NaHCO_3 dissociates to



- Both the products are not desirable. Since NaOH may lead to caustic embrittlement and CO₂ makes the condensed water into acidic and corrosive. Thus, it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.
- Compared to ion-exchange process, water treated by zeolite process contains 25% ore dissolved salts. The higher cost of the plant and materials are also limiting factors.

Advantages:

- The hardness is nearly completely removed and water of about 10ppm hardness is produced.
- The equipment used is compact and occupies less space.
- It is quite clean and rapid process that requires less time for softening.
- Less skill is needed for maintainance as well as operations.
- Impurities are not precipitated, so there is no danger of sludge formation.
- The process automatically adjusts itself to waters of different hardness.

Comparison of zeolite process with lime-soda process:

Zeolite process	Lime-soda process
1. The process produces water of 10-15ppm residual hardness.	1. Depending on whether it is hot or cold process, water of generally, 15-50ppm residual hardness is obtained.
2. Water treated by zeolite process contains large amounts of sodium salts than in the original raw water.	2. Treated water contains lesser percentage of sodium salts.
3. The cost of plant and zeolite are higher. Hence the capital cost is higher.	3. The capital cost is lower
4. Operation expenses are lower as NaCl(cheap) is used for regeneration.	4. Operation expenses are higher as costly chemicals are consumed.
5. The method cannot be used for treating acidic water, because the zeolite undergoes disintegration	5. There is no such limitation
6. The plant occupies less space as it is compact.	6. Plant occupies more space, as it depends on the amount of water to be softened.
7. The raw water to be softened	7. The process is form such limitation
	8. The process cannot be operated under pressure.
	9. The process involves difficulty

<p>must be free from suspended matter; otherwise the pores of zeolite material are blocked and the bed loses its exchange capacity.</p> <p>8. It can operate under pressure and can be designed for fully automatic operation.</p> <p>9. The process involves no problem of settling, coagulation, filtration and removal of the sludges and precipitates.</p> <p>10. Control test comprises only in checking the hardness of treated water. The process adjusts itself to water of different hardness.</p> <p>11. Treated-water contains more NaHCO_3 that creates problem when used as feed water in boilers.</p>	<p>in settling, coagulation, filtration and removal of precipitates.</p> <p>10. In order to meet the changing hardness of incoming water, frequent control and adjustments of reagents is needed.</p> <p>11. Treated water is completely free from NaHCO_3 because it is removed in the form of insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$.</p>
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4.10 Ion-exchange process:

Ion exchange is “a process in which ions held on a porous, essentially insoluble solid are exchanged for ions in solution that is brought in contact with it”.

Ion exchange resins:

The ion exchange resins are insoluble, cross-linked, high molecular weight organic polymers with a porous structure. The functional groups attached to the chains are responsible for ion-exchange properties.

Classification:

The ion-exchange resins may be classified as –

A) Cation exchange resins (R^-H^+): These resins are mainly styrene divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water. Such resins have acidic functional groups like – SO_3H , – COOH , – OH (phenolic) capable of exchanging the cationic portion of minerals by their hydrogen

ions and hence they are termed as cation exchangers. Ex: Amberlite IR-120, Dowex – 50

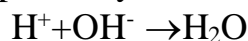
B) Anion exchange resins (R^+OH^-): These resins are styrene-divinyl benzene or amine-formaldehyde copolymers that contain basic functional groups like amino or quaternary ammonium ($-^+NR_3$) or quaternary phosphonium or tertiary sulphonium groups an integral part of the resin matrix. These resins after treatment with dilute NaOH solution, become capable of exchanging their OH^- ions with anions in water and therefore known as anion exchangers.

Ex: Amberlite – 400, Dowex-3

The hard water is first passed through cation exchange column, when all the cations like Ca^{2+} , Mg^{2+} are removed from it and the equivalent amount of H^+ ions are released from the column to water.

After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO_4^{2-} , Cl^- present in the water are removed and equivalent amount of OH^- ions are released from the column to

H^+ and OH^- ions released from cation exchange and anion exchange columns respectively combine to form water molecule.



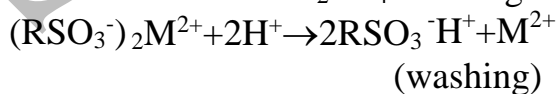
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as deionized or demineralized water. It is also free from acidity or alkalinity. Thus it is as pure as distilled water.

Finally, the demineralized water is passed through a degasifier, a tower whose sides are heated and which is connected to a vacuum pump. High temperature and low pressure reduces the amount of dissolved gases like CO_2 and O_2 in water.

Regeneration:

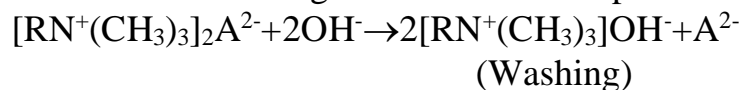
When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, then they are said to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of dilute HCl or H_2SO_4 . The regeneration can be represented as



The column is washed with deionized water and washing is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dilute NaOH solution. The regeneration can be represented as



The column is washed with deionized water and washing is passed to sink or drain.

Then the regenerated ion exchange resins are used again.

Advantages:

- i) The process can be used to soften highly acidic or, alkaline waters.
- ii) The process produces water of very low hardness (2ppm), SO, the treated water is very good for use in high pressure boilers.

Disadvantages:

- i) Capital cost is high since chemical and equipment both are costly.
- ii) If water contains turbidity then the efficiency of the process is reduced.

S.No	Characteristic	Ion-exchange process	Zeolite process	Lime-soda process
1	Requirements	Cation and anion exchangers	Zeolite	Lime, soda and coagulants
2	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions
3	Capital cost	Very high	High	Low
4	Operating expenses	High	Low	High
5	Raw water	i) Should be non-turbid ii) Both acidic or alkaline water can be treated iii) Prior knowledge of hardness not	i) Should be non-turbid ii) Should not be acidic iii) Prior knowledge of hardness not required.	Prior knowledge or hardness is essential

		required		
6	Automation	Possible	Possible	Not possible
7	Residual hardness	Least (0-2ppm)	Low (0-15ppm)	High (15-50ppm)

UNIT 5 SURFACE CHEMISTRY

5.1 Adsorption and types of adsorption

The phenomenon of accumulation of a substance on the surface of a solid or a liquid is known as adsorption.

Terms:

1. **Absorption:** A substance is uniformly distributed throughout the body.
Example: water vapors are absorbed by anhydrous CaCl_2 .
2. **Adsorption :** The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption.
Example: charcoal when mixed with a colored solution of sugar, adsorbs the coloring matter and is used as decoloriser.
3. **Adsorbent:** The solid that takes up a gas or vapor or a solute from a solution is known as adsorbent.
4. **Adsorbate:** The gas or vapor or the solute that is held at the surface of the solid is known as adsorbate.

Difference between absorption and adsorption:

Absorption	Adsorption
(1) A substance is uniformly distributed throughout the body.	(1) It is the phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid or liquid.
(2) It is a bulk phenomenon	(2) It is a surface phenomenon
(3) it is a slow process	(3) It is a fast surface
(4) Attainment of equilibrium takes some time.	(4) Equilibrium is attained easily.
(5) It requires porous structure in a substance that absorbs simple molecules.	(5) It depends on the surface area of the adsorbent.

Types of adsorption:

(1) Physical adsorption or van der waal's adsorption:

When a gas is adsorbed on the surface of a solid by van der waal's forces without resulting in the formation of any chemical bond between the adsorbate and adsorbent, it is known as physical adsorption or van der waal's adsorption.

- (i) Physical adsorption is characterized by low heats of adsorption i.e. about 20-40 kJ/mole.
- (ii) This is reversible.
- (iii) Increase of pressure causes more gas to be adsorbed and the release of pressure frees the adsorbed gas.
- (iv) Decrease of temperature increases adsorption but the gas adsorbed at low temperature can be freed again by heating.
- (v) Physical adsorption is usually multilayer.
- (vi) In physical adsorption, the adsorbate molecules are held by comparatively weak van der waal's forces. Hence, the activation energy of desorption is very low.
- (vii) Physical adsorption occurs appreciably at very low temperatures i.e. below the boiling point of the adsorbate.
- (viii) Physical adsorption takes place between every gas and a solid i.e. is not specific in nature because it involves van der waal's forces.

(2) Chemical adsorption or chemisorption:

When a gas is held on the surface of a solid by forces similar to that of a chemical bond, the type of adsorption is known as chemical adsorption or chemisorption.

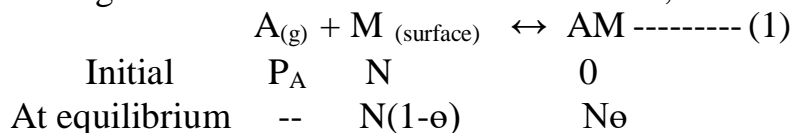
- (i) The fact that forces involved are similar to those of a chemical bond is confirmed by the fact that the heats evolved during chemisorption are high i.e. 40-400 kJ/mole.
- (ii) The magnitude of chemisorption increases with the rise in temperature.
- (iii) The chemisorption is irreversible.
- (iv) Chemisorption is specific in nature.
- (v) Chemisorption is monolayer since the chemical forces operate within short distance only.
- (vi) In chemisorption the adsorbate molecules are held by comparatively strong valence forces. Hence, the activation energy of desorption is very high.

5.2 Langmuir adsorption isotherm:

Langmuir considered the surface of the solid to be made up of elementary sites each of which adsorb one gas molecule. It is assumed that all adsorption sites are equivalent and the ability of the gas molecule to get bound to any one site is independent whether the neighboring sites are occupied or not.

It is also assumed that a dynamic equilibrium exists between the adsorbed molecules and free molecules.

If A is the gas molecule and M is the surface site, then



Where k_a and k_d are the rate constants for adsorption and desorption respectively.

P_A = pressure of gas molecule A

N = total number of sites

$N\theta$ = number of adsorbed molecules

$N(1-\theta)$ = number of vacant sites on surface and

θ = fraction of surface sites occupied by the gas molecules

Rate of adsorption \propto pressure of A (P_A)

\propto number of vacant sites on the surface ($N(1-\theta)$)

Therefore, the rate of adsorption $\propto P_A N(1-\theta)$

$$= k_a P_A N(1-\theta) \text{ ---- (2)}$$

Rate of desorption \propto number of adsorbed molecules ($N\theta$)

Therefore, rate of desorption = $k_d N\theta$

At equilibrium,

Rate of adsorption = rate of desorption

$$k_a P_A N(1-\theta) = k_d N\theta$$

$$k_a/k_d P_A (1-\theta) = \theta$$

$$K P_A (1-\theta) = \theta$$

$$\theta = \frac{K P_A}{1 + K P_A}$$

This equation is known as Langmuir adsorption isotherm.

Multilayer adsorption and BET Theory:

The theory of multilayer adsorption is proposed by Stephen Brunauer, Paul Emmet and Edward Teller (BET Theory, 1938).

Assumptions:

- (1) Physisorption results in the formation of multilayer adsorption.
- (2) The solid surface has uniform sites of adsorption and that adsorption at one site does not affect adsorption at neighbouring sites.

After the formation of monolayer, the adsorption can continue with the formation of multilayer involving the second layer, third layer and so on. The surface area available for the n^{th} layer is assumed to be the same as that for $(n-1)^{\text{th}}$ layer.

The BET equation derived on the basis of the above assumptions is

The constant 'C' depends on the nature of the gas at a given temperature T and is given by the expression

$$C = \exp(E_1 - E_L)/RT$$

Where

E_1 = energy of adsorption in the first layer = constant

E_L = energy of adsorption of the succeeding layers
= heat of liquefaction of the gas

The volume V_m is a constant for a given adsorbate gas-adsorbent system and 'C' is also a constant for the given gas.

Determination of surface area of solids:

The BET method is widely used in the calculation of surface areas of adsorbents.

The total surface area, S_{total} is obtained by the following equation.

5.3 Applications of adsorption:

- (1) Activated charcoal is used in gas masks in which all toxic gases and vapors are adsorbed by the charcoal while pure air passes through its pores practically unchanged.
- (2) Animal charcoal is used as decoloriser in the manufacture of cane sugar.
- (3) Adsorption plays an important role in the heterogeneous catalysis.
Ex. The role of finely divided iron in the manufacture of ammonia.
- (4) Recovery and concentration of desired solutes as part of downstream processing in chemical and biochemical industries.
Ex. Adsorption of antibiotics, fine chemicals, proteins etc
- (5) Purification of organic products by adsorbing coloring matter and impurities.
Ex. Refining of edible oils, sugar etc.

- (6) Removal/recovery and concentration of metals from industrial effluents.
- (7) Separation of compounds of a mixture by adsorption both in column chromatography as well as in thin layer chromatography for analytical purposes.
- (8) Ion-exchange adsorption process.
Ex. (a) demineralization of water.
(b) separation of lanthanides by adsorption followed by eluting out with chelating buffers.
- (9) Use of surface active agents in detergents, paints, lubrication, water proofing, surface cleaners etc.,
- (10) Charcoal adsorption filters are used for removing organic matter from drinking water.
- (11) Fuller's earth is used in large quantities for refining petroleum and vegetable oils due to its good adsorption capacity for unwanted materials.
- (12) Adsorption process is used by using activated charcoal in Dewar's flask.
- (13) In cloth dying, mordants like alums are used that absorb the dye particles.
- (14) Silica and alumina gels are used as absorbent for removing moisture and for controlling room humidities.
- (15) In medicine: For the treatment of arsenic poisoning, colloidal $\text{Fe}(\text{OH})_3$ is administered that adsorbs the arsenic poison and can be removed from the body by vomiting.

5.4 Colloids

Graham classified all the substances into crystalloids and colloids on the basis of diffusion experiments.

- (1) Crystalloids are the substances that diffuse readily through semi permeable membrane (vegetable or animal) and which can be obtained in the crystalline form easily.
Ex. Sugar, urea, potassium hydroxide, magnesium sulphate etc.
- (2) Colloids are the substances that diffuse very slowly in solution. The colloids are the substances whose particles show little or no tendency to diffuse through semi permeable membrane.
Ex. Starch, gums, glue, gelatin, albumin etc.
Ostwald regarded colloidal solutions as heterogeneous two-phase system that consists of dispersed phase in a dispersion medium.

Classification of Colloids:

Colloidal solutions are generally known as sols. Colloidal solutions can be classified into two categories based on the affinity of the two phases.

- (1) Lyophilic sols or solvent-loving sols are the sols in which the dispersion medium has greater affinity for the dispersed phase.
Ex. Starch, gelatin, glue, and agar sols in water.
- (2) Lyophobic sols or solvent hating sols: These are the sols in which there is no apparent affinity between the dispersion medium and the dispersed phase.
Ex. Gold sol, silver sol, arsenic sulfide sol in water.

Electrical properties of colloids:

- (1) **Electrophoresis** : U-tube is partly filled with a colloidal solution of $\text{Al}(\text{OH})_3$ and the rest of the U-tube is filled by distilled water.
When a potential difference is applied, positively charged $\text{Al}(\text{OH})_3$ colloidal particles move towards cathode. At cathode, those particles get coagulated or precipitated by losing their charge.
“The movement of the colloidal particles under the influence of an applied electric field is known as electrophoresis”.
If the movement of colloidal particles is towards cathode, it known as cataphoresis.
The speed of colloidal particles when the applied field strength is 1 volt m^{-1} is known as electrophoretic or cataphoretic mobility.
The electrophoretic mobility depends upon the molecular size of the colloidal particles. The difference in the electrophoretic mobility is used in the separation of mixtures.

- (2) **Electro osmosis:**

“The phenomenon of movement of the dispersion medium of a colloidal solution under the influence of electric field when the dispersed particles are prevented from moving is known as electro osmosis”.

The rate at which the dispersion medium moves is a measure of the electro osmosis.

- (3) **Isoelectric point:**

The charge in the case of proteins, amino acids, polypeptides is a function of pH of the medium.

Due to the protonation of the basic groups of the molecules in acidic medium, the molecules have positive charge while due to the

ionization of the acidic groups in alkaline medium, the molecules have negative charge.

“The pH at which the net charge on the molecule is zero is known as isoelectric point “.

The molecule at the isoelectric point exist as zwitter ions. At the isoelectric point of lyophilic sol, the particles of the dispersed phase do not migrate either to cathode or to anode when subjected to electric field.

At the isoelectric point, coagulation of colloidal particles starts.

5.5 Optical properties:

Tyndall effect:

If a beam of light is passed through colloidal solution in dark, the solution becomes luminescent when viewed through microscope at right angles to the path of the incident. This phenomenon of scattering of light by colloidal particles is known as **Tyndall effect**.

It is found that the scattered beam to be polarized and the intensity of the scattered light by a colloidal solution is related to the concentration of the dispersed phase particles(N), radius of the particles(r) and the wavelength of light.

Tyndall effect is used in R&D. It also proves the heterogeneous character of the colloidal system.

Applications of colloids in industry:

- (1) Emulsion polymerization for the synthesis of polymers.
- (2) Fiber dyeing.
- (3) In warfare: Animal charcoal is used in gas masks for adsorption of poisonous gases.
- (4) Tanning of leather:
- (5) In the bread baking industry.
- (6) Colloidal antimony is an effective medicine for kalaazar.
- (7) Clotting of blood by alum or ferric chloride solution.
- (8) Colloidal sulfur is used as a germ killer for plants.
- (9) Smoke precipitation.
- (10) Removal of dirt from sewage.
- (11) Purification of water
- (12) Electroplating of rubber.

5.6 Nano materials-Introduction

The term nano materials is used to describe the preparation and applications of materials with at least one dimension in the nanometer (10^{-9}m) scale range. Nano science and nanotechnology are emerging areas of technological importance with profound impact on a variety of physical sciences, engineering, biology and medical fields.

The unique properties of nano materials have been attributed to two important characteristics. They are

- (1) Large surface area.
- (2) Size effect or quantum effect.

Examples:

- (1) Nano materials and clusters of metals, semi conductors and magnetic materials.
- (2) Nano particles of ceramic oxides and two-dimensional arrays of metals, semiconductors and magnetic materials.
- (3) Nano tubes of carbon and layered metal chalcogenides.
- (4) Thin films and surfaces of a wide variety of materials.
- (5) Super lattices of 3-dimensional structures of metals, semiconductors and magnetic materials.

Preparation of nanomaterials:

There are two broad approaches for the preparation of nano materials. They are

- (1) Top-down approach
- (2) Bottom-up approach
 - (1) Top-down approach involves mostly mechanical and electromechanical methods for cutting down the bulk materials to give colloid sized particles which are stabilized by protecting agents.
 - (2) Bottom-up approach involves mostly wet chemical methods such as chemical reduction of metal salts, electrochemical methods, controlled decomposition of meta stable organo metallic compounds. This make use of self-assembly and self-organization capabilities of molecules to build nano materials.

Synthetic methods for the preparation of nano particles and nano crystals:

- (1) Precipitation methods:
- (2) Thermolysis of organometallic compounds.
- (3) Hydrothermal or solvothermal synthesis.
- (4) Vapor phase reactions
- (5) Sonochemical reduction.

Nano tubes and nano wires can be prepared by

- (1) Nano wire growth in vapor phase:
 - (a) Vapor-liquid-solid growth
 - (b) Oxide-assisted growth
 - (c) CVD thermal processes.
- (2) Solution based methods:
 - (a) Template-based synthesis
 - (b) Solution-liquid-solid process
 - (c) Solvothermal synthesis.

5.7 Applications of nano materials:

- (1) Catalytic activity of nano particles in the form of colloids and nano clusters have been investigated in different reactions in homogeneous as well as heterogeneous phases.
- (2) Potential applications of nano particles as zero-dimensional quantum dots have been reported in the design of new super conductors.
- (3) Nano particles are potential components in the generation of biometallic nano structures and nano mechanical devices based on DNA.
- (4) Nano tubes are used in drug delivery vessels.
- (5) Nano wires exhibit distinct optical, chemical, thermal and electrical properties because of their large surface area.

UNIT 6 ENERGY SOURCES

6.1 Fuels:

Definition:

- (1) A fuel may be defined as any combustible substance which during combustion gives a large amount of industrially and domestically useful heat.
- (2) A fuel may be defined as energy rich chemical which yields energy by a process of combustion and get converted to energy poor compound.
- (3) A fuel may be defined as any combustible substance which (a) is insoluble in bulk (b) may be burnt in atmospheric air to evolve heat capable of using in domestic and industrial purposes.

Classification:

- (A) Classification based on the occurrence:
 - (i) Primary or natural fuels: The fuels which occur in nature as such.
Example: wood, coal, peat, lignite, anthracite, petroleum, natural gas etc.
 - (ii) Secondary or artificial fuels: The fuels which are derived from the primary fuels.
Example: coke, kerosene oil, petrol, coal gas, pulverized coal, Thiokol, hydrazine, liquefied petroleum gas (LPG) etc.
- (B) Classification based on the physical state:
 - (i) solid fuels
 - (ii) liquid fuels
 - (iii) gaseous fuels

A complete classification of fuels with suitable examples is represented in **Table**.

Classification of Fuels

Type of Fuel	Solid Fuels	Liquid Fuels	Gaseous Fuels
Primary or Natural fuels	Wood, peat, lignite, brown coal, anthracite, oil shales, tar sands, bitumen	Crude oil or petroleum	Natural gas
Secondary or Artificial Fuels	Charcoal, coke, semicoke, petroleum coke, pulverized coal, colloidal fuels, solid rocket fuels like Thiokol, hydrazine, nitro cellulose etc.	Gasoline or motor spirit, diesel, kerosene, coal tar, and its fractions, alcohols and synthetic spirits	Coal gas, coke oven gas, water gas, producer gas, carbureted water gas, oil gas, biogas, blast furnace gas, refinery oil gas, synthetic gas, acetylene and liquid petroleum gas(LPG)

6.2 Characteristics of a Good Fuel:

- (1) **High calorific value:** The calorific value of a fuel is the direct measure of its efficiency of a fuel. If the calorific value of the fuel is high, the fuel is said to be more efficient. Therefore, a good fuel must have high calorific value.
- (2) **Moderate ignition temperature:** Ignition temperature is the minimum temperature to which the fuel is to be heated to start combustion. The fuel having very low ignition temperature causes fire hazards during handling, applications, storage and transportation. It is very difficult to ignite the fuel with ignition temperature. Hence moderate ignition temperature is the most desired property of the fuel.
- (3) **Low moisture content:** The presence of high percentage of moisture in the fuel reduces the efficiency of a fuel. It also increases the ignition temperature and fuel cost. It decreases the calorific

value since some of the heat produced is utilized to vaporize the moisture. Hence the moisture content in a good must be at negligible level.

- (4) **Low ash content:** Formation of ash during combustion is due to the presence of inorganic matter in the fuel. High ash content in the fuel causes the following problems.
- (a) lowering the calorific value.
 - (b) problems in disposal.

Hence, a good fuel must be free from ash content.

- (5) **Combustion control:** A large wastage of valuable fuel can be avoided by
- (a) regulating the combustion rate properly and
 - (b) stopping the process immediately as when desired.

- (6) **Ease of availability:** Fuel must be readily available in abundant and its cost must be minimum.

- (7) **Harmless combustion products:** A good fuel must not produce harmful combustion products like CO, SO₂, NO, H₂S, smoke and clinkers during combustion. Therefore, a good fuel must burn with clean flame without producing undesirable by products.

- (8) **Low cost.**

- (9) **Easy to transport.**

- (10) **Low storage cost.**

- (11) **Uniform size:** In the case of a solid fuel, the size should be uniform so that the combustion is regular.

- (12) A fuel must burn in air with efficiency without much smoke.

Solid Fuels:

The main solid fuels include wood, peat, lignite, coal, charcoal etc.

In addition to these, certain agricultural and industrial such as spent tan, rice husk, coconut and nutshells are also employed as fuels.

Coal:

Coal is regarded as a fossil fuel produced from large accumulation of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years.

Classification of Coal:

There are four kinds of coal based on their carbon content and calorific value.

The process of conversion of wood into coal occurs in several stages by geographical process known as "coalification".

The process may be complete or may be stopped at any state thus giving rise to material of varying carbon content.

wood → peat → lignite → bituminous coal → anthracite coal
Carbon content and calorific value increases → → → →

Peat:

It is a brown fibrous mass and is considered as first stage of coal formation. It contains 57% carbon and its calorific value is about 5400 kcal/kg.

Lignite:

It is soft brown colored and is a low grade fuel. It contains 60% to 70% carbon and its calorific value is about 6500 to 7500 kcal/kg.

Bituminous coal: The bituminous coals are 3 types.

(a) **Sub bituminous:** Black and smooth in appearance have 75 to 83% carbon content and its calorific value is about 7000 kcal/kg.

(b) **Bituminous:** Carbon content is from 78 to 90% and calorific value is from 8000 to 8500 kcal/kg.

(c) **Semi bituminous:** Carbon content is 90 to 95% and has calorific value of about 8500 to 8600 kcal/kg.

Anthracite: Highest grade of coal dense and lustrous in appearance. The carbon content is 92-98% and the calorific value ranges between 8650 to 8700 kcal/kg.

6.3 Analysis of Coal:

The composition of coal varies widely and hence it is necessary to analyze and interpret the results.

The quality of coal is ascertained by the following 2 types of analysis:

- (1) Proximate analysis
- (2) Ultimate analysis.

Proximate analysis:

In proximate analysis, the data collected vary with the procedure adopted. The quality of coal can be assessed by proximate analysis. The

analysis includes the determination of moisture, volatile matter, ash and fixed carbon.

(i) Moisture: About 1 g of finely powdered air-dried coal sample is weighed in a crucible. The crucible is heated in an electric hot-air oven ($105-110^{\circ}\text{C}$) for one hour. The crucible is taken out, cooled in dessicator and weighed. Loss in weight is noted.

(ii) Volatile matter: The dried sample of coal left in the crucible in (i) is covered with lid and placed in an electric furnace (muffle furnace) at $925^{\circ}\text{C} \pm 20^{\circ}\text{C}$ for 7 minutes. The crucible is taken out, cooled first in air, then in a dessicator and weighed. Loss in weight is noted.

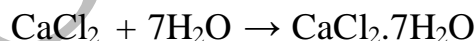
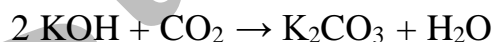
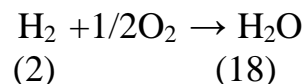
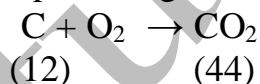
(iii) Ash: The residual coal in the crucible in (ii) is then heated without lid in muffle furnace for half an hour at $700 \pm 50^{\circ}\text{C}$. The crucible is taken out, cooled first in air, then in a dessicator and weighed. Heating, cooled and weighing is repeated until a constant weight is obtained. The residue is reported as ash on percentage basis.

(iv) Fixed carbon:

Percentage of fixed carbon = 100 - percentage of moisture + volatile matter + ash

Ultimate analysis: The ultimate analysis is useful for combustion calculations. It includes the determination of ultimate constituents present in dry coal like carbon, hydrogen, nitrogen, sulfur, ash and oxygen.

(i) Carbon and Hydrogen: A known amount of coal sample (about 1-2 g) is burnt in a current of dry oxygen in a combustion apparatus. Carbon and hydrogen of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights. After the completion of the absorption of the products, the tubes are weighed again, and percentage of the elements are calculated from the results.



Nitrogen: Nitrogen in coal sample is estimated by kjeldahl method.

In this method nitrogen of coal is converted into ammonia and is estimated.

The powdered coal sample is exactly weighed and is heated with concentrated H_2SO_4 , K_2SO_4 and mercuric

sulfate till the solution becomes clear. Then the solution is treated with excess KOH or NaOH solution and distilled. The ammonia liberated is absorbed in a known volume of standard dilute H_2SO_4 solution. The excess of acid is determined by back titration with standard NaOH solution.

(iii) **Sulfur:** Known amount of powdered coal is taken and it is burnt in oxygen at high pressure in bomb calorimeter. Sulfur in coal gets oxidized to SO_2 . It is dissolved in water and treated with BaCl_2 solution to precipitate sulfate as BaSO_4 . The precipitate is filtered and washed, dried and weighed.

Ash determination is carried on as in proximate analysis.

The sum of the percentage of C, H, N, S and ash are subtracted from 100 and recorded as percentage of oxygen.

Significance of Proximate analysis:

The proximate analysis is an assay rather than true analysis.

Each constituent determined in proximate analysis has own implication in the assessment of the coal sample.

(1) **Moisture content:** Presence of moisture in coal is objectionable. Moisture in coal evaporates during burning of coal absorbing some of the liberated heat in the form of latent heat of evaporation. Moisture increases transport cost and reduces the calorific value.

(2) **Volatile mater:** The volatile matter of coal causes long flame, high smoke and relatively low heating values.

The volatile matter content of coal influences the furnace design. If volatile matter is high, large space is required. The percentage of volatile matter in coal denotes the proportion of the coal which will be converted into gas and tar products by heat.

High volatile matter content is preferable in coal gas manufacture and in carbonization plants.

For the manufacture of metallurgical coke, coal with low volatile matter is preferred.

Ash: The amount of ash and nature of ash in coal are important in determining the quality of coal. In good quality coal, the ash content should be low.

High ash content in coal

- (i) reduces the calorific value of coal.
- (ii) Does not allow free flow of air and heat which results in low efficiency.
- (iii) Increases transport, handling, storage and disposal costs.
- (iv) If clinkers are formed, they block the inter space of the grate on which coal is generally burnt which results in irregular burning of coal.

Fixed carbon: Higher the percentage of fixed carbon, greater is the calorific value

6.4 Liquid Fuels-Petroleum:

Petroleum is the principle source of aliphatic organic compounds. It is a dark greenish brown highly viscous oil found in deep in the earth's crust. Usually oil is floating upon a layer of brine and has a layer of gas on the top of it.

It contains various hydrocarbons together with small amounts of organic compounds having oxygen, nitrogen and sulfur.

The average composition of petroleum is

Carbon : 79.5 - 87.1%; Hydrogen: 11.5 - 14.8%; Sulfur: 0.1 - 3.5%;

Nitrogen and Oxygen: 0.1-0.5%.

Refining of Petroleum:

The process of separation of crude oil or petroleum into different fractions on the basis of their boiling points is known as refining or fractionation of petroleum. The refining process mainly involves 3 steps.

- (1) Separation of water
- (2) Removal of harmful sulfur compounds
- (3) Fractional distillation.

(1) Separation of water (Cottrell's process):

The crude oil is an extremely stable emulsion of oil and salt water. To separate water from crude oil, the crude oil is allowed to flow between two highly charged electrodes. The colloidal water droplets combine to form large drops and get separated from oil.

(2) Removal of sulfur compounds:

To remove sulfur from the crude oil or petroleum, the crude oil is treated with copper oxide. The sulfur gets precipitated as copper sulfide and is separated by filtration.

(3) Fractional distillation:

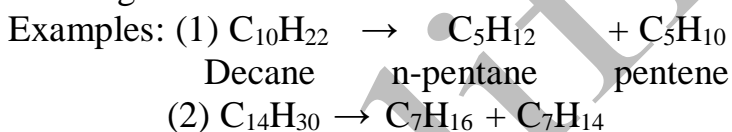
The crude oil is heated to about 400°C in an iron retort. All volatile constituents get evaporated. The hot vapors are passed up through a fractionating column. Fractionating column is a tall cylindrical tower having number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. As vapors go up, they become gradually cooler and fractional condensation takes place at different heights of column.

Name of the fraction	Boiling range	Approximate composition in terms of carbon atoms	Uses
1. Uncondensed gas	Below 30°C	$\text{C}_1\text{-C}_4$	Domestic or industrial fuel, LPG
2 Petroleum ether	$30^{\circ}\text{C-}70^{\circ}\text{C}$	$\text{C}_5\text{-C}_7$	As a solvent
3 Gasolene or petrol or motor spirit	$40^{\circ}\text{C-}120^{\circ}\text{C}$	$\text{C}_5\text{-C}_9$	Motor fuel, solvent and in dry cleaning
4 Naphtha or solvent spirit	$120^{\circ}\text{C-}180^{\circ}\text{C}$	$\text{C}_9\text{-C}_{10}$	Solvent and in dry cleaning
5 Kerosene oil	$180^{\circ}\text{C-}250^{\circ}\text{C}$	$\text{C}_{10}\text{-C}_{16}$	Domestic fuel, jet fuel
6 Diesel oil or	$250^{\circ}\text{C-}320^{\circ}\text{C}$	$\text{C}_{10}\text{-C}_{18}$	Diesel engine

fuel oil or gas oil			oil
7 Heavy oil (lubricating oil, petroleum jelly, grease, paraffin wax)	320 ⁰ C-400 ⁰ C	C ₁₇ -C ₃₀	Lubricant
8 Residue (asphalt, petroleum coke)	4000C	C30 and above	Water proofing of roofs, road making, fuel and in moulding arc light rods

6.5 Cracking:

The process of breaking or degradation of higher molecular weight hydrocarbons into lower molecular weight hydrocarbons is known as cracking.



Purpose of cracking:

- To convert high boiling substances which have low demand into low boiling substances suitable for automobiles.
- To produce raw materials for petrochemical industries.

Methods for cracking:

The process of cracking is mainly of two types.

- (1) Thermal cracking
 - (2) Catalytic cracking
- (1) **Thermal cracking:** This method is also called Burton process.

In this process, heavier hydrocarbon molecules are converted into light hydrogen rich molecules at higher temperature.

If heavy oil is subjected to high temperature and pressure, the larger hydrocarbon molecules breakdown to smaller molecules.

- I. Liquid-phase thermal cracking: The heavy oil or gas oil is cracked at 475 to 530°C and high pressure in the range 15 to 100 kg/cm². The products are separated by fractional distillation. The cracked products have octane number up to 70.
- II. Vapor-phase thermal cracking: Vapor phase cracking is carried out for oils that have low boiling temperature. The oil is first vaporized and then subjected to cracking at 600°C to 650°C and comparatively low pressure of 10-20 kg/cm². This method is less time consuming.

The process may be carried out either in liquid phase or vapor phase.

Catalytic cracking:

This method of cracking involves the use of catalysts. The catalysts include alumino silicate with some metal oxides of Ca, Mg, Fe, Cr, Na. The process completes at low temperature and pressure compared to thermal process.

Catalytic cracking is of 2 types.

- (i) Fixed bed cracking
 - (ii) Moving bed catalytic cracking
- (i) **Fixed bed catalytic cracking:**

- The heavy oil vapors are heated in a pre heater to cracking temperature 420°C-450°C. The vapors are forced to a catalytic chamber maintained at 425°C-450°C and pressure of 1.5 kg/cm². During catalytic cracking 40% is converted into gasoline and 2-4% carbon is formed.
- The vapors coming out of catalytic chamber are passed through fractionating column, where heavy oil fractions condense. Then the vapors are passed through cooler where some gases are condensed along with gasoline. Uncondensed gases move on. The gasoline having some dissolved gases is sent to a stabilizer to remove the gases. After 8-10 hours, the catalyst stops functioning due to deposition of black layer of carbon. This is reactivated by removing carbon by burning.

▪ **Moving bed catalytic cracking:**

In moving bed catalytic cracking, the finely divided catalyst is agitated by gas. So that it can be handled like a fluid system and can be pumped as a true liquid. This method provides good contact between the catalyst and reactant.

The optimum conditions for the method include

Catalyst: $\text{Al}_2\text{O}_3 + \text{SiO}_2$ agitated with gas

Temperature : 550°C

Pressure : just above normal pressure.

The finely divided catalyst bed is fluidized by passing heavy oil or gas oil vapors, in a cracking chamber. The cracked vapors are sent into fractionating column to separate into gases, gasoline and un cracked gases.

The un cracked oils are further subjected to cracking.

The deactivated catalyst is regenerated by burning off the carbon deposited and is mixed with fresh heavy oil and returned to the cracking chamber.

Differences between catalytic cracking and thermal cracking.

Thermal cracking	Catalytic cracking
(1) The heavy oil is converted into lower hydrocarbons by means of high temperature.	(1) The cracking is carried out at a temperature of 400°C - 450°C in the presence of catalyst.
(2) The yield of gasoline is low.	(2) The yield of gasoline is high.
(3) High pressure is required for thermal cracking.	(3) Low pressure is required for catalytic cracking.
(4) The products mainly contain lower hydrocarbons.	(4) The products contain high amount of aromatics.
(5) The gasoline produced has a low octane rating.	(5) The gasoline produced has a high octane rating.

6.6 Knocking:

Premature and instantaneous ignition of petrol-air (fuel-air) mixture in a petrol engine, leading to the production of explosive violence known as knocking.

In an internal combustion engine the fuel-air mixture must burn smoothly and rapidly. Due to compression, sometimes the fuel-air mixture may get heated to a temperature higher than the ignition temperature. This results in spontaneous combustion even before sparking. Due to this premature ignition, the rate of oxidation is high and the mixture detonates producing rattling noise which is known as knocking.

Reasons for knocking:

- (1) Faulty engine design.
- (2) Running conditions of engine
- (3) Chemical structure of fuel.

Example:

- (i) Knocking tendency decreases in the order
n-alkanes > mono substituted alkanes > cycloalkanes > alkenes > poly substituted alkenes > aromatics.
- (ii) For straight chain hydrocarbons, the tendency to knock increases with molecular weight and boiling point.
n-hexane > n-pentane > n-butane

Adverse effects of knocking:

- (1) Early ignition
- (2) Mechanical damage due to over heating.
- (3) Decrease in efficiency and increase in fuel consumption.
- (4) Increase in fuel consumption.
- (5) Noise and roughness.

Remedial measures for knocking:

- (1) By using anti-knocking agents like tetra ethyl lead (TEL).
- (2) By the use of high octane fuel.
- (3) By reducing pressure in the inlet by throttling.
- (4) By using critical compression ratio.

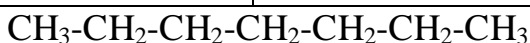
Octane number:

The performance of gasoline in internal combustion engines is related on the basis of octane number.

Definition: The octane number of gasoline is defined as the percentage of isooctane (2,2,4-trimethyl pentane) present in a mixture of isooctane and n-heptane.

The straight chain hydrocarbon i.e. n-heptane that has poor combustion characteristics and knocks badly is arbitrarily given an octane number of zero where as the branched chain hydrocarbon i.e. isooctane that has an excellent combustion characteristics and very little knocking tendency is given an octane number of 100.

Fuel	Octane number	Combustion characteristics	Knocking characteristics
n-heptane	0	Poor combustion characteristics	Knocks severely
Isooctane	100	Excellent combustion characteristics	High resistant to knocking



n-heptane



2,2,4-trimethyl pentane

(isooctane)

Octane number = 0

Octane number = 100

80-octane fuel is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.

Cetane number:

Cetane number is a measure of the ease with which a fuel will ignite under compression. Cetane number of fuel mainly depends on the nature and composition of its hydrocarbons.

Definition: The percentage of hexadecane in a mixture of hexadecane and α -methyl naphthalene is known as cetane number.

Two hydrocarbons α -methyl naphthalene (aromatic) and n-cetane (hexadecane) are specified as standards. n-cetane has low ignition lag. Hence its cetane number is fixed as 100 while α -methyl naphthalene has long ignition lag and its cetane number is fixed as zero.

Diesel fuel	Cetane number	Remarks
Cetane (n-hexadecane)	100	Very short ignition delay
α -methyl naphthalene	0	Longer ignition delay

Example: consider the following series.

n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics.

- (1) Ignition delay increases from left to right.
- (2) Ignition quality increases from right to left.
- (3) Cetane number increases from right to left.

As straight chain alkanes like n-cetane have low ignition delay and ignite readily on compression while the aromatics do not readily ignite on compression, we can conclude that high cetane number fuels eliminate diesel knock.

The cetane number of fuel may be increased by the addition of pre-ignition dopes such as ethyl nitrite, iso amyl nitrite, acetone peroxide.

2,2,4,4,6,8,8-heptamethyl nonane (HMN) with a cetane number of 15 is now considered as the low quality diesel in view of its availability and purity.

On the revised scale (HMN reference) the cetane number represents the percentage cetane in the blend with HMN plus 15/100 of the % HMN.

Example; A blend of 50% cetane and 50% HMN has a cetane number of $50 + 15/100 \times 50 = 57.5\%$.

Differences between Octane number and Cetane number:

Octane number	Cetane number
1. It is the percentage of isooctane in a mixture of isooctane and n-heptane that matches the fuel under test in knocking characteristics.	1. It is the percentage of hexadecane in a mixture of hexadecane and α -methyl naphthalene which have the same knocking characteristics as the diesel fuel.
2. It is used to find the suitability of gasoline or any other internal combustion engine fuel.	2. It is used to find the suitability of a diesel fuel.

3. The octane number of internal combustion fuels can be increased by the addition of tetraethyl lead (TEL) $(C_2H_5)_4Pb$ and diethyl telluride, $(C_2H_5)_2Te$.	3. The cetane number of diesel fuel can be increased by the addition of 'pre ignition dopes' such as ethyl nitrite, isoamyl nitrite, acetone peroxide etc.
4. The octane number of internal combustion fuels can be increased by the addition of tetraethyl lead (TEL) $(C_2H_5)_4Pb$ and diethyl telluride, $(C_2H_5)_2Te$.	4. The cetane number of diesel fuel can be increased by the addition of 'pre ignition dopes' such as ethyl nitrite, isoamyl nitrite, acetone peroxide etc.
5. Hydrocarbons which are poor diesel fuels are quite good gasoline fuels.	5. The order of ignition quality among hydrocarbon constituent of a diesel fuel is n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics. Thus, the hydrocarbons which are poor gasoline fuels are quite good diesel fuels.
6. Straight chain hydrocarbons are worst fuels as they have low octane number	6. Straight chain hydrocarbons are best fuels as they have high cetane number.

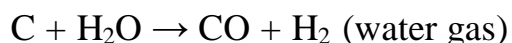
6.7 Synthetic petrol:

Synthesis of petrol from coal can be made from coal by 2 methods.

(1) Fischer- Tropsch method.

(2) Bergius method.

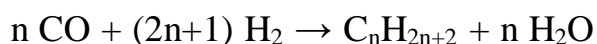
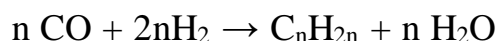
(1) Fischer-Tropsch method: The raw material i.e. hard coke is converted into water gas ($CO + H_2$) by passing steam over red hot coke.



A mixture of hydrogen and water gas is first purified by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$ (to remove organic sulfur compounds).

The purified gas is compressed to 5 to 25 atm and then passed through a converter maintained at about $200\text{--}300^\circ\text{C}$. The converter is packed with a catalyst consisting of a mixture of cobalt (Co, 100 parts), thoria (5 parts), magnesia (MgO , 8 parts) and keiserguhr earth (200 parts).

A mixture of saturated and unsaturated hydrocarbons result.



The out coming hot gaseous mixtures from the exothermic reaction are led to a cooler, where a liquid resembling crude oil is obtained. The crude oil obtained is fractionated to give gasoline and high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

(2) Bergius process: Coal is a raw material in bergius process. In this process, the low ash coal is powdered and made into a paste with heavy oil and catalyst (tin or nickel oleate).

The paste is heated with hydrogen at 450°C and 200-250 atm pressure for about one and half an hour. The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at high temperature and pressure to form low-boiling liquid hydrocarbons. The liberated gases are led to condenser where a liquid resembling crude oil is obtained. This on fractionation gives (a) gasoline (b) middle oil and (c) heavy oil.

Heavy oil is used again for making paste with fresh coal dust. Middle oil is hydrogenated in vapor phase in the presence of solid catalyst to give more gasoline. The yield of gasoline is about 60% of the coal dust used.

6.8 Gaseous fuels:

The important gaseous fuels are

- (i) Natural gas (Primary fuel)
- (ii) Producer gas (Secondary fuel)
- (iii) Water gas (Secondary fuel)

- (iv) Carbureted gas (Secondary fuel)
- (v) Coal gas (Secondary fuel)

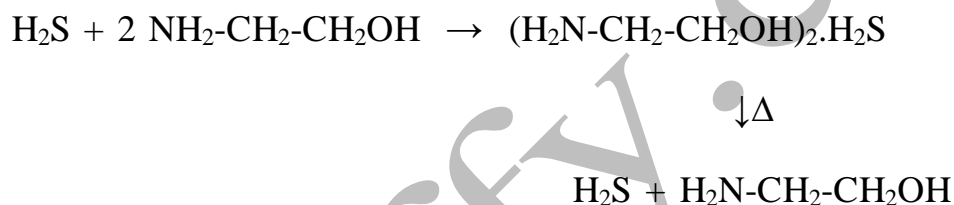
Natural gas:

Natural gas is primarily methane gas. It is a fossil fuel.

If lower hydrocarbons like methane and ethane are present, the natural gas is known as dry or lean gas. If higher hydrocarbons are present along with methane, the natural gas is known as wet or rich gas.

Composition: Methane = 88.5%, Ethane = 5.5%, propane = 3.7%, Butane = 1.8%, Pentane, H_2 , CO, CO_2 and others = 0.5%.

Sometimes natural gas contains H_2S which is removed by scrubbing with 2-amino ethanol.



Applications:

- (1) It is very good domestic fuel.
- (2) Used in synthesis of synthetic proteins which are used as animal food.
- (3) Used as raw material for the manufacture of carbon black, methanol, formaldehyde and other chemicals.

Producer gas: Producer gas is the mixture of CO + N_2 .

Water gas: It is a mixture of CO (40%) and H_2 (50%) along with some CO_2 and N_2 .

Carbureted gas: It is a mixture of CO (35%), H_2 (35%), 20% of various lower hydrocarbons and 10% of CO_2 and N_2 .

Coal gas: Coal gas contains 50% H_2 , 30% hydrocarbons, 5% CO

6.9 Analysis of flue gas by ORSAT'S method:

The mixture of gases (CO_2 , CO and O_2) coming out of the combustion chamber is known as flue gas. The analysis of flue gas gives an idea about the efficiency of combustion process.

If flue gas contains considerable amount of CO , it indicates incomplete combustion and insufficient supply of oxygen.

If flue gas contains considerable amount of O_2 , it indicates excess of oxygen which results in loss of heat.

The analysis of flue gas is carried out with the help of ORSAT'S apparatus.

The orsat's apparatus consists of horizontal tube. One end of tube is connected to 3 way stop cock and stop cock is further connected to U-tube. The U-tube is packed with fused CaCl_2 and glass wool for drying and to avoid the incoming smoke particles.

The other end of horizontal tube is connected to graduated burette surrounded by water-jacket, to maintain constant temperature. The burette is connected to water reservoir with the help of rubber tubing. The water level in the burette can be adjusted with the help of reservoir.

The burette is further connected to 3 absorption bulbs fitted with stopcocks. The bulbs are filled with KOH , alkaline pyrogalllic acid and ammonical cuprous chloride, which can absorb CO_2 , CO and O_2 .

KOH absorbs CO_2 . Pyrogalllic acid can absorb O_2 and CO_2 . Ammonical cuprous chloride can absorb CO , O_2 and CO_2 .

Procedure:

The air is expelled from ORSAT's apparatus and 100mL of flue gas is carefully sucked into graduated burette. 3 way stopcock is closed.

The stopcock at KOH bulb is opened and flue gas is forced into KOH bulb by adjusting reservoir. CO_2 gets absorbed and for complete absorption the gas is sent repeatedly.

The unabsorbed gas is taken back into the burette and stopcock at KOH bulb is closed. The decrease in volume gives the volume of CO_2 in 100mL of flue gas.

The volumes of O_2 and CO are similarly determined by passing through absorption bulbs filled with alkaline pyrogalllic acid and ammonical cuprous chloride.

The gas remaining in burette after absorption of CO_2 , CO and O_2 is taken as N_2 .

Calorific value:

Definition: Calorific value of a fuel may be defined as the amount of heat released when a unit quantity (mass or volume) of a fuel is burnt completely in air or oxygen.

Units:

- For solid or liquid fuel: calorie/gram, kilocalorie/gram, Joule/kg, British Thermal Unit/lb.
- For gaseous fuels: kilocalorie/cubic meter, British Thermal Unit/cubic feet

6.10 Higher calorific value or Gross calorific value:

Definition: Higher calorific value is defined as the amount of heat released when unit quantity of fuel is burnt completely in air and the combustion products are cooled to room temperature.

Hydrogen is present in almost all fuels, when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to room temperature, the latent heat of condensation of steam is also included in the measured heat. This is known as higher or gross calorific value (HCV or GCV).

Net calorific value or low calorific value (NCV or LCV) :

LCV is the net heat produced when unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.

NCV or LCV = GCV or HCV - Latent heat of combustion of water vapor produced.

Determination of calorific value of fuel by Junker's calorimeter:

Junker's calorimeter consists of a vertical cylindrical combustion chamber where the combustion of fuel can be carried out with the help of Bunsen burner. The supply of gaseous fuel is regulated with the help of pressure governor. The volume of gas flowing in a particular time is measured with the help of gasometer. The combustion chamber is surrounded by an annular water space. Radiative and convective heat loss from the calorimeter is prevented with the help of chromium plated outer jacket. The outer jacket contains air which is very good heat insulator. Around the combustion chamber, there is an annular space where water is made to circulate. The thermometers are placed at appropriate places to measure the temperatures of the inlet and outlet water.

A known volume of gas is burnt in excess of air at a constant rate in combustion chamber such that all the heat absorbed in water. Water is flowing at a constant in annular space around the combustion chamber. The increase in temperature of the water is measured and the heat evolved from the burning of gas can be calculated. The weight of water flowing is recorded for the calculation of calorific value of gaseous fuel.

Let V = volume of gas burnt in certain time t at STP

W = weight of water collected in time t

T_1 = temperature of incoming water

T_2 = temperature of outgoing water

Then, Higher calorific value(HCV) = $W(T_2 - T_1)/V$ kCal/m³

Suppose m = mass of steam condensed in certain time t in graduated cylinder from V m³ of gas and latent heat of steam = 587 kcal/kg.

Lower calorific value (LCV) = {HCV - $m/v \times 587$ } kcal/m³

UNIT 7 PHASE RULE

7.1 Phase rule:

The Phase rule was derived by Gibbs and states that, for a system at equilibrium

$$F = C - P + 2$$

Where,

F = degrees of freedom

C = number of components

P = number of phases in the system

The phase rule is defined as the number of degrees of freedom (F) exceeds the difference of the number of components (C) and the number of phases (P) by 2.

Phase: Phase is physically distinct, mechanically separable part of a system, which is separated from other parts of system by real or imaginary boundaries.

Example: Water system

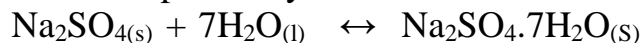
At freezing point water contains three different phases



Component: The number of components in a system is the maximum number of independently variable chemical species necessary to describe the composition of each phase.

Example: (1) In water system all the three phases ice, water, water vapor has the same chemical composition i.e. H_2O . Hence it is called 'one component system'.

(2) If we take Na_2SO_4 -water system to describe composition of different phases two independently variable chemical species are required. Hence it is called 'two component system'.



Degrees of freedom: The minimum number of independently variable factors such as temperature, pressure and composition, which must be fixed in order to represent the condition of a system is known as 'degrees of freedom'

If degrees of freedom (F) is **zero**, the system is known as **non variant** (or) **invariant**.

If degrees of freedom (F) is **one**, the system is **uni variant**.

If degrees of freedom (F) is **two**, the system is **bi variant**.

Example: In water system, if all the three phases are in equilibrium, then the degrees of freedom is zero and the system is invariant.

If two phases are in equilibrium, then the degrees of freedom is one and the system is uni variant.

If only one phase is present, then the degrees of freedom is two and the system is bi-variant.

7.2 Applications of Phase rule:

- (1) Useful in understanding the properties of materials such as metals, alloys and composites.
- (2) Used in several metallurgical processes, solvent extraction, steam distillation.
- (3) In the quality control of ultrapure materials like semi-conductors, it is used to check impurity concentration.

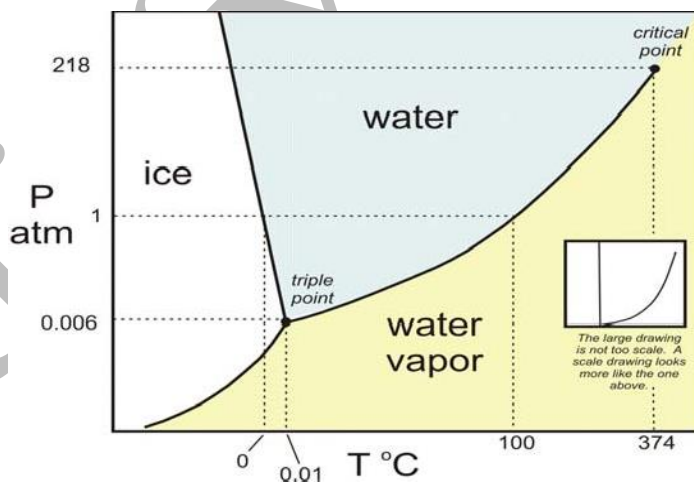
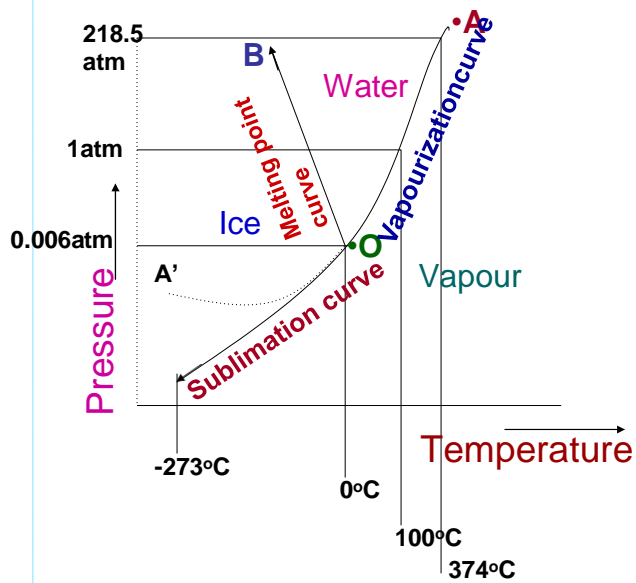
Water System

Water system is typical example for one component system.

Water system has three phases ice, water and water vapor which show the following different equilibria

- | | |
|-------|---------------------|
| (i) | Ice ↔ water |
| (ii) | Ice ↔ water vapor |
| (iii) | Water ↔ water vapor |

• PHASE DIAGRAM OF WATER:



The above phase diagram has

- (a) Curves OA, OB and OC
- (b) Areas AOC, AOB and BOC
- (c) Triple point 'O'

(A) Curves:

- (i) Vaporization curve, OA: Water at any given temperature is associated with vapor. With increase in temperature, there is an

increase in vapor and vapor pressure. The rate of increase is higher at higher temperature than at lower temperature.

The vaporization curve starts at freezing point and extends till critical temperature of 374°C and critical vapor pressure 217.5 atm . Beyond the point 'A' only water exists and vapor is incompressible beyond 'A'.

Point 'O' is lower part of vaporization curve which represents freezing point of water. The temperature and pressure corresponding to this point are 0.0098°C and 0.006 atm .

Along vaporization curve water and vapor are in equilibrium with each other.

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

The degrees of freedom along vaporization curve is one and the system is univariant.

- (ii) Sublimation curve, OB: Sublimation curve represents the equilibrium between ice and vapor. With decrease in temperature initially the vapor pressure drops steeply followed by slow decrease. The sublimation curve can be extended below 'B'.

Along sublimation curve, two phases solid ice and vapor are in equilibrium with each other.

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

The degrees of freedom is one and the system is univariant.

- (iii) Fusion Curve: The fusion curve represents equilibrium between ice and water. The curve slopes towards pressure axis indicating melting point of ice is decreased by increasing pressure.

Ice occupies more volume than water. Whenever pressure is increased ice melts to form water which is accompanied by a decrease in fusion temperature.

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

The system is univariant. This curve is extendable beyond 'C'.

- (iv) Super cooling curve, OA': Water always does not freeze at 0°C . If the vessel containing water and vapor is perfectly clean and free from dust, it is possible to super cool water below its freezing point. The curve OA' represents vapor pressure curve of super cooled water. This curve represents meta stable system, which reverts to stable system on slight disturbance.

(B) Triple point: The curves OA, OB and OC meet at the triple point 'O' where all the three phases ice, water, vapor are in equilibrium. The triple point of water is 0.006 atm and 0.0098°C . At triple point, the system is non-variant and the system changes from non-variant to univariant when the pressure or temperature are changed.

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

(C) Areas: Areas in one component system represent the existence of single phase. These areas are the fields of existence of vapor, liquid and ice respectively. On applying phase rule to these one phase one component system

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

The system is bi variant.

7.3 Silver-lead system:

Silver-Lead system is an example for two-component system.

The four possible phases of silver-lead system are

- (i) Solid silver
- (ii) Solid lead
- (iii) Solution of silver and lead in molten state
- (iv) Vapor

Silver and lead have very high boiling point, the vapor is practically absent. The pressure changes have negligible impact on phase diagram. The phase diagram is plotted between composition and temperature at constant pressure of one atmosphere. The variance of system reduces by factor of one and corresponding phase rule equation is called reduced or condensed phase rule.

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

In the phase diagram 'A' represents the melting point of pure silver and 'B' that of pure lead. The phase diagram contains curves OA, OB and areas AOB, AOD, BOE and point 'O'.

Curves:

(i) **Curve 'OA':** This is freezing point curve of silver. The melting point of pure silver is 961°C . Addition of small quantities of lead lower the melting point of silver.

Along 'OA' solid silver and melt of silver and lead are in equilibrium. The melting point of Ag falls gradually by addition of lead till the silver melt gets saturated with lead.

Along curve 'OA', the system is two phase two component system.

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

The system is univariant.

(ii) **Curve 'OB':** This is freezing point curve of lead. The melting point of pure lead is 327°C . Addition of small quantity of silver lower the melting point of lead till point 'O'.

Along curve OB

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

The system is univariant.

Eutectic point 'O':

The lines OA and OB meet at eutectic point 'O'.

At 'O' the silver solution becomes saturated with lead and lead solution is saturated with silver. On further addition of silver or lead solid will get separated. This saturation limit is represented by 'O' called eutectic point.

The temperature and composition of the eutectic mixture corresponding to eutectic point at 1 atm pressure are 303°C and 2.4 % Ag + 97.6 % Pb respectively.

At this point all 3 phases i.e., solid Ag, solid Pb, liquid solution are in equilibrium.

On applying reduced phase rule equation

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

The system is non-variant.

The eutectic point refers to lowest freezing point of liquid mixture of two metals.

Areas

(1) **Area AOB:** This area represents a homogeneous solution of Ag and Pb.

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

The system is bivariant.

- (2) Area AOC: Here solid silver and melt coexist.

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

The system is univariant.

- (3) Area BOD: Here solid lead and melt are in equilibrium.

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

The system is univariant.

- (4) Area COE: The area COE has solid eutectic and solid lead in equilibrium.

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

The system is univariant.

- (5) Area DOE: The area has solid eutectic and solid silver in equilibrium.

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

The system is univariant.

Pattinson's process for desilverization of lead:

Silver is generally recovered from lead or copper ores. Galena (PbS) is a lead ore that contains 0.1% silver. The enrichment of silver in this ore to 2.4% is done with the help of Ag-Pb phase diagram. This process is called pattinson's process or desilverisation process.

On cooling melt of silver-lead vertically above the eutectic point along line 'BO' as soon as it reaches any temperature on freezing curve, solid lead starts solidifying. On further the composition of melt approaches composition of eutectic i.e., 2.4% Ag and 97.6% Pb. This solid eutectic rich in Ag is profitably then used for subsequent recovery of silver employing electrochemical techniques. The relative increase in the amount of lead in the solids and increase of silver in melt is known as desilverization.

7.4 Iron-carbon system

Iron has 3 allotropic forms

- (i) α - iron BCC Exists up to 890°C
- (ii) β -iron FCC exists up to 890°C-1400°C
- (iii) δ -iron BCC exists up to 1400°C-1535°C

Iron melts at 1535°C.

Iron-carbon system represents interstitial solid solutions.

Pure iron is weak and not suitable for fabrication. Iron-carbon alloy improves the mechanical properties.

Cooling curve of Iron: Depending on the temperature, iron may exist in BCC or FCC structures. At room temperature, iron is in BCC and at 910°C it changes to FCC and then at 1400°C back to BCC.

770°C is called curie point. At this temperature, the magnetic properties of iron disappear. When temperature drops back to curie point then the magnetic properties reappear.

7.5 Heat treatment:

Heat treatment is combined operations of heating and cooling of metal or an alloy in solid state in order to get the desired properties.

During heat treatment, the size and shape of grain or the composition of the phase undergoes changes with respect to the micro constituents and internal stress will be relieved.

Heat treatment aims at

- (1) Increasing strength, toughness, hardness, ductility to steel.
- (2) Relieving internal stress and strain.
- (3) Normalizing steel which has been subjected to mechanical or heat treatment.

The heat treatment methods include

- (I) Transformation hardening
- (II) Tempering
- (III) Annealing
- (IV) Normalizing
- (V) Case hardening

(I) Transformation hardening: When plain carbon steel is heated to a temperature above 723°C for long time, dissolution of more carbon takes place with the formation of austenite phase in FCC structure. This on slow cooling FCC changes to BCC and excess carbon forms cementite.

If steel is quenched, carbon atoms do not have sufficient time to form cementite but remain trapped in BCC. Excess carbon gets precipitated in hot metal and prevents slipping of planes. This transformation of austenite to cementite which is a hard steel, by heat treatment is known as “Transformation hardening”.

(II) Tempering: If simple carbon steel, which is in austenite state is quenched by plunging in to water or brine, the unstable δ -iron in FCC and held carbon in solid solution changes to stable α -iron at that temperature carbon is soluble in α -iron which has BCC structure.

Quenching lowers temperature rapidly, atomic adjustments cannot take place totally, there is little time for carbon to diffuse. Due to this new constituent martensite is formed.

The quenched steel is reached to transition temperature of α - iron to δ -iron. At this elevated temperature there is greater atomic mobility. Consequently highly strained atoms readjust removing hardness and brittleness. The sample is then cooled in air, water or oil to get desired properties. This process is known as “Tempering”. This removes internal strain and metal is quite hard and tough.

- (III) Annealing:** When steel is cooled very slowly, equilibrium is established and stress free steel is obtained. The process involves dissolution of carbon in δ -iron followed by slow and controlled cooling.

By annealing the steel becomes soft, ductile and machinable. If steel is heated to higher temperature, the grain size increases and material becomes weak. This is used for drawing wires.

Annealing consists of 3 types.

- (a) Heating to the right temperature.
- (b) Soaking or keeping at that temperature.
- (c) Slow cooling in a furnace.

Advantages :

- (a) Annealing removes internal stress.
- (b) It changes ductility toughness, electrical and magnetic properties.
- (c) Improves machinability.

- (IV) Normalizing:** Normalizing means bringing back the structure and properties that are normal for a sample. By normalization process fine and stronger pearlite is produced.

Normalizing produces steel with high tensile strength, yield strength and impact resistance. Normalizing makes steel soft and homogeneous. In normalizing hyper and hypo-eutectoid steels are heated above upper critical range. In this process rate of cooling is faster which prevents the formation of coarser grains which reduce strength.

- (V) Case hardening or carburizing:** This technique is used for surface modification. In case hardening carbon is introduced into a solid ferrous alloy by heating the metal in contact with a carbonaceous solid, liquid or gas.

Case hardening is done in 2 ways.

- (i) Pack carburizing
- (ii) Liquid carburizing

In pack carburizing the material is packed in carburizing cases of 1 cm thick layer of packing material. It gives carbon to steel.

In liquid carburizing the article is heated in a bath of molten cyanides, carbonates, chlorides at 900 to 950°C.

Gas carburizing is used for hardening small articles.

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UNIT 8 MATERIALS CHEMISTRY

8.1 Cement:

Cement is construction material which possess adhesive and cohesive properties and used for binding the building blocks, bricks, stones.

Cement is classified into 4 types based on chemical composition.

- (1) Natural cement
- (2) Puzzalona cement
- (3) Slag cement
- (4) Portland cement

(1) Natural cement:

It is made by subjecting the argillaceous lime stone to calcinations at high temperature and then the calcinated mass is pulverized. It possesses low strength and used in preparation of mortars.

(2) Puzzalona cement:

Natural puzzalona is deposit of volcanic ash which is produced by rapid cooling of lava mixed with slaked lime.

It is a mixture of aluminium silicate, calcium silicate and silicates of iron.

Puzzalona cement is not used directly but used by mixing with Portland cement.

(3) Slag cement:

Slag cement is mixture of slag i.e. aluminium silicate and calcium. The mixture is poured into cold water, granular cement produced is dried and mixed with lime and pulverized to fine powder.

Slag cement is low setting cement. It can be hardened by adding accelerators like clay, salt or caustic soda.

It is used for making concrete for construction in waterlogged area where much tensile strength is not required.

(4) Portland cement:

Portland cement is made by calcination of calculated amounts of clay and lime followed by gypsum. It is a mixture of calcium silicate and aluminium silicate with small amount of gypsum. It is hydraulic in nature.

Chemical composition of Portland cement:

The composition of Portland cement should satisfy the following conditions.

- (i) The ratio of the percentage of lime to that of SiO_2 , Al_2O_3 and Fe_2O_3 when calculated by formula $\text{CaO} / (2.8 \text{SiO}_2 + (1.2\text{Al}_2\text{O}_3) + (0.65\text{Fe}_2\text{O}_3))$ should be greater than 1.02 and not less than 0.66.
- (ii) Ratio of the percentages of Al_2O_3 to Fe_2O_3 should not be less than 0.66.
- (iii) Weight of MgO should not be more than 6%.
- (iv) Weight of insoluble residue should not exceed 2%.
- (v) Total sulfur content should not exceed 2.75%.
- (vi) Total loss of ignition should not exceed 4%.

Chemical composition range of Portland cement:

Ingradiant	Formula	% limit	Functions
Lime	CaO	60-67	Increases strength and setting time
Silica	SiO_2	17-25	Gives strength and prolongs setting time
Alumina	Al_2O_3	3-8	Increases strength
Iron oxide	Fe_2O_3	0.5-6.0	Imparts grey color and strength
Magnesia	MgO	0.1-4.0	Excess % contributes to unsoundness.
Sulfur trioxide	SO_3	1.2	Imparts soundness
Alkali	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0.5-3.0	Causes efflorescence

8.2 Manufacture of Portland cement:

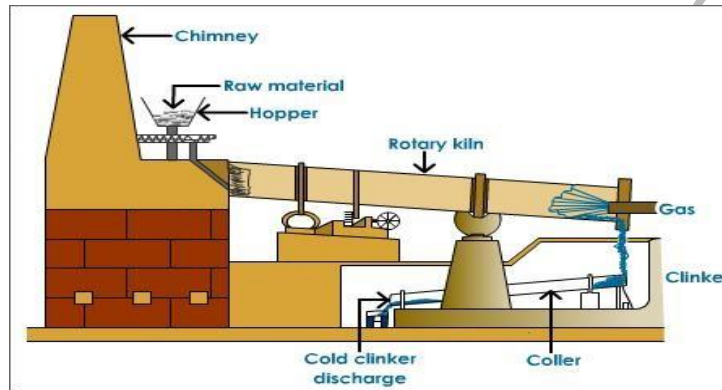
There are 2 different methods for the manufacture of Portland cement;

- (1) Dry process.
- (2) Wet process.

(1) Dry process:

The dry process involves different steps:

- (a) Mixing of raw materials
- (b) Burning mixture in rotary kiln
- (c) Grinding clinkers with gypsum.



The process is used when raw materials lime stone and clay are hard.

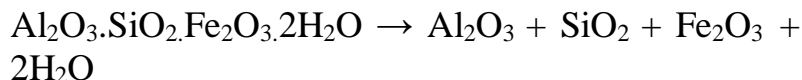
(c) Mixing of raw materials:

The dry process produces fine powder of cement. This process is employed if limestone and clay are hard. The lime stone is crushed into pieces and it is mixed with clay in 3:1 ratio. The mixture is pulverized to fine powder and stored in storage bins and then introduced into upper end of rotary kiln for calcinations.

(d) Burning of mixture in rotary kiln:

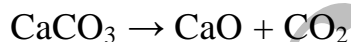
The rotary kiln consists of an inclined steel cylinder 15-200 ft long and 10 ft diameter. It is mounted on rollers and can be rotated with desired speed. The cylinder is lined inside with fire bricks. The kiln has different zones.

- (i) The drying zone: The zone is present in upper part of kiln and temperature is around 400°C . Here water present in the slurry gets evaporated and clay is cleaved to Al_2O_3 , SiO_2 and Fe_2O_3 .



- (ii) Calcination zone or decarbonating zone:

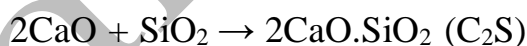
This is middle portion of kiln, where the temperature is 1000°C . Here the lime stone is completely decomposed into CaO which exists in the form of small lumps called nodules.



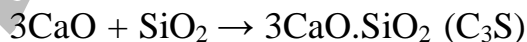
- (iii) Burning zone or clinkering zone:

This is bottom most and hottest zone in rotary kiln. The temperature is around 1400°C - 1500°C . In this zone the mixture melts and forms little rounded pasty mass called clinkers. The clinkers are greenish black and have rough texture.

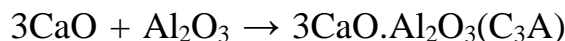
In the burning zone or clinkering zone the following reactions take place.



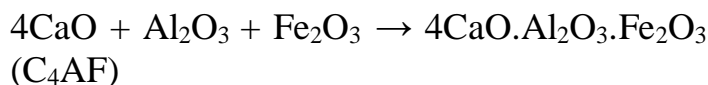
Dicalcium silicate



Tricalcium silicate



Tricalcium aluminate



(tetracalcium aluminoferrite)

The $C_3A + C_4AF/C_3S$ ratio is known as burn ability index. This is generally in the range 0.45-0.85.

(C) Grinding or mixing of cement clinkers with gypsum:

The clinkers are cooled and finely ground. The finely ground clinkers have low setting time and by absorption of moisture they set quickly. To reduce rate of setting it is mixed with 2-3% gypsum ($CaSO_4 \cdot 2H_2O$).

The fast setting Al_2O_3 in clinkers reacts with gypsum and form crystals of tricalcium sulfo aluminate which is insoluble. This prevents early setting and hardening. The mixture of clinkers and gypsum is known as Portland cement.

Compound composition of Portland cement:

Name of the compound	Chemical formula	Average percentage
1 Tricalcium silicate	$3CaO \cdot SiO_2$	45%
2 dicalcium silicate	$2CaO \cdot SiO_2$	25%
3 Tricalcium aluminate	$3CaO \cdot Al_2O_3$	1%
4 Tetracalcium aluminoferrate	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	9%
5 Calcium sulfate	$CaSO_4$	5%
6 Calcium oxide	CaO	2%
7 Magnesia	MgO	4%

Manufacture of cement by wet process:

The manufacture of cement by wet process involves 3 different steps.

- (1) Mixing of raw materials
- (2) Burning mixture in rotary kiln
- (3) Grinding or mixing of cement clinkers with gypsum

This method is used when both the raw materials lime stone and clay are hard.

- (1) Mixing of raw materials:

The organic matter and foreign materials present in the clay are removed by washing with water. The lime stone is mixed with clay in 3:1 proportion and then homogenized. The resulting slurry contains 40% water. The slurry is fed into rotary kiln.

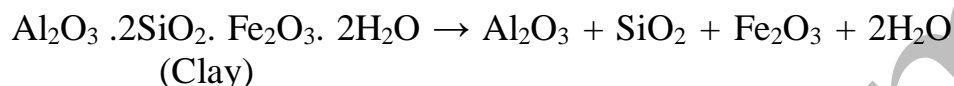
- (2) Calcinations or burning of mixture in rotary kiln:

The slurry of raw mixture is fed into rotary kiln. The kiln consists of an inclined rotating cylinder 150-200 ft long and 10 ft in

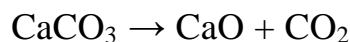
diameter, lined with fire bricks. The kiln rotates at the rate of one revolution per minute.

Due to rotary motion of kiln the slurry moves downwards and gets heated, by blast of hot air. The chemical reactions taking place at various zones of rotary kiln are

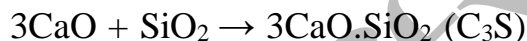
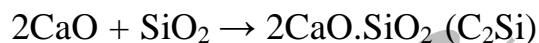
- (a) Drying zone: The temperature in the zone is 750°C , the moisture present in the slurry is evaporated and the clay is broken into Al_2O_3 , SiO_2 and Fe_2O_3 .



- (b) Calcinations zone: The temperature in this zone is 1000°C and lime stone gets decomposed to CaO



- (c) Reaction zone or clinkering zone: The temperature in this zone is about 1600°C , the mixture partly gets melted and following chemical reactions takes place.



The resulting product called clinker, is allowed to cool in cooler.

- (3) Mixing of clinkers of cement with gypsum:

The clinkers are mixed with 3% gypsum to reduce the rate of setting. The fast setting constituent Al_2O_3 of clinker reacts with gypsum to form calcium sulpho aluminate.

8.3 Setting and hardening of Portland cement:

When cement is mixed with water to produce a plastic like cement paste. The paste when subjected to hydration and gelation, finally crystalline products are formed.

- (1) Initial setting of cement involves hydration of tricalcium aluminate.
- (2) Second step involves gelation in which tobermonite gel is formed, along with calcium hydroxide and hydrated tricalcium aluminate.
- (3) Crystallization of tri calcium takes place. Initial reaction involves the formation of tetra calcium aluminate, hardening

of tri calcium aluminate takes place finally through crystallization.

Finally setting and hardening of cement paste is due to the formation of tobermonite gel with crystallization of calcium hydroxide and hydrated calcium aluminate.

8.4 Lubricants:

Lubricant may be defined as a substance which reduces the friction when introduced between two surfaces. The phenomenon is known as lubrication.

Criteria of a good lubricant or functions of lubricant:

- (1) Lubricant should keep moving parts apart.
- (2) It helps in reducing frictional forces between two sliding surfaces.
- (3) It prevents loss of heat produced by frictional forces and acts as coolant.
- (4) It should reduce wear and tear as well as surface deformation caused due to friction.
- (5) It prevents rust formation and corrosion and hence reduces the running cost of machinery.
- (6) It acts as seal in internal combustion engines and prevents the leakage of gases.
- (7) It reduces loss of heat energy there by increasing the efficiency of engine.

Classification of lubricants:

On the basis of physical state lubricants can be classified as

- (1) Lubricating oils (liquid lubricants)
- (2) Greases (semi solids)
- (3) Solid lubricants
 - (1) Lubricating oils: The oil provide a continuous fluid film over the moving or sliding surfaces. They also act as a cooling and sealing agents and prevent corrosion.

Examples:

Animal oils: whale oil, lard oil etc.

Vegetable oils: olive oil, palm oil, castor oil etc.

Mineral oil or petroleum oil.

As single oil does not possess all the good qualities of lubrication, certain additives are added to achieve desired characteristics.

These are called blended oils.

- (2) Greases or semi-solid lubricants: Greases are obtained by combining lubricating oil with thickening agent. Greases are classified on the basis of the soap used in their manufacture as soda-based greases, lithium based greases.etc.
- (3) Solid lubricants: In certain aero-space devices, semi-solid lubricants cannot be used. Solid lubricants can withstand heavy load and low speed.

Example: MoS_2 , mica, chalk, wax, soap, graphite.

Solid lubricants consist of a number of layers of three layer atoms held together by weak vander waal's forces which make them soft and smooth to act as lubricants.

8.5 Mechanisms to explain action of lubricants:

The following 3 mechanisms have been proposed to explain the action of lubricants:

- (1) Thin film or boundary lubrication
 - (2) Fluid film or hydrodynamic lubrication
 - (3) Extreme pressure lubrication
- (1) Thin film or boundary lubrication:

In this type of lubrication, thin film of lubricant is adsorbed on the surface and held by vander waal's forces due to which friction is reduced.

Thin film lubrication is applied when

- (a) The speed is very low.
- (b) The shaft moves from rest position to operation
- (c) The load is high.
- (d) The oil has low viscosity.

Some peaks may have higher thickness than the film of lubricant that results in wearing and tearing. Hence, the chemical or physical forces on some metal surfaces would avoid a thin layer of lubricating oil.

Therefore, the coefficient of friction is reduced due to oiliness.

(2) Fluid film or hydrodynamic lubrication:

This is also known as thick film lubrication. It is varied out with the help of liquid lubricants. In this process, the two sliding surfaces are separated by thick film of about 1000^0A , which is applied to prevent direct surface to surface contact. Wear and tear of metal is minimized.

Example: In a ball bearing, irregularities of the shaft and bearing surfaces are covered by a thick film of lubricant and thereby preventing the contact of metallic surfaces with each other.

Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, sewing machines etc.

(3) Extreme pressure lubrication:

Extreme pressure lubrication involves chemical action on the part of the lubricant.

Under heavy load and high speed conditions, high local temperature is generated. Due to this temperature liquid film may not stick, it may decompose and vaporize. Under these conditions special additives called extreme pressure additives are used.

Extreme pressure additives are blended with lubricating oils to form more durable film to withstand high temperature and pressure.

Examples: Chlorinated esters, sulfurised oils and tricresyl phosphates.

The extreme pressure lubricants actually do not reduce friction but prevent welding between the surfaces.

Selection of the lubricant:

The selection of the lubricant depends on the operation

Operating condition	Types of lubricant
1. High speed and heavy load	Extreme pressure lubricant
2. Low speed and heavy load	High oiliness boundary film lubricants
3. Less load and high speed	Oil with low viscosity
4. Low temperature	High fluidity
5. High temperature	Oxidation resistance and less viscosity

Differences between fluid film lubrication and boundary lubrication:

Fluid film lubrication	Boundary lubrication
1. Lubricants having low viscosity are used in fluid film lubrication	1. Lubricants having high viscosity are used.
2. Thickness of oil film is more than 1000^0A	2. Thickness of oil film is less than 1000^0A
3. These are used in the machines working under high load and high speed	3. These are used in the machines working under heavy load and low speed
4. These are used as such. No metallic surface is required for adsorption	4. The thin lubricating oil is adsorbed by physical or chemical forces
5. Watches, clocks, guns, sewing machines require fluid film lubrication	5. Gears, rollers, tractors, etc. require thin film lubrication

8.6 Properties of lubricants:

Important properties of the lubricants:

(A) Cloud point:

The lubricating oils are derivatives of petroleum and contain dissolved paraffin wax and other resinous impurities. These impurities tend to separate from the oil at lower temperatures. The solidification of lubricant causes jamming of machines.

“The temperature at which the impurities begin to separate from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point”

“The cloud point is the temperature at which crystallization of solids in the form of cloud or haze first becomes noticeable, when the oil is cooled at a standard rate.”

Significance:

- (i) The cloud point indicate stability of lubricants in cold conditions.
- (ii) Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engine clogged because of separation of wax.

(B) Pour point:

It is useful to understand the stability of lubricants in cold conditions.

“The pour point is the temperature at which the oil just ceases to flow when cooled at a standard apparatus.” OR

“The temperature at which the lubricating oil ceases to flow and pour is called pour point”

Significance:

- (i) It indicates the stability of lubricants in cold conditions
- (ii) Pour point values of petroleum and non-petroleum lubricants are necessary when functioning under sub-freezing conditions.
- (iii) It determines suitability of lubricant or hydraulic oil for low temperature installations.

(C) Flash point:

“ Flash point is defined as the minimum temperature at which the lubricating oil gives off its vapors that ignite for a moment, when a flame is brought near it.

Significance

- (i) The flash point do not indicate directly the lubricating value of oil but it is important when the oil is exposed to high temperature.
- (ii) Oil of high flash point is suppose to offer more resistance to spontaneous combustion.
- (iii) The knowledge of flash point of lubricant aids in precautionary measures against fire hazards.

(D) Fire point:

Fire point is the lowest temperature at which the vapors of lubricating oil burn continually for at least 5 seconds, when flame is brought near it.

In most of the cases, the fire point of an oil is about 5-40°C higher than the flash point.

Significance:

- (i) The knowledge fire point of lubricating oil aids in precautionary measures against fire hazards.
- (ii) In the case of lubricating oils, it is an index of danger in using them for lubrication

8.7. Refractories:

Refractories are the inorganic substances which can withstand very high temperatures without softening deformation.

The main function of refractories varies depending on the purpose.

They are used for the construction of kilns, ovens, crucibles, retorts, furnaces etc.

Classification of refractories:

Refractories are broadly classified into 3 categories on their chemical nature:

- (1) Acidic refractories: They are made of acidic materials such as alumina, silica. These are resistant to acidic slags, but attacked by basic materials.

Ex. Silica, alumina, fireclay refractories

- (2) Basic refractories: Basic refractories are those which consist of basic materials, but attacked by acidic materials.

Ex. Magnesite, dolomite, chrome magnesite refractories

- (3) Neutral refractories: They are not completely neutral in chemical sense. They consist of weakly basic/acidic materials like carbon, zircon chromite, graphite and silicon carbide.

Characteristics of a refractory:

Good refractory material should possess

- (1) High temperature resistance under working conditions.
- (2) Good abrasion resistance by dusty gases and molten metals.
- (3) Low permeability or ability to contain heat.
- (4) High mechanical strength, structural strength and crack resistance to withstand overlying load.
- (5) Thermal strength to withstand thermal shock due to rapid and repeated temperature fluctuations.
- (6) They should possess low thermal coefficient of expansion

8.8 Insulators

Insulators are the substances which are capable of retarding the flow of heat or electricity through them.

Classification of insulators:

Insulators are broadly classified into 2 types.

- (1) Thermal insulators
 - (2) Electrical insulators or dielectrics.
- (1) Thermal insulators: The substances having extremely low thermal conductivity are known as thermal insulators. Thermal insulators are mainly used to prevent the loss of heat which takes place by conduction, convection and radiation
- Thermal insulators are normally employed when flow of has to be stopped from outside environment.
- Characteristics of a good thermal insulator:
- (1) Its thermal conductivity is extremely low.
 - (2) It should be water proof and fire proof
 - (3) It should be chemically stable to the surrounding conditions.
 - (4) It should have low density
 - (5) It should be mechanically stable and capable of bearing load.

(2) Electrical insulators or dielectrics: An insulator, also called a dielectric, is a material that resists the flow of electric current. An insulating material has atoms with tightly bonded valence electrons. These materials are used in parts of electrical equipment, also called insulators or insulation, intended to support or separate electrical conductors without passing current through themselves. The term is also used more specifically to refer to insulating supports that attach electric power transmission wires to utility poles or pylons.

Ex: Glass, Paper or Teflon

Characteristics of electrical insulators:

- (1) The electrical charges cannot pass through the insulator.
- (2) They possess low conductivity i.e. high resistivity.
- (3) They have low thermal contraction and expansion.
- (4) For an ideal insulator di electrical loses should be minimum
- (5) They should be resistant to chemicals, solvents, acids, alkalis, oils and other organic solvents.
- (6) They should have low dielectric constant.

Semi conductors:

The electrical resistivity of many metals decreases with decrease in temperature. The phenomenon in which the electrical resistivity of many materials suddenly falls to nearly zero when it is cooled to a very low temperature is known as superconductivity and the materials under this condition is known as super conductor.

The temperature at which the materials undergo a phase transition from a state of normal conductor to superconductor is known as critical temperature or transition temperature. Above critical temperature the material exhibits normal conductivity.

These materials in their superconducting state are diamagnetic and repel in magnetic field. The phenomenon of exclusion of magnetic field is known as “Meissner effect”. It is useful in determination of critical temperature of super conductors.

Applications of super conductors:

- (1) Some super conductors act as excellent catalysts for industrial processes.
- (2) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a good sensor for alcohol vapours on contact with certain gases, the electrical resistivity of super conductor changes sharply.
- (3) Super clips made of super conductors for computers. These can function 1000-times faster than silicon clips.

- (4) Super conducting magnets capable of generating high fields with low power consumption are being employed in scientific tests and research equipments.
- (5) Because of small size and less energy consumption, super conductors are used in magneto-hydrodynamic power generators to maintain plasma.
- (6) Super conductors are used in MRI scans.
- (7) Magnetic resonance spectroscopy is used in the chemical analysis of body tissues.
- (8) Super conducting cables can be used to transmit electrical power over long distances without resistive losses.
- (9) High efficiency separating machines are built using super conductors which are used to separate tumor cells from healthy cell by high gradient magnetic separation method.
- (10) Using superconducting elements extremely fast and large scale computer can be built in compact size.

QUESTION BANK

UNIT 1

ELECTRO CHEMISTRY

Long answer questions:

1. State and explain Kohlrausch's law of independent mobility of ions. Give its applications.
2. Write an account on Conductometric titrations.
3. Define the terms
 - (a) Specific conductance
 - (b) equivalent conductance
 - (b) Molar conductance
4. (a) What is ion selective electrode? Explain the working of ion-selective electrode.
(b) What are reference electrodes? Explain the construction of calomel electrode.
5. Explain the composition, application and advantages of the following cells
 - (a) Ni-Cd cell
 - (b) Lithium cell
6. Explain the application of quinhydrone electrode.
7. Explain the following terms
 - (a) single electrode potential
 - (b) reference electrode
 - (c) standard hydrogen electrode
8. Explain the effect of dilution on conductivity.
9. State Kohlrausch law. Explain how it can be used to determine the dissociation constant of a weak acid.
10. Define the terms specific conductance and equivalent conductance. Explain clearly why on dilution the specific conductance decreases but equivalent conductance increases.

Multiple choice questions:

- (1) The resistance of a conductor is directly proportional to
 - (a) Current passed
 - (b) Area of the cross section of conductor
 - (c) Length of the conductor
 - (d) Equivalent conductance
- (2) The resistance of the conductor is 5×10^{-2} ohms. Conductance in mhos is
 - (a) 200
 - (b) 20
 - (c) 500
 - (d) 50

- (3) The equivalent conductivity of an electrolytic solution
- Increases with dilution
 - Decreases with dilution
 - Independent of dilution
 - None of the above
- (4) Specific conductance = cell constant \times _____
- (5) In a galvanic cell
- chemical energy is converted into electrical energy
 - Electrical energy is converted into chemical energy
 - Chemical energy is converted into heat energy
 - Electrical energy is converted into heat energy.
- (6) Sodium chloride is poor conductor of electricity but transforms into a good conductor in molten state because
- The covalent bonds are broken in molten state
 - The degree of dissociation increases
 - It forms liquid crystals
 - The ions get mobility.
- (7) If 'l' is the distance between the electrodes of cross sectional area 'a', then the cell constant is given by the ratio
- l/a
 - a/l
 - $a \times l$
 - $a - l$
- (8) The conductivity of 0.1N KCl is $0.01120 \text{ mho cm}^{-1}$. If the cell constant is equal to 0.5 cm^{-1} , the conductance in mhos is equal to
- 2.24×10^{-2}
 - 5.6×10^{-3}
 - 224
 - 560
- (9) With increase in dilution, the conductivity of a solution
- Increases
 - Decreases
 - Does not change
 - Increase first and then decrease
10. The cell constant of a conductometric cell
- Increases with dilution
 - decreases with dilution
 - depends on the nature of the electrode
 - independent of the nature of the electrolyt
- (11) Equivalent conductivity of any electrolyte is the algebraic sum of _____ conductivities.

UNIT 2**CORROSION AND ITS CONTROL**

- 1) Explain the process of wet corrosion by evolution of hydrogen and absorption of oxygen
- 2) Describe the electrochemical theory of corrosion.
- 3) Differentiate the following with suitable examples.
 - a) Galvanic series and electrochemical series.
 - b) Pitting corrosion and stress corrosion.
- 4) (a) What is meant by differential aeration corrosion? Illustrate with suitable examples.
 (b) How is rate of corrosion influenced by
 - i. Nature of corrosion product
 - ii. Relative anodic to cathodic areas
 - iii. Temperature and moisture.
- 5) (a) What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion.
 (b) Describe the various factors influencing the rate of chemical corrosion.
- 6) Write down the equation for the hydrogen evolution in an electrochemical corrosion reaction?
- 7) (a) What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion.
 (b) Describe the various factors influencing the rate of chemical corrosion.
- 8) What are the factors effecting corrosion?
- 9) a) Explain the following factors influencing the rate of corrosion
 - i. Nature of corrosion product
 - ii. Position in electrochemical series
 - iii. pH.
 (b) Differentiate between dry corrosion and wet corrosion 3. Define corrosion? Explain any 4 factors that affect the rate of corrosion & explain any 4 corrosion control methods.
10. Explain how corrosion control can be brought about by the following methods.
 - a) Modifying the environment
 - b) Cathodic protection.
11. Write a short note on Inhibitors & Cathode protection.
12. (a) Write short notes on chromizing
 (b) How pH of an electrolyte affects electrodeposit?
 (c) Explain the method of coating for protection of furnace parts
13. (a) Describe the mechanism of drying of conjugated oils.

- (b) Name any four important drying oils.
 (c) Define the following:
 i. Acid value of an oil ii. Saponification Value iii. Iodine Value.
14. Write notes on Surface preparation.
15. (a) Discuss how the surface of a metal is prepared prior to the application of a protective coating.
 (b) Write the important applications of protective coating.
 (c) Why is moderate current density employed during electroplating? What is metallic coating? Name the metallic coating methods.
16. (a) Describe the process of sheradizing? Mention its applications?
 (b) Distinguish between anodizing and electroplating.
 (c) Define Anodizing
17. (a) List the differences between anodic coating and cathodic coating.
 (b) How zinc coated on iron prevents corrosion?
 (c) Explain sand blasting method of surface preparation?
18. Explain in detail the various methods of Chemical conversion coatings
19. (a) Explain the following: (i). Alkali Cleaning (ii). Mechanical cleaning.
 (b) Describe the principles involved in electro plating.
 (c) Anodized coating is preferred for Aluminium - Give Reasons.

Multiple choice questions

1. Corrosion is (a)
 (a) Oxidation
 (b) Reduction
 (c) Both of these
 (d) None of these
2. Volatile oxide film is seen in (c)
 (a) Al (b) Na (c) Mo (d) Ag
3. Pitting-Bed worth rule is related to (a)
 (a) Dry corrosion
 (b) Wet corrosion
 (c) Both of these
 (d) None of these
4. In electrochemical corrosion, oxidation takes place at (a)
 (a) Anode
 (b) Cathode
 (c) Both of these
 (d) None of these

5. Rusting of iron takes place in which environment (c)
(a) Acidic
(b) Basic
(c) Neutral
(d) None of these
6. Impure metals can generate (a)
(a) Galvanic cells
(b) Stress structure
(c) Homogeneity
(d) None
7. When two dissimilar metals are connected, to reduce corrosion, the anode should be (a)
(a) Large
(b) Small
(c) Medium
(d) No relation
8. To prevent corrosion, the medium should have (a)
(a) Low O_2
(b) High O_2
(c) Medium O_2
(d) Excess of O_2
9. Protection to the paint is given by (b)
(a) Driers
(b) Pigment
(c) Thinner
(d) Drying oil
10. The chief component of paint is (b)
(a) Driers
(b) Pigment
(c) Thinner
(d) Drying oil
11. Galvanizing is the process of coating iron with
(a) Ni (b) Zn (c) Cu (d) Sn
12. During galvanic corrosion the more active metal acts as

- (a) Anode
 - (b) Cathode
 - (c) Anode as well as cathode
 - (d) None of the above
13. The principle of electroplating is
- (a) Electrolysis
 - (b) Oxidation
 - (c) Reduction
 - (d) Anodization
14. The metal which is protected by a layer of its own oxide
- (a) Cu (b) Fe (c) Au (d) Al
15. A metal will be easily corroded if it is
- (a) Less acidic (b) more acidic (c) less basic (d) more basic
16. Corrosion of zinc containing an impurity of copper is known as
- (a) Water-line corrosion
 - (b) Galvanic corrosion
 - (c) Drip corrosion
 - (d) Crevice corrosion
17. The type of corrosion occurring in a wire fence is
- (a) Galvanic corrosion
 - (b) Differential aeration
 - (c) Inter granular corrosion
 - (d) Water-line corrosion
18. In chromium electroplating electrolyte used is _____
19. An acid which is used in the phosphate coatings is _____
20. Function of pigment in paint is _____

UNIT 3

POLYMERS

1. Write the differences between
 - a) compression-Injection moulding
 - b) additional polymerization-condensation polymerization
 - c) thermoset-thermoplasts.
2. Explain any one of the mechanism of additional polymerization, using suitable example.

3. Write a note on thermo setting plastics? Write a note on properties and uses of Teflon.
4. Describe the manufacture , properties ,uses of
 - a)polyethylene b) Teflon c) Thiokol d) PVC
- 5.(a) How is HDPE is prepared? Give its properties and uses?
 (b) Explain the injection moulding process with a neat diagram?
 Mention its advantages
6. What is moulding of plastics? Explain compression moulding technique in detail.
- 7.How is Bakelite manufactured? Discuss its important uses and properties.
8. Identify the thermosets & thermoplasts among the following:
 PVC, polyethylene, silicon, polyester fiber, bakelite.
 What is Bakelite? How is it manufactured and mention its uses.
- 9(a) Differentiate between LDPE & HDPE.
 (b) What are the drawbacks of raw rubber?
 (c) Write the repeating unit for the following:
 - i. Nylon 6,6 ii. PVC
- 10..Describe the preparation, properties and engineering uses of Polythylene.
11. (a) Explain the preparation, properties and uses of Bakelite.
 (b) Describe with a neat sketch, the process of compression moulding
12. (a) How will you synthesis nylon 6,6 from 1,3 butadiene?
 (b) Describe the method of preparation of polyester and mention its properties and uses.
 (c) What is the repeating unit of (i). natural rubber ii. Teflon.
13. (a) What are elastomers? Give the preparation, properties and uses of Buna S.
 (b) Describe a method for moulding of thermoplastic resin
14. (a) Differentiate between elastomer and plastic.
 (b) Which rubbers are used in the preparation of automobile parts? Discuss their manufacture and vulcanization.
15. Write preparation, properties and uses of nylon, polyester, and polyurethanes.
 - (a) Why are Silicones called inorganic polymers? Discuss the synthesis of linear chain Silicones.
 - (b) Why Bakelite can't be remoulded and write its repeating unit?
 - (c) Describe condensation polymerization with an example

Multiple choice questions:

1. Number of monomers in a polymer is (c)
 - (a) Tacticity
 - (b) Functionality
 - (c) Degree of polymerization
 - (d) All
2. Poly functional molecules can give the following type of polymer (d)
 - (a) Only linear
 - (b) Only straight
 - (c) Both (a) and (b)
 - (d) Only cross linked
3. In which of the following polymerization, the rate is fast (a)
 - (a) Addition polymerization
 - (b) Condensation polymerization
 - (c) Both equal
 - (d) None
4. Accelerators are added in which type of polymerization (c)
 - (a) Addition
 - (b) Condensation
 - (c) Both
 - (d) None
5. In which type of moulding, the continuous strips can be obtained (d)
 - (a) Compression
 - (b) Injection
 - (c) Transverse
 - (d) Extrusion
6. The polymer used in optical instruments is (c)
 - (a) PMMA
 - (b) PTFE
 - (c) PE
 - (d) Nylon
7. Urea formaldehyde resins are (b)
 - (a) Phenoplasts
 - (b) Amono plastics

- (c) Both of these
(d) None of these
8. Adipic acid is _____functional
(a) Mono
(b) Bi
(c) Tri
(d) Tetra
9. Vulcanization was first done by (d)
(a) MRF
(b) Ceat
(c) JK
(d) Good year
10. Isocyanate rubber is (b)
(a) Polyamide
(b) Polyurethane
(c) Polyester
(d) Polythene
11. Which one among the following is a copolymer
(a) Nylon 6,6
(b) Teflon
(c) PVC
(d) Polybutadiene
12. Polyester belong to the following type of polymer
(a) Addition, thermoplastic
(b) Addition, thermosetting
(c) Condensation, thermoplastic
(d) Condensation, thermosetting
13. Bakelite is prepared by the condensation of
(a) Phenol and formaldehyde
(b) Phenol and acetaldehyde
(c) Cresol and formaldehyde
(d) Urea and formaldehyde
14. Chloroprene is the repeating unit in

(a) PVC

(b) SBR

(c) Neoprene

(d) Teflon

15. Cellulose acetate is a

(a) Thermoplastic

(b) Thermosetting plastic

(c) Both of these

(d) None of these

16. Vulcanization of rubber improves _____

17. Nylon 6 is used for making _____

18. Thermoplastic resins are formed by _____

19. Natural rubber is a polymer of _____

20. Thiokol rubber is made by reaction between _____

UNIT 4 WATER

1. Define hardness of water. What are the units of hardness of water. Give the relationship between different units.
2. Explain the EDTA method for the determination of hardness of water.
3. Discuss briefly the boiler troubles and their treatment.
4. Write short note on the following
 - (a) Scale formation
 - (b) Sludge formation
 - (c) Caustic embrittlement
5. Give a brief note on the following
 - (a) priming
 - (b) foaming
 - (c) electro dialysis
6. Explain the following
 - (a) Reverse osmosis
 - (b) Colloidal conditioning
 - (c) Calgon conditioning
7. Discuss the lime soda process for softening of hard water.
8. How can you differentiate scale and sludge formation of hard water?

9. Describe the ion-exchange process used for softening of water.
10. How can you differentiate the following.
 - a. Temporary hardness and permanent hardness
 - b. Scales and sludges
11. a) What is meant by “hardness” of water. And what are the disadvantages of hard water?
b) Distinguish between temporary and permanent hardness of water.
c) What are its units?
d) How do you express the hardness of water?
12. (a) What is the principle of EDTA method? Explain the estimation of hardness of water by complex metric method.
(b) Mention the dis-advantages of using hard water for industrial purpose.
13. (a) Explain the terms temporary and permanent hardness of water.
(b) How do you estimate the temporary hardness of water by EDTA method?
(c) 50 ml of a sample of hardwater was titrated against 0.01 M EDTA, required 48 ml of EDTA for titration. 50 ml of the same hardwater after boiling and filtering etc. required 35ml of the EDTA for titration. Calculate the total and temporary hardness of water in degree Clark.
14. (a) Estimation of free chlorine in water samples.
(b) Discuss the impurities in water and their effects.
(C) Explain the sedimentation process for the treatment of municipal water
15. Write a short notes on the following:
 - a) Break - point chlorination
 - (b) Dissolved oxygen
 - (c) Hardness of water
 - (d) Sedimentation and coagulation.
16. Distinguish the following:
 - (a) Hard water and soft water
 - (b) carbonate and non-carbonate hardness
 - (c) mg/litre and ppm
 - (d) Sedimentation and filtration.

17. 0.5 g of CaCO_3 was dissolved in dil. HCl and diluted to 1000 mL. 50 mL of this solution required 48 mL of EDTA solution for titration. 50 mL of hard water sample required 15 mL of EDTA solution for titration. 50 mL of same water sample on boiling, filtering etc, required 10 mL of EDTA solution. Calculate the different kinds of hardness in ppm.
18. Write short notes on the following:
- Units of hardness of water
 - Break point chlorination
 - Filtration of water
 - Impurities in water
19. Write short notes on the following:
- Carry over
 - Phosphate conditioning
 - Caustic embrittlement
20. a) Write short notes on Internal treatment methods
b) State the disadvantages of scale formation in boilers.
21. Distinguish between the following:
- Scales and Sludges
 - Soft water and dematerialized water.
 - Lime soda process and demineralization of water.
22. What are boiler scales? How their compositions effect the boiler? What are their ill effects? Discuss the measures for their prevention.
23. Compare the lime soda process with zeolite process of water softening.
24. (a) Describe the demineralisation of water by ion - exchange method.
(b) Mention the disadvantages of using hard water for any two industries
25. Explain the Ion-exchange method for the removal of dissolved impurities and its advantages over lime soda process
26. (a) Explain the cold lime soda process and hot lime soda process. What are the advantages of lime soda process?
(b) 100 ml of a water sample contains hardness equivalent to 25 ml of 0.08 N MgSO_4 .
(i). What is the hardness of water sample in ppm?
(ii). What is the amount of lime and soda required for the treatment of the water sample?
27. Explain the Ion-exchange method for the removal of dissolved impurities and its Advantages over lime soda process.

28. a) What is the chemical composition of Zeolite? How are they classified? Explain the mechanism of the treatment of hard water by Zeolites.
- b) A Zeolite softener was exhausted and regenerated by passing 100 liters of NaCl solution containing 585 gms per liter. Calculate the total hardness of the water sample in ppm, if the Zeolite softener can soften 1000 liters of water before regeneration.
29. Write a comparative statement on lime soda & Zeolite process.
30. Calculate the lime and soda needed for softening 50,000 litres of water containing the following salts: $\text{CaSO}_4 = 136 \text{ mg/lit}$; $\text{MgCl}_2 = 95 \text{ mg/lit}$; $\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/lit}$; $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/lit}$. Given that the molar mass of $\text{Ca}(\text{HCO}_3)_2$ is 162 and that of MgCl_2 is 95 4) Determine the amount of soda and lime required in Kg's to soften 5000 lit of water containing the following salts $\text{MgCl}_2 = 15.5 \text{ ppm}$, $\text{Ca}(\text{HCO}_3)_2 = 32.5 \text{ ppm}$, $\text{Ca}(\text{NO}_3)_2 = 22.4 \text{ ppm}$, $\text{NaCl} = 50 \text{ ppm}$, $\text{KCl} = 22.5 \text{ ppm}$.
31. Hydrazine is having an advantage over its counterpart sodium sulphite in the boiler-corrosion problem. What is it?
32. Mention the various boiler troubles and explain them in detail

Multiple choice questions:

1. Which of the following is a source of surface water (d)
(a) Rain water (b) river water (c) sea water (d) all
2. Hard water (b)
(a) Gives lather with soap (b) does not give lather with soap
(c) Hard to touch (d) solid
3. Equivalent weight of CaCO_3 (b)
(a) 100 (b) 50 (c) 10 (d) 1000
4. Indicator in EDTA method is (b)
(a) Fast sulphon (b) eriochrome Black T (c) methyl orange (d) phenolphthalein
5. Break point chlorination refers to (d)
(a) Titration (b) coagulation (c) sedimentation (d) disinfection
6. Caustic embrittlement is (a)
(a) Boiler corrosion
(b) Method of softening
(c) Internal treatment
(d) External treatment

7. Forming of wet steam is known as (a)
- Priming
 - Foaming
 - Both of these
 - None of these
8. Foaming can be avoided by (c)
- Adding anti-foaming agent
 - Removing oil from water
 - Both of these
 - None of these
9. Zeolite is known as (b)
- Calgon
 - Permutit
 - Alum
 - Salt
10. In reverse osmosis (a)
- Water gets separated
 - Contaminants are separated
 - Both of these
 - None of these
11. The process of removing extra common salt is called (c)
- deionization
 - softening
 - desalination
 - disinfection
14. A semi permeable membrane allows (a)
- only solvent particle
 - only solute particle
 - both solute and solvent particles
 - neither of them
15. Presence of NaCl imparts hardness to water – true or false
16. Hard water is water containing (a)
- Ca^{2+} , Mg^{2+} , Fe^{3+}
 - Na^+ & K^+
 - NO_3^- and PO_4^{3-}
 - dissolved gases
17. A semi permeable membrane allows
- only solvent particle
 - only solute Particle
 - both solute and solvent particles
 - neither of them
18. High alkaline water causes the problem of boiler scales – True or False.
19. Temporary hardness is caused by _____
20. Formation of _____ causes caustic embrittlement.

21. Dissolved oxygen in water can be removed by_____
 22. Radioactive conditioning prevents the formation of _____
 23. In hot-lime soda process the function of lime is to remove _____ type of hardness.
 24. The process of removal of extra common salt from water is known as_
 25. O_3 acts as _____
 26. Chlorine is used in purification of drinking water for _____
 27. Removal of microorganisms from water is known as _____
 28. A water sample contains 136 grams of calcium sulfate per liter. The hardness of water in terms of calcium carbonate is _____
1. Presence of NaCl imparts hardness to water – true or false
 2. The disinfecting action of bleaching powder is due to ---
 3. Anion exchange resin is regenerated by (a) alkali (b) acid (c) neutral solution
 4. Hard water is water containing
(a) Ca^{2+} , Mg^{2+} , Fe^{3+} (b) Na^+ & K^+ (c) NO_3^- and PO_4^{3-} (d) dissolved gases
 5. High alkaline water causes the problem of boiler scales – True or False
 6. Calculate the lime and soda requirement for treating 10,000 liters of water which analyses as follows: Total hardness: 400ppm $CaCO_3$ eq; M-alkalinity 200ppm $CaCO_3$ eq; Ca alkalinity: 2250ppm $CaCO_3$ eq.

UNIT 5

SURFACE CHEMISTRY

- 1) Differentiate the following:
 - (a) adsorption and absorption
 - (b) physical adsorption and chemical adsorption
 - (c) Lyophilic and lyophobic colloids
- 2) Derive Langmuir adsorption isotherm.
- 2) State and explain the BET equation for multilayer adsorption. How can you determine the surface area of an adsorbent with the help of BET equation.
- 3) Write short notes on the following:
 - (a) Tyndall effect
 - (b) Gold number
 - (c) Electrophoresis
- 4) What is nanotechnology? Explain the application of nanotechnology in the following fields.

- (a) space
 - (b) defence
 - (c) automotive industry
- 5) What are colloids? How they are classified?
- 6) Explain the factors that influence the adsorption of gases on the solid surface with suitable examples.
- 7) Give a brief note on the following:
- (a) electro osmosis
 - (b) protective colloids
- 8) micelles

1. The charge on the colloidal particle can be distributed by

- (a) Tyndall effect
- (b) Brownian movement
- (c) Osmosis
- (d) Cataphoresis

2. The precipitation of colloidal solution is difficult in the presence of

- a. NaCl (b) aerosol (c) gelatin (d) none of these

3. Fog is a colloidal solution of

- (a) Liquid dispersed in gas
- (b) Gas dispersed in liquid
- (c) Solid dispersed in liquid
- (d) Liquid dispersed in liquid

4. Smoke is an example of

- (a) Emulsion (b) gel (c) aerosol (d) jelly

5. The Brownian movement increases as

- (a) The size of the colloidal particle reduces
- (b) The size of the colloidal particle increases
- (c) None of the above

6. Cheese is the example of

- (a) Gel (b) emulsion (c) aerosol (d) hydrophil
7. In coagulating a positively charged colloidal particle the coagulating power of PO_4^{3-} is
- (a) Greater than SO_4^{2-}
 (b) Less than SO_4^{2-}
 (c) Less than Br^-
 (d) Less than HCO_3^-
8. Gold number is minimum in the case of
- (a) NaCl
 (b) Silica gel
 (c) Starch
 (d) Gelatin
9. Coagulation of 10 ml of gold solution by 10% NaCl is just prevented by the presence of 0.25 g of starch. The gold number of starch is
- (a) 0.25 (b) 2.5 (c) 250 (d) 0.025
10. Example of positively charged solution
- (a) $\text{Fe}(\text{OH})_2$ (b) Ag_2S_3 (c) protein (d) gold colloid

UNIT 6

ENERGY SOURCES

- (a) What is a fuel? Explain the classification of fuel with suitable examples.
 (b) What are the characteristics of a good fuel?
- Write an account on the analysis of flue gas by orsat's apparatus.
- Write an account on the analysis of coal and its significance.
- Explain HCV and LCV of a fuel. How can you determine the calorific value of a fuel by Junker's gas calorimeter.
- Write short note on the following:
 - Bergius process
 - Fischer-Tropsch's process
 - Octane number

6. Give a brief note on the following:
 - (a) Cetane number
 - (b) Knocking
 - (c) Cracking
7. How can you differentiate the following?
 - (a) Thermal cracking and Catalytic cracking
 - (b) Octane number and Cetane number
8. Describe the proximate analysis of coal and discuss the significance of each.
9. Describe the ultimate analysis of coal and discuss the significance of each.
10. (a) Distinguish between thermal and catalytic cracking.
(b) How the gasoline is prepared by fixed bed catalytic cracking process

Multiple choice questions:

1. A substance on burning if produces some energy, then it is called
 - (a) lubricant
 - (b) refractory
 - (c) insulator
 - (d) fuel
2. Natural gas is
 - (a) Primary fuel
 - (b) secondary fuel
 - (c) tertiary fuel
 - (d) none of these
3. water gas is
 - (a) primary fuel
 - (b) secondary fuel
 - (c) tertiary fuel
 - (d) none of these
4. Which will have higher value
 - (a) GCV
 - (b) NCV
 - (c) Both are equal
 - (d) cannot be predicted
5. Which is the elemental analysis
 - (a) Proximate analysis
 - (b) ultimate analysis
 - (c) both of these

- (d) none of these
6. Best quality of coal
- (a) wood
 - (b) peak
 - (c) lignite
 - (d) anthracite
7. In the determination of NCV, the problems are
- (a) escaped (b) condensed (c) oxidized (d) reduced
8. Conversion of coal to coke is called
- (a) Coalification
 - (b) carbonization
 - (c) bituminization
 - (d) none of the above
9. Cottrell's process is for
- (a) separation for sulfur
 - (b) separation for water
 - (c) separation for oxygen
 - (d) none of the above
10. sulfur can be removed by adding
- (a) Cu
 - (b) CuO
 - (c) Fe_2O_3
 - (d) H_2O
11. Octane number indicates the purity of _____
12. Cetane number indicates the purity of _____
13. Flue gas analysis is done by _____
14. In the Orsat's apparatus the first bulb is filled with _____
15. Calorific value of a gaseous fuel is determined by _____

UNIT 7

PHASE RULE

1. Write short note on the following:
- (a) Critical point
 - (b) Triple point
 - (c) Phase rule
- (4) Give a brief note on the following:
- (a) Phase
 - (b) Component
 - (c) Degrees of freedom

(5) Explain the following:

- (a) Annealing
- (b) Normalizing
- (c) Hardening

(6) Explain water system with the help of neat phase diagram.

(7) (a) What is Gibbs phase rule? Explain the terms involved in phase rule.

(b) Give an application of phase rule to lead-silver system.

(8) Give a brief note on eutectic characteristics and applications.

Multiple Choice Questions:

1. Gibbs phase rule for general system:

(a) $P+F=C-1$ (b) $P+F=C+1$ (c) $P+F=C-2$ (d) $P+F=C+2$

2. In a single-component condensed system, if degree of freedom is zero, maximum number of phases that can co-exist_____.

(a) 0 (b) 1 (c) 2 (d) 3

3. The degree of freedom at triple point in unary diagram for water

_____.

(a) 0 (b) 1 (c) 2 (d) 3

4. Above the following line, liquid phase exist for all compositions in a phase diagram.

(a) Tie-line (b) Solvus (c) Solidus (d) Liquidus

5. Following is wrong about a phase diagram.

(a) It gives information on transformation rates.

(b) Relative amount of different phases can be found under given equilibrium conditions.

(c) It indicates the temperature at which different phases start to melt.

(d) Solid solubility limits are depicted by it.

6. Not a Hume-Ruthery condition:

(a) Crystal structure of each element of solid solution must be the same.

(b) Size of atoms of each two elements must not differ by more than 15%.

(c) Elements should form compounds with each other.

(d) Elements should have the same valence.

7. Pick the odd one in the following:

(a) Isomorphous alloy (b) Terminal solid solution

(c) Intermediate solid solution (d) Compound

8. The boundary line between (liquid) and (liquid+solid) regions must be part of_____.

(a) Solvus (b) Solidus (c) Liquidus (d) Tie-line

9. The boundary line between (liquid+solid) and (solid) regions must be part of_____.

(a) Solvus (b) Solidus (c) Liquidus (d) Tie-line

10. The boundary line between (α) and (α + β) regions must be part of_____.

(a) Solvus (b) Solidus (c) Liquidus (d) Tie-line

11. Horizontal arrest in a cooling curve represents:

(a) Continuous cooling (b) Invariant reaction (c) Both (d) None

12. Relative amounts of phases in a region can be deduced using

(a) Phase rule (b) Lever rule (c) Either (d) None

13. An invariant reaction that produces a solid up on cooling two liquids:

(a) Eutectic (b) Peritectic (c) Monotectic (d) Syntectic

14. A solid + a liquid result in a liquid up on heating during _____ reaction.

(a) Eutectic (b) Peritectic (c) Monotectic (d) Syntectic

15. A solid + a liquid result in a solid up on cooling during _____ reaction.

(a) Eutectic (b) Peritectic (c) Monotectic (d) Syntectic

16. On heating, one solid phase results in another solid phase plus on liquid phase during____reaction.

(a) Eutectic (b) Peritectic (c) Monotectic (d) Syntectic

17. A solid phase results in a solid plus another solid phase up on cooling during_____reaction.

(a) Eutectoid (b) Peritectoid (c) Eutectic (d) Peritectic

18. A solid phase results in a solid plus another solid phase up on heating during _____ reaction.
 (a) Eutectoid (b) Peritectoid (c) Monotectoid (d) None
19. A liquid phase produces two solid phases during _____ reaction up on cooling.
 (a) Eutectic (b) Eutectoid (c) Peritectic (d) Peritectoid
20. Liquid phase is involved in the following reaction:
 (a) Eutectoid (b) Peritectoid (c) Monotectoid (d) None
21. Not a basic step of precipitation strengthening
 (a) Solutionizing (b) Mixing and compacting (c) Quenching (d) Aging
22. wt.% of carbon in mild steels
 (a) <0.008 (b) 0.008-0.3 (c) 0.3-0.8 (d) 0.8-2.11
23. Eutectic product in Fe-C system is called
 (a) Pearlite (b) Bainite (c) Ledeburite (d) Spheroidite
24. Eutectoid product in Fe-C system is called
 (a) Pearlite (b) Bainite (c) Ledeburite (d) Spheroidite
25. Phases that exist on left side of an invariant reaction line are called
 (a) Pro-phase (b) Hypo-phase (c) Hyper-phase (d) None
26. Alloying element that decreases eutectoid temperature in Fe-C system
 (a) Mo (b) Si (c) Ti (d) Ni

UNIT 8

MATERIAL CHEMISTRY

1. Discuss any FOUR essential properties of a good refractory in detail.
2. What are electrical insulators? Discuss their characteristics & engineering applications.
3. What are thermal insulators? Discuss their engineering applications and characteristics
4. (a) What are refractories? How important are the properties – refractoriness under load and thermal conductivity for industrial applications?

- (b) Compare acidic and basic refractories with examples
5. What do you understand by 'refractoriness'. Explain its measurement. Write a note on 'refractoriness-under-load (RUL)'.
6. (a) Define Refractories and what are the criteria of a good refractory?
- (b) Give the classification of refractories with suitable examples
7. (a) What is pyrometric cone equivalent? How it is determined for a refractory? What is its significance?
- (b) Write a short note on: i. porosity ii. Thermal Conductivity iii. Dimensional Stability.
8. Write a short note on principle and function of Lubricants
9. (a) Give the functions of lubricants.
- (b) Describe the mechanism of extreme pressure lubrication.
- C) How a viscous lubricant is converted into grease?
10. Write a note on lubricants with special reference to their classification, mode of action, examples and uses.
11. Explain the various mechanisms of lubrication in detail.
12. Explain the following two theories for the mechanism of the lubricants.
- a) Boundary lubrication
- b) Extreme pressure lubrication
13. (a) Give the functions of lubricants.
- (b) Describe the mechanism of extreme pressure lubrication.
- C) How a viscous lubricant is converted into grease?
- 14.. Define lubricant. Discuss the Classification and important properties of the lubricants.
15. What are the chemical constituents of Cement? Discuss the function of each constituent.
16. (a) Why cements are called hydraulic cements?
- (b) By writing the various chemical reactions involved explain the setting and hardening of cement.
17. (a) Discuss the chemical and physical changes that occur during the setting of cement with relevant chemical equations.
- (b) Write a note on types of Portland cements.
18. What is Portland cement? Give its composition. What are the raw materials required for its manufacture? Discuss the chemistry of setting and hardening of cement.
19. a. Write a short note on Additives for cement.
- b. Write a note on type of Portland cement.

20. With the help of flow diagram explain the manufacture of Portland cement by dry and wet process

Multiple choice questions:

1. Any material which can with stand high temperature with out softening from deformation (b)
 - (a) Insulating material
 - (b) Refractory
 - (c) Lubricant
 - (d) Fuel
2. Ability to with stand higher temperature is known as (d)
 - (a) Thermal spalling
 - (b) Thermal conductivity
 - (c) Thermal resistivity
 - (d) Refractories
3. Refractory fails due to (d)
 - (a) Rapid changes due to temperature
 - (b) Over firing
 - (c) Due to dimensional changes
 - (d) All
4. Halogenated organic liquid insulator (d)
 - (a) Silicones
 - (b) Silicates
 - (c) Esters
 - (d) None
5. Boundary lubrication is also known as (b)
 - (a) Thick film lubrication
 - (b) Thin film lubrication
 - (c) Medium film lubrication
 - (d) All the above
6. Saponification of fat with alkali gives (a)
 - (a) Liquid lubricant
 - (b) Solid lubricant
 - (c) Both of the above
 - (d) None of the above
7. Calcining the argillaceous material alone produces (a)

- (a) Natural cement
 - (b) Puzzalona cement
 - (c) Porland cement
 - (d) Slag cement
8. Initial setting of cement is due to the gelation of (b)
- (a) Clinker
 - (b) Slag
 - (c) Silos
 - (d) Flux
9. Initial setting of cement should not be less than (d)
- (a) 5 minutes
 - (b) 10 minutes
 - (c) 15 minutes
 - (d) 30 minutes
10. Mixing and grinding of valconoic ash produces (b)
- (a) Natural cement
 - (b) Puzzalona cement
 - (c) Portland cement
 - (d) Slag cement
11. Porosity in an impurity by weathering of
- (a) Chemical stability
 - (b) Resistance to corrosion
 - (c) Thermal conductivity
 - (d) Resistance to thermal spalling
12. High refractotiness under load is shown by
- (a) Dolomite
 - (b) Magnesia
 - (c) Alumina
 - (d) Silica
13. Lubricants are aimed to reduce
- (a) Abrasion
 - (b) Corrosion
 - (c) Wearing
 - (d) All the above

14. Lubricant used in machines working at low temperature should have

- (a) High pour point
- (b) Low pour point
- (c) High flash point
- (d) Low flash point

15. Graphite dispersed in oil is known as

- (a) Dispersion lubricant
- (b) Grease
- (c) Oildag
- (d) Graoil

University previous question papers:**Code No: 09A1BS03 Set No. 1****EXTERNAL EXAM****I B.Tech. II Mid Examinations, March – 2010****ENGINEERING CHEMISTRY****Objective Exam****Name: _____ Hall Ticket No. A****Answer All Questions. All Questions Carry Equal Marks. Time: 20 Min. Marks: 10.****I. Choose the correct alternative:**

1. The following is an example of polyamide resin []
a) Bakelite b) Nylon c) fluon d) polyaniline
2. Quantum dots are often referred to as []
a) Artificial atoms b) atoms c) molecules d) compounds
3. The polymers with alternate arrangement of functional groups are called []
a) atactic polymers b) isotactic polymers
c) syndiotactic polymers d) oligopolymers
4. Caustic embrittlement in boilers can be prevented by using []
a) sodium chloride b) sodium sulphate c) sodium phosphate d) sodium hydroxide
5. The protective action of different colloids is expressed in terms of []
a) Oxidation number b) Avagadro number c) atomic number d) goldnumber
6. The size of the nanoparticles is between []
a) 1-100nm b) 1-1000nm c) 1-10 nm d) 1-10000nm
7. The composition of natural rubber is []
a) Polyisoprene b) Chloroprene c) polyisobutene d) polysulphide
8. Freundlich adsorption isotherm is a plot of []
a) Mass and volume b) Mass and temperature c) Mass and pressure d) Mass and concentration
9. The method in which the ions present in saline water migrate towards their respective electrodes under applied emf through ion-selective membrane is called []
a) Osmosis b) Reverse Osmosis c) Electrodialysis d) Dialysis
10. Castor oil is a []
a) Antiskinning agent b) Antifoaming agent c) Anti ageing agent d) Anti corrosive agent

Code No: 09A1BS03 :2: Set No. 1

II Fill in the Blanks:

11. The exhausted zeolite is regenerated by _____
12. The composition of solution used in the estimation of hardness of water by EDTA method is _____
13. The dispersion of liquid dispersed phase in gas dispersion medium is called _____
14. 22.2 mg/l of chlorides in water cause _____ hardness in terms of CaO equivalents.
15. The adsorption of H_2 or O_2 on charcoal is an example of _____
16. The indicator used during the estimation of hardness of water by EDTA method is _____
17. The amount of lime required for the removal of 65mg/l of hardness in terms of CaO equivalents is _____
18. A monomer with more than three reactive sites is called _____
19. The soft, loose, slimy precipitates formed inside the boiler are _____
20. The visibility of dust particles in a semidarkened room when a sun beam enters is an example of _____

-oOo-

Code No: 09A1BS03 Set No. 2

EXTERNAL EXAM

I B.Tech. II Mid Examinations, March – 2010

ENGINEERING CHEMISTRY

Objective Exam

Name: _____ Hall Ticket No. A

Answer All Questions. All Questions Carry Equal Marks. Time: 20 Min. Marks: 10.

I. Choose the correct alternative:

1. Caustic embrittlement in boilers can be prevented by using []
a) sodium chloride b) sodium sulphate c) sodium phosphate d) sodium hydroxide
2. The protective action of different colloids is expressed in terms of []
a) Oxidation number b) Avagadro number c) atomic number d) goldnumber
3. The size of the nanoparticles is between []
a) 1-100nm b) 1-1000nm c) 1-10 nm d) 1-10000nm
4. The composition of natural rubber is []
a) Polyisoprene b) Chloroprene c) polyisobutene d) polysulphide
5. Freundlich adsorption isotherm is a plot of []
a) Mass and volume b) Mass and temperature c) Mass and pressure d) Mass and concentration
6. The method in which the ions present in saline water migrate towards their respective electrodes under applied emf through ion-selective membrane is called []
a) Osmosis b) Reverse Osmosis c) Electrodialysis d) Dialysis
7. Castor oil is a []
a) Antiskinning agent b) Antifoaming agent c) Anti ageing agent d) Anti corrosive agent
8. The following is an example of polyamide resin []
a) Bakelite b) Nylon c) fluon d) polyaniline
9. Quantum dots are often referred to as []
a) Artificial atoms b) atoms c) molecules d) compounds
10. The polymers with alternate arrangement of functional groups are called []
a) atactic polymers b) isotactic polymers
c) syndiotactic polymers d) oligopolymers

Cont...2

Code No: 09A1BS03 :2: Set No. 2

II Fill in the blanks:

11. 22.2 mg/l of chlorides in water cause _____ hardness in terms of CaCO_3 equivalents.
12. The adsorption of H_2 or O_2 on charcoal is an example of _____

13. The indicator used during the estimation of hardness of water by EDTA method is _____

14. The amount of lime required for the removal of 65mg/l of hardness in terms of CaO equivalents is _____

15. A monomer with more than three reactive sites is called _____

16. The soft, loose, slimy precipitates formed inside the boiler are _____

17. The visibility of dust particles in a semidarkened room when a sun beam enters is an example of _____

18. The exhausted zeolite is regenerated by _____

19. The composition of solution used in the estimation of hardness of water by EDTA method is _____

20. The dispersion of liquid dispersed phase in gas dispersion medium is called _____

-oOo-

Code No: 09A1BS03 Set No. 3

EXTERNAL EXAM

I B.Tech. II Mid Examinations, March – 2010

ENGINEERING CHEMISTRY

Objective Exam

Name: _____ Hall Ticket No. A

Answer All Questions. All Questions Carry Equal Marks. Time: 20 Min. Marks: 10.

I. Choose the correct alternative:

1. The size of the nanoparticles is between []
a) 1-100nm b) 1-1000nm c) 1-10 nm d) 1-10000nm
2. The composition of natural rubber is []
a) Polyisoprene b) Chloroprene c) polyisobutene d) polysulphide
3. Freundlich adsorption isotherm is a plot of []
a) Mass and volume b) Mass and temperature c) Mass and pressure d) Mass and concentration
4. The method in which the ions present in saline water migrate towards their respective electrodes under applied emf through ion-selective membrane is called []
a) Osmosis b) Reverse Osmosis c) Electrodialysis d) Dialysis
5. Castor oil is a []
a) Antiskinning agent b) Antifoaming agent c) Anti ageing agent d) Anti corrosive agent
6. The following is an example of polyamide resin []
a) Bakelite b) Nylon c) fluon d) polyaniline
7. Quantum dots are often referred to as []
a) Artificial atoms b) atoms c) molecules d) compounds
8. The polymers with alternate arrangement of functional groups are called []
a) atactic polymers b) isotactic polymers
c) syndiotactic polymers d) oligopolymers
9. Caustic embrittlement in boilers can be prevented by using []
a) sodium chloride b) sodium sulphate c) sodium phosphate d) sodium hydroxide
10. The protective action of different colloids is expressed in terms of []
a) Oxidation number b) Avagadro number c) atomic number d) goldnumber

Cont....2

Code No: 09A1BS03 :2: Set No. 3

II Fill in the Blanks:

11. The indicator used during the estimation of hardness of water by EDTA method is _____

12. The amount of lime required for the removal of 65mg/l of hardness in terms of CaCO_3 equivalents is _____

13. A monomer with more than three reactive sites is called _____

14. The soft, loose, slimy precipitates formed inside the boiler are _____

15. The visibility of dust particles in a semidarkened room when a sun beam enters is an example of _____

16. The exhausted zeolite is regenerated by _____

17. The composition of solution used in the estimation of hardness of water by EDTA method is _____

18. The dispersion of liquid dispersed phase in gas dispersion medium is called _____

19. 22.2 mg/l of chlorides in water cause _____ hardness in terms of CaCO_3 equivalents.

20. The adsorption of H_2 or O_2 on charcoal is an example of _____

-oOo-

Code No: 09A1BS03 Set No. 4

EXTERNAL EXAM

I B.Tech. II Mid Examinations, March – 2010

ENGINEERING CHEMISTRY

Objective Exam

Name: _____ Hall Ticket No. A

Answer All Questions. All Questions Carry Equal Marks. Time: 20 Min. Marks: 10.

I. Choose the correct alternative:

1. Freundlich adsorption isotherm is a plot of []
a) Mass and volume b) Mass and temperature c) Mass and pressure d) Mass and concentration
2. The method in which the ions present in saline water migrate towards their respective electrodes under applied emf through ion-selective membrane is called []
a) Osmosis b) Reverse Osmosis c) Electrodialysis d) Dialysis
3. Castor oil is a []
a) Antiskinning agent b) Antifoaming agent c) Anti ageing agent d) Anti corrosive agent
4. The following is an example of polyamide resin []
a) Bakelite b) Nylon c) fluon d) polyaniline
5. Quantum dots are often referred to as []
a) Artificial atoms b) atoms c) molecules d) compounds
6. The polymers with alternate arrangement of functional groups are called []
a) atactic polymers b) isotactic polymers
c) syndiotactic polymers d) oligopolymers
7. Caustic embrittlement in boilers can be prevented by using []
a) sodium chloride b) sodium sulphate c) sodium phosphate d) sodium hydroxide
8. The protective action of different colloids is expressed in terms of []
a) Oxidation number b) Avagadro number c) atomic number d) goldnumber
9. The size of the nanoparticles is between []
a) 1-100nm b) 1-1000nm c) 1-10 nm d) 1-10000nm
10. The composition of natural rubber is []
a) Polyisoprene b) Chloroprene c) polyisobutene d) polysulphide

Cont...2

Code No: 09A1BS03 :2: Set No. 4

II Fill in the Blanks:

11. A monomer with more than two reactive sites is called _____
12. The soft, loose, slimy precipitates formed inside the boiler are _____

13. The visibility of dust particles in a semidarkened room when a sun beam exerts is an example of

14. The exhausted zeolite is regenerated by _____

15. The composition of solution used in the estimation of hardness of water by EDTA method is _____

16. The dispersion of liquid dispersed phase in gas dispersion medium is called _____

17. 22.2 mg/l of chlorides in water cause _____ hardness in terms of CaCO_3 equivalents.

18. The adsorption of H_2 or O_2 on charcoal is an example of _____

19. The indicator used during the estimation of hardness of water by EDTA method is _____

20. The amount of lime required for the removal of 65mg/l of hardness in terms of CaCO_3 equivalents is

-oOo-

Code No: 09A1BS03

R09

Set No. 2

I B.Tech Regular Examinations, JUNE 2010**ENGINEERING CHEMISTRY**

Common to CE, ME, CHEM, BME, IT, MECH, MEP, AE, BT, AME, ICE,
E.COMP.E. MMT, ETM, EIE, CSE, ECE, EEE

Time: 3 hours**Max Marks: 75****Answer any FIVE Questions****All Questions carry equal marks**

1. (a) What is Gibbs phase rule, its significance and limitations?
(b) Explain with suitable examples the terms involved in Gibb's phase rule. [8+7]
2. Write an account on the refining of petroleum by explaining the composition, boiling range and uses of different fractions obtained during refining. [15]
3. (a) What are concentration cells? How can the EMF of a concentration cell be evaluated?
(b) Write short notes on single electrode potential and its significance. [9+6]
4. Explain the following statements with proper illustrations.
(a) Tyndal cone is observed when a beam of light is concentrated on colloidal systems.
(b) Alums are used for the treatment of water supplied by municipalities. [8+7]
5. Write a brief account on the following:
(a) Heat capacity of a refractory material.
(b) Porosity of a refractory material.
(c) Thermal expansion and contraction.
(d) Refractoriness. [15]
6. (a) How are synthetic high polymers classified?
(b) Discuss the preparation, properties and uses of various grades of polythene. [8+7]
7. (a) What are the factors that lead to caustic embrittlement in boilers? How can this be prevented?
(b) Distinguish between Zeolite process and Ion-Exchange process. [8+7]
8. (a) Explain the process of galvanizing and tinning.
(b) What are organic paints? Describe their constituents. [8+7]

Code No: 09A1BS03

R09

Set No. 4

I B.Tech Regular Examinations, JUNE 2010

ENGINEERING CHEMISTRY

Common to CE, ME, CHEM, BME, IT, MECT, MEP, AE, BT, AME, ICE, E.COMP.E,
MMT, ETM, EIE, CSE, ECE, EEE

Time: 3 hours

Max Marks: 75

Answer any FIVE Questions

All Questions carry equal marks

1. What is meant by a phase diagram? With the help of a phase diagram, explain the following ?

- (a) Triple point
- (b) Eutectic point. [15]

2. Classify the following fuels space by furnishing proper reasons.

- (a) Coke
- (b) Petroleum
- (c) Benzol
- (d) Biogas
- (e) Lignite
- (f) LPG
- (g) Natural gas
- (h) Anthracite. [15]

3. What is meant by coagulation of colloids? How is it brought out? [15]

4. (a) Why is hard water harmful to boilers?

(b) Describe the causes and harmful effects of scale formation.

(c) One liter of water from Khammam Dist. in Andhra Pradesh showed the following analysis: $\text{Mg}(\text{HCO}_3)_2 = 0.0256$ gms, $\text{Ca}(\text{HCO}_3)_2 = 0.0156$ gms, $\text{NaCl} = 0.0167$ gms, $\text{CaSO}_4 = 0.0065$ gms, and $\text{MgSO}_4 = 0.0054$ gms. Calculate the lime & soda required for softening of 10,000 litres of water. [4+4+7]

5. (a) What is the difference between free-radical and ionic chain polymerization?

(b) Write a note on preparation, properties and uses of i. bakelite ii. PVC. [5+5+5]

6. How are the following properties influence the stability of refractories?

- (a) Chemical inertness.
- (b) Refractoriness under load.
- (c) Refractoriness.
- (d) Dimensional stability. [15]

7. (a) What do you understand by electrochemical series? How is this series useful in the determination of corrosion of metals. 8M

(b) The resistance of a 0.1N solution of an electrolyte of 40 ohms. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm². calculate equivalent conductivity. [8+7]

8. (a) Discuss the influence of following factors on corrosion:-

- i. Over voltage
- ii. Nature of the metal
- iii. Nature of environment.

(b) Explain the nature and role of constituents of organic paints. [9+6]

Code No: 09A1BS03

R09

Set No. 1

I B.Tech Regular Examinations, JUNE 2010

ENGINEERING CHEMISTRY

Common to CE, ME, CHEM, BME, IT, MECT, MEP, AE, BT, AME, ICE,
E.COMP.E, MMT, ETM, EIE, CSE, ECE, EEE

Time: 3 hours

Max Marks: 75

Answer any FIVE Questions

All Questions carry equal marks

1. (a) Explain the electrochemical theory of corrosion of metals with special reference to rusting of iron.
(b) Write a note on galvanizing and metal cladding. [8+7]
2. Write a brief account on the following:
(a) Wet Process for the manufacture of cement.
(b) Setting and hardening of cement. [8+7]
3. (a) What are colloids? How are they classified?
(b) Differentiate the dispersed phase from dispersion medium. [8+7]
4. What is meant by cracking of hydrocarbons? What are its objectives? With the help of neat sketches explain the production of petrol by catalytic cracking. [15]
5. Give proper explanations for the following statements
(a) The fusion curve of ice has a negative slope whereas the sublimation curve has positive slope in the phase diagram
(b) In lead-silver system, isobaric phase diagrams are studied. [7+8]
6. Explain the synthetic methods, properties and applications of the following elastomers:-
(a) Buna-S rubber
(b) Butyl rubber
(c) Thiokol rubber. [5+5+5]
7. (a) Differentiate between lime-soda and zeolite processes for softening of water giving merits and demerits of the two processes.
(b) How is the hardness of water expressed? What are the various units employed? Explain their interconversion. [9+6]
8. (a) Give reasons for the following statements:-
i. When a zinc rod is dipped in a solution of aq. copper sulphate, copper is precipitated out.
ii. Nernst equation is applicable for the determination of emf of a concentration cell.
(b) State and explain the Kohlrausch's law and its applications. [6+9]

Code No: 09A1BS03

R09

Set No. 3

I B.Tech Regular Examinations, JUNE 2010

ENGINEERING CHEMISTRY

Common to CE, ME, CHEM, BME, IT, MECH, MEP, AE, BT, AME, ICE,
E.COMP.E, MMT, ETM, EIE, CSE, ECE, EEE

Time: 3 hours

Max Marks: 75

Answer any FIVE Questions

All Questions carry equal marks

1. (a) What are fuels? How are they classified? What are the advantages of gaseous fuels?
- (b) Give an account of the analysis of coal by ultimate analysis and its significance. [7+8]
2. (a) How are metals protected by impressed current method?
- (b) Explain the galvanisation and tinning processes of metals. [6+9]
3. Differentiate the following with suitable examples:-
 - (a) Polymer from monomer
 - (b) Homo polymer from co-polymer
 - (c) Step growth polymerization from chain polymerisation. [5+4+6]
4. (a) Define the terms specific, equivalent and molar conductivities. How do they vary with dilution.
- (b) Calculate the cell constant of a cell having a solution of concentration N/30 gm. equiv/litre of an electrolyte which showed the equivalent conductance of 120 Mhos cm² gm equiv⁻¹: [8+7]
5. (a) Explain the various reasons for failure of a refractory material.
- (b) Differentiate refractories from insulators. [7+8]
6. (a) Write a note on complexometric titrations used for estimation of hardness of water by EDTA.
- (b) Explain the process of electrodialysis. [8+7]
7. Explain how iron-carbon phase diagram provides information about the formation of different phases in iron-carbide system. [15]
8. What are fullerenes? Present an account of applications of fullerenes. [15]

SET-1 NR Code.No: NR10104
EXTERNAL EXAM B.TECH – SUPPLEMENTARY EXAMINATIONS
JUNE - 2010

ENGINEERING CHEMISTRY

(Common to CE, ME, MEP, MCT, AE)

Time: 3hours Max

Marks:80

Answer any FIVE questions

All questions carry equal marks

1. How are the metals protected by the following methods?
 - a) Sacrificial anode method
 - b) Cementation
 - c) Organic coating like varnish. [16]
2. Differentiate the following with suitable examples.
 - a) Thermoplastic resins from thermosetting resins
 - b) Polymer from monomer
 - c) Chain polymerization from step polymerization. [16]
- 3.a) Explain the lime-soda process with relevant chemical reactions involved.
b) A sample of water contains 16.4 mg/l of $\text{Ca}(\text{HCO}_3)_2$, 11.2 mg/l of CaCl_2 , 9.6 mg/l of MgCl_2 , 10 mg/l of turbidity. Calculate the amount of lime and soda required for the treatment of 10,000 litres of water. [8+8]
4. Write a detailed account on the following:
 - a) Knocking
 - b) Ultimate analysis
 - c) Metallurgical coke. [16]
- 5.a) What are refractories? How are they classified? Explain refractoriness.
b) Explain the characteristics and engineering applications of thermal insulators. [8+8]
6. Explain the setting and hardening of cement with the chemical changes involved. [16]
7. Explain the following properties of lubricants and their significance:
 - a) Viscosity
 - b) Flash and fire point
 - c) Aniline point. [16]
8. Write short notes on the following:
 - a) Junker's calorimeter
 - b) Zeolite process. [16]

SET-2

NR

Code.No: NR10104

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY
HYDERABAD

I B.TECH – SUPPLEMENTARY EXAMINATIONS JUNE - 2010
ENGINEERING CHEMISTRY

(Common to CE, ME, MEP, MCT, AE)

Time: 3hours Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) Explain the lime-soda process with relevant chemical reactions involved.
- b) A sample of water contains 16.4 mg/l of $\text{Ca}(\text{HCO}_3)_2$, 11.2 mg/l of CaCl_2 , 9.6 mg/l of MgCl_2 , 10 mg/l of turbidity. Calculate the amount of lime and soda required for the treatment of 10,000 litres of water. [8+8]
2. Write a detailed account on the following:
 - a) Knocking
 - b) Ultimate analysis
 - c) Metallurgical coke. [16]
- 3.a) What are refractories? How are they classified? Explain refractoriness.
- b) Explain the characteristics and engineering applications of thermal insulators. [8+8]
4. Explain the setting and hardening of cement with the chemical changes involved. [16]
5. Explain the following properties of lubricants and their significance:
 - a) Viscosity
 - b) Flash and fire point
 - c) Aniline point. [16]
6. Write short notes on the following:
 - a) Junker's calorimeter
 - b) Zeolite process. [16]
7. How are the metals protected by the following methods?
 - a) Sacrificial anode method
 - b) Cementation
 - c) Organic coating like varnish. [16]
8. Differentiate the following with suitable examples.
 - a) Thermoplastic resins from thermoset resins
 - b) Polymer from monomer
 - c) Chain polymerization from step polymerization. [16]

SET-3

NR

Code.No: NR10104

EXTERNAL EXAM

I B.TECH – SUPPLEMENTARY EXAMINATIONS JUNE - 2010

ENGINEERING CHEMISTRY

(Common to CE, ME, MEP, MCT, AE)

Time: 3hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) What are refractories? How are they classified? Explain refractoriness.
- b) Explain the characteristics and engineering applications of thermal insulators. [8+8]
2. Explain the setting and hardening of cement with the chemical changes involved. [16]
3. Explain the following properties of lubricants and their significance:
 - a) Viscosity
 - b) Flash and fire point
 - c) Aniline point. [16]
4. Write short notes on the following:
 - a) Junker's calorimeter
 - b) Zeolite process. [16]
5. How are the metals protected by the following methods?
 - a) Sacrificial anode method
 - b) Cementation
 - c) Organic coating like varnish. [16]
6. Differentiate the following with suitable examples.
 - a) Thermoplastic resins from thermoset resins
 - b) Polymer from monomer
 - c) Chain polymerization from step polymerization. [16]
- 7.a) Explain the lime-soda process with relevant chemical reactions involved.
- b) A sample of water contains 16.4 mg/l of $\text{Ca}(\text{HCO}_3)_2$, 11.2 mg/l of CaCl_2 , 9.6 mg/l of MgCl_2 , 10 mg/l of turbidity. Calculate the amount of lime and soda required for the treatment of 10,000 litres of water. [8+8]
8. Write a detailed account on the following:
 - a) Knocking
 - b) Ultimate analysis
 - c) Metallurgical coke. [16]

SET-4

NR

Code.No: NR10104

EXTERNAL EXAM

I B.TECH – SUPPLEMENTARY EXAMINATIONS JUNE - 2010

ENGINEERING CHEMISTRY

(Common to CE, ME, MEP, MCT, AE)

Time: 3 hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

1. Explain the following properties of lubricants and their significance:
 - a) Viscosity
 - b) Flash and fire point
 - c) Aniline point. [16]
2. Write short notes on the following:
 - a) Junker's calorimeter
 - b) Zeolite process. [16]
3. How are the metals protected by the following methods?
 - a) Sacrificial anode method
 - b) Cementation
 - c) Organic coating like varnish. [16]
4. Differentiate the following with suitable examples.
 - a) Thermoplastic resins from thermoset resins
 - b) Polymer from monomer
 - c) Chain polymerization from step polymerization. [16]
- 5.a) Explain the lime-soda process with relevant chemical reactions involved.
- b) A sample of water contains 16.4 mg/l of $\text{Ca}(\text{HCO}_3)_2$, 11.2 mg/l of CaCl_2 , 9.6 mg/l of MgCl_2 , 10 mg/l of turbidity. Calculate the amount of lime and soda required for the treatment of 10,000 litres of water. [8+8]
6. Write a detailed account on the following:
 - a) Knocking
 - b) Ultimate analysis
 - c) Metallurgical coke. [16]
- 7.a) What are refractories? How are they classified? Explain refractoriness.
- b) Explain the characteristics and engineering applications of thermal insulators. [8+8]
8. Explain the setting and hardening of cement with the chemical changes involved. [16]

Code No: R07A1BS07

R07

Set No. 2

I B.Tech Supplementary Examinations, June 2010

ENGINEERING CHEMISTRYCommon to Mechanical Engineering, Mechatronics, Production
Engineering, Automobile Engineering

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. Briefly discuss the various metallic coatings that prevent corrosion. [16]
2. (a) What are the ratio of phenol and formaldehyde in Novolac and resol?
(b) Name any two synthetic rubbers and give their preparation. Compare the properties natural rubber with vulcanized rubber. [4+12]
3. (a) Distinguish between extreme pressure lubrication & boundary lubrication.
(b) Describe the functions of viscosity index improvers? Give examples.
(c) In what situations semi-solid lubricants are preferred. [8+4+4]
4. (a) Explain proximate analysis of coal and its significance
(b) What is petrol knock? How is related to chemical structure? Explain octane number. [8+8]
5. (a) Distinguish between hard water and soft water. What is break point chlorination and what is its importance?
(b) Discuss the methods for the determination of
 - i. Alkalinity
 - ii. Dissolved oxygen. [8+8]
6. (a) How can scale formation be prevented by :
 - i. Phosphate conditioning
 - ii. Calgon conditioning
 - iii. Carbonate conditioning.
 (b) Compare and contrast lime soda process with that of demineralization process. [9+7]
7. (a) What is electrochemical corrosion and how does it occur? Describe its mechanism.
(b) What are corrosion inhibitors? Discuss anodic and cathodic inhibitors with suitable examples. [8+8]
8. (a) Define Refractories and what are the criteria of a good refractory?
(b) Give the classification of refractories with suitable examples. [6+10]

Code No: R07A1BS07 R07 Set No. 4
 I B.Tech Supplementary Examinations, June 2010
ENGINEERING CHEMISTRY
 Common to Mechanical Engineering, Mechatronics, Production
 Engineering, Automobile Engineering
 Time: 3 hours Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) What is electrochemical corrosion and how does it occur? Describe its mechanism.
 (b) What are corrosion inhibitors? Discuss anodic and cathodic inhibitors with suitable examples. [8+8]
2. Briefly discuss the various metallic coatings that prevent corrosion. [16]
3. (a) Explain proximate analysis of coal and its significance
 (b) What is petrol knock? How is related to chemical structure? Explain octane number. [8+8]
4. (a) What are the ratio of phenol and formaldehyde in Novolac and resol?
 (b) Name any two synthetic rubbers and give their preparation. Compare the properties natural rubber with vulcanized rubber. [4+12]
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 (b) Give the classification of refractories with suitable examples. [6+10]
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 (b) Discuss the methods for the determination of
 - i. Alkalinity
 - ii. Dissolved oxygen. [8+8]
7. (a) How can scale formation be prevented by :
 - i. Phosphate conditioning
 - ii. Calgon conditioning
 - iii. Carbonate conditioning.
 (b) Compare and contrast lime soda process with that of demineralization process. [9+7]
8. (a) Distinguish between extreme pressure lubrication & boundary lubrication.
 (b) Describe the functions of viscosity index improvers? Give examples.
 (c) In what situations semi-solid lubricants are preferred. [8+4+4]

Code No: R07A1BS07

R07

Set No. 1

I B.Tech Supplementary Examinations, June 2010

ENGINEERING CHEMISTRYCommon to Mechanical Engineering, Mechatronics, Production
Engineering, Automobile Engineering

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) Distinguish between hard water and soft water. What is break point chlorination and what is its importance?
(b) Discuss the methods for the determination of
 - i. Alkalinity
 - ii. Dissolved oxygen. [8+8]
2. (a) Explain proximate analysis of coal and its significance
(b) What is petrol knock? How is related to chemical structure? Explain octane number. [8+8]
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(b) What are corrosion inhibitors? Discuss anodic and cathodic inhibitors with suitable examples. [8+8]
8. (a) Define Refractories and what are the criteria of a good refractory?
(b) Give the classification of refractories with suitable examples. [6+10]

Code No: R07A1BS07

R07

Set No. 3

I B.Tech Supplementary Examinations, June 2010

ENGINEERING CHEMISTRYCommon to Mechanical Engineering, Mechatronics, Production
Engineering, Automobile Engineering

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) Distinguish between extreme pressure lubrication & boundary lubrication.
(b) Describe the functions of viscosity index improvers? Give examples.
(c) In what situations semi-solid lubricants are preferred. [8+4+4]
2. (a) Explain proximate analysis of coal and its significance
(b) What is petrol knock? How is related to chemical structure? Explain octane number. [8+8]
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i. Alkalinity
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SET-1 R05 Code.No: R05010301
EXTERNAL EXAM
I B.TECH – SUPPLEMENTARY EXAMINATIONS, JUNE - 2010
ENGINEERING CHEMISTRY
(COMMON TO ME, MCT, MEP, AME)

Time: 3hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) What is break point chlorination? Explain.
- b) Explain EDTA method for the estimation of hardness of water.
- c) What is reverse osmosis? Explain desalination of brackish water. [6+5+5]
- 2.a) What is galvanic corrosion? Explain with neat diagram.
- b) Explain corrosion control methods in detail. [6+10]
- 3.a) What is natural rubber? How is it isolated?
- b) Describe (i) Compression moulding and
(ii) Extrusion moulding with neat diagrams. [6+10]
4. Write short notes on the following
 - (i) Thiokol rubber
 - (ii) Buna-s
 - (iii) Nylon
 - (iv) Teflon [16]
- 5.a) What is calorific value of a fuel? Differentiate HCV from LCV.
- b) What is carbonization? Explain the by-product over method. [8+8]
- 6.a) What is the composition of portland cement ?
- b) Write about the manufacture of portland cement with the help of a neat diagram.
Write the chemical reactions involved in the process. [4+12]
- 7.a) Write an account on the classification of refractories.
- b) Write a brief note on
 - (i) RUL test
 - (ii) Thermal & palling of refractory
 - (iii) Dimensional stability
 - (iv) Porosity [6+10]
8. Give an account of the following
 - (a) Thermal insulators
 - (b) Galvanic series
 - (c) Dry corrosion [5+4+7]

SET-2

R05

Code.No: R05010301

EXTERNAL EXAM

I B.TECH – SUPPLEMENTARY EXAMINATIONS, JUNE - 2010

ENGINEERING CHEMISTRY

(COMMON TO ME, MCT, MEP, AME)

Time: 3hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) What is natural rubber? How is it isolated?
- b) Describe (i) Compression moulding and (ii) Extrusion moulding with neat diagrams. [6+10]
2. Write short notes on the following
 - (i) Thiokol rubber
 - (ii) Buna-s
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 - (iv) Teflon [16]
- 3.a) What is calorific value of a fuel? Differentiate HCV from LCV.
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 - (i) RUL test
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 - (a) Thermal insulators
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 - (c) Dry corrosion [5+4+7]
- 7.a) What is break point chlorination? Explain.
- b) Explain EDTA method for the estimation of hardness of water.
- c) What is reverse osmosis? Explain desalination of brakish water. [6+5+5]
- 8.a) What is galvanic corrosion? Explain with neat diagram.
- b) Explain corrosion control methods in detail. [6+10]

SET-3

R05

Code.No: R05010301

EXTERNAL EXAM

I B.TECH – SUPPLEMENTARY EXAMINATIONS, JUNE - 2010

ENGINEERING CHEMISTRY

(COMMON TO ME, MCT, MEP, AME)

Time: 3hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) What is calorific value of a fuel? Differentiate HCV from LCV.
- b) What is carbonization? Explain the by-product over method. [8+8]
- 2.a) What is the composition of portland cement ?
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Write the chemical reactions involved in the process. [4+12]
- 3.a) Write an account on the classification of refractories.
- b) Write a brief note on
 - (i) RUL test
 - (ii) Thermal & palling of refractory
 - (iii) Dimensional stability
 - (iv) Porosity [6+10]
4. Give an account of the following
 - (a) Thermal insulators
 - (b) Galvanic series
 - (c) Dry corrosion [5+4+7]
- 5.a) What is break point chlorination? Explain.
- b) Explain EDTA method for the estimation of hardness of water.
- c) What is reverse osmosis? Explain desalination of brakish water. [6+5+5]
- 6.a) What is galvanic corrosion? Explain with neat diagram.
- b) Explain corrosion control methods in detail. [6+10]
- 7.a) What is natural rubber? How is it isolated?
- b) Describe (i) Compression moulding and
(ii) Extrusion moulding with neat diagrams. [6+10]
8. Write short notes on the following
 - (i) Thiokol rubber
 - (ii) Buna-s
 - (iii) Nylon
 - (iv) Teflon [16]

SET-4

R05

Code.No: R05010301

EXTERNAL EXAM
I B.TECH – SUPPLEMENTARY EXAMINATIONS, JUNE - 2010
ENGINEERING CHEMISTRY
(COMMON TO ME, MCT, MEP, AME)

Time: 3hours

Max.Marks:80

Answer any FIVE questions**All questions carry equal marks**

- 1.a) Write an account on the classification of refractories.
- b) Write a brief note on
 - (i) RUL test
 - (ii) Thermal & palling of refractory
 - (iii) Dimensional stability
 - (iv) Porosity [6+10]
2. Give an account of the following
 - (a) Thermal insulators
 - (b) Galvanic series
 - (c) Dry corrosion [5+4+7]
- 3.a) What is break point chlorination? Explain.
- b) Explain EDTA method for the estimation of hardness of water.
- c) What is reverse osmosis? Explain desalination of brakish water. [6+5+5]
- 4.a) What is galvanic corrosion? Explain with neat diagram.
- b) Explain corrosion control methods in detail. [6+10]
- 5.a) What is natural rubber? How is it isolated?
- b) Describe (i) Compression moulding and
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 - (i) Thiokol rubber
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 - (iii) Nylon
 - (iv) Teflon [16]
- 7.a) What is calorific value of a fuel? Differentiate HCV from LCV.
- b) What is carbonization? Explain the by-product over method. [8+8]
- 8.a) What is the composition of portland cement ?
- b) Write about the manufacture of portland cement with the help of a neat diagram.
Write the chemical reactions involved in the process. [4+12]

Code No: RR10301

Set No. 1

I B.Tech Supplementary Examinations, Aug/Sep 2008

ENGINEERING CHEMISTRY

(Common to Mechanical Engineering, Mechatronics, Production Engineering, Aeronautical Engineering and Automobile Engineering)

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) What are the various factors which influence corrosion?
(b) Write any four corrosion control methods. [8+8]
2. (a) Identify the thermo sets and thermoplastics among the following:
 - i. PVC.
 - ii. Polyethylene.
 - iii. Silicone.
 - iv. Polyester fibre.
 - v. Bakelite.
 (b) What is bakelite? How is it manufactured and mention its uses? [5+11]
3. (a) Explain the difference between municipal water and the water used for industrial purposes such as the one used in steam boilers.
(b) Describe the sand filter used for the purification of municipal water. [8+8]
4. A sample of Water contains the following impurities per lit: $\text{Mg}(\text{HCO}_3)_2 = 73, \text{g}$, $\text{CaCl}_2 = 222 \text{mg}$, $\text{MgSO}_4 = 120 \text{mg}$, $\text{Ca}(\text{NO}_3)_2 = 164 \text{mg}$. Calculate the amounts of lime and soda needed for 50,000 lit of water if the lime is 70% pure and soda is 85% pure and 10% excess chemicals are to be added. [16]
5. (a) How petroleum is formed in nature? Discuss the classification of petroleum based on their composition:-
(b) What is cetane number? How the cetane number of the Fuel can be improved. [8+8]
6. (a) Describe the method of determination of calorific value of a solid fuel by bomb calorimeter.
(b) Calculate the gross and net calorific value of a coal sample from the following data obtained from a bomb calorimeter. Weight of coal 0.73 gm, weight of water in the calorimeter 1500 gm, water equivalent of calorimeter 470 gm initial temp 25.00°C , and final temp, 28°C , percentage of hydrogen in coal 2.5%, latent heat of steam 587 cal/gm . [8+8]
7. What are Refractories? Explain Thermal spalling, strength and porosity of the refractories. [16]
8. Write a note on lubricants with special reference to their classification, mode of action, examples and applications. [16]

Code No: RR1030

Set No. 2

I B.Tech Supplementary Examinations, Aug/Sep 2008

ENGINEERING CHEMISTRY

(Common to Mechanical Engineering, Mechatronics, Production Engineering, Aeronautical Engineering and Automobile Engineering)

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) Write down the equation for the hydrogen evolution in an electro chemical corrosion reaction.
(b) What are fillers and extenders? Give examples.
(c) Describe the process
 - i. galvanizing
 - ii. anodizing. [5+5+6]
2. (a) Write down any two distinguishing features of PVC.
(b) Explain the differences between thermo set and thermo plastics.
(c) What is moulding of plastics? Explain compression moulding technique in detail. [5+5+6]
3. (a) Write a note on the use of coagulants used in sedimentation of water.
(b) Give the reactions involved in lime-soda process. [8+8]
4. Calculate the amount of soda and lime required to soften 15,000 lit of water which showed the following analysis.
NaCl = 15.5 ppm, KCl = 25 ppm, CO_2 = 5.5 ppm, Mg SO_4 = 120 ppm, CaCl_2 = 22 ppm, $\text{Ca}(\text{HCO}_3)_2$ = 15 ppm, $\text{Mg}(\text{HCO}_3)_2$ = 3.30 ppm, Suspended matter = 15 ppm, Organic impurities = 35 ppm. [16]
5. (a) How is coal is graded? Explain what is calorific value of coal.
(b) Give the advantages and disadvantages of Coal over gaseous fuels. [8+8]
6. (a) Discuss in detail Bergius procedure for the manufacture of synthetic petrol.
(b) What are the characteristics of a good Fuel? [8+8]
7. What are Refractories? Explain Thermal spalling, strength and porosity of the refractories. [16]
8. Explain the following two theories for the mechanism of the lubricants.
 - (a) Boundary lubrication
 - (b) Extreme pressure lubrication. [8+8]

Code No: RR10301

Set No. 3

I B.Tech Supplementary Examinations, Aug/Sep 2008

ENGINEERING CHEMISTRY

(Common to Mechanical Engineering, Mechatronics, Production Engineering, Aeronautical Engineering and Automobile Engineering)

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) Describe the cathodic protection of corrosion control
(b) Write a note on Electroplating. [8+8]
2. (a) What are the draw backs of raw rubber? How are its properties improved?
(b) How is Buna - S Rubber prepared? Write its uses. [8+8]
3. (a) What is meant by "softening" of water?
(b) How is the "Softening" of water carried out using the Zeolite Process?
(c) What is alkalinity of water due to and how it is estimated? [4+6+6]
4. Calculate the quantities (in Kgs) of lime and soda required to soften 50,000 litres of hard water containing the following salts:-
 $\text{MgCl}_2 = 95 \text{ PPM}$; $\text{Mg}(\text{HCO}_3)_2 = 146 \text{ PPM}$; $\text{CaSO}_4 = 136 \text{ PPM}$; $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ PPM}$
 Assume that the lime used is only 85% pure and soda is only 95% pure and the molar masses of $\text{Mg}(\text{HCO}_3)_2$ and CaSO_4 are respectively 146 and 136. [16]
5. (a) What is coal? How it is formed? Discuss the qualities of a good coal.
(b) Give the Classification of coal and explain each class with example. [8+8]
6. (a) With a neat diagram describe the orsat gas analysis method. What are the special precaution to be taken in the measurement .
(b) Define calorific values of a fuel. Distinguish gross and net calorific value. [8+8]
7. What are Refractories? Explain Thermal spalling, strength and porosity of the refractories. [16]
8. Explain the following two theories for the mechanism of the lubricants.
(a) Boundary lubrication
(b) Extreme pressure lubrication. [8+8]

Code No: RR10301

Set No. 4

I B.Tech Supplementary Examinations, Aug/Sep 2008

ENGINEERING CHEMISTRY

(Common to Mechanical Engineering, Mechatronics, Production Engineering, Aeronautical Engineering and Automobile Engineering)

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions

All Questions carry equal marks

1. (a) What is a drying oil? Give two examples.
(b) Compare the uniform corrosion and pitting corrosion.
(c) Explain Sacrificial anode method in detail. [5+6+5]
2. (a) Write the repeat unit in Bakelite, PVC and Nylon?
(b) Mention any two important compounding ingredients of rubber.
(c) Write a note on Silicones. [5+6+5]
3. (a) What is meant by "hardness" of water?
(b) What are the major disadvantages of hard water when used for
i. domestic purposes.
ii. industrial purposes and
iii. steam generation in boilers? [4+12]
4. 2 litres of water obtained from a borewell in Patancheru near Hyderabad gave the following analysis for salts :- $\text{FeSO}_4 = 30.4 \text{ mg}$; $\text{CaSO}_4 = 13.6 \text{ mg}$; $\text{MgCl}_2 = 38 \text{ mg}$; $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg}$; $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg}$; $\text{NaCl} = 11.7 \text{ mg}$.
Find out the total hardness of water in ppm units, giving temporary and permanent hardness assuming the atomic mass of Fe to be 56, that of Ca to be 40, that of Mg to be 24 and that of Na to be 23. [16]
5. (a) What are the Constituents of petroleum? Describe the Origin of petroleum.
(b) Give an account of production of petrol from crude oil. [8+8]
6. (a) The analysis of fuel gases was found to contain the following percentage by Volume $\text{CO}_2 = 13\%$, $\text{O}_2 = 6\%$. Find the air per kg of coal if the carbon content of coal is 85%.
(b) A producer gas has the following composition by volume. $\text{H}_2 = 10.4\%$, $\text{CH}_4 = 35\%$, $\text{CO} = 25\%$, $\text{CO}_2 = 10.8\%$, $\text{N}_2 = 50.3\%$. Calculate the quantity of air required per m^3 of gas. If 20% excess air is supplied, find the percentage composition of the products of combustion. [8+8]
7. (a) How are the refractories are classified? Give one example for each class.
(b) Write a note on the conditions leading to failure of a refractory material. [8+8]
8. Write a note on lubricants with special reference to their classification, mode of action, examples and applications. [16]