Hall Ticket Number: **18CY001**

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I/IV B.Tech (Regular) DEGREE EXAMINATION

DECEMBER, 2018 **CSE/ECE/EI/IT BRANCHES**

First Semester **Engineering Chemistry**

Time: Three Hours **Maximum : 50 Marks**

Answer Question No.1 compulsorily. (1X10 = 10 Marks)

Answer ONE question from each unit. (4X10=40 Marks)

1. Answer all questions (1X10=10 Marks)

a What is meant by coagulation?
b Define foaming.
c What is meant by Calgon conditioning?
d What is pitting corrosion?
e What is ''Pilling-Bedworth rule''?
f Define Anti knocking agent. Give an example
g Define Higher calorific value of fuel.
h Write the main constituents of LPG.
i Define Elimination reactions?
j Write any two applications of Bakelite?

UNIT – I

2.a Define Hardness of water. Discuss the estimation of hardness of water by EDTA method. 6M
2.b Calculate temporary hardness and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3 mg/L, $Ca(HCO_3)_2$= 16.2 mg/L, $MgCl_2$= 9.5 mg/L, $CaSO_4$= 13.6 mg/L. 4M

(OR)

3.a Explain Ion exchange process for the softening of water. 6M
3.b Explain the method of treatment of brackish water by Reverse Osmosis 4M

UNIT – II

4.a Derive Nernst equation for single electrode potential. 4M
4.b Explain i). Galvanic Corrosion ii). Differential aeration corrosion 6M

(OR)

5.a Explain how corrosion of a material is controlled by Cathodic protection method. 6M
5.b Write short note on Electroplating of Gold. 4M

UNIT – III

6.a Discuss the determination of calorific value of solid fuel by Bomb calorimeter. 7M
6.b Write short note on cetane number 3M

(OR)

7.a Write short note on refining of crude petroleum. Write various fractions obtained from petroleum. 7M
7.b What are Bio Fuels? Write any two advantages of Bio diesel. 3M

UNIT – IV

8.a Explain with mechanism the "Markownikoff"s and Anti-Markownikoff"s rule" 6M
8.b Explain a method of synthesis of "Paracetamol" 4M

(OR)

9.a Distinguish between Thermoplastic and Thermosetting polymers 6M
9.b Explain the preparation, properties and applications of PVC 4M

Bapatla Engineering College (Autonomous): Bapatla
Department of Chemistry
1/4BTech-Engineering Chemistry; Semester-I: December -2018
Scheme of Evaluation(Common for CSE, IT,EIE & ECE branches)
Paper Code: 18CY001

1.Answer all question each question carries 1 mark

UNIT-I

2.a) Definition -1M

Principle -1M

Procedure -2M

Calculation - 2M

2.b) Temporary hardness - 2M

permanent hardness - 2M

(OR)

3.a) principle - 2M

Process - 3M

Diagram - 1M

3.b) Definition - 1M

Method - 2M

Diagram - 1M

UNIT-II

4.a) Derivation - 4M

4.b) i) Galvanic corrosion - 3M

ii) Differential aeration corrosion- 3M

(OR)

5.a) Any method of cathodic protection - 6M

5.b) Composition - 1M

Process - 2M

Equation – 1M

UNIT-III

6.a) Diagram - 1M

Construction -1M

Working - 2M

Calculation -2M

Correction -1M

6,b) Definition - 1M

Explanation - 2M

(OR)

7.a) Diagram - 1M

Refining of Crude oil - 4M

Fractions -2M

7,b) Definition - 1M

Any two advantages - 2M

UNIT-IV

8.a) Markownikoff's statement - 1M

Mechanism - 2M

Anti-Markownikoff's statemrnt - 1M

Mechanism -2M

8.b) Structure - 1M

Method - 1 M

Synthesis - 2M

(OR)

9.a) Any six Differences - 6M

9.b) Preparation - 2M

Properties - 1M

Applications -1M

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1 a) Finely divided silica, clay etc. do not settle down easily and hence cannot be removed by sedimentation. Most of these are in colloidal form and are -vely charged and hence don't coalesce because of mutual repulsion. Such impurities are removed by coagulation method by adding chemicals called coagulants. These coagulants may be either inorganic or organic in nature.

b) Foaming is the production of persistent foam or bubbles in boilers,which do not break easily

c) *Calgon conditioning:* Calgon i.e., sodium hexa meta phosphate when added to boilerwater,reacts with scale forming $CaSO_4$ and forms highly soluble complexes.

$$2CaSO_4 + [Na_4(PO_3)_6]^{2-} \longrightarrow [Ca_2(PO_3)_6]^{2-} + 2Na_2SO_4$$

d) Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively unattacked.

e) Pilling-Bedworth rule: According to it "an oxide is protective or non-porous, if the volume of the oxide is atleast as great as the volume of the metal from which it is formed". On the other hand, "if the volume of the oxide is less than the volume of metal, the oxide layer is porous (or non-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below".

f) An anti-knocking agent is a gasoline additive used to reduce engine knocking and increase the fuels octane rating by raising the temperature and pressure at which auto- ignition occurs)

Example:- Tetra ethyl lead , Diethyl telluride

g) High or gross calorific value (HCV/GCV):

Total amount of heat produced, when unit mass or volume of the fuel is burnt completely and the combustion products are allowed to cool to room temperature (15°C or 60°F). Example, hydrogen present in the fuel is converted into steam. They are condensed back to room temperature. Thus the latent heat of condensation of steam is also included in the measured heat.

h) The main constituents of LPG are n-butane (38.5%), isobutene (36.7%), and propane (24.7%), with little or no propylene and ethane

i) An Elimination reaction is atype of organic reaction in which two substituent's are removed from an adjacent carbon atoms of a molecule to form unsaturated compound

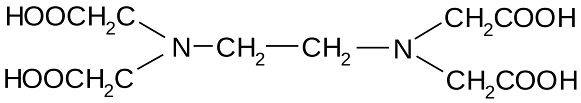
j) Applications: Used as an adhesive in plywood lamination and in grinding wheels etc. It is also widely used in paints and varnishes

UNIT-1

2 a) Hardness: The water which does not produce lather with soap is known as hard water. This propertiy is known as hardness.

Determination of hardness of water by EDTA method

EDTA method is the most common and accurate method of determination of hardness of water. EDTA (Ethylene Diamine Tetra Acetic acid) is also called versinate solution and the method is called complexometric method as EDTA forms stable complex with metal ions.



Ethylene Diamine Tetra Acetic acid

Theory: In order to determine the hardness, water sample is buffered to a pH value of 10 using NH_4OH-NH_4Cl buffer and few drops of Eriochrome black-T (EBT) indicator are added. EBT forms a weak unstable wine red colour complex with the metal ions present in water.

$$M^{2+} + \text{EBT} \longrightarrow \underset{\text{Wine red}}{\text{M-EBT complex (unstable)}}$$

Where, $M^{2+} = Ca^{2+}, Mg^{2+}$ ions

During the course of titration ofwater sample against EDTA, EDTA combines with free metal ions to give very stable M-EDTA complex which is colourless. After all free metal ions are consumed, the next drop of added EDTA solution displaces the indicator to form M-EDTA complex.

$$\underset{\text{Wine red}}{\text{M-EBT complex}} + \text{EDTA} \longrightarrow \underset{\text{colourless}}{\text{M-EDTA complex}} + \underset{\text{blue colour}}{\text{EBT}}$$

Thus at equivalence point, there is change in colour from wine red to blue.

Procedure: Standardization of EDTA solution: The burette is cleaned and filled with EDTA solution. Now 50 ml of standard hard water is pipette out into a clean conical flask. Add 10 ml of buffer solution and 2-3 drops of EBT indicator to water sample. Now it is titrated against EDTA, till wine red colour changes to blue.

Let the volume of EDTA consumed be V_1 ml.

1. Determination of Total Hardness: As per the same above procedure titrate 50 ml of unknown hard water sample against EDTA. Let the volume of EDTA solution consumed be V_2 ml.
2. Determination of permanent Hardness:Take 250 ml of water sample in 500 ml beaker and boil it the volume reduces to about 50 ml. This causes decomposition of all bicarbonates into $CaCO_3$ and $Mg(OH)_2$. Filter and quantitatively collect the filtrate and washings in a 250 ml conical flask and make the volume to 250 ml with distilled water.

50 ml of this water sample is titrated against EDTA as done in the step-1. Let the volme of EDTA solution consumed be V_3 ml

Calculation:Step-1:

V_1 ml of EDTA solution = 50 ml of standard hard water

= 50 mg of $CaCO_3$ (1 ml contains 1 mg of $CaCO_3$)

1 ml of EDTA solution = 50/ V_1 mg of $CaCO_3$ equivalent hardness

Step-2:

50 ml of hard water sample = V_2 ml of EDTA solution

= V_2 x 50/ V_1 mg of $CaCO_3$ equivalent hardness

1000 ml hard water sample = $\frac{1000 \times V_2 \times 50}{50 \times V_1}$

= 1000 x V_2/V_1 mg of $CaCO_3$ equivalent hardness

Hence, *total hardness* = 1000 x V_2/V_1 mg/litre or ppm

Step3:

50 ml of boiled water sample = V_3 ml of EDTA solution

= V_3 x 50/ V_1 mg of $CaCO_3$ equivalent hardness

1000 ml hard water sample = $\frac{1000 \times V_3 \times 50}{50 \times V_1}$

= 1000 x V_3/V_1 mg of $CaCO_3$ equivalent hardness

Hence, *permanent hardness* = 1000 x V_3/V_1 mg/litre or ppm

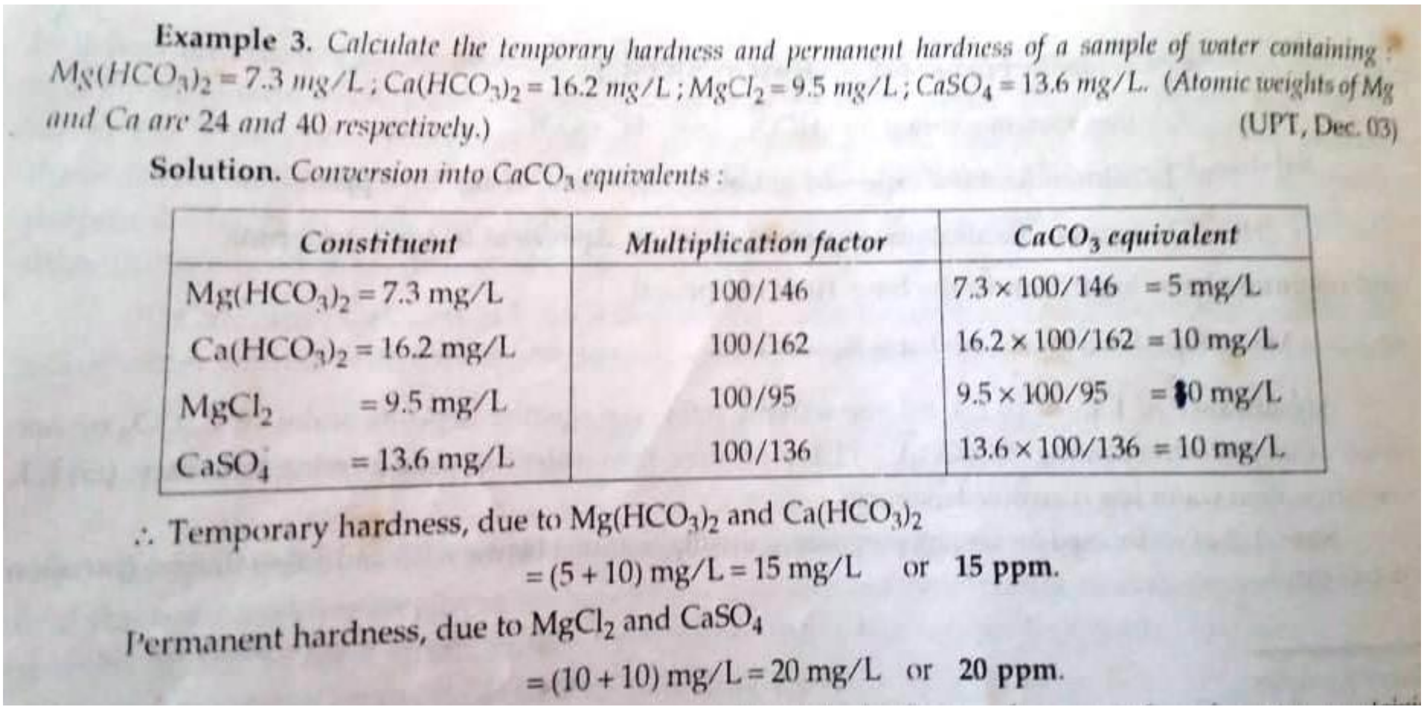
Step4:

Temporary hardness = total hardness - permanent hardness

= 1000 x V_2/V_1 - 1000 x V_3/V_1

= 1000 $(V_2-V_3)/V_1$ ppm

2 b)



Example 3. *Calculate the temporary hardness and permanent hardness of a sample of water containing : $Mg(HCO_3)_2 = 7.3$ mg/L ; $Ca(HCO_3)_2 = 16.2$ mg/L ; $MgCl_2 = 9.5$ mg/L ; $CaSO_4 = 13.6$ mg/L. (Atomic weights of Mg and Ca are 24 and 40 respectively.)* (UPT, Dec. 03)

Solution. *Conversion into $CaCO_3$ equivalents :*

Constituent	*Multiplication factor*	*$CaCO_3$ equivalent*
$Mg(HCO_3)_2 = 7.3$ mg/L	100/146	7.3 × 100/146 = 5 mg/L
$Ca(HCO_3)_2 = 16.2$ mg/L	100/162	16.2 × 100/162 = 10 mg/L
$MgCl_2 = 9.5$ mg/L	100/95	9.5 × 100/95 = 10 mg/L
$CaSO_4 = 13.6$ mg/L	100/136	13.6 × 100/136 = 10 mg/L

∴ Temporary hardness, due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$

= (5 + 10) mg/L = 15 mg/L or **15 ppm.**

Permanent hardness, due to $MgCl_2$ and $CaSO_4$

= (10 + 10) mg/L = 20 mg/L or **20 ppm.**

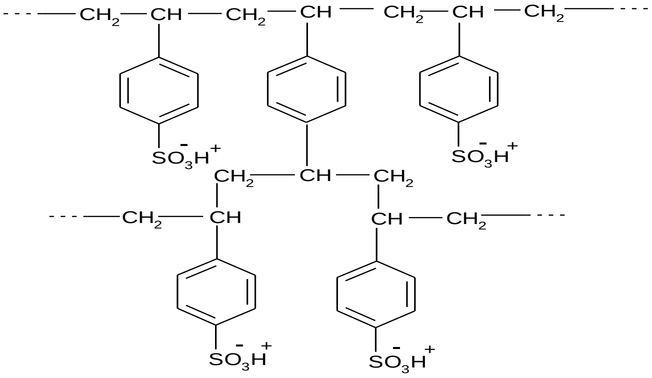
OR

3. a) . Ion-exchange process: (Demineralization or deionization)

Principle: In the method ion exchange resins are used for softening of water. Ion exchange resins are porous, insoluble, cross linked long chain organic polymers. The functional groups attached to the resins are responsible to the ion exchange properties.

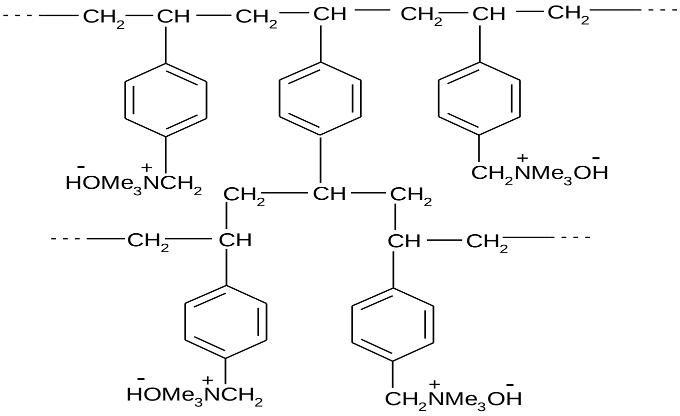
Resins containing acidic groups like –COOH, $-SO_3H$, –OH are capable of exchanging their H^+ ions with other cations in solution. Resins containing basic groups like $-NH_2$, $-NHCH_3$, $-N(CH_3)_3^+$ are capable of exchanging their OH^- ions with other anions present in water. The ionic exchange resins are two types.

1. Cation exchange resins (CER): These are styrene - divinyl benzene co-polymers, which on sulphonatin or carboxylation become capable of exchanging their H^+ ions with the cations present in raw watwer. Cation exchange resins are represented by the general formula RH^+.



Cation-Exchange Resin

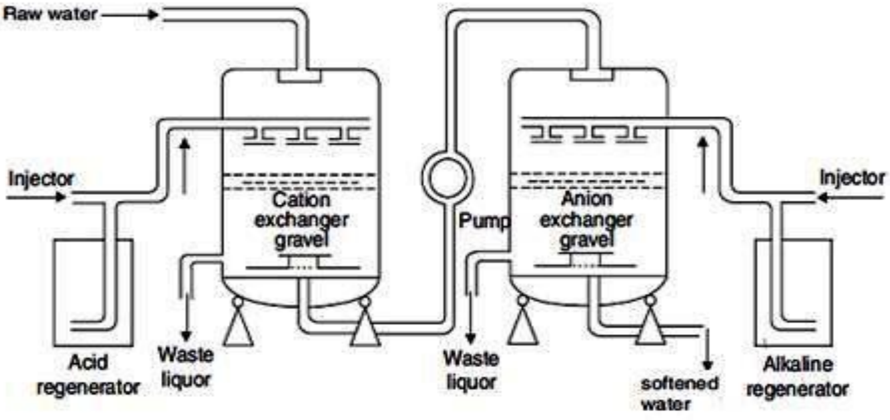
2. Anion exchange resins (AER): These are styrene-divinyl benzene or amino formaldehyde co-polymers containing amino or quaternary ammonium groups as integral part of resin. These after treatment with dilute NaOH become capable of exchanging their OH^- ins with the anions of water. Anion exchange resins are represented by the general formula ROH^-.



Anion-Exchange Resin

Process:

The CER is arranged in the form of bed in a cylinder made of steel or plastic. The AER used is also arranged as a bed in another cylinder. Both the cylinders are connected to a de-gasifier which removes dissolved gases.



Demineralisation of water.

Raw water is passed through the CER bed. All the cations present in water are exchanged by Hydrogen ions of the resin as shown below.

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

The water free from cations is now passed through anion exchange resin bed. Here all the anions of water are exchanged by the OH^- of the resins as shown below.

$$ROH^- + Cl^- \longrightarrow RCl^- + OH^-$$
$$2ROH^- + SO_4^{2-} \longrightarrow R_2SO_4^{2-} + 2OH^-$$

The H^+ ions released cation exchanger and OH^- ions released from anion exchanger combine to produce water molecule.

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

Now the water coming out of the exchanger is free from all the cations and anions. This ion free water is known as deionized or demineralized water.

Regeneration:

When the CER bed is exhausted, it is regenerated by passing a dilute solution of HCl or H_2SO_4 followed by washing with distilled water.

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

Exhausted Resin	regenerating solution	regenerated resin	washings

When the AER bed is exhausted, it is regenerated by passing a dilute solution of NaOH or Na_2CO_3 followed by washing with distilled water.

$$RCl^- + OH^- \longrightarrow ROH^- + Cl^-$$
$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4^{2-}$$

Exhausted Resin	regenerating solution	regenerated resin	washings

Now-a-days mixed bed deionizers are used for softening of water. Mixed bed deionizers contain cation and anion exchange resin beds in the same equipment.

3 b) Reverse osmosis

The flow of solvent molecules from a dilute solution to the concentrated solution when these two are separated by a semi permeable membrane is called osmosis.

The flow of solvent depends on the concentration gradient and the consequent osmotic pressure existing across the membrane.

The flow of solvent is reversed i.e. migration of solvent molecules from concentration solution to dilute solution, when hydrostatic pressure is applied on the concentrated solution. This is known as reverse osmosis.

In reverse osmosis (R.O) method pure solvent is separated from its contaminants rather than removing contaminants from the water. This membrane filtration is sometimes also called super filtration or hyper filtration.

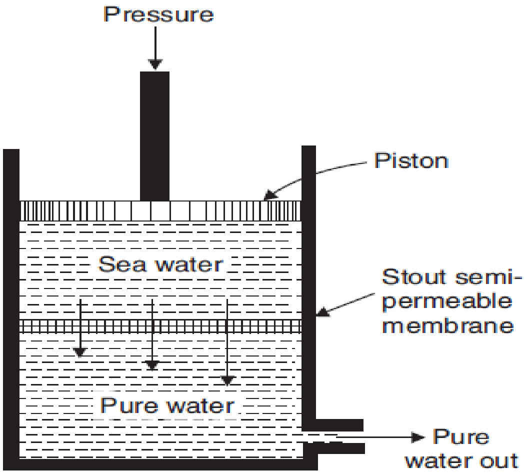


Fig. 17.8 Reverse osmosis cell.

In this process, pressure of the order 15 to 40 Kg/m^2 is applied to sea water to force its pure water out through the semi permeable membrane, leaving behind the dissolved salts and other impurities. The membrane consists of very thin films of cellulose acetate affixed to either side of a perforated tube. However, more recently membranes made of poly methacrylate, poly amide and polysulphone polymers are being used. With the help of this method, dissolved salts, non ionic, organic matter are also removed. Also it deals with the problem of removing colloidal silica which is not removed by demineralization.

Advantages:

1. Maintenance cost is low.
2. Life time of membrane is 2 years and it can be replaced easily without interruption to supply of water.
3. The water used in high pressure boilers is produced by reverse osmosis.
4. It removes micro-organisms, colloidal and organic impurities along with ions of salt.

UNIT-II

4 a) Nernst equation:

Consider a general reversible redox reaction,

$$M^{n+}_{(aq)} + n\,e^{-} \rightleftharpoons M_{(s)} \;\ldots\ldots\ldots\; (1)$$

Now for a reversible reaction the free energy change (ΔG) and its equilibrium constant (K) are inter-related as,

$$\Delta G = - RT \ln K + RT \ln \{[\text{Products}] / [\text{Reactants}]\} \quad (2)$$

We know that $\Delta G^0 = - RT \ln K$ (3) and Apply the equation (3) in (2), We get

$$\Delta G = \Delta G^0 + RT \ln \{[\text{Products}] / [\text{Reactants}]\} \;\ldots\ldots\; (3)$$

Where ΔG^0 is the standard free energy change. The equation (3) is known as Van't Hoff reaction isotherm.

In a reversible reaction, the electrical energy is produced is the same as decrease in free energy. i.e. $-\Delta G = nFE$ and -- $\Delta G^0 = nFE^o$ …. (4)

Where, E = electrode potential, E^0 = standard electrode potential and F = Faraday (96,500 Coulomb).

Apply the equations (1) and (4) in equation (3), we get

$$-nFE = -nFE^0 + RT \ln \{[M] / [M^{n+}]\}$$

Since the concentration of metal, M is unity, we have

$$-nFE = -nFE^0 + RT \ln \{1 / [M^{n+}]\}$$

$$-nFE = -nFE^0 - RT \ln [M^{n+}]$$

Divide this equation by –nF, we get

$$E = E^0 + (RT / nF) \ln [M^{n+}]$$

$$E = E^0 + (2.303\, RT / nF) \log [M^{n+}] \;\ldots.\; (5)$$

This equation (5) is known as Nernst's equation for electrode potential.

At 25^0C, $E = E^0 + (0.0592/ n) \log [M^{n+}]$

Similarly Oxidation potential-Nernst Equation

$$E = E^0 - (0.0592/ n) \log [M^{n+}]$$

E – Electrode potential

E^o – Standard electrode potential

R – Gas constant

T – 298 K

n – No of electrons involved

F – 96500 coulomb

4 b) i) Galvanic Corrosion:

When two dissimilar metals (eg., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as a anode while the less active metal (with less negative electrode potential) acts as cathode.

In the above example, zinc (higher in electrochemical series) forms the anode and is attacked

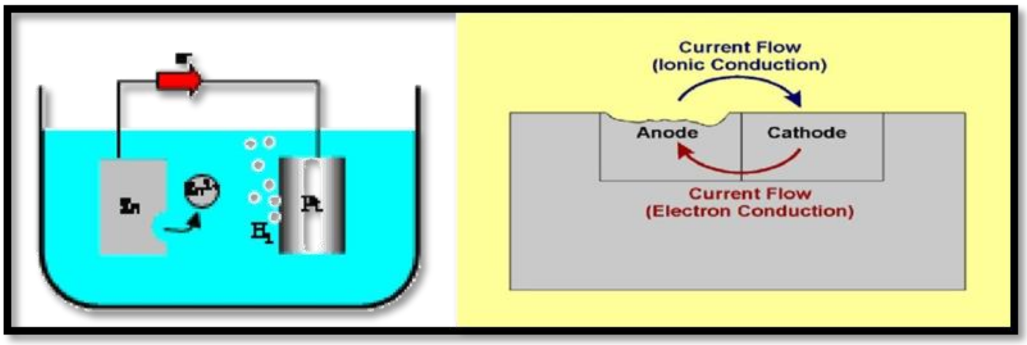
and gets dissolved; whereas copper (lower in electrochemical series or more noble)acts as cathode. Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows

from the anode metal, zinc to the cathode metal, copper.

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

Thus it is evident that the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

Example: (i) Steel screws in a brass marine hardware (ii)Lead-antimony solder around copper wise; (iii) a steel propeller shaft in bronze bearing (iv Steel pipe connected to copper plumbing.



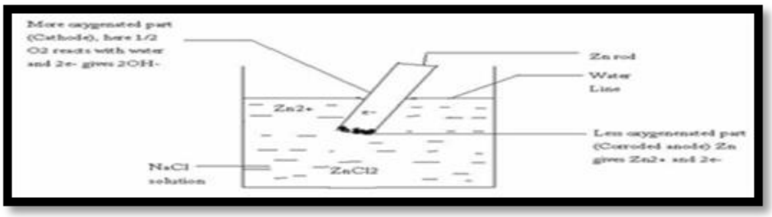
ii) Differential aeration Corrosion:

It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration.

It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that poor-oxygenated parts are anodic.

Examples: i) The metal part immersed in water or in a conducting liquid is called water line corrosion. ii) The metal part partially buried in soil.

Explanation: If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers crrosion



At anode: Corrosion occurs (less aerated): $M \longrightarrow M^{2+} + 2e^-$

At cathode: OH- ions are produced (more aerated): $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

(OR)

5 a) CATHODIC PROTECTION:

The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur. There are two methods of applying cathodic protection to metallic structures.

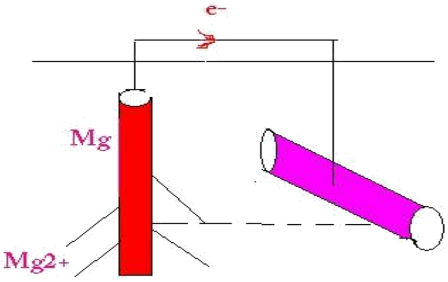
i. Sacrificial anodic protection (galvanic protection)
ii. Impressed current cathodic protection

i. SACRIFICIAL ANODIC PROTECTION METHOD

In this method, the metallic structure to be protected is made cathode by connection it with more active metal (anodic metal). Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.

Applications:

1. Protection as buried pipelines, underground cables from soil corrosion.
2. Protection from marine corrosion of cables, ship hulls, piers etc.
3. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
4. Calcium metal is employed to minimize engine corrosion.



In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (eg., a pipeline, bridge, ship hull or boat).

ii. IMPRESSED CURRENT CATHODIC PROTECTION METHOD

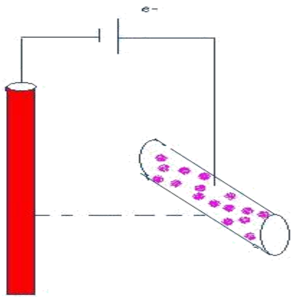
In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

Usually the impressed current is derived from a direct current sources (like battery or rectifier on AC line) with an insoluble, inert anode (like graphite, scrap iron, stainless steel, platinum or high silica iron).

A sufficient DC current is applied *to* an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is, usually, a back fill, composed of coke breeze or gypsum, so as to increase the electrical contact with the surrounding soil.

Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid up ships etc.

This kind of protection technique is particularly useful for large structures for long term operations.



In Impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

5 b) ELECTROPLATING OR ELECTRODEPOSITION

Electroplating is a coating technique. It is the most important and most frequently applied industrial method of producing metallic coating.Electroplating is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.The base metal to be plated is made cathode whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

Objectives: Electroplating is carried out for

i. Decoration or better appearance
ii. Increasing the resistance to corrosion of the coated metal.
iii. Improving the hardness of the metal
iv. Increasing the resistance to chemical attack
v. Electro refining.

Procedure:The article is to be plated first treated with organic solvent like carbon tetrachloride, acetone, tetrachloro ethylene to remove oils, greases etc. Then it is made free from surface scale, oxides, etc. by treating with dil. HCl or H_2SO_4 (acid pickling). The cleaned article is then made as the cathode of the electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity. The electrolyte is a solution of soluble salt of the coating metal.When direct current is passed, coating metal ions migrate to the cathode and get deposited there. Thus, a thin layer of coating metal is obtained on the article made as the cathode.In order to get strong, adherent and smooth deposit, certain types of additives (glue, gelatin, boric acid) are added to the electrolytic bath.In order to improve the brightness of the deposit, brightening agents are added in the electrolytic bath.The favourable conditions for a good electrodeposit are; i) optimum temper ii) optimum current density iii) Low metal ion concentrations.

Gold Electroplating:

Anode: Gold

Cathode: Metal article

Electrolyte: Gold + KCN

Temperature: 60 deg C.

Current density (mA cm-2): 1-10

Use:

i. This is used for electrical and electronic applications.
ii. ii)It is used for high quality decorations and high oxidation resistant coatings
iii. Usually for ornamental jewellery, a very thin goldcoating (about 1x10-4 cm) is given.

UNIT-III

6 a)Measurement of Calorific Value of a Solid Fuel:

Bomb calorimeter:
This apparatus is used for the determination of calorific value of solid fuel and non-volatile liquid fuels.

Construction:

It consists of a strong cylindrical stainless steel bomb in which combustion of the fuel takes place. The bomb has a lid which is screwed to the body of the bomb to make a perfect gas tight seal. The lid has two stainless steel electrodes and an oxygen inlet valve (fig. 1). To one of the electrodes a small ring is attached on which a stainless steel crucible is supported. The bomb is placed in a copper calorimeter surrounded by air and water jacket (which prevents heat loss due to radiation). An electrically operated stirrer and a Beckmann's thermometer (which measures th of a degree) is placed in the water jacket to maintain uniform distribution of heat and measure the increase in temperature respectively.

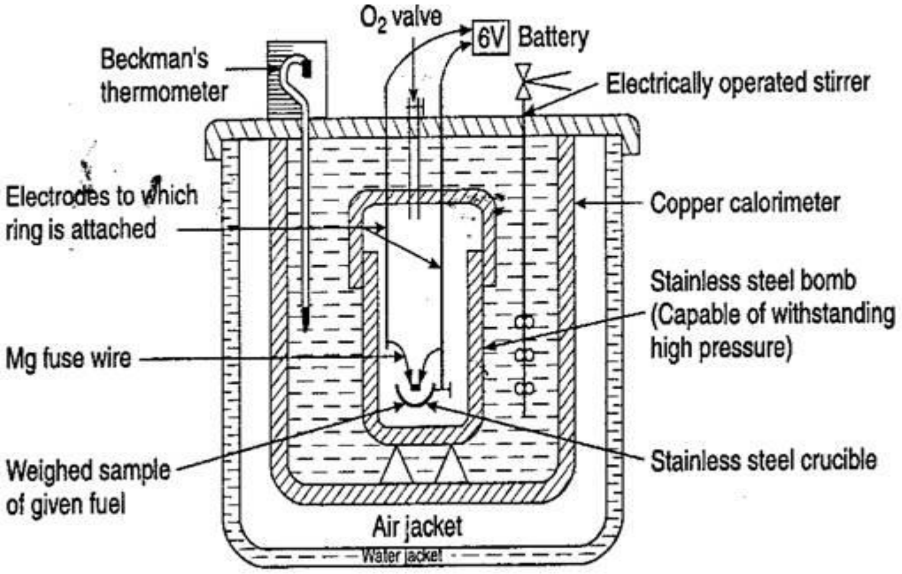


fig. 1

Working of bomb calorimeter

A known mass (0.5- 1.0 g) of a fuel is taken in a clean crucible, supported over a ring. A fine mercury wire, touching the fuel sample, is stretched across the electrodes. The lid is tightly screwed and filled with oxygen to a pressure of 25 atm. The bomb is lowered into a copper calorimeter containing known mass of water. The water is stirred and the initial temperature is noted. The electrodes are connected to a 6 V battery and the circuit is completed. The sample burns and heat is liberated. Uniform stirring is continued and the maximum temperature attained is recorded.

Calculation

X = mass; in g of fuel sample taken in crucible
W = mass of water in calorimeter
w = water equivalent in g of calorimeter, stirrer, thermometer, bomb
t_1 = initial temperature of water in calorimeter
t_2 = final temperature of water in calorimeter
L = higher calorific value of fuel in cal/g
Heat liberated by burning of a fuel = XL
Heat absorbed by water and apparatus = $(W + w)(t_2 - t_1)$
Heat liberated = heat absorbed
$XL = (W + w)(t_2 - t_1)$

Thus, HCV of the fuel $L = (W + w)(t_2 - t_1)/x$ cal/g or kcal/kg

The water equivalent of the calorimeter is determined by burning a fuel of known calorific value and using the above equation.

Example, Water equivalent of benzoic acid (HCV = 6325 kcal/7kg) and naphthalene (HCV = 9688kcal/kg).

If H is the percentage of hydrogen in the fuel
Then 9Hg/100 = Mass of H_20 from 1 g fuel = 0.09 Hg
Heat taken by water in the form of steam = 0.09 H x 587
LCV = HCV - Latent heat of water formed

= HCV-0.09 × H × 587 cal/g (or kcal/kg)   (latent heat of steam is 587 kcal/kg)

Corrections:

i. Fuse wire correction: The heat liberated includes the heat given out by ignition of the fuse wire used.
ii. Acid correction: Fuels containing sulphur and nitrogen are oxidized under high pressure and temperature of ignition to sulphuric acid and nitric acid.

$S + 0_2 \rightarrow SO_2$
$2S0_2 + 0_2 + 2H_20 \rightarrow 2H_2S0_4$ + heat (H = -144000 cal)
$2N_2 + 2H_20 + 5O_2 \rightarrow 4HN0_3$ + heat (H = - 57160 cal)

Formation of these acids is an exothermic reaction, thus the measured heat also includes the heat given out during acid formation.

Amount of these acids can be analyzed from the washings. Sulphuric acid is precipitated as $BaS0_4$. Correction for 1 mg sulphur is 2.25 cal while for 1 ml N/10 HNO_3 is 1.43 cal.

iii. Cooling correction: Time taken to cool the water from maximum temperature to room temperature is noted. From the rate of cooling (dt0 /min) and actual time for cooling (t min), the cooling correction dt x t is added to rise in temperature.

L (HCV) = $(W-w)(t_2-t_1$+cooling correction)–(Acid + fuse wire correction)/X

6 b) 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 which has same ignition delay as the fuel under test 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, isoamyl nitrite and 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+15/100X50 = 57.5%.

(OR)

7 a) Refining of crude oil:

The crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The process is called ‘refining of crude oil’ and the plants set up for the purpose, are called the oil refineries. The refining involves

Step 1: Separation of water (Cottrell’s process):

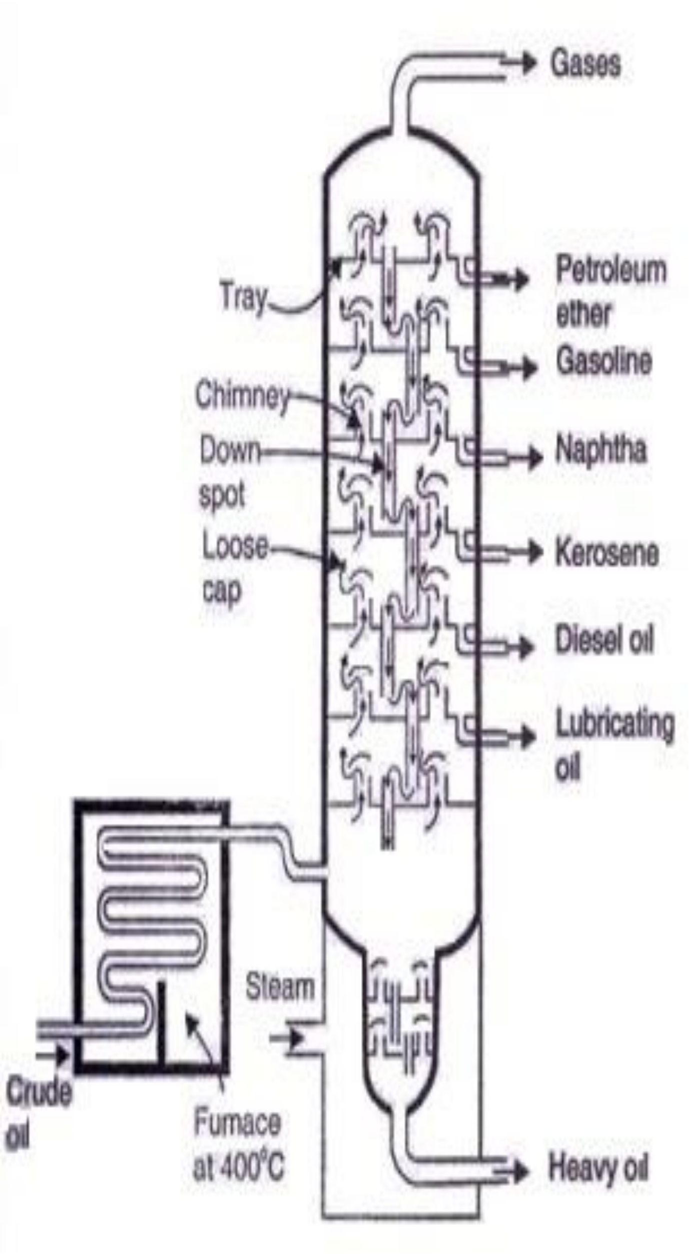
The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

Step 2: Removal of harmful sulphur compounds:

This involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide (a solid), which is then removed by filtration.

Step 3: Fractional distillation:

The crude oil is then heated to about 400^0C in an iron retort whereby all volatile constituents, except the residue (asphalt or coke) are evaporated. The hot vapours are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney, covered with a loose cap. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fraction condenses first, while the lower boiling fractions turn-by-turn.



Name of Fraction	Boiling range	Approximate Composition	Uses
Uncondensed gas	Below 30^{0}C	C_1-C_4	Domestic or industrial fuel, LPG
etroleum ether	30^{0}C-70^{0}C	C_5-C_7	As a solvent
Gasolene or Petrol or Motor spirit	40^{0}C-120^{0}C	C_5-C_9	Motor fuel, solvent and in dry cleaning
Naphtha or solvent spirit	120-180^0 C	C_9-C_{10}	As solvent and in dry cleaning
Kerosene oil	180-250^{0}C	C_{10}-C_{16}	As an illuminant, jet engine fuel and for preparing laboratory gas.
Diesel oil or fuel oil or gas oil	250-320^0 C	C_{15}-C_{18}	Diesel engine fuel.
Heavy oil i) Lubricating oil ii) Petroleum jelly iii) Grease iv) Paraffin wax	320-400^0 C	C_{17}-C_{30}	For getting gasoline by cracking process As lubricant As lubricant and in cosmetics and medicines. As lubricant In candles, boot polishes, wax paper, tarpolin cloth etc.
Residue may be either i) Asphalt or ii) Petroleum coke	Above 400^0 C.	C_{30} and above	Water proofing of roofs and road making As a fuel and in moulding arc light rods.

7 **(b) Definition :** A fuel which is produced from biological raw materials

(Or)

Any fuel whose energy is obtained through a process of biological carbon fixation

Advantages of biodiesel fuel

- ✓ Biodiesel fuel is a renewable energy source unlike petroleum-based diesel.
- ✓ It is less polluting than petroleum diesel.
- ✓ The lack of sulphur in 100% biodiesel extends the life of catalytic converters.
- ✓ It can also be blended with other energy resources and oil.
- ✓ Biodiesel fuel can also be used in existing oil heating systems and diesel engines without making any alterations.
- ✓ The lubricating property of the biodiesel may lengthen the lifetime of engines.
- ✓ It releases less greenhouse gas eg: B20 reduces Co_2 by 15%.

UNIT-IV

8 a) Markownikoff's rule :-

When an unsymmetrical reagent adds to an unsymmetrical alkene, the positive part of the reagent becomes attached to the double bonded carbon, which bears the greatest no. of Hydrogen atoms

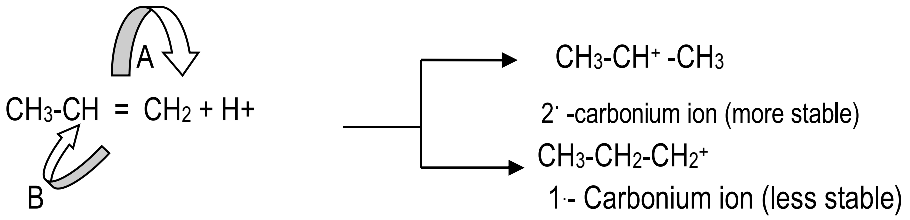
Example : - Addition of HBr to propene gives isopropyl bromide

Mechanism: It involves the following steps

Step-1:- HBr ionises to give a Proton(Electrophile) and a Bromide ion (Nucleophile)

$$HBr \xrightarrow[\text{Proton}]{} H^+ + Br^-$$

Step-2:- The proton attacks the double bond to form a more stable Carbonium ion



$CH_3\text{-}CH = CH_2 + H+$

$CH_3\text{-}CH^+\text{-}CH_3$

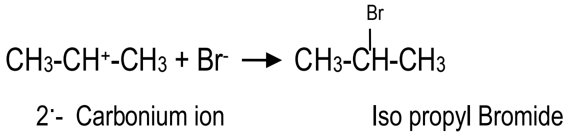
$2^{\cdot}$ -carbonium ion (more stable)

$CH_3\text{-}CH_2\text{-}CH_2^+$

$1^{\cdot}$- Carbonium ion (less stable)

Stability order of Carbonium ions:- $3^{\cdot} - > - 2^{\cdot} > 1^{\cdot}$

Step-3:- The bromide ion attacks the more stable secondary carbonium ion to give the major product



$$CH_3\text{-}CH^+\text{-}CH_3 + Br^- \rightarrow CH_3\text{-}\overset{Br}{C}H\text{-}CH_3$$

$2^{\cdot}$- Carbonium ion Iso propyl Bromide

Anti –Markownikoffis rule :-

When an unsymmetrical reagent adds to an unsymmetrical alkene , the positive part of the reagent becomes attached to the double bonded carbon which bears the least no. of hydrogen atoms

Example: - Addition of HBr to propene in the absence of peroxides gives n-propyl bromide

Mechanism:

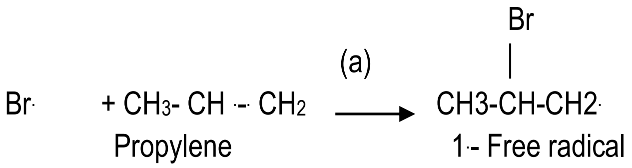
Step-1:- Peroxide dissociates to give alkoxy free radicals

$$R\text{-}0\text{-}0\text{-}R \xrightarrow{\triangle} 2R\text{-}0^{\cdot}$$

Step-2 :- Alkoxy free radical attacks HBr

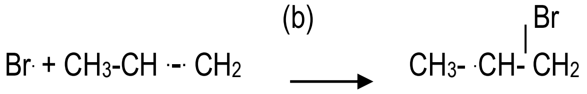
$$R\text{-}0^{\cdot} + H:Br \longrightarrow R\text{-}OH + Br^{\cdot}$$

Step-3:- Bromine atom can attack propylene to give a primary free radical and a secondary free radical



$$Br^{\cdot} + CH_3\text{-}\,CH \cdot\!\text{-}\!\cdot\, CH_2 \xrightarrow{(a)} CH3\text{-}\overset{\overset{\displaystyle Br}{|}}{CH}\text{-}CH2^{\cdot}$$

Propylene 1·- Free radical



$$Br^{\cdot} + CH_3\text{-}CH \cdot\!\text{-}\!\cdot\, CH_2 \xrightarrow{(b)} CH_3\text{-}\,{}^{\cdot}CH\text{-}\overset{\overset{\displaystyle Br}{|}}{CH_2}$$

2$^{\cdot}$- Free radical

Stability of free radicals is 3$^{\cdot}$>2$^{\cdot}$>1$^{\cdot}$

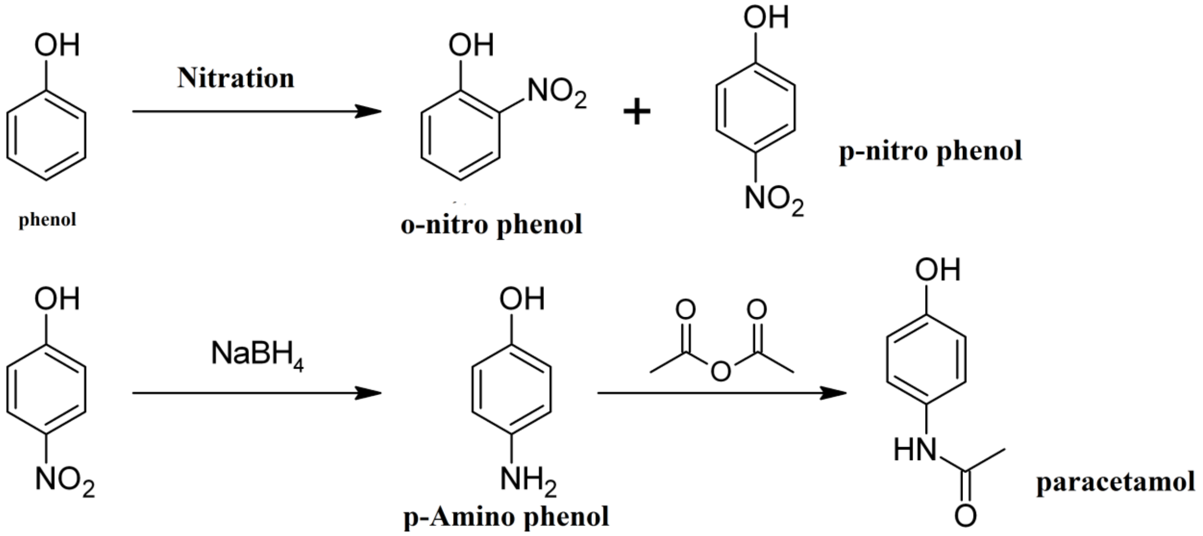
Step-4:-

$$CH_3\text{-}\,{}^{\cdot}CH\text{-}\,CH_2Br + H:Br \longrightarrow CH_3 - CH_2\text{-}\,CH_2Br + Br^{\cdot}$$

n-propyl bromide

8 b) Synthesis of paracetamol :

Paracetamol is easily prepared by nitrating phenol with sodium nitrate gives Ortho and Para-nitro phenol . Para nitro phenol is seperated from Ortho nitro phenol and on further reduction of P-nitrophenol with sodium borohydride gives P-amino phenol which is then Acetylated with acetic anhydride gives paracetamol.

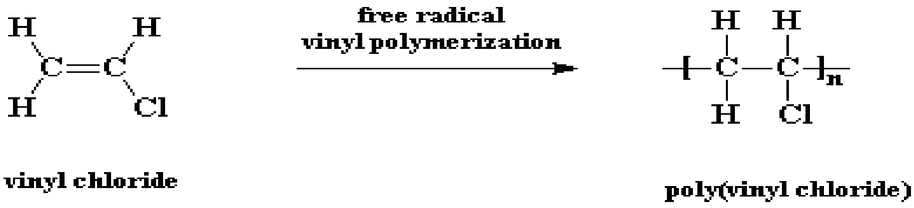


(OR)

9 a) Differences between Thermoplastics & Thermosets:

Thermoplastics	Thermosets
1. They are formed either by addition or by condensation polymerisation reactions.	1. They are formed by condensation reactions.
2. They have either linear or branched structures.	2. They have three dimensional, cross linked net work structures.
3. Adjacent polymeric chains are held together by vanderwaal or dipole-dipole or 'H' bonds.	3. Adjacent polymeric chains are held together by cross links (covalent bonds).
4. They soften on heating and stiffen on cooling.	4.They do not soften on heating.
5. They are soluble in suitable solvents.	5. They are insoluble.
6. They can be remoulded, reshaped and reused.	6. They cann't be remoulded and hence cann't be reused.
7.They can be recycled from wastes.	7. They cann't be recycled.
8. There is no change in their chemical composition while moulding.	8. There is formation of cross linkings through strong covalent bonds while moulding.
9. They are tough materials. Ex; Polyethylene, Polypropylene, PVC etc .	9. They are brittle materials. Ex; Urea formaldehyde, Phenol formaldehyde,.

9 (b) Polyvinyl chloride(PVC): It's produced by the free radical polymerization of vinyl chloride in presence of benzyl peroxide or hydrogen peroxide inb an autoclave under pressure.



Properties of PVC:PVC is colourless odourless, non-inflammable and chemically inert powder.

- Very good thermal and acoustic insulation;
  The multi-groove PVC profiles exhibit very low thermal conductivity which means greater thermal insulation.
- No maintenance: coating or surface treatment;
  PVC is not altered by atmospheric agents like light, atmospheric oxygen, inorganic acids and alkalies.
- Flexibility in design;
  PVC can safely be used in all contexts.
- PVC is self-extinguishing or flame retardant;
  therefore it is very safe for all types of application and construction. Moreover PVC does not pollute the environment and can be fully recycled.

Applications of PVC :

Regarding mechanical-physical properties, there are essentially two types of PVC:

- RIGID PVC, without plasticizers, it exhibits high surface strength and very good rigidity. It is used mainly for extrusion of profiles for windows, piping and other applications in widely differing sectors.
- PLASTICIZED PVC added with plasticizers thanks to which a flexible material is obtained used in manufacture of films, gaskets, expanded products, sheets, jacketing for electrical cables, etc.conc. And hot acids & bases.

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