

First Semester B.E. Degree Examination, Dec.2018/Jan.2019
Engineering Chemistry

Time: 3 hrs.

Max. Marks: 100

Note: Answer any FIVE full questions, choosing ONE full question from each module.

Module-1

- 1 a. Define terms : (i) Free energy (ii) Entropy (iii) Cell potential. (06 Marks)
- b. For the cell, $\text{Fe} \mid \text{Fe}^{2+}(0.01\text{M}) \parallel \text{Ag}^+(0.1\text{M}) \mid \text{Ag}$, write the cell reaction and calculate the e.m.f of cell at 298 K, if standard potentials of Fe and Ag electrodes are -0.44 V and $+0.8\text{V}$ respectively. (07 Marks)
- c. What are Secondary Batteries? Explain the construction and working of Nickel – metal hydride (Ni - MH) battery. Mention its applications. (07 Marks)

OR

- 2 a. Define Primary, Secondary and Reserve batteries with examples. (06 Marks)
- b. What are concentration cells? The cell potential of copper concentration cell $\text{Cu} \mid \text{CuSO}_4(0.005\text{M}) \parallel \text{CuSO}_4(\text{X}) \mid \text{Cu}$ is 0.0295 V at 25°C . Calculate the value of X. (06 Marks)
- c. Explain the construction and working of glass electrode giving its application in determination of pH of solution. (08 Marks)

Module-2

- 3 a. Define corrosion. Describe the electrochemical theory of corrosion taking rusting of iron as an example. (07 Marks)
- b. Explain (i) Water line corrosion (ii) Pitting corrosion. (06 Marks)
- c. What is electroless plating? Explain electroless plating of Nickel. (07 Marks)

OR

- 4 a. What is meant by metal finishing? Mention (any five) technological importance of metal finishing. (06 Marks)
- b. Explain the process of (i) Galvanizing (ii) Anodising of Al. (07 Marks)
- c. What is electroplating? Explain electroplating of chromium. Mention why chromium cannot be used as anode. (07 Marks)

Module-3

- 5 a. Define calorific value of fuel. Explain the experimental determination of calorific value of solid / liquid fuel using Bomb calorimeter. (08 Marks)
- b. What are fuel cells? Describe the construction and working of Solid Oxide Fuel Cell (SOFC). (06 Marks)
- c. What are Solar cells? Explain the construction and working of photovoltaic (PV) cell. (06 Marks)

OR

- 6 a. Explain the preparation of solar grade Silicon by Union Carbide process. (07 Marks)
b. Write a note on (i) Power alcohol (ii) Unleaded petrol. (06 Marks)
c. 0.75 g of coal sample (Carbon 90%, H₂ 5% and ash 5%) was subjected to combustion in Bomb calorimeter. Mass of water taken in calorimeter was 2.5 kg and the water equivalent of calorimeter is 0.65 kg. The rise in temperature was found to be 3.2°C. Calculate higher and lower calorific values of the sample. Latent heat of steam = 2457 kJ/kg and specific heat of water = 4.187 kJ/kg/°C. (07 Marks)

Module-4

- 7 a. What are the causes, effects and disposal methods of e-waste? (07 Marks)
b. What are the sources, effects and control of lead pollution? (Pb pollution). (07 Marks)
c. In a COD test, 30.2 cm³ and 14.5 cm³ of 0.05 N FAS solutions are required for a Blank and Sample titration respectively. The volume test sample used was 25 cm³. Calculate the COD of the sample solution. (06 Marks)

OR

- 8 a. Explain the sources, effects and control of oxides of nitrogen. (07 Marks)
b. Explain softening of water by ion exchange method. (07 Marks)
c. Explain the Activated sludge treatment of sewage water. (06 Marks)

Module-5

- 9 a. Explain the theory, instrumentation and application of Atomic absorption spectroscopy. (07 Marks)
b. Explain the theory and instrumentation of potentiometry. (07 Marks)
c. Write a note on Fullerene. Mention its application. (06 Marks)

OR

- 10 a. What are Nanomaterials? Explain the synthesis of nanomaterials by precipitation method. (07 Marks)
b. Explain the synthesis of Nano materials by Sol-Gel technique. (06 Marks)
c. Explain the theory and instrumentation of conductometry. (07 Marks)

ANSWERS

1. a)

Free energy :

Gibbs free energy is the part of total energy of a system which is available to do useful work.

$$G = H - T S.$$

Where, H = Enthalpy

T = Temperature

S = Entropy

Entropy: It represents the unavailability of a system's energy for conversion into useful work, due to degree of disorder or randomness in the system. **It is the measure of degree of disorder or randomness in the system.** It is represented by "S". Entropy is expressed in terms of J/K/mol.

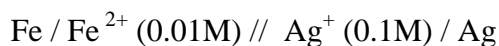
$$dS = T/dq$$

$$= \frac{\text{Heat absorbed}}{\text{Absolute temperature}}$$

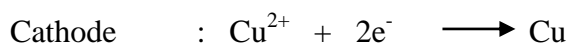
Cell potential (EMF of a cell): It is the potential difference between the two electrodes of a galvanic cell which causes the flow of current from one to other.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

1.b)



Cell reaction :



$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]}$$

$$E_{\text{cell}}^0 = E_{\text{c}}^0 - E_{\text{a}}^0 = 0.8 - (-0.44)$$

$$= 1.24 \text{ V}$$

$$E_{\text{cell}} = 1.24 + \frac{0.0591}{2} \log \frac{[0.1]^2}{[0.01]}$$

$$E_{\text{cell}} = 2.28 + \frac{0.0591}{2} \log \frac{[0.01]}{(0.01)}$$

$$E_{\text{cell}} = 2.28 \text{ V}$$

1.c)

Nickel-metal hydride battery:

Construction:

In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed.

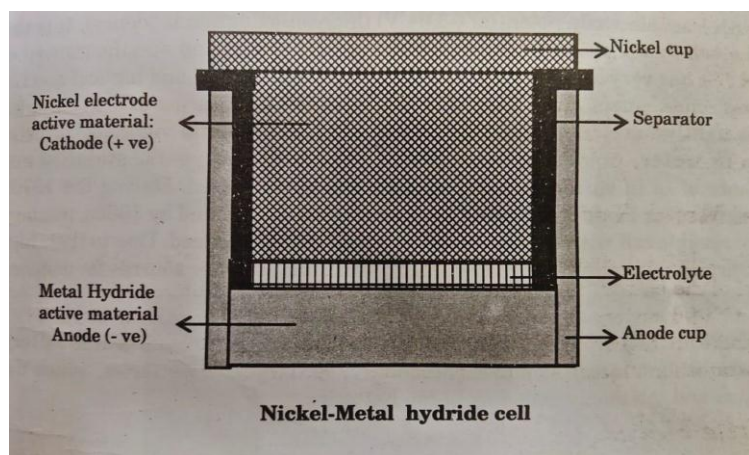
Anode – Porous nickel grid pasted with **metal hydride** (such as TiH_2 , VH_2 ,) and a hydrogen storage alloy (such as LaNi_5).

Cathode - Porous nickel grid pasted with **Ni(OH)_2 , NiO(OH)** .

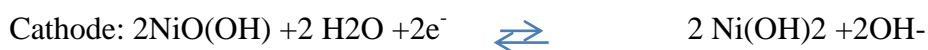
Electrolyte- KOH .

Separator- Polypropylene.

Representation: $\text{MH}_2 \mid \text{KOH} \mid \text{Ni(OH)}_2, \text{NiO(OH)}$



Working:



Uses: Used in cellular phones, camcorders and laptop computers.

2.a. Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reaction.

Classification of the Battery:

1. Primary Batteries: A battery which cannot be recharged because the cell reactions are irreversible is called primary battery. Once the cell get completely discharged, later these are of no use. e.g. Zn-MnO_2 , Li-MnO_2 .

2. Secondary Battery: A battery which can be recharged because the cell reactions are reversible is called secondary battery. This is also known as storage battery.

e.g. Lead-acid battery, Li-ion battery, Ni-MH₂ battery.

3. Reserve battery: In this battery, one of the components is stored separately and used whenever required. Commonly in reserve batteries, electrolyte is stored separately. Reserve batteries deliver high power in short period of time and these batteries will have long life.

e.g. In Mg-CuCl, Mg-AgCl and Zn-Ag₂O in these batteries, water is an electrolyte and this is inserted whenever required.

2.b.

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$0.0595 = \frac{0.059}{2} \log \frac{x}{0.005}$$

$$0.0295 = 0.0295 \log \frac{x}{0.005}$$

$$1 = \log x - \log 0.005$$

$$\log x = 1 + \log 0.005$$

$$= 1 - 2.301$$

$$\log x = -1.301$$

$$x = 0.05\text{M}$$

2.c. Glass electrode (Glass pH electrode):

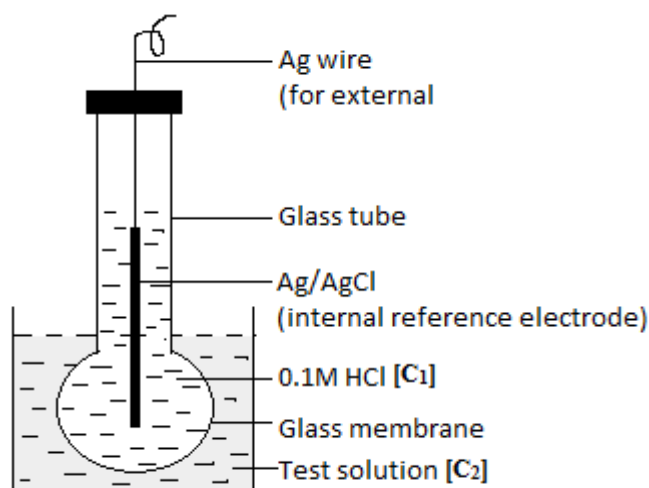
It is more selective towards H⁺ ions, in the solution containing mixture of ions. Hence used in the measurement of concentration of H⁺ ions in the solution.

Glass electrode can be represented as ,

Ag | AgCl | HCl_(0.1M) | glass membrane

Construction:

- A glass electrode consists of a long glass tube with thin walled glass membrane bulb at the bottom.
- Glass membrane bulb is made up of silicate corning glass with composition 22% Na₂O, 6% CaO and 72% SiO₂.
- The bulb is filled with 0.1M HCl.
- A silver-silver chloride electrode, used as an internal reference electrode is dipped in HCl inside the bulb, provides an electrical contact. The bulb of the glass electrode is dipped into analyte solution containing hydrogen ions.



Working:-

- If the hydrogen ion concentrations of the solution inside and outside the glass membrane are different then the potential develops across the glass membrane.

i.e Glass membrane-



(Boundary potential is the potential raised across the membrane due to the movement of H^+ ions between two solutions of different H^+ ion concentration.)

$$E_b = E_2 - E_1$$

$$E_b = (E^0 + 0.0591 \log [C_2]) - (E^0 + 0.0591 \log [C_1])$$

Where C_2 and C_1 are the concentrations of analyte and internal standard solution respectively.

Since C_1 is constant, then

$$E_b = L + 0.0591 \log C_2 \quad (\text{Where } L = -0.0591 \log C_1)$$

$$E_b = \boxed{L + 0.0591 \log [\text{H}^+]} \quad \text{Since, } C_2 = [\text{H}^+]$$

$$E_b = L - 0.0591 \text{pH} \quad \text{Since } \text{pH} = -\log [\text{H}^+]$$

Theoretically $E_b = 0$, when $C_1 = C_2$. But a small potential is developed even when $C_1 = C_2$ it is due to the unevenness of glass membrane. Small additional potential developed due to the curvature difference of glass membrane is called Asymmetric potential.

Overall potential of the glass electrode is the sum of 3 potentials,

1. Boundary Potential (E_b)
2. Potential of Ag/AgCl ($E_{Ag/AgCl}$)
3. Asymmetric potential ($E_{asymmetric}$)

$$\text{i.e., } E_G = E_b + E_{Ag/AgCl} + E_{asymmetric}$$

$$= L - 0.0591\text{pH} + E_{Ag/AgCl} + E_{asymmetric}$$

$$E_G = E_G^0 - 0.0591\text{pH}$$

Where $E_G^0 = L + E_{Ag/AgCl} + E_{asymmetric}$ is constant for a particular material.

The above equation for potential of glass electrode can be used to measure the pH of the solution

3.a.

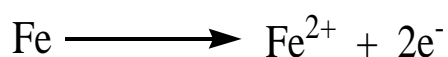
Electrochemical Theory Of Corrosion: According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur.

A large number of tiny galvanic cells with anodic and cathodic regions are formed.

- Oxidation of metal takes place at the anodic region. e.g. $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
- The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.
- The electrons travel through the metal from the anodic region to cathodic region.

Reactions:

Reaction at anodic region: As mentioned above, oxidation of metal takes place at anode.

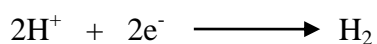


Reactions at cathodic region: At cathode, the reaction is either

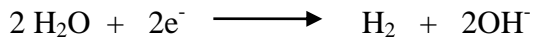
a) Liberation of hydrogen or b) absorption of oxygen.

A) **Liberation of hydrogen** (In the Absence of Oxygen)

1) In acidic medium the reaction is :



2) In neutral/alkaline medium, the reaction is:

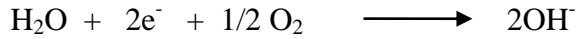


B) **Absorption of oxygen** (In the Presence Of Oxygen)

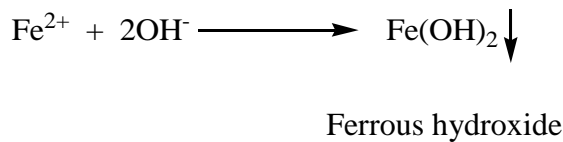
3) In acidic medium, the reaction is:



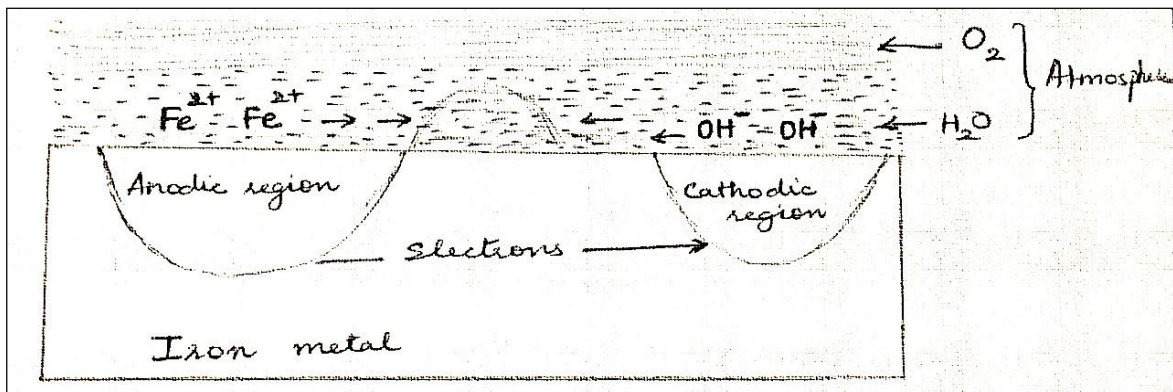
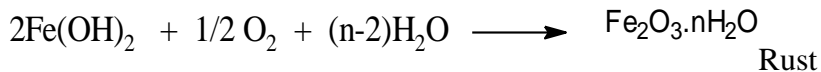
4) In neutral/alkaline medium, the reaction is :



Overall Reaction:



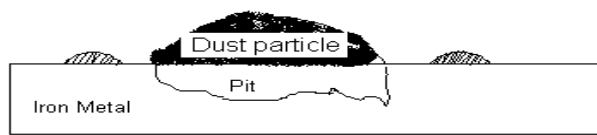
Since the layer of rust formed is highly porous, oxygen and moisture from the environment pierce deeper and increase the rate of corrosion.



3.b. Pitting corrosion: This is an example of differential aeration corrosion.

- When a small dust particle or water droplets gets deposited on a steel surface, the **region below the dust particle is exposed to less oxygen** compared to the remaining part.
- As a result, the region below the dust particle acts as anode undergoes corrosion and forms a pit. The remaining region of the metal acts as cathode and is unaffected.

The reactions may be represented as follows:



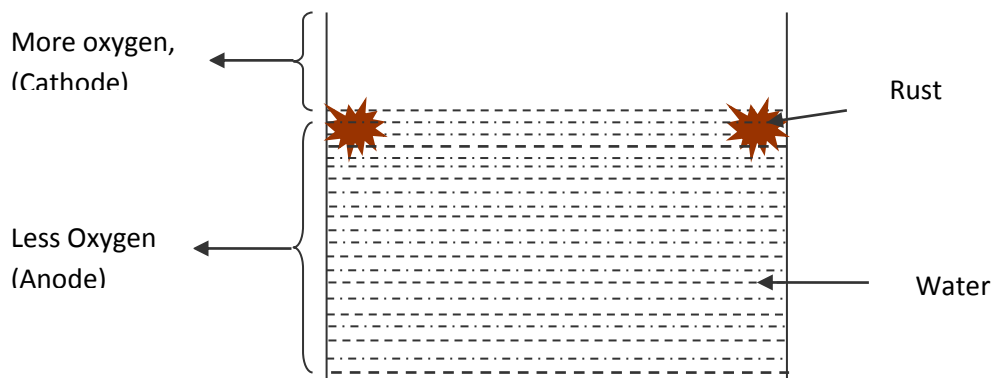
Cell reactions:

At anode : $M \longrightarrow M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^-$

Formation of a small anodic area and a large cathodic area results in intense corrosion below the dust particle.

Water line corrosion: This is an example of differential aeration corrosion.



- When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolve oxygen, whereas, the portion above the water line is exposed to more oxygen.
- Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected.

A distinct brown line is formed just below the water line due to the deposition of rust.

The reactions may be represented as follows:

Cell reactions:

At anode : $M \longrightarrow M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^-$

3.c

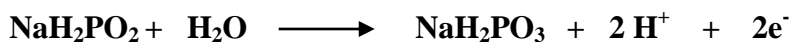
ELECTROLESS PLATING OF NICKEL:

Pretreatment:

- ❖ Article to be plated is degreased by organic solvent and etched by dil. H_2SO_4 .
- ❖ Metals like Fe, Al and brass do not need further treatment.
- ❖ Non-metallic materials (e.g. glass, plastics, printed circuit boards, PCB) are activated by first dipping in SnCl_2 and HCl solution, at 25°C followed by dipping in PdCl_2 solution and dried.
- ❖ SnCl_2 reduces palladium ions on the surface of the object to palladium which catalyse the deposition reaction.

Plating bath solution	Nickel chloride
Reducing agent	Sodium hypo phosphite
Complexing agent	Sodium succinate
Buffer	Sodium acetate
pH	4.5
Temperature	$70-90^\circ\text{C}$

Reactions:



- H^+ released during electroless plating will decrease the pH of plating bath. This results in burnt deposits of Ni. This is overcome by adding a buffer (sodium acetate)

Applications :

1. Used in electronic appliances
2. Domestic and automotive fields
3. Electroless Ni plated polymer are used for decorative purposes.

4.a

Metal finishing: Metal finishing is the process of surface modification of a metal by deposition of a layer of metal or by converting the surface layer metal into its oxide film.

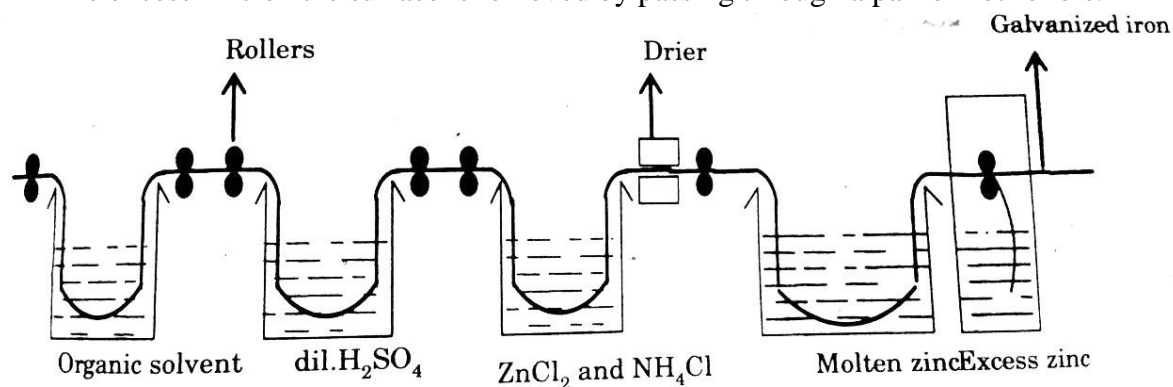
Technological importance of metal finishing: Metal finishing is carried out to obtain technologically important surface properties. These properties are:

1. A decorative appearance.
2. An improved corrosion resistance.
3. An improved heat resistance.
4. Improved surface hardness.
5. Improved solder ability.
6. Good thermal conductivity, electrical conductivity.

4.b.

i) Galvanizing: Galvanizing is the process of coating zinc on iron by hot dipping method. It involves the following steps.

- The iron sheet is washed with organic solvents to remove organic matter on the surface.
- Then it is treated with dilute sulphuric acid to remove rust or oxide layer. This is called pickling. The sheet is then washed with distilled water and dried.
- The iron sheet is then treated with a mixture of aqueous solution of $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$, which acts as a flux and dried. This helps the molten zinc to adhere strongly on the surface.
- The article is then dipped in a bath of molten zinc (450°C).
- The excess zinc on the surface is removed by passing through a pair of hot rollers.



Galvanizing

Application: Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

ii)

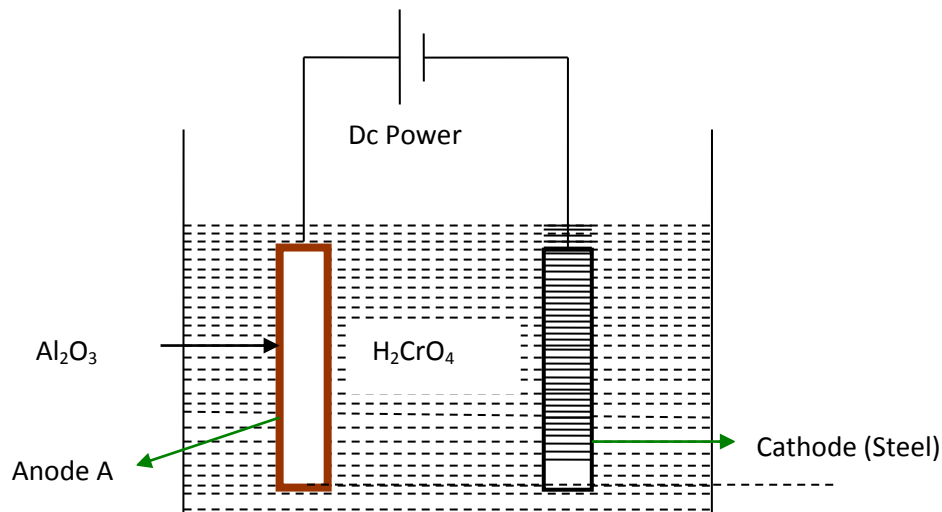
Anodizing

Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as a protective layer

Anodizing of aluminum:

In anodisation of aluminium, clean, polished aluminium is taken as anode and immersed in an electrolytic cell containing 5-10% chromic acid. Inert electrode like stainless steel or graphite is taken as the cathode. Temperature is maintained at 35°C and a suitable voltage is applied to get the desired thickness of oxide layer on aluminium. The aluminium oxide layer thus formed is porous. The pores are finally sealed by dipping in hot water to produce $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which occupies higher volume and thereby the pores are sealed. This non-porous protective layer

prevents aluminium from corrosion. Metals such as Mg, Ti etc. can also be anodised to prevent corrosion.



At anode: $2 \text{Al} \rightarrow 2\text{Al}^{3+} + 6\text{e}^-$

At cathode: $6 \text{H}^+ + 6\text{e}^- \rightarrow 3 \text{H}_2$

$2 \text{Al}^{3+} + 1 \frac{1}{2} \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$

Applications: anodized aluminium is used as an attractive highly durable, corrosion resistant material in roof, buildings, home appliances and computer parts

4.C.

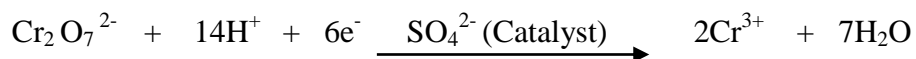
Electroplating is the process of electrolytic deposition of a metal on the surface of substrate; the substrate may be any metal, a polymer, a ceramic or a composite.

ELECTROPLATING OF CHROMIUM

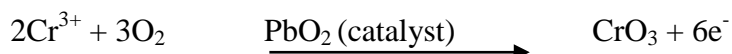
- The surface of the object is cleaned thoroughly. Oil and grease removed by organic solvent and then, treated with dilute H_2SO_4 to remove oxide layer.
- Finally, the surface is washed with distilled water. Then, chromium plating is done under the following conditions.

	Decorative Chromium Electroplating	Hard Chromium Electroplating
Plating bath composition	Chromic acid (H ₂ CrO ₄) + H ₂ SO ₄ in ratio 100 : 1	Chromic acid (H ₂ CrO ₄) + H ₂ SO ₄ in ratio 100 : 1
Operating temperature	45-60 °C	45-60 °C
Current density	100 – 200 mA cm ⁻²	200-400 mA cm ⁻²
Anode	Insoluble anode: Pb-Sn alloy coated with PbO ₂ .	Insoluble anode: Pb-Sn alloy coated with PbO ₂
Cathode	Object to be plated	Object to be plated
Anodic reaction	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
Cathodic reaction	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
Applications	1.Used in decorative coating in taps, handles, automobile bumpers, wheel rims 2. Used in corrosion resistant coating.	1. Cutting edges of milling machine 2. Hand guns, aircraft landing parts.
Thickness	0.25- 0.75micrometre	0.005-0.75 mm

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3⁺ state by a complex anodic reaction in the presence of sulphate ions. The Cr³⁺ then gets reduced to Cr on the substrate surface.



- For a good deposit, the Cr³⁺ concentration must be low. The PbO₂ oxidizes Cr³⁺ to Cr⁶⁺, thus reduce (control) the concentration of Cr³⁺.



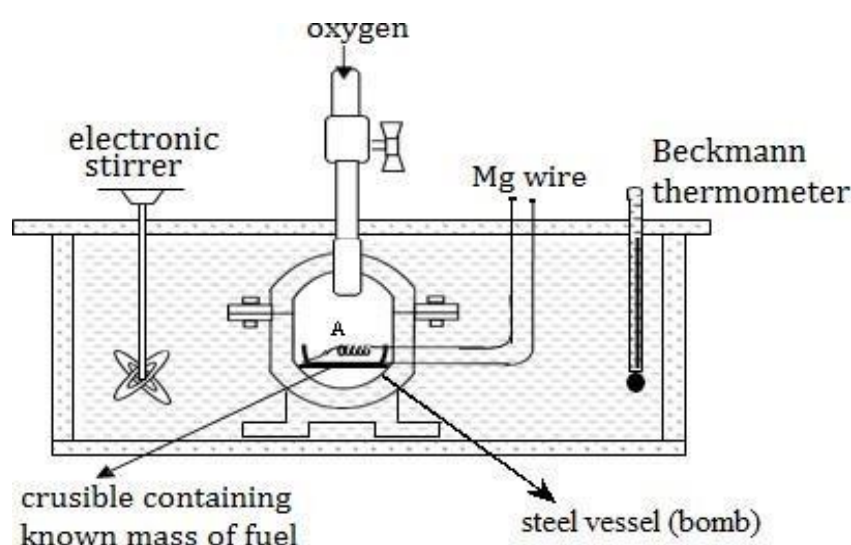
In chromium plating we do not use chromium metal as anode due to the following reasons.

- If chromium dissolves at anode, there will be a high concentration of Cr^{3+} in solution. In such cases, a black, (bad, burnt) deposit is obtained.
- In acidic solutions, chromium may undergo passivation.

5.a.

Calorific Value: The quality of a fuel is determined by the amount of energy released per unit mass or volume referred to as calorific value.

Principle: A known mass of the solid sample is burnt in excess oxygen. The surrounding water and the calorimeter absorb the heat liberated. The heat liberated by the fuel is equal to the absorbed by the water and the calorimeter.



Construction

- ❖ The bomb calorimeter (shown in the fig.) consists of a strong inner cylindrical steel vessel (bomb) with an airtight lid and an inlet for oxygen.
- ❖ The bomb has a crucible with a loop of wire. The ends of the wire project out and are connected to a source of electric current.
- ❖ The bomb is immersed in a rectangular copper vessel (calorimeter) of known weight and containing known volume of water, which is continuously stirred by mechanical stirrer.
- ❖ A Beckmann thermometer is introduced into the calorimeter to measure the temperature.

Working

- A known mass of water is taken in the calorimeter and is closed with the lid.
- The initial temperature of water is noted, $t_1^{\circ}\text{C}$
- A known mass of the fuel is taken in the crucible, inside the bomb.
- Oxygen is passed through the bomb.
- The ends of the wire are connected to an electric source so as to ignite the fuel.
- On passing an electric current through the ignition coil, the fuel gets ignited.
- The fuel burns liberating heat. Heat liberated is taken up by the water and calorimeter. The water is continuously stirred using the stirrer.
- The maximum temperature attained by the water, $t_2^{\circ}\text{C}$, is noted.

Observation and calculations:

$\text{Gross calorific value} = \frac{(w_1 + w_2) s \Delta t}{m} \quad \text{kJ kg}^{-1}$

where

w_1 = mass of water in the calorimeter, in kg

w_2 = water equivalent of the calorimeter, in kg

s = specific heat of water, in $\text{kJ kg}^{-1} \text{ } ^\circ\text{C}^{-1}$

$\Delta t = t_2 - t_1$ = rise in temperature, in $^\circ\text{C}$

m = mass of the fuel, in kg

5.b. Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

Solid oxide fuel cell (SOFC)

Anode – NiZrO_2

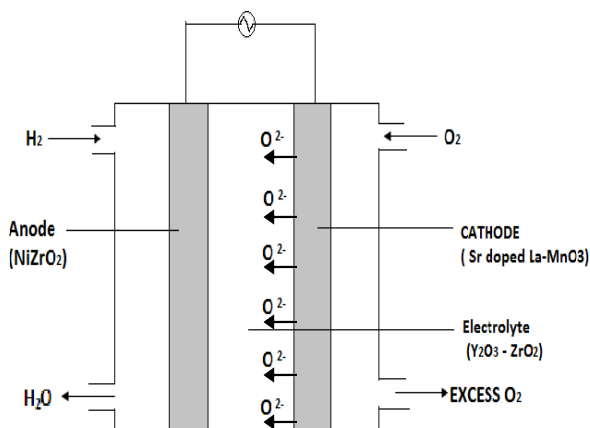
Cathode – Strontium doped lanthanum manganite (Sr-La MnO_3)

Fuel – H_2 or CO or mixture of both

Oxidant – O_2

Electrolyte – Solid $\text{ZrO}_2 - \text{Y}_2\text{O}_3$

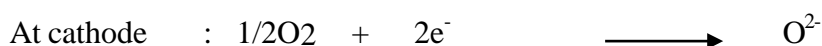
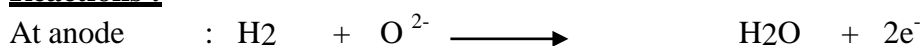
Operating temperature – 1000°C



Hydrogen gas (fuel) flows across anode. Hydrogen combines with oxygen ions

(O^{2-}) liberating water and electron. Liberated electrons move to cathode by external circuit.

At cathode, air (O_2) flows across porous cathode. When oxygen reaches the cathode, O_2 gets reduced to oxygen ion (O^{2-}). These oxygen ions diffuse through the electrolyte i.e by solid state diffusion from cathode to anode.

Reactions :

Applications - SOFC systems are being developed for military.

Locomotives (trains, ships)

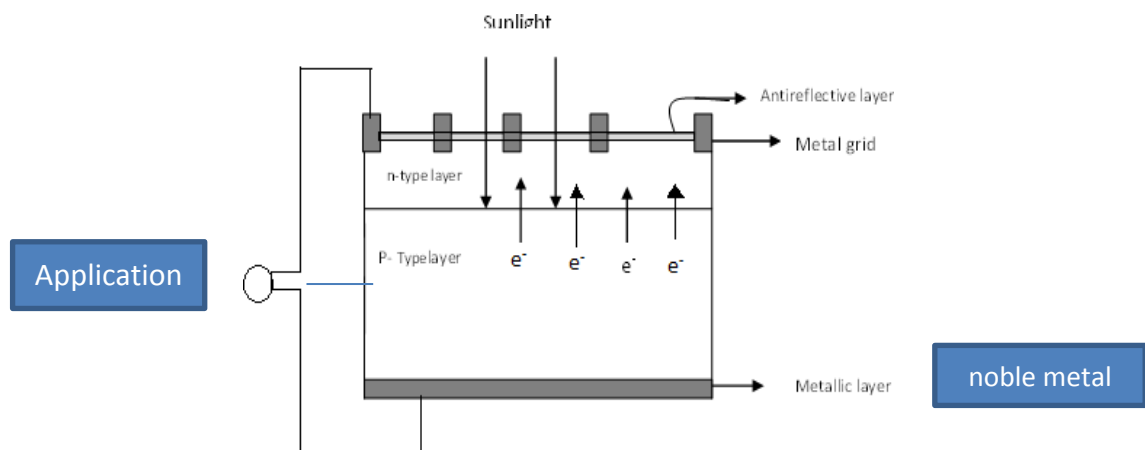
5.c.

Photovoltaic cells are semiconductor device which convert solar energy into electrical energy.

(Photovoltaic cell is based on the principle of photoelectric effect).

Construction of Photovoltaic Cell:

- A typical silicon PV cell is composed of a thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon.
- Hence a p-n junction is formed between the two.
- A **metallic grid** forms one of the electrical contacts of the PV cell, over n-type semiconductor and coated with an **antireflective layer** (TiO_2) between the grid lines increase the amount of light transmitted to the semiconductor (prevent reflection of solar radiation).
- The PV cell's other electrical contact is formed by a layer of noble metal (like silver) on the back of p-type semiconductor.



Working of PV cell :

- Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy
h = Planck constant
 ν = frequency
c = speed of light
 λ = wavelength

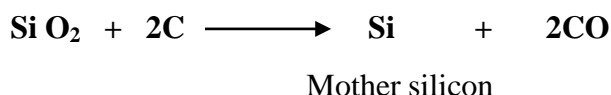
- When electromagnetic radiation (sunlight) is incident to the plane of solar cell, the photons, which possess energy sufficient to overcome the barrier potential are absorbed and electrons are ejected (from p-type semiconductor and move towards n-type through p-n junction to recombine with holes).
- Since p-n junction allows only one way movement of electrons, these electrons must flow through the external circuit to **recombine with holes**. This movement of electrons through the external circuit generate an electric current.

6.a.

PRODUCTION OF SOLAR GRADE SILICON: BY UNION CARBIDE PROCESS

The Union Carbide process: This process involves the following steps:

Silica(Quartz) is treated with coal in an electric arc furnace

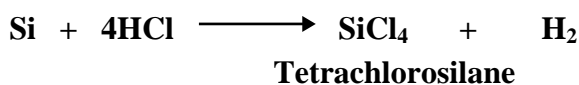
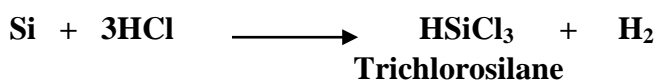


Carbon monoxide is further oxidized to carbon dioxide and released into the atmosphere.

In next step mother silicon is mixed with an oxygen and silica to remove the impurities such as Al, Ca and Mg. These impurities are removed in the form of slag (silicates) to get **Metallurgical grade silicon**



Metallurgical grade silicon is treated with dry HCl at 300⁰C to obtain trichlorosilane and tetrachlorosilane.



The trichlorosilane is separated by distillation.

Tetrachlorosilane is converted into trichlorosilane by **hydrogenating** in a reactor at 1000⁰ C.



The purified trichlorosilane is passed through a ion exchange column filled with **quaternary ammonium ion exchange resin** acting as catalyst.

- **Trichlorosilane gets converted into dichlorosilane.**



dichlorosilane

The products are separated by distillation, tetrachlorosilane is recycled to the hydrogen reactor and dichlorosilane is passed through a second ion exchange column filled with quaternary ammonium ion exchange resin.

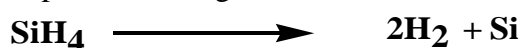
- **Dichlorosilane is converted into silane.**



Silane

The above products are separated by distillation and trichlorosilane is recycled to the ion exchange column.

- **Silane** is further purified by distillation and then pyrolyzed (heated at high temperature) to produce solar grade silicon which is 99.99% pure.



The silicon obtained is further purified by zone refining

6.b.

POWER ALCOHOL (gasohol)

- This is alcohol-blended petrol.
- Gasohol is a blend of 15 – 85% of absolute ethanol and 85 – 15% of petrol by volume.
- Gasohol with 85% of absolute ethanol & 15% of petrol can be used with engine modification. Gasohol with 15% of absolute ethanol & 85% of petrol can be used without engine modification.
- Absolute alcohol is used in the preparation of Power alcohol to prevent phase separation.
- Alcohol contains higher percentage of oxygen than MTBE and hence brings about complete oxidation of petrol more effectively.
- Therefore power alcohol has better anti-knocking characteristics than unleaded petrol.

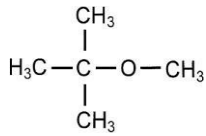
Advantages of power alcohol:

1. Power output is higher than petrol
2. Ethanol is better anti-knocking agent than MTBE.

3. Ethanol is cheaper than petrol.
4. It reduces emission of CO, NO hence causes less pollution.
5. Biodegradable.

Unleaded petrol:

In unleaded petrol, methyl-t-butyl ether (MTBE) and ethyl-t-butyl ether (ETBE) are used as anti-knocking agents.



MTBE has oxygen in its structure (in the form of ether group). This oxygen used for the complete combustion of the petrol, thus formation of peroxide compounds is minimized.

Advantages of unleaded petrol:

1. Increases the efficiency of the engine.
2. Helps in complete combustion of fuel hence, less air pollution
3. Increases the octane number of petrol.
4. Exhaust does not contain harmful gases

6.c.

$$\begin{aligned} \text{GCV} &= \frac{(w_1 + w_2) s \Delta t}{m} \\ &= \frac{(2.5+0.65) \times 3.2 \times 4.187}{0.75 \times 10^{-3}} \\ &= 56273 \text{ KJ/kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - (0.09 \times \% \text{ of H}_2 \text{ in fuel} \times \text{Latent heat of steam}) \\ &= 56273 - (0.09 \times 5 \times 2457) \\ &= 56273 - 1105.65 \\ &= 55167.35 \text{ KJ/Kg} \end{aligned}$$

7.a

e- WASTE or ELECTRONIC WASTE MANAGEMENT:

e-waste refers to electronic & electrical goods which can no longer be used. They contain hazardous & toxic materials which cannot be disposed off with other solid waste.

Source:

- Mobile phones, batteries, telephones, switch, socket, cable wires, computer, hardware, monitor, keyboard, refrigerator, washing machines, TV etc.
- Kitchen equipment (microwave ovens), laboratory with equipment's (microscopes, calorimeters)

Characteristics: e-waste is generally characterised by analysing the components & composition of waste.

- **Hazardous components in e- waste:**

Number of components contain hazardous components that need to be removed for separate treatment. Flame retardants are widely used in plastics to prevent developing fire in electronic equipment almost 12% of all plastics used in the electric & electronic equipment contains flame retardants, (television housing, computer monitors)

- **Material composition of waste:**

Electronic waste contains a mixture of various metals, particularly Cu, Al, steel, Hg covered with various types of plastics & ceramics.

Disposal:**1. RECYCLING OF e-WASTE:**

e-waste can be re-utilized with help recycling process.

It involves dismantling of the electronic device, separation of the parts having hazardous substances like CRT(cathode ray tube), printed circuit boards & then recovery of the precious metals like Cu, gold, lead, can be done with the help of a e-waste recycler.

2. REUSE:

This is the most desirable e-waste recycling where with slight modifications the mobile phones, computer, laptop, printers can reused or given as second hand product.

7.b**LEAD:****Source:**

1. Lead comes from metal smelting , lead- acid battery, steel industries ,
2. Burning of waste oil, paint industries.
3. Lead enters water through contact with plumbing , lead based pipes.

Ill effects:

1. **Air borne lead** can enter into human system and get accumulated into **blood**.
2. When the concentration of lead increases , it can enter brain and also get **deposited in bones**.(because the similarity in sizes of Ca^{2+} & Pb^{2+}
3. When bone starts dissolving due to old age or illness , it can enter blood stream.
4. It inhibits the production of haemoglobin & causes **anaemia** ,it adverse effect to kidney function & **permanent brain damage**.
5. Lead has serious effects on the children **IQ**.

Control:

1. Replacement of conventional lead based products by lead free products.
2. The effect of lead on human can be controlled by following proper disposal method.
3. Eliminate lead contamination in drinking water by process such as reverse osmosis, distillation, filtration using carbon filters specially manufactured for lead removal.

7.c.

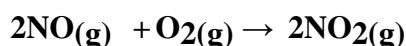
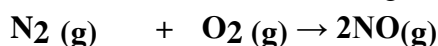
$$\begin{aligned}
 \text{NFAS} &= \text{MFAS} \\
 \text{COD} &= \frac{8 \times \text{NFAS} \times (X-Y) \times 1000}{V} \\
 &= \frac{8 \times 0.05 \times (30.2-14.5) \times 1000}{25} \\
 &= 251.2 \text{ mg of oxygen/liter}
 \end{aligned}$$

8.a.

OXIDES OF NITROGEN (NO_x): NO, NO₂ ,& N₂O are the common oxides of nitrogen

Source:

1. N₂ & O₂ are the main constituents of air these gases don't react with each other at a normal temperature, **when lightning strikes**, they combine to form oxides of nitrogen.
2. When fossil fuel is burnt , di nitrogen & di oxygen combine to yield NO & NO₂



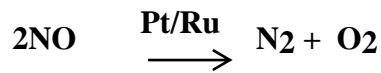
3. Nitrogen fixation, bacterial decay of nitrogenous compounds leads NO_x in atmosphere.
4. From acid pickling plants

Ill effect:

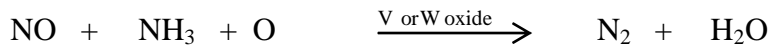
1. Higher levels of NO₂ can cause damage to the human respiratory tract, respiratory infections & Asthma.
2. It is unpleasant in odour and leads to irritation of eyes and even lung's congestion.
3. Long- term exposure to high levels of nitrogen di oxygen can cause chronic disease.
4. Formation of photochemical smog, which limits in visibility of road.
5. Causes acid rain – NO₂ and N₂O₅ reacts with H₂O and O₃ to form HNO₃ .

Control:

1. **Oxides of nitrogen & carbon monoxide** can be controlled by passing these gases through a catalyst converter containing **Pt-Rh** catalyst ,which coverts these toxic gases to non-toxic nitrogen and carbon dioxide.



2. Treatment of flue gas by injecting into NH_3 , powdered limestone or aluminum dioxide.
3. Selective catalytic reduction at $300\text{--}400^\circ\text{C}$ by vanadium oxide or tungsten oxide as a catalyst.



8.b.

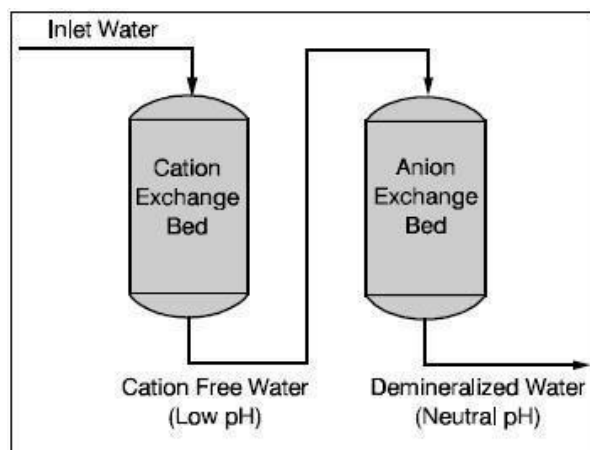
SOFTENING OF WATER BY ION EXCHANGE PROCESS:

The process of removal of Ca, Mg, Fe salts and other metallic ions from water is called softening of water.

1. Softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin.
2. Ion exchange resins are high molecular weight, cross linked polymers with a porous structure.
3. The functional groups which are attached to the chains are responsible for ion exchange properties.

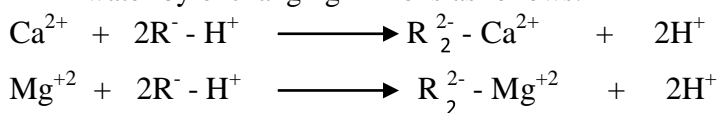
Cation exchange resins: The resins containing acidic groups which are capable of exchanging H^+ ions for cations (Ca^{+2} or Mg^{+2}) present in water.

Anion exchange resins: The resins containing basic groups which are capable of exchanging OH^- ions for anions (Cl^- , SO_4^{2-} , HCO^-) present in water.

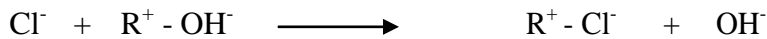


Process

- ◆ In this process, cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{+2} , Mg^{+2} are removed from hard water by exchanging H^+ ions as follows.



- ◆ Hard water is then passed through anion exchange resin where anions like Cl^- , SO_4^{2-} are exchanged with OH^- ions as follows.



The H^+ and OH^- ions released combine to form water molecule.

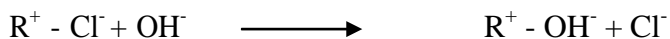
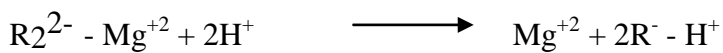
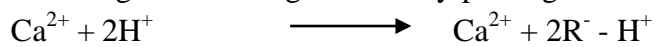
- ◆ Thus water coming out of two resin is free from metallic ions and called as ion exchanged water.

Regeneration:

When the resins lose their capacity to exchange ions, they should be regenerated. The process of regeneration is the reversal of the reaction taking place for ion exchange.

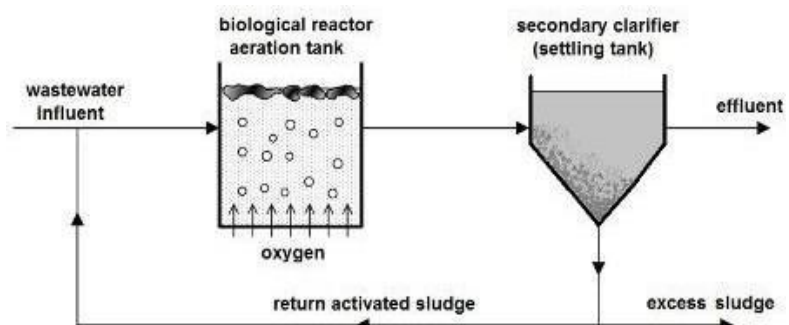
Cation exchange resin is regenerated by passing a solution of dil HCl or H_2SO_4 .

Anion exchange resin is regenerated by passing a solution of NH_4OH or NaOH respectively. R_2^{2-} -



8.c.

SECONDARY TREATMENT(Activated sludge method) :



This stage is to remove biologically oxidizable impurities present in polluted water. Here, waste water sample after primary treatment is mixed with activated sludge under aerobic condition.

Activated sludge: Activated sludge is a water sample containing higher concentration of microorganisms like azobacter etc.

The water is mixed with proper quantity of activated sludge and the mixture is sent to aeration tank. During the process, microorganisms present in activated sludge attack on biologically oxidizable compounds of sewage and decompose them into CO_2 and H_2O . The effluent, after this treatment is passed to sedimentation tank (clarifier) where sludge is settled down. The clear effluent (which has much lower organic load) is sent to tertiary treatment. A part of sludge is used for further treatment and rest is disposed off.



9.a.

ATOMIC ABSORPTION SPECTROSCOPY

It deals with the absorption of energy (electromagnetic radiation) by the gaseous atoms of a substance in their ground state.

It is a technique for measuring the concentration of various elements in the sample through their absorption of light.

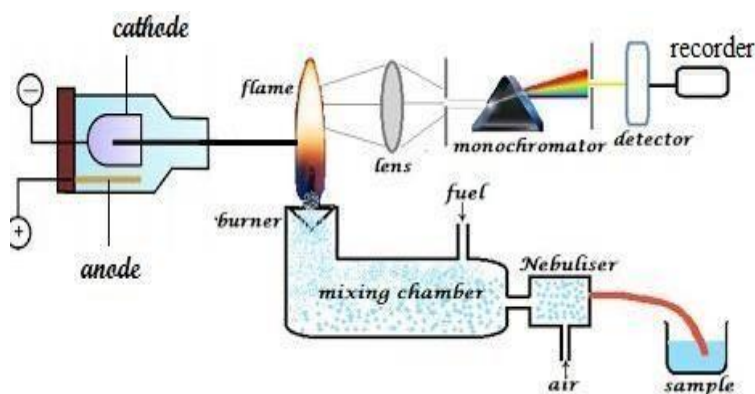
THEORY: Here, when a solution having a mixtures of metallic species is introduced into the flame. The solvent evaporates and vapor of metallic species is obtained.

These atoms are promoted to excited state for a short period of time (nanoseconds) by absorbing radiation of their own specific resonance wavelength . The amount of wavelength absorbed(energy), is specific to a particular atom.

The absorption of radiation will be proportional to the intensity of atoms in the sample. The intensity of light absorbed is related to concentration by, **Beer-Lambert law**.

$A = \epsilon ct$ Where ' ϵ ' is the absorption coefficient, c is the concentration; t is the path length.

INSTRUMENTATION



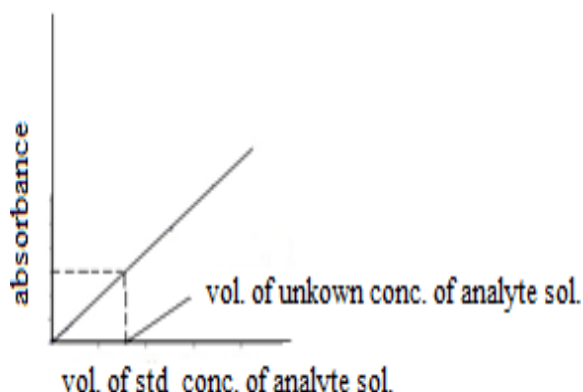
The burner (atomizer): Here the sample is burned with the flame produced by the fuel and oxidant combination. The sample after evaporation leaves a fine residue of neutral atoms.

Fuel and Oxidant: This is a very important part of the entire process. If the heat produced is not sufficient then the sample doesn't form atoms. If the heat of burner is more, the sample molecule may ionize instead of forming atoms. So the proper combination of fuel and oxidant are to be used.

Radiation source: It's a **hollow cathode lamp** which consists of a glass tube filled with noble gas. An anode and a cathode is placed. Cathode should be is coated with a metal of analyte to be analyzed. The cathode emits radiation characteristic of the metal to be analyzed.

Monochromator and detector: The radiation first passes through the sample and then passes through a monochromator in order to separate the element specific radiation from any other radiation emitted by the source, which is finally measured by a detector. Then the calibration curve is obtained by plotting the absorbance against the concentration of the standard solutions.

From the calibration curve, the concentration of the sample solution can be determined.



Applications:

- i) Used in medical research and laboratories to analyze metal ions like Na, K, Mg, Ca and other body fluids in blood, saliva and urine samples .
- ii) To determine heavy metal like Fe, Mn, Cu, Zn, Hg, Pb, Sn etc in environmental samples.
- iii) To determine metal elements in the food industry.

9.b.

POTENTIOMETRY

It deals with a estimation of chemical substances in the solution by measuring the potential value.

THEORY:

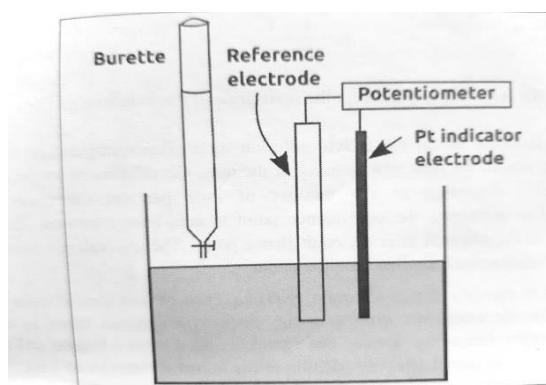
In potentiometry the amount of substance (metal ion) in the solution is estimated by measuring the EMF between 2 electrodes that are dipped in the solution.

The relation between electrode potential and metal ion concentration is given by the Nernst equation.

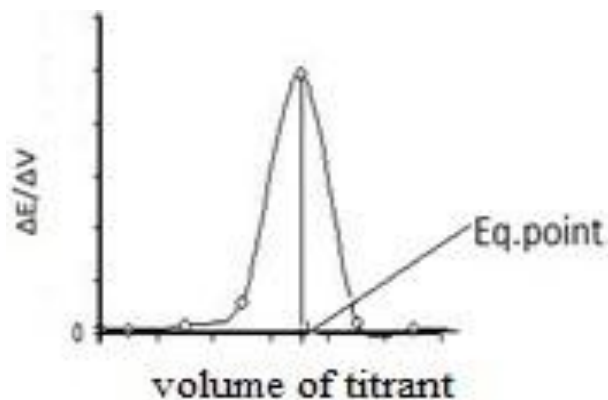
$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

It can be seen from the equation that the potential of an electrode E depends upon the concentration of the ion M^{n+}

Instrumentation:



- Potentiometer consists of 2 electrodes i.e a reference electrode and an indicator electrode which are connected to a device (potentiometer) for measuring the potential.
- The indicator electrode responds rapidly to the changes in the potential due to the concentration changes of the analyte.
- A known volume of the analyte is taken in a beaker and its potential is measured by connecting the assembly to a potentiometer.
- The titrant is added in increments of 0.5ml and the potential is measured each time.
- Near the equivalence point there is sharp increase in the potential. The end point is determined by plotting change in potential against the volume of titrant.



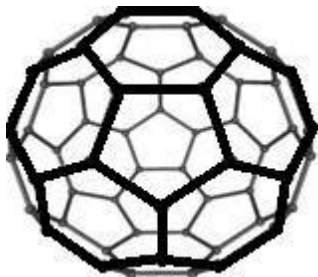
Applications:

- Used in precipitation titrations, which involves insoluble salt metals. (For example titration of silver ion with a halide ion. Silver electrode is used as indicator electrode)
- Used in complexometric titrations.

9.c.

FULLERENES:

1. Fullerenes are class of molecules made of only carbon atoms having closed cage like structure.
2. Many number of fullerene molecules with different carbon atoms like C₆₀, C₇₀, C₇₄, C₇₈ etc., have been prepared.
3. **C₆₀** is the smallest, stable and abundant fullerene, obtained by usual preparation methods.



4. C₆₀ has **spherical** shape and resembles a football and commonly known as buckyball.
5. Fullerenes are made up of pentagons and hexagons. Pentagons give curvature required to form closed structure.
6. All fullerenes contain **12 pentagons** and different numbers of hexagons.
7. Each fullerene has 2(10+M) number of carbon atoms corresponding to 12 pentagons and M number of hexagons.

Properties and Application.

1. Single C₆₀ molecule theoretically can take up maximum of 60 hydrogen atoms.

Application- Hydrogen storage material for fuel cells

Electrode material in secondary batteries. Ex- Nickel Metal Hydride battery.

- Each C₆₀ molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

***Application-**Used as optical limiters. Optical limiters are used to protect materials from damage, by intense incident light radiation.*

- A polymer composite of C₆₀ molecule and polyvinylcarbazole exhibits very high photoconductivity.

***Application-** Used in Photocopying applications.*

10.a.

PRECIPITATION METHOD

Nano material refers to a material with at least one of its dimension (length, width or breadth) in nano scale.i.e 10^{-9} m.

Precursor-Inorganic metal salt (usually nitrate, or acetate of metal)dissolved in water.

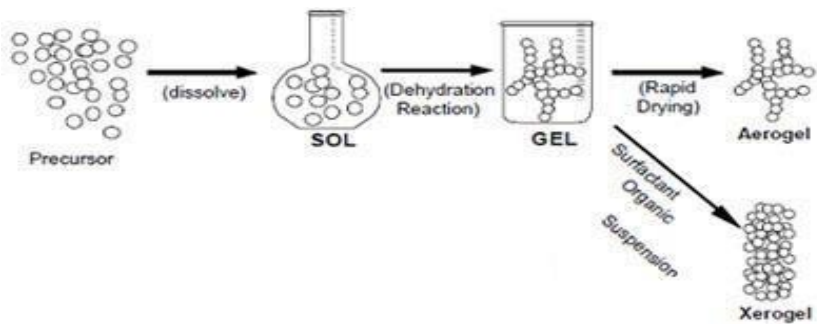
- Metal cations exist in the form of metal hydrate species, such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.
- To this addition of precipitating agent such as NaOH, NH₄OH, NaBr or Na₂CO₃ results in change in pH, increase in ions and condensation of precursor.
- The concentration of ions in the solution increases and reaches a critical level called as Supersaturation
- At supersaturation, Nucleus formation is initiated.
- Nucleus grows into particles, which gets precipitated.
- The product obtained is filtered, washed with water, air dried and calcinated at higher temperature.
- If super saturation and rate of nucleation are slow then the precipitate with wide particle size is formed.
- If super saturation and rate of nucleation are rapid then nucleus formed will burst, so particles with small size formed.
- Thus nano particle of **desired size** can be obtained by controlling **super saturation and rate of nucleation**.

10.b.

SOL-GEL PROCESS

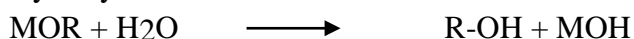
- In sol-gel process, either **metal salt or alkoxide** is used as precursor (starting material).
 - It is mainly used in the synthesis of uniform nanoparticles of **metal oxides**. Steps involved in synthesis
- Preparation of Sol**
 - Conversion of Sol to Gel.**
 - Aging of Gel.**
 - Drying of the Gel (evaporation)**

5. Heating at high temperature(calcination)

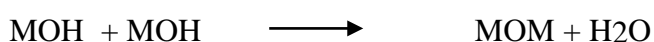


- **Step 1 : Sol** is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)
- **Step 2:** Sol is further converted into a gel by hydrolysis and condensation of precursors.(adding acid or base as catalyst)

Hydrolysis of alkoxides



Condensation of hydrolysed species with each other(releases water)



- **Step 3:** Aging (keeping for a known period of time) of colloid solutions takes place, i.e.colloids can increase their particle size and grows into a sol-gel.
- **Step 4:**Then the gel is dried by evaporation (solvent get evaporated)
- **Step 5:**Calcinated (heating to high temperature) to produce nanoparticles.

10.C.

CONDUCTOMETRIC TITRATION

Determination of quantity of material present in the solution by measuring its electrical conductivity.

THEORY:

Conductivity is a measure of ability of a solution to carry an electric current. Electrolyte solution conducts current by the migration of ions under the influence of an electric field. This obeys Ohm's law,

$$E = IR$$

where, E = Applied potential

I = Current

R = Resistance

Conductance is a reciprocal of resistance, i.e $C = \frac{1}{R}$

Resistance depends on length and cross sectional area of the conductor (resistance is directly proportional to the length of conductor and inversely proportional to the cross sectional area of the conductor)

$$\text{i.e } R = s \frac{l}{a}$$

where, s = specific resistance

l = length of conductor

a = cross sectional area of the conductor

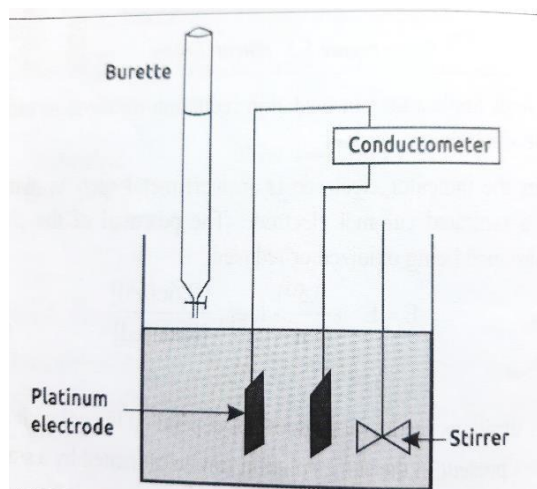
The unit of specific conductance is $\text{ohm}^{-1}\text{cm}^{-1}$. In this neutralization point is given by sudden change in conductance.

INSTRUMENTATION:

1. Conductivity cell: Two Pt electrodes of area 1cm^2 and at 1cm apart
2. Conductivity meter: To display the reading during titration.
3. Magnetic stirrer: To maintain uniform concentration.

Analyte solution is taken in the beaker, and a magnetic stirrer is placed. Conductivity cell is dipped in the solution which is connected to the conductometer. Initial reading is noted. The titrating reagent (known ml) is added and conductance is measured after stirring. The addition of titrating agent is continued until at least 5 readings beyond the equivalence point.

A graph of conductance vs volume of titrant is plotted. And the equivalence point is noted.



Applications:

1. Displacement titration (salt of weak acid titrated against strong acid)
2. Used in estimation of acid or base present in the sample solution
3. Precipitation titration (silver nitrate against sodium chloride)
4. Complexation titrations (EDTA vs metal ion)

First/Second Semester B.E. Degree Examination, June/July 2019
Engineering Chemistry

Time: 3 hrs.

Max. Marks: 100

Note: Answer any FIVE full questions, choosing ONE full question from each module.

Module-1

- 1 a. What is single electrode potential? Derive Nernst's equation for single electrode potential. (06 Marks)
- b. What are batteries? Demonstrate the construction and working of Ni-MH battery, mention its applications. (07 Marks)
- c. What voltage will be generated by a cell that consists of an iron electrode immersed in 0.5M FeSO₄ solution and a copper electrode immersed in 1M CuSO₄ solution at 298 K. Given $E_{Fe}^{\circ} = -0.44\text{ V}$ and $E_{Cu}^{\circ} = 0.34\text{ V}$. Write the cell representation and cell reactions. (07 Marks)

OR

- 2 a. What is Battery? Explain primary and secondary with examples. (06 Marks)
- b. Describe the construction and working of Li-ion battery. Mention its applications. (07 Marks)
- c. What are concentration cells? Emf of the cell $Cd | CdSO_4 (XM) || CdSO_4 (0.025M) | Cd$ at 28°C is 0.035 V. Find the concentration of CdSO₄ at anode. Given $R = 8.314\text{ J/K/mol}$, $F = 96500\text{ C}$. (07 Marks)

Module-2

- 3 a. Discuss the following types of corrosion:
i) Differential metallic corrosion ii) Water line corrosion (06 Marks)
- b. What is corrosion? Illustrate electrochemical theory of corrosion taking iron as an example. (07 Marks)
- c. What is electroless plating? Outline the electroless plating of copper. (07 Marks)

OR

- 4 a. Explain the factors affecting the rate of corrosion:
i) Nature of corrosion product ii) Ratio of anodic to cathodic areas (06 Marks)
- b. What is meant by metal finishing? Highlight any five technological importance of metal finishing. (07 Marks)
- c. What is electroplating? Discuss the electroplating of chromium. (07 Marks)

Module-3

- 5 a. What are fuel cells? Describe the construction and working of Methanol-Oxygen fuel cell. (06 Marks)
- b. Describe the experimental determination of calorific value of solid fuel using Bomb Calorimeter. (07 Marks)
- c. 0.95 g of coal sample (C = 93%; H₂ = 6% and ash 1%) was subjected to combustion in Bomb calorimeter. Mass of water taken in the calorimeter was 2.6 kg and the water equivalent of calorimeter was 0.75 kg. The rise in temperature was found to be 3.2°C. Calculate the gross and net calorific values of the sample. Latent heat of steam = 2457 kJ/kg/°C and $S = 4.187\text{ kJ/kg/°C}$. (07 Marks)

OR

- 6 a. Explain the preparation of solar grade silicon by union-carbide process. (06 Marks)
b. What are pv-cells? Illustrate the construction and working of a typical pv-cell. (07 Marks)
c. What is knocking? Explain the mechanisms of knocking. Mention its ill effects. (07 Marks)

Module-4

- 7 a. Outline the softening of water by ion-exchange method. (06 Marks)
b. What are the sources, effects and control of lead pollution? (07 Marks)
c. Define COD. In a COD test, 30.6 cm³ and 15.5 cm³ of 0.05N FAS solution are required for blank and sample titration respectively. The volume of the test sample used was 25 cm³. Solve the COD of the water sample solution. (07 Marks)

OR

- 8 a. What is Desalination? Describe the process of reverse osmosis of water. (06 Marks)
b. What is boiler corrosion? Explain the boiler corrosion with CO₂, O₂ and MgCl₂. (07 Marks)
c. Define COD. Illustrate the determination of COD of waste water sample. (07 Marks)

Module-5

- 9 a. Describe the synthesis of nano-material by sol-gel technique. (06 Marks)
b. Discuss the theory and instrumentation of conductometry. (07 Marks)
c. Outline the theory, instrumentation and applications of colorimetry. (07 Marks)

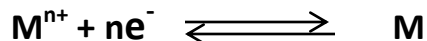
OR

- 10 a. Explain size dependent properties of nano material:
i) Surface area
ii) Electrical
iii) Optical properties (06 Marks)
b. Write a note on fullerenes. Mention its properties and applications. (07 Marks)
c. What are nanomaterials? Explain the synthesis of nanomaterial by chemical vapour deposition method. (07 Marks)

ANSWERS

1.a Single electrode potential: It is the potential developed at the junction of a metal and solution when a metal is in contact with its own ions due to loss or gain of electrons.

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature.
Consider a reversible electrode reaction,



Equilibrium constant for the above reaction is,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[M]}{[M^{n+}]} \dots\dots\dots (1)$$

According to thermodynamics, for a reversible process, equilibrium constant (K) is related to decrease in change in free energy ($-\Delta G$) as, by Vant Hoff equation.

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots (2)$$

Where, ΔG^0 = Standard change in free energy

R = Universal gas constant

T = Temperature

Substituting 1 in 2 we have,

$$\Delta G = \Delta G^0 + RT \ln \frac{[M]}{[M^{n+}]} \dots\dots\dots (3)$$

The decrease free energy ($-\Delta G$) for any reversible process is equal to the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\max} \dots\dots\dots (4)$$

In case of a Galvanic cell, W_{\max} = Electrical energy supplied by the cell

$$= [(\text{difference in potential between two electrodes}) \times (\text{total charge flowing through the cell})]$$

If 'n' moles of electrons are flowing from anode to cathode, then the total quantity of charges flowing through the cell is 'n' Faradays(nF).

$$\therefore W_{\max} = E_{\text{cell}} \times nF = nFE \quad (5)$$

By comparing equation 4 and 5,

$$- \Delta G = nFE \quad \text{.....(6) or } \Delta G = -nFE$$

Under standard conditions,

$$- \Delta G^\circ = nFE^\circ \quad (7) \text{ or } \Delta G^\circ = -nFE$$

Substituting the values equation (6) and (7) in equation (3)

$$nFE = -nFE^\circ + RT \ln K_c \quad \text{.....(8)}$$

Dividing throughout by -nF,

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \quad \text{.....(9)}$$

$$E = E^\circ + 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \left\{ \frac{2.303RT}{nF} \log [M] - \frac{2.303}{nF} \log [M^{n+}] \right\} \quad \text{.....(10)}$$

In case of metal-metal ion electrode, as 'M' is solid metal, [M] = 1

$$\therefore E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

(R is a gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; T= temperature in absolute scale (298K);

F is Faraday = $96,500 \text{ C mol}^{-1}$)

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}] \quad \text{at 298 K}$$

1.b.

Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reaction.

Nickel-metal hydride battery:

Construction:

In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed.

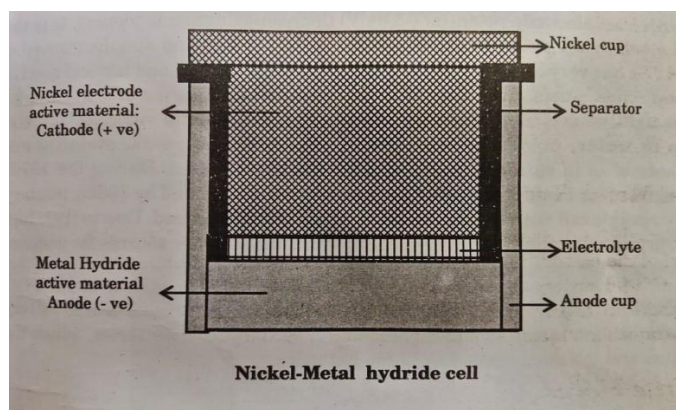
Anode – Porous nickel grid pasted with **metal hydride** (such as TiH_2 , VH_2 ,) and a hydrogen storage alloy (such as LaNi_5).

Cathode - Porous nickel grid pasted with **Ni(OH)_2 , NiO(OH)** .

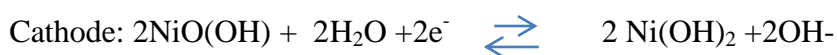
Electrolyte- KOH .

Separator- Polypropylene.

Representation : $\text{MH}_2 \mid \text{KOH} \mid \text{Ni(OH)}_2, \text{NiO(OH)}$



Working:

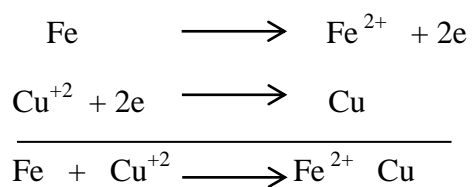




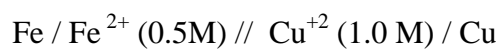
Uses: Used in cellular phones, camcorders and laptop computers.

1.c.

Cell reaction:



Cell Representation:



$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \left[\frac{M^{n+} \text{ at cathode}}{M^{n+} \text{ at anode}} \right]$$

$$E_{0\text{cell}} = E_{0\text{Cu}^{2+}/\text{Cu}} - E_{0\text{Fe}^{2+}/\text{Fe}}$$

$$= 0.34 - (-0.44)$$

$$E_{0\text{cell}} = 0.78\text{V}$$

$$E_{\text{cell}} = 0.748 + \frac{0.0591}{2} \log \left[\frac{1.0}{0.5} \right]$$

$$= 0.74 + 0.0295 \log 2$$

$$E_{\text{cell}} = 0.74 + 0.0295 \times 0.3$$

$$E_{\text{cell}} = 0.74885\text{V}$$

2.a

Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reaction.

Classification of the Battery:

1.Primary Batteries: A battery which cannot be recharged because the cell reactions are irreversible is called primary battery. Once the cell get completely discharged, later these are of no use. e.g. Zn-MnO₂, Li-MnO₂.

2. Secondary Battery: A battery which can be recharged because the cell reactions are reversible is called secondary battery. This is also known as storage battery.

e.g. Lead-acid battery, Li-ion battery, Ni-MH₂ battery.

2.b

Lithium-ion battery:

Construction:

Anode-Lithium intercalated graphite.

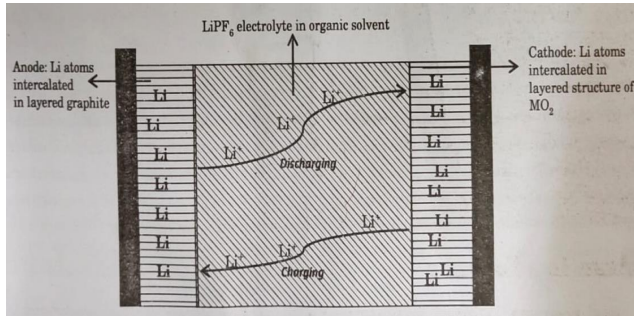
Cathode – Lithium metal oxide such as (LiCoO₂).

Electrolyte -A solution of lithium salt (LiPF₆) in organic solvent.

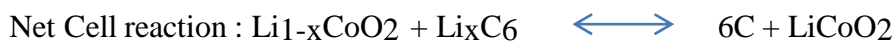
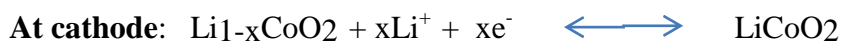
Separator- non-woven **polypropylene**.

Representation : *Li,C / LiPF₆, in organic solvent / LiCoO*

- It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers.
- Lithium ions move between anode and cathode during discharging and charging process. Since both anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.



Working



Applications: Portable electronics , mobile phones , laptop, ipod etc.

2.c

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log \frac{C_2}{C_1}$$

$$0.035 = \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log \frac{C_2}{C_1}$$

$$0.035 = \frac{0.0597}{2} \log \frac{0.025}{x}$$

$$0.035 - 0.02986 = \log 0.025 - \log x$$

$$0.00514 = -1.602 - \log x$$

$$\log x = -1.602 - 0.00514$$

$$\log x = -1.607719$$

$$x = \text{antilog}(-1.6077)$$

$$= 0.024 \text{ M}$$

3a.

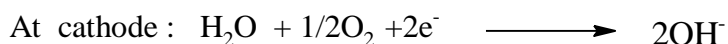
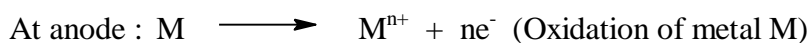
i) Differential metal corrosion:



- This type of corrosion occurs when two **dissimilar metals** are in contact with each other and are exposed to a corrosive environment. The two metals differ in their electrode potentials. The metal with lower electrode potential acts as anode and the other metal with higher electrode potential acts as cathode.
- The anodic metal undergoes oxidation and gets corroded. A reduction reaction occurs at the cathodic metal. The cathodic metal does not undergo corrosion.

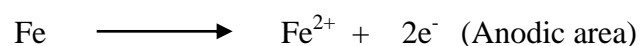
The general cell reactions may be represented as follows:

Cell reactions:

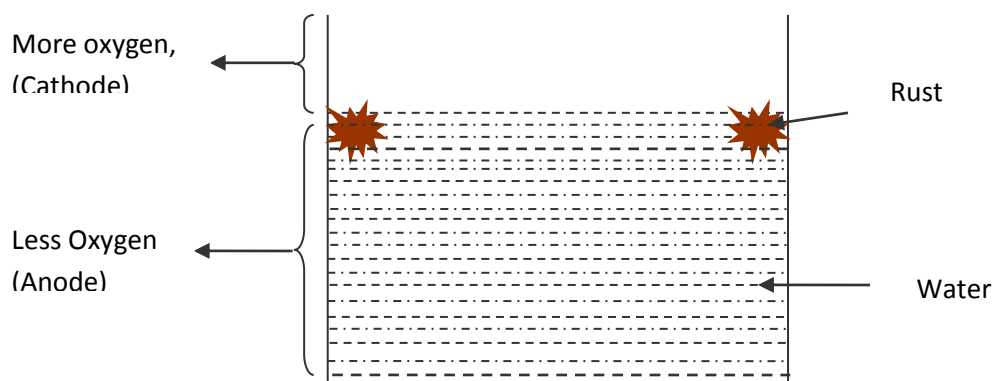


Higher the potential difference between the anodic and cathodic metals, **higher is the rate of corrosion.**

Example: When Fe(-0.44V) is in contact with Cu(0.34V), iron acts as anode and Cu acts as cathode because Fe has lower electrode potential compared to Cu. Therefore Fe undergoes corrosion.



ii) Water line corrosion: This is an example of differential aeration corrosion.



- When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolved oxygen, whereas, the portion above the water line is exposed to more oxygen.
- Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected.

A distinct brown line is formed just below the water line due to the deposition of rust.

The reactions may be represented as follows:

Cell reactions:

At anode : $M \longrightarrow M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^-$

3.b

Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

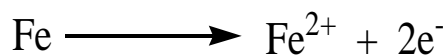
Electrochemical Theory Of Corrosion: According to electrochemical theory, when a metal such as iron is exposed to a corrosive environment, following changes occur.

A large number of tiny galvanic cells with anodic and cathodic regions are formed.

- Oxidation of metal takes place at the anodic region. e.g. $Fe \rightarrow Fe^{2+} + 2e^-$
- The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.
- The electrons travel through the metal from the anodic region to the cathodic region.

Reactions:

Reaction at anodic region: As mentioned above, oxidation of metal takes place at anode.

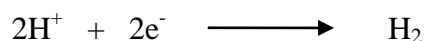


Reactions at cathodic region: At cathode, the reaction is either

a) Liberation of hydrogen or b) absorption of oxygen.

A) **Liberation of hydrogen** (In the Absence of Oxygen)

5) In acidic medium the reaction is :

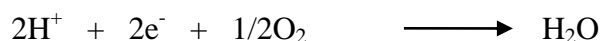


6) In neutral/alkaline medium, the reaction is:

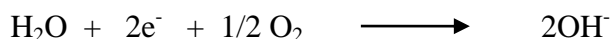


B) **Absorption of oxygen** (In the Presence Of Oxygen)

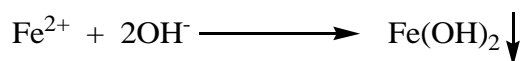
7) In acidic medium, the reaction is:



8) In neutral/alkaline medium, the reaction is :

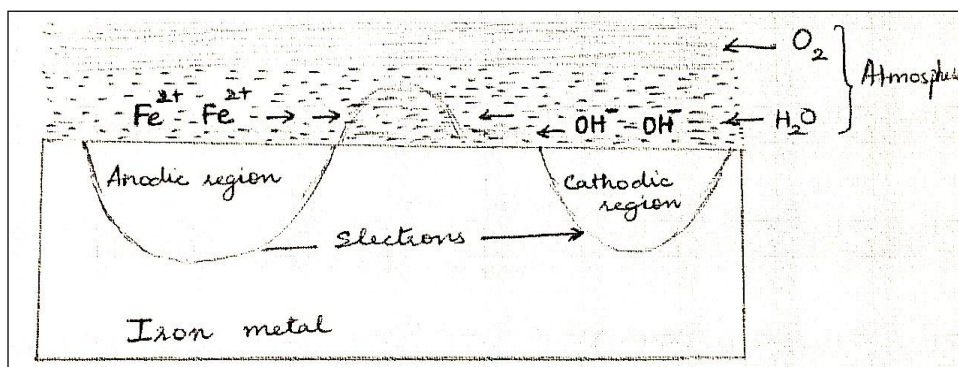
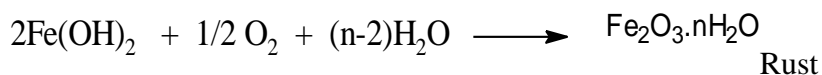


Overall Reaction:



Ferrous hydroxide

Since the layer of rust formed is highly porous, oxygen and moisture from the environment pierce deeper and increase the rate of corrosion



3.c.

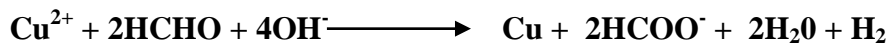
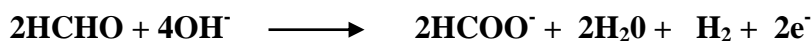
Electroless plating of Copper/Electroless plating on PCB:

Pretreatment and activation of the surface:

- ❖ Article to be plated is degreased by organic solvent and etched by dil. H_2SO_4 .
- ❖ Metals like Fe, Co, Ni etc do not need further treatment.
- ❖ Non-metallic materials (e.g. glass, plastics, printed circuit boards, PCB) are activated by first dipping in SnCl_2 and HCl solution, followed by dipping in PdCl_2 solution and dried.

Plating bath solution	Copper sulphate
Reducing agent	Formaldehyde
Complexing agent	EDTA
Buffer	Sodium hydroxide and Rochelle salt
pH	11
Temperature	25°C

Reactions:



Applications:

1. Mainly used in **printed circuit boards (PCB)**.
2. For plating on non-conductors.

Advantages of electroless plating:

1. Electrical equipment is not required.
2. Semiconductors and insulators can also be plated.
3. Electroless plating baths have better throwing power.
4. Electroless coatings are harder than the electrodeposited coatings

4.a

Nature of corrosion product:

- If the corrosion product is insoluble, stable and non-porous, then it acts as a protective film which prevents further corrosion.
- The film acts as a barrier between metal surface and the corrosive environment.
- On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

Example: Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of Cr_2O_3 on the surface.

Ratio of Anodic to cathodic areas:

Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. When cathodic area is large, demand for electrons for reduction reaction is high. To meet this demand oxidation reaction occurs more intensely at anodic area.

For example, a broken coating of tin on iron surface, results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.

A broken coating of zinc on iron surface, results in less corrosion at the broken region. Iron is cathodic to zinc. Exposed region of iron acts as cathode with small area. Zinc acts as anode which has large area.

4.b

Metal finishing: Metal finishing is the process of surface modification of a metal by deposition of a layer of metal or by converting the surface layer metal into its oxide film.

Technological importance of metal finishing: Metal finishing is carried out to obtain technologically important surface properties. These properties are:

- A decorative appearance.
- An improved corrosion resistance.
- An improved heat resistance.
- Improved surface hardness. (An improved resistance to wear and tear, Abrasion.)
- Improved solder ability.

4.c.

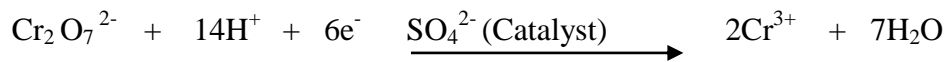
Electroplating is the process of electrolytic deposition of a metal on the surface of substrate; the substrate may be any metal, a polymer, a ceramic or a composite.

ELECTROPLATING OF CHROMIUM

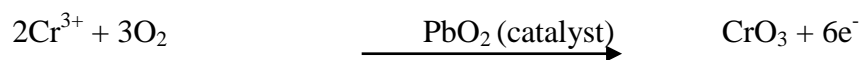
- The surface of the object is cleaned thoroughly. Oil and grease removed by organic solvent and then, treated with dilute H_2SO_4 to remove oxide layer.
- Finally, the surface is washed with distilled water. Then, chromium plating is done under the following conditions.

	Decorative Chromium Electroplating	Hard Chromium Electroplating
Plating bath composition	Chromic acid (H_2CrO_4) + H_2SO_4 in ratio 100 : 1	Chromic acid (H_2CrO_4) + H_2SO_4 in ratio 100 : 1
Operating temperature	45-60 °C	45-60 °C
Current density	100 – 200 mA cm^{-2}	200-400 mA cm^{-2}
Anode	Insoluble anode: Pb-Sn alloy coated with PbO_2 .	Insoluble anode: Pb-Sn alloy coated with PbO_2
Cathode	Object to be plated	Object to be plated
Anodic reaction	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
Cathodic reaction	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
Applications	1.Used in decorative coating in taps, handles, automobile bumpers, wheel rims 2. Used in corrosion resistant coating.	1. Cutting edges of milling machine 2. Hand guns, aircraft landing parts.
Thickness	0.25- 0.75micrometre	0.005-0.75 mm

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3⁺ state by a complex anodic reaction in the presence of sulphate ions. The Cr³⁺ then gets reduced to Cr on the substrate surface.



- For a good deposit, the Cr³⁺ concentration must be low. The PbO₂ oxidizes Cr³⁺ to Cr⁶⁺, thus reduce (control) the concentration of Cr³⁺.



In chromium plating we do not use chromium metal as anode due to the following reasons.

- If chromium dissolves at anode, there will be a high concentration of Cr³⁺ in solution. In such cases, a black, (bad, burnt) deposit is obtained.
- In acidic solutions, chromium may undergo passivation.

5.a.

Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

Methanol – Oxygen fuel cell

Construction:

Anode & Cathode – Made up of porous nickel sheets impregnated with Pt/Ru electrocatalysts

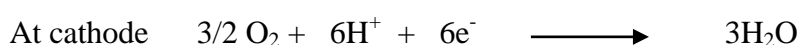
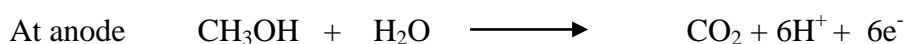
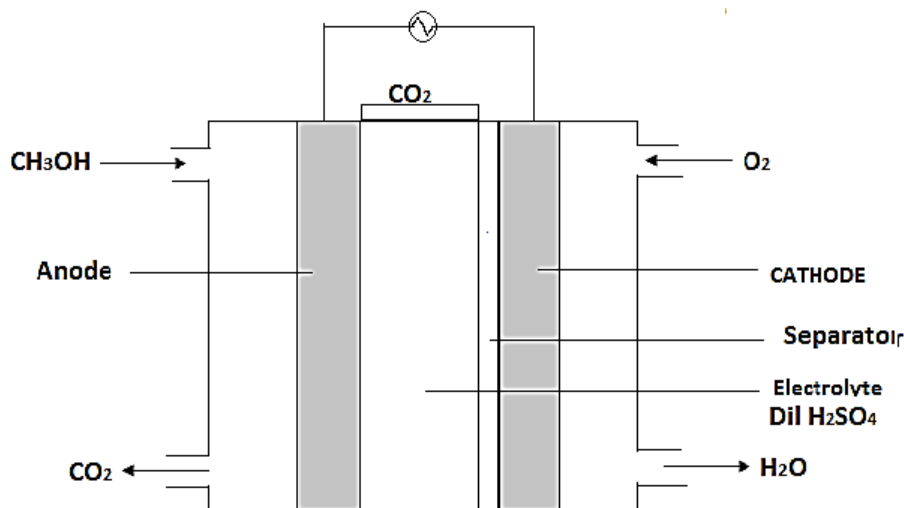
Fuel – Methanol

Oxidant – O₂

Electrolyte – Sulphuric acid(dilute)

Separator – Sulphonic acid polymer membrane.

Operating temperature – 25⁰C

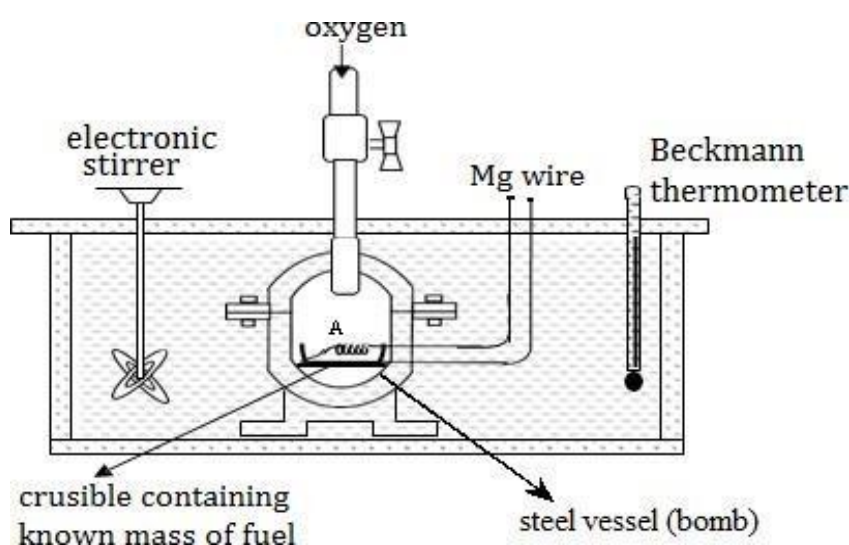


A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and thereby prevents the oxidation of methanol at cathode. Methanol – H_2SO_4 mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

5.b

Construction

❖ The bomb calorimeter (shown in the fig.) consists of a strong inner cylindrical steel vessel (bomb) with an airtight lid and an inlet for oxygen.



❖ The bomb has a crucible with a loop of wire. The ends of the wire project out and are connected to a source of electric current.

❖ The bomb is immersed in a rectangular copper vessel (calorimeter) of known weight and containing known volume of water, which is continuously stirred by mechanical stirrer.

❖ A Beckmann thermometer is introduced into the calorimeter to measure the

temperature.

Working

- A known mass of water is taken in the calorimeter and is closed with the lid.
- The initial temperature of water is noted, $t_1^{\circ}\text{C}$
- A known mass of the fuel is taken in the crucible, inside the bomb.
- Oxygen is passed through the bomb.
- The ends of the wire are connected to an electric source so as to ignite the fuel.
- On passing an electric current through the ignition coil, the fuel gets ignited.
- The fuel burns liberating heat. Heat liberated is taken up by the water and calorimeter. The water is continuously stirred using the stirrer.
- The maximum temperature attained by the water, $t_2^{\circ}\text{C}$, is noted.

Observation and calculations:

$$\text{Gross calorific value} = \frac{(w_1 + w_2) s \Delta t}{m} \quad \text{kJ kg}^{-1}$$

where

w_1 = mass of water in the calorimeter, in kg

w_2 = water equivalent of the calorimeter, in kg

s = specific heat of water, in $\text{kJ kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$

$\Delta t = t_2 - t_1$ = rise in temperature, in $^{\circ}\text{C}$

m = mass of the fuel, in kg

5.c.

$$\begin{aligned} \text{GCV} &= \frac{(w_1 + w_2) s \Delta t}{m} \\ &= \frac{(2.6 + 0.75) \times 3.2 \times 4.187}{0.95 \times 10^{-3}} \\ &= 47,246 \text{ KJ/kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - (0.09 \times \% \text{ of H}_2 \text{ in fuel} \times \text{Latent heat of steam}) \\ &= 47,246 - (0.09 \times 6 \times 2457) \\ &= 47,249 - 1326.78 \\ &= 45919.2 \text{ KJ/Kg} \end{aligned}$$

6.a.

PRODUCTION OF SOLAR GRADE SILICON: BY UNION CARBIDE PROCESS

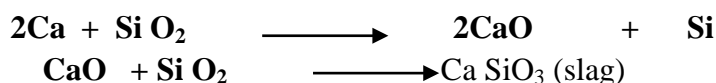
The Union Carbide process: This process involves the following steps:

Silica(Quartz) is treated with coal in an electric arc furnace

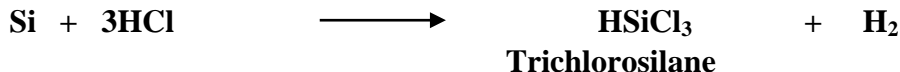


Carbon monoxide is further oxidized to carbon dioxide and released into the atmosphere.

In next step mother silicon is mixed with an oxygen and silica to remove the impurities such as Al, Ca and Mg. These impurities are removed in the form of slag (silicates) to get **Metallurgical grade silicon**

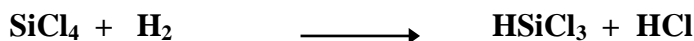


Metallurgical grade silicon is treated with dry HCl at 300⁰C to obtain trichlorosilane and tetrachlorosilane.



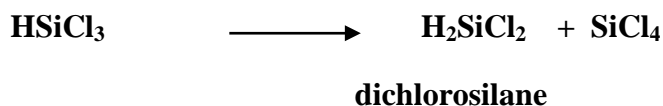
The trichlorosilane is separated by distillation.

Tetrachlorosilane is converted into trichlorosilane by **hydrogenating** in a reactor at 1000⁰ C.



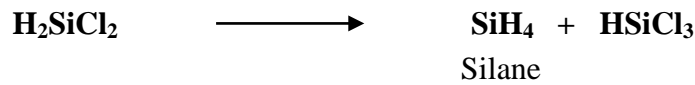
The purified trichlorosilane is passed through a ion exchange column filled with **quaternary ammonium ion exchange resin** acting as catalyst.

- **Trichlorosilane gets converted into dichlorosilane.**



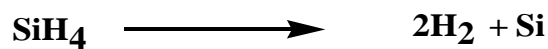
The products are separated by distillation, tetrachlorosilane is recycled to the hydrogen reactor and dichlorosilane is passed through a second ion exchange column filled with quaternary ammonium ion exchange resin.

- **Dichlorosilane is converted into silane.**



The above products are separated by distillation and trichlorosilane is recycled to the ion exchange column.

- **Silane** is further purified by distillation and then pyrolyzed (heated at high temperature) to produce solargrade silicon which is 99.99% pure.



The silicon obtained is further purified by zone refining

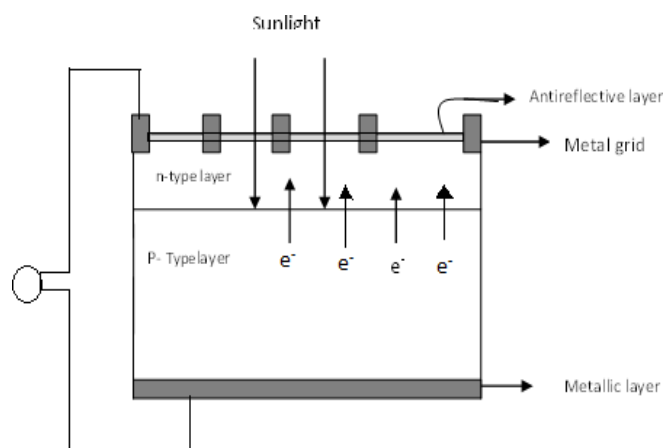
6.b.

Photovoltaic cells are semiconductor device which convert solar energy into electrical energy.

(Photovoltaic cell is based on the principle of photoelectric effect).

Construction of Photovoltaic Cell:

- A typical silicon PV cell is composed of a thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon.
- Hence a p-n junction is formed between the two.
- A **metallic grid** forms one of the electrical contacts of the PV cell, over n-type semiconductor and coated with an **antireflective layer** (TiO_2) between the grid lines increase the amount of light transmitted to the semiconductor (prevent reflection of solar radiation).
- The PV cell's other electrical contact is formed by a layer of noble metal (like silver) on the back of p-type semiconductor.



Working of PV cell :

- Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy
h = Planck constant
v = frequency
c = speed of light
 λ = wavelength

When electromagnetic radiation (sunlight) is incident to the plane of solar cell, the photons, which possess energy sufficient to overcome the barrier potential are absorbed and electrons are ejected (from p- type semiconductor and move towards n-type through p-n junction to recombine with holes).

- Since p-n junction allows only one way movement of electrons, these electrons must flow through the external circuit to **recombine with holes**. This movement of electrons through the external circuit generate an electric current.

6.c

Knocking in petrol engine:

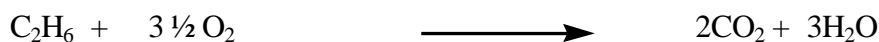
In petrol engines, the mixture of petrol and air is drawn into the cylinder. The fuel-air mixture is compressed by the piston and is ignited by an electric spark.

Definition of knocking:

The rattling sound produced by shock waves in a petrol engine due to explosive combustion of fuel-air mixture at higher compression ratio.

Mechanism of knocking in chemical terms:

A. Under ideal conditions, when petrol sample has hydro carbons (like aromatic, branched, cyclic) can withstand high pressure, undergoes smooth and complete combustion by the spark produced in an engine. So there is no knocking. (Ideal case or normal case)



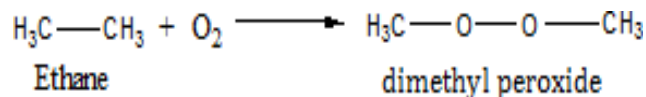
B. But, if hydrocarbon molecules(straight chain) present in the petrol cannot withstand the high pressure, undergoes incomplete combustion and forms unstable peroxides.

- These unstable peroxides decompose rapidly to give a number of gaseous compounds and increase the compression ratio beyond the limit.
- These products are **pre-ignited** (self-ignited i.e before spark produced)
- Due to this, petrol –air mixture suddenly burst into flames. This explosive combustion increases the pressure and leads to the production of **shock waves**.

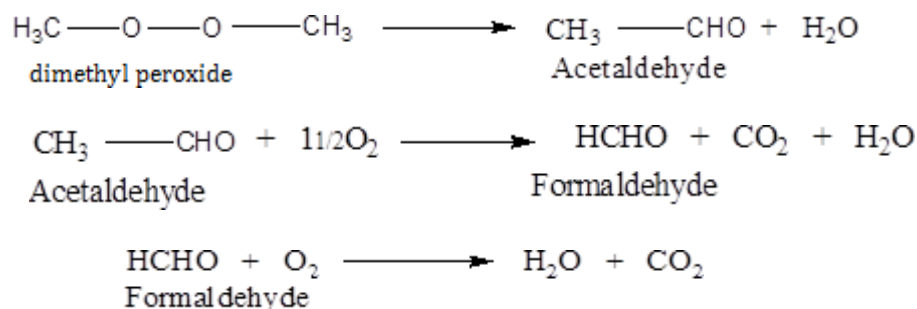
The shock waves dissipate its energy by hitting the walls of cylinder and piston. This causes rattling sound referred to as **Knocking**.

Under knocking conditions, the rate of combustion is very high. It involves following steps.

1. Oxygen combines with hydrocarbon molecule forming peroxides.



2. The peroxides decompose readily to give a number of gaseous products. For example,



Effects of knocking in petrol engine:

- Decreases the life of petrol engine
- Causes mechanical damage due to overheating.
- Consumption of petrol is more, results in less power output

7.a

SOFTENING OF WATER BY ION EXCHANGE PROCESS:

The process of removal of Ca, Mg, Fe salts and other metallic ions from water is called softening of water.

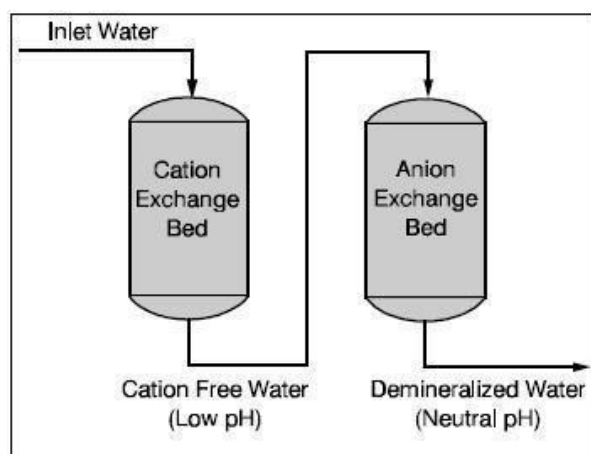
Softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin.

Ion exchange resins are high molecular weight, cross linked polymers with a porous structure.

The functional groups which are attached to the chains are responsible for ion exchange properties.

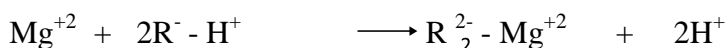
Cation exchange resins: The resins containing acidic groups which are capable of exchanging H^+ ions for cations (Ca^{+2} or Mg^{+2}) present in water.

Anion exchange resins: The resins containing basic groups which are capable of exchanging OH^- ions for anions (Cl^- , SO_4^{2-} , HCO^-) present in water.

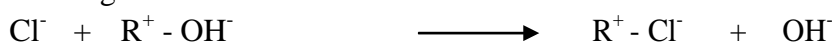


Process

◆ In this process, cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{+2} , Mg^{+2} are removed from hard water by exchanging H^+ ions as follows.



◆ Hard water is then passed through anion exchange resin where anions like Cl^- , SO_4^{2-} are exchanged with OH^- ions as follows.



The H^+ and OH^- ions released combine to form water molecule.

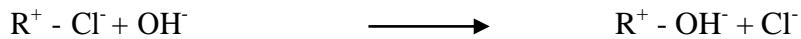
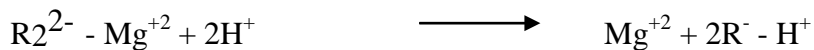
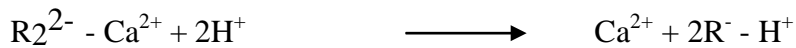
◆ Thus water coming out of two resin is free from metallic ions and called as ion exchanged water.

Regeneration:

When the resins lose their capacity to exchange ions, they should be regenerated. The process of regeneration is the reversal of the reaction taking place for ion exchange.

Cation exchange resin is regenerated by passing a solution of dil HCl or H₂SO₄ .

Anion exchange resin is regenerated by passing a solution of NH₄OH or NaOH respectively.



7.b.

LEAD:

Source:

4. Lead comes from metal smelting , lead- acid battery, steel industries ,
5. Burning of waste oil, paint industries.
6. Lead enters water through contact with plumbing , lead based pipes.

Ill effects:

6. **Air borne lead** can enter into human system and get accumulated into **blood**.
7. When the concentration of lead increases , it can enter brain and also get **deposited in bones**.(because the similarity in sizes of Ca²⁺ & Pb²⁺
8. When bone starts dissolving due to old age or illness , it can enter blood stream.
9. It inhibits the production of haemoglobin & causes **anaemia** ,it adverse effect to kidney function & **permanent brain damage**.
10. Lead has serious effects on the children **IQ**.

Control:

4. Replacement of conventional lead based products by lead free products.
5. The effect of lead on human can be controlled by following proper disposal method.
6. Eliminate lead contamination in drinking water by process such as reverse osmosis, distillation, filtration using carbon filters specially manufactured for lead removal.

7.c

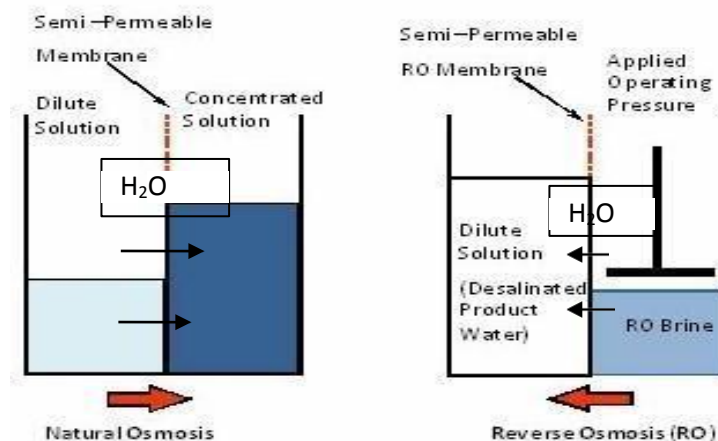
$$\begin{aligned} \text{COD} &= \frac{8 \times \text{NFAS} \times (X-Y) \times 1000}{V} \\ &= \frac{8 \times 0.05 \times (30.6-15.5) \times 1000}{25} \\ &= 241.6 \text{ mg of oxygen/liter} \end{aligned}$$

8.a.

DESALINATION OF WATER:

The process of removal of dissolved salts present in water is called desalination. This can be achieved by reverse osmosis method.

Reverse osmosis (R.O): If pure water (dilute solution) and salt water (concentrated solution) are separated by a semipermeable membrane, the water molecules flow from pure water to salt water. This process is called as OSMOSIS. The pressure exerted on membrane due to osmosis is called as osmotic pressure. The water molecules can be made to flow in reverse direction by applying pressure on salt water which is greater than the osmotic pressure. This process is called as reverse osmosis.



“The movement of water molecule through semipermeable membrane from higher concentration to lower concentration by applying pressure on higher concentration” is called reverse osmosis.

In R.O tube, saltwater and fresh water is separated by semipermeable membrane made up of cellulose acetate, nylon, polymethylacrylate and polyamide. When the saltwater supplied with high pressure, water flow from saltwater to fresh water. Fresh water is collected from fresh water outlet and salt water is discharged in to the environment.

8.b.

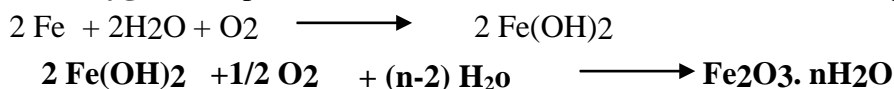
BOILER CORROSION:

The process of degradation of the boiler surface by the attack of boiler feed water is called as boiler corrosion. Corrosion may occur due to presence of dissolved oxygen, carbon dioxide and low pH in the feed water.

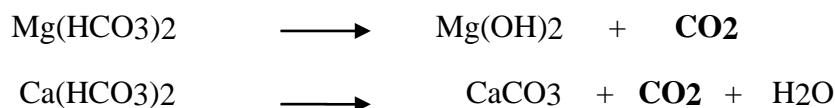
Causes:

- Presence of dissolved O₂
- Presence of dissolved CO₂
- Acid formation due to Hydrolysis
- Presence of free acids

Dissolved oxygen: DO present in feed water can attack boiler surface and produce rust as follows



Dissolved carbon dioxide: CO₂ present in the boiler water either from air or due to the presence of residual temporary hardness.



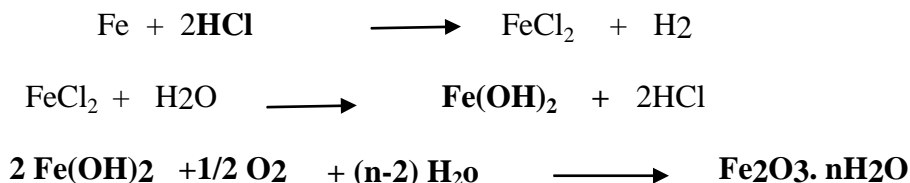
This carbon dioxide dissolves in water to produce carbonic Acid, which is slightly acidic in nature and hence corrosion occurs.



Acid may be formed due to the presence of magnesium compounds in feed water which results in **drop of pH** below 8.5



The resultant Acid attacks the boiler to form rust.



8.c

CHEMICAL OXYGEN DEMAND:

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds(impurities) present in 1 liter of waste water using strong oxidizing agent K₂Cr₂O₇

Procedure:

- A known volume waste water (V cm³), 1g mercuric sulphate and 1g silver sulphate are added to 250 cm³ conical flask, followed by the addition of a known amount potassium dichromate and sulphuric acid.
- The above mixture is refluxed for two hours and cools the mixture.
- Titrated the mixture against standard FAS solution, till the colour changes from green to brown using Ferrion as an indicator.

Blank: The same procedure is repeated for 25 cm³ of distilled water

Observation and calculation:

Normality of FAS solution = N_{FAS}

Volume of FAS solution consumed for back titration = y cm³ Volume of FAS consumed for blank titration = x cm³

1 cm³ of 1N FAS solution = 8 mg of oxygen

(x-y) cm³ N_{FAS} solution = 8 . N_{FAS} . (x-y) mg of oxygen

i.e., V cm³ of waste water sample = 8 . N_{FAS} . (x-y) mg of oxygen

1000 ml of the waste water sample = $\frac{8 \cdot N_{FAS} \cdot (x-y) \times 1000}{\text{Volume of water sample take}}$ mg of oxygen

COD of the waste water sample	$\frac{8 \cdot N_{FAS} \cdot (x-y) \times 1000}{\text{Volume of water sample}}$	mg of
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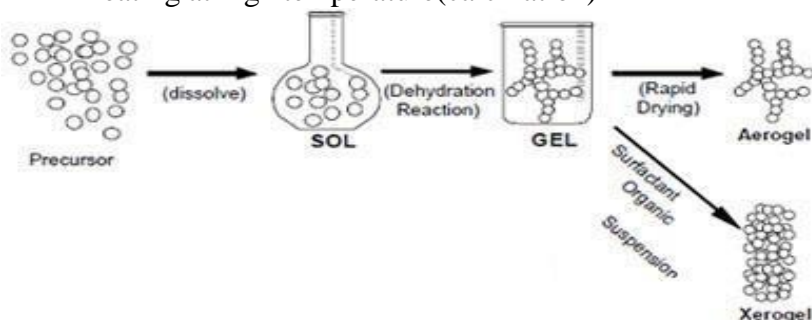
(Volume of water sample taken can be 20, 25, 30 ml....)

9.a.

SOL-GEL PROCESS

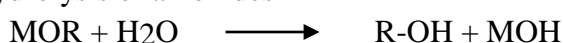
- In sol-gel process, either **metal salt or alkoxide** is used as precursor (starting material).
- It is mainly used in the synthesis of uniform nanoparticles of **metal oxides**. Steps involved in synthesis

- **Preparation of Sol**
- **Conversion of Sol to Gel.**
- **Aging of Gel.**
- **Drying of the Gel (evaporation)**
- **Heating at high temperature (calcination)**



- **Step 1 : Sol** is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)
- **Step 2:** Sol is further converted into a gel by hydrolysis and condensation of precursors. (adding acid or base as catalyst)

Hydrolysis of alkoxides



Condensation of hydrolysed species with each other (releases water)



- **Step 3:** Aging (keeping for a known period of time) of colloid solutions takes place, i.e. colloids can increase their particle size and grows into a sol-gel.
- **Step 4:** Then the gel is dried by evaporation (solvent get evaporated)
- **Step 5:** Calcinated (heating to high temperature) to produce nanoparticles.

9.b.

CONDUCTOMETRIC TITRATION

Determination of quantity of material present in the solution by measuring its electrical conductivity.

THEORY:

Conductivity is a measure of ability of a solution to carry an electric current. Electrolyte solution conducts current by the migration of ions under the influence of an electric field. This obeys Ohm's law,

$$E = IR \quad \text{where, } E = \text{Applied potential} \quad I = \text{Current}$$

R = Resistance

Conductance is a reciprocal of resistance, i.e. $C = \frac{1}{R}$

Resistance depends on length and cross sectional area of the conductor (resistance is directly proportional to the length of conductor and inversely proportional to the cross sectional area of the conductor)

$$\text{i.e. } R = s \cdot \frac{l}{a} \quad \text{where, } s = \text{specific resistance}$$

l = length of conductor

a = cross sectional area of the conductor

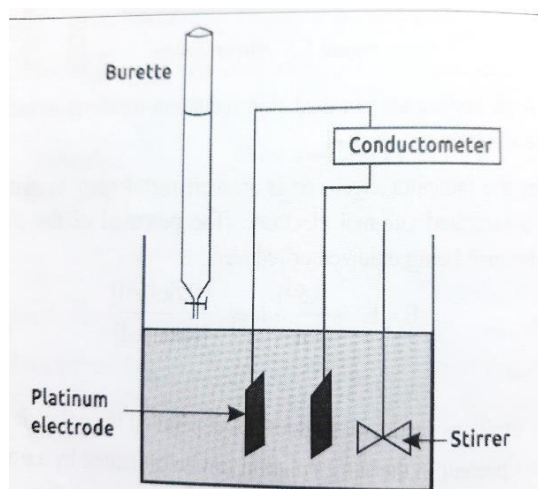
The unit of specific conductance is $\text{ohm}^{-1}\text{cm}^{-1}$. In this neutralization point is given by sudden change in conductance.

INSTRUMENTATION:

- Conductivity cell: Two Pt electrodes of area 1cm^2 and at 1cm apart
- Conductivity meter: To display the reading during titration.
- Magnetic stirrer: To maintain uniform concentration.

Analyte solution is taken in the beaker, and a magnetic stirrer is placed. Conductivity cell is dipped in the solution which is connected to the conductometer. Initial reading is noted. The titrating reagent (known ml) is added and conductance is measured after stirring. The addition of titrating agent is continued until at least 5 readings beyond the equivalence point.

A graph of conductance vs volume of titrant is plotted. And the equivalence point is noted.



Applications :

- Used in estimation of acid or base present in the sample solution.
- Displacement titration (salt of weak acid titrated against strong acid)
- Precipitation titration (silver nitrate against sodium chloride)
- Complexation titrations (EDTA vs metal ion)

9.c

COLORIMETRY

Colorimetry is used to determine the concentration of compounds in a solution. This method is used for solution which are themselves coloured or which gives colour with a suitable reagent. The intensity of colour is directly proportional to concentration of the solution.

Theory : This method is based on **Beer-Lamberts law**.

According to **Beer-Lamberts law**, when a monochromatic light is passed through a solution, part of light is absorbed by solution. The extent of absorption depends on the concentration of the solution and path length of the light through the solution.

$$A = \epsilon \cdot c \cdot t$$

Where, A = Absorbance

ϵ = molar extinction coefficient, c = concentration of the solution;

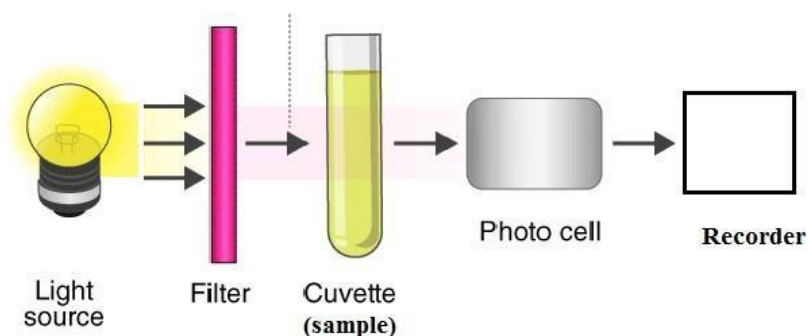
t = path length & is constant for a given substance at a given wavelength.

If t, is kept constant, then, A directly proportional C. Hence a plot of absorbance against concentration gives a straight line.

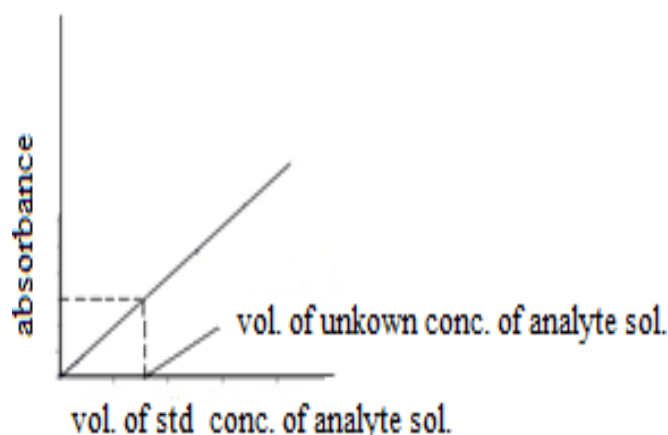
INSTRUMENTATION: Calorimeter are made of following components

- Light source.
- A filter which provides desired wavelength range.
- A sample cell.
- A photocell detector.
- Recorder.

• First, a blank solution is taken in the sample cell and monochromatic light of suitable wavelength is allowed to fall. Its absorbance is adjusted to zero.



- Then the different analyte solutions of known concentration are placed in sample cell one by one and its absorbance is noted.
- The absorbance for **analyte solution of unknown concentration** is noted.
- A plot of absorbance versus standard concentrations of analyte is used to find unknown concentration of analyte in the sample.



Application:

- Determination of the composition of colored complex
- Used in soil testing for analysis of soil and plant nutrients.
- Used in food testing laboratories to check concentration of chemical parameters.
- Used in clinical laboratories for analysis of biomolecules such as glucose, urea.

10.a)

SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

1. Surface area

- Some properties like **catalytic activity**, **gas adsorption** and **chemical reactivity** depend on the surface area of the material.
- When bulk material is subdivided into nanomaterial, the total volume of the material remains same, but the collective surface area is greatly increased. Due to increased surface

area, the material becomes catalytically active or chemically reactive or gets good gasadsorption property.

Ex: **Bulk Gold** - Catalytically **inactive**, **Nano Gold** – Catalytically **active**

2. Electrical properties

- In bulk material electronic bands are continuous, due to overlapping of orbitals of billions of atoms, the material acts as conductor.
- But, in nanosize materials, very few atoms or molecules will be present, so electronic bands become separate.
- Hence, some metals which are good conductors in bulk become semiconductors and insulators as their size is decreased to nano level.

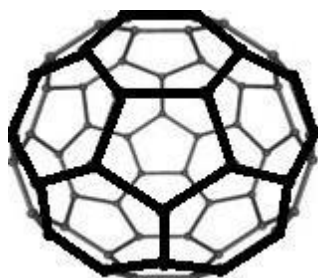
3. Optical properties

- The separate electronic states of nanomaterials allow absorption and emission of light of specific wavelength. Hence they exhibit unique colors different from bulk materials.
- Nanoparticles of metals exhibit unique optical property called as **surface plasmon resonance**.
- When light hits the surface of metal particle, surface electrons starts oscillating back and forth in synchronized way in a small space this is called as **Surface Plasmon Resonance**.
- Resonating electrons have cross sectional area very much higher than the nanoparticle.
- Depending on the frequency of oscillation, resonating electrons can capture radiation of different wavelength.
- Ex : **Bulk Gold** - Yellow colour
 Nano Gold - Red colour

10.b)

FULLERENES:

- Fullerenes are class of molecules made of only carbon atoms having closed cage like structure.
- Many number of fullerene molecules with different carbon atoms like C₆₀, C₇₀, C₇₄, C₇₈ etc., have been prepared.
- **C₆₀** is the smallest, stable and abundant fullerene, obtained by usual preparation methods.



- C₆₀ has **spherical** shape and resembles a football and commonly known as buckyball.
- Fullerenes are made up of pentagons and hexagons. Pentagons gives curvature required to form closed structure.
- All fullerenes contain **12 pentagons** and different numbers of hexagons.
- Each fullerene has **2(10+M)** number of carbon atoms corresponding to 12 pentagons and **M** number of hexagons.

Properties and Application.

1. Single C₆₀ molecule theoretically can take up maximum of 60 hydrogen atoms.

Application- *Hydrogen storage material for fuel cells*

Electrode material in secondary batteries. Ex- Nickel Metal Hydride battery.

2. Each C₆₀ molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

Application- *Used as optical limiters. Optical limiters are used to protect materials from damage, by intense incident light radiation.*

3. A polymer composite of C₆₀ molecule and polyvinylcarbazole exhibits very high photoconductivity.

Application- *Used in Photocopying applications.*

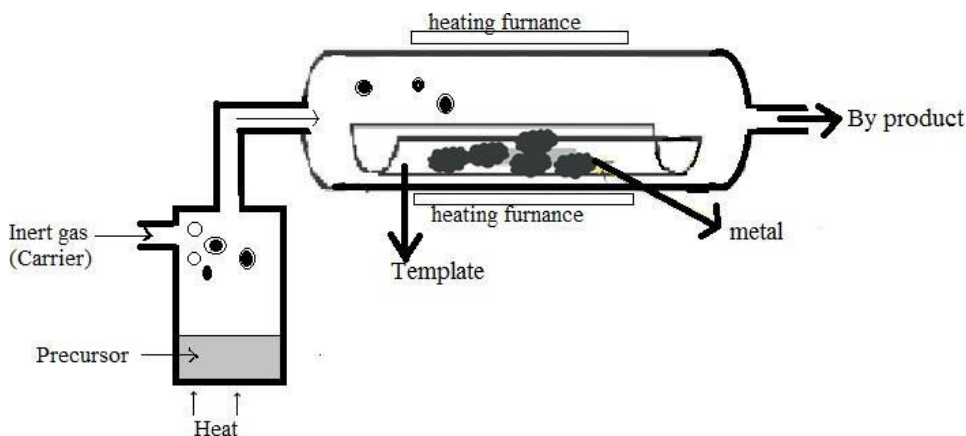
4. C₆₀ molecule readily accepts electron and forms C₆₀ meta stable anion and becomes catalytically active.

Application : *Catalyst in organic reactions such as hydrogenation-dehydrogenation reactions.*

10.c)

CHEMICAL VAPOUR DEPOSITION:

- In CVD process, nanoparticles are synthesized from the gaseous phase by a chemical reaction or decomposition of precursors at high temperature.
- In this method precursor is vaporized and mixed with inert carrier gas like N₂ and mixture fed in to a reactor.
- Reactor is maintained at high temperature required for the reaction
- Precursors undergo reaction, producing a product which is deposited over the substrate.
- The by-products and leftovers from reactions are easily removed from the reaction chamber.
- Reaction is catalyzed by the catalyst present on the substrate.
- Precursors should be highly pure, stable at room temperature with sufficient volatility.
- Commonly used precursors are halides, carbonyls, hydrides of metal.
- In this method it is possible to produce almost any metal and nonmetallic material as well compounds such as oxides, nitrides etc



First/Second Semester B.E. Degree Examination, Dec.2019/Jan.2020
Engineering Chemistry

Time: 3 hrs.

Max. Marks: 100

Note: Answer any FIVE full questions, choosing ONE full question from each module.

Module-1

- 1 a. Define Free Energy. Derive Nernst equation for single electrode potential. (07 Marks)
- b. What are Reference Electrodes? Describe the construction and working of Calomel electrode. (06 Marks)
- c. Explain the construction and working of Ni – Metal Hydride battery. Give the reaction during charging and discharging mode. Give any two applications. (07 Marks)

OR

- 2 a. Describe the construction and working of Lithium – ion battery. Give its applications. (07 Marks)
- b. Write a note on Primary, Secondary and Reserve batteries. (06 Marks)
- c. What are Concentration Cells? EMF of the cell $\text{Ag}/\text{AgNO}_3(\text{C}_1) // \text{AgNO}_3(\text{C}_2 = 0.2\text{m}) / \text{Ag}$ is 0.8V. Calculate C_1 of the cell. (07 Marks)

Module-2

- 3 a. What is Corrosion? Explain the Electrochemical theory of corrosion by taking iron as an example. (07 Marks)
- b. Explain i) Differential Metal Corrosion ii) Pitting Corrosion. (07 Marks)
- c. What do you mean by metal finishing? Mention any five technological importances. (06 Marks)

OR

- 4 a. Define and explain any two terms :
 i) Polarisation ii) Decomposition potential iii) Over voltage. (06 Marks)
- b. What is Electroless Plating? Explain the Electroless plating of copper. (07 Marks)
- c. Explain the process of Galvanization. (07 Marks)

Module-3

- 5 a. What is Knocking? Explain the mechanism. (07 Marks)
- b. On burning 0.96 grams of solid fuel in bomb calorimeter the temperature of 3500 grams of water increased by 2.7°C water equivalent of calorimeter and latent heat of steam are 385 grams and 587 cal/gram respectively. If the fuel contains 5% H_2 , calculate its gross and net calorific value. Specific heat of water = 4.187 kJ/kg K. (06 Marks)
- c. What are Fuel Cells? Describe the construction and working of $\text{CH}_3\text{OH} - \text{O}_2$ fuel cell. (07 Marks)

OR

- 6 a. What are Solar Cells? Explain the construction and working of a typical P.V. Cell. (07 Marks)
- b. Explain the production of solar grade Si by Union Carbide Process. (07 Marks)
- c. Write a note on : i) Power alcohol ii) Unleaded petrol. (06 Marks)

Module-4

- 7 a. What are the main sources, effects and control of lead pollution? (07 Marks)
b. Mention the various causes, effects and disposal methods of e – waste. (07 Marks)
c. 50 ml of an industrial sewage has consumed 11.5 ml of 0.4N $K_2Cr_2O_7$ solution for complete oxidation. Calculate C.O.D of industrial sewage. (06 Marks)

OR

- 8 a. Explain the activated sludge treatment of sewage water. (07 Marks)
b. What is Desalination? Describe the desalination of seawater by reverse Osmosis process. (07 Marks)
c. Write a note on Ozone depletion. (06 Marks)

Module-5

- 9 a. Explain the theory, Instrumentation and Application of Calorimetry. (06 Marks)
b. What is Potentiometric titration? Explain the principle involved in Potentiometric titration. (07 Marks)
c. Write a note on Fullerene. Mention its application. (07 Marks)

OR

- 10 a. What are Nano – materials? Give their synthesis by Sol – gel techniques. (07 Marks)
b. Write a note on Graphenes. Mention their applications. (07 Marks)
c. Explain the theory and applications of Atomic Absorption Spectroscopy. (06 Marks)

Answers of VTU question paper Dec 2019/Jan 2020

1a. Free energy

Gibbs free energy is the part of total energy of a system which is available to do useful work.

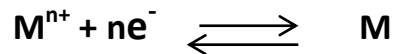
$G = H - T S$. Where, H = Enthalpy, T = Temperature, S = Entropy.

Single electrode potential: It is the potential developed at the junction of a metal and solution when a metal is in contact with its own ions due to loss or gain of electrons.

1.b)

Nernst equation for single electrode potential:

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature. Consider a reversible electrode reaction,



Equilibrium constant for the above reaction is,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[M]}{[M^{n+}]} \dots\dots\dots (1)$$

According to thermodynamics, for a reversible process, equilibrium constant (K) is related to decrease in change in free energy ($-\Delta G$) as, by Vant Hoff equation.

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots (2)$$

Where, ΔG^0 = Standard change in free energy
 R = Universal gas constant
 T = Temperature

Substituting 1 in 2
 we have,

$$\Delta G = \Delta G^0 + RT \ln \frac{[M]}{[M^{n+}]} \dots\dots (3)$$

The decrease free energy ($-\Delta G$) for any reversible process is equal to the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\max} \dots\dots\dots (4)$$

In case of a Galvanic cell, W_{\max} = Electrical energy supplied by the cell

$$= [(\text{difference in potential between two electrodes}) \times (\text{total charge flowing through the cell})]$$

If 'n' moles of electrons are flowing from anode to cathode, then the total quantity of charges flowing through the cell is 'n' Faradays (nF).

$$\therefore W_{\max} = E_{\text{cell}} \times nF = nFE \dots\dots\dots (5)$$

By comparing equation 4 and 5,

$$-\Delta G = nFE \dots\dots\dots (6) \text{ or } \Delta G = -nFE$$

Under standard conditions,

$$-\Delta G^\circ = nFE^\circ \dots\dots\dots (7) \text{ or } \Delta G^\circ = -nFE^\circ$$

Substituting the values equation (6) and (7) in equation (3)

$$nFE = -nFE^\circ + RT \ln K_c \dots\dots\dots (8)$$

Dividing throughout by -nF,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \dots\dots (9)$$

$$E = E^\circ - 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \left\{ \frac{2.303RT}{nF} [M] - \frac{2.303RT}{nF} \log [M^{n+}] \right\} \dots\dots (10)$$

In case of metal-metal ion electrode, as 'M' is solid metal, $[M] = 1$

$$\therefore E = E^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}]$$

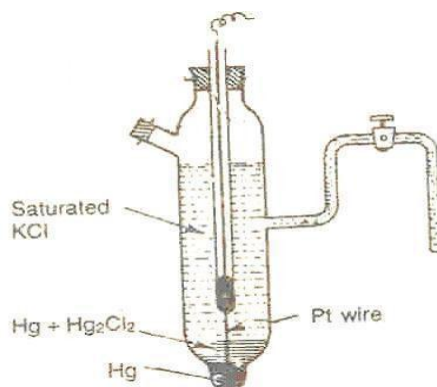
(R is a gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; T= temperature in absolute scale (298K); F is Faraday = $96,500 \text{ C mol}^{-1}$)

$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$	at 298 K
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1b. Reference electrodes are the electrodes whose potential is known and with reference to those, the electrode potential of any other electrode can be measured.

Construction and working of calomel electrode

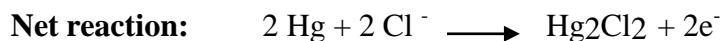
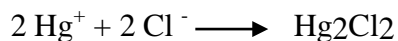
1. Calomel electrode is a **Metal-metal salt electrode**
2. A Metal-metal salt electrode consists of Mercury, Mercurous Chloride and a solution of KCl.
3. Mercury is placed at the bottom of a glass tube.
4. A paste of Mercury and Mercurous Chloride (calomel) is placed above the Mercury. The space above the paste is filled with a KCl solution of known concentration.
5. A platinum wire is kept immersed into the mercury to obtain external electrical contact.
6. It is internally connected through salt bridge.



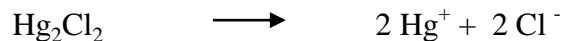
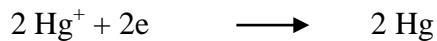
Calomel electrode can be represented as ,



The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.



When it is Cathode:-



1c.

Nickel-metal hydride battery:

Construction:

In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed.

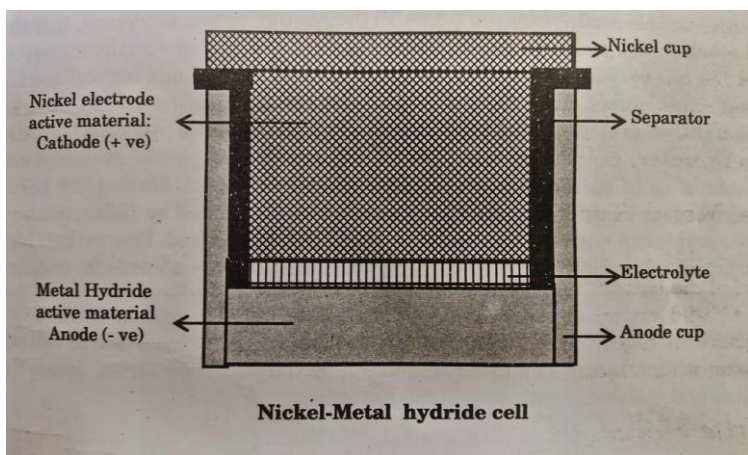
Anode – Porous nickel grid pasted with **metal hydride** (such as TiH_2 , VH_2 ,) and a hydrogen storage alloy (such as LaNi_5).

Cathode - Porous nickel grid pasted with **$\text{Ni}(\text{OH})_2$, $\text{NiO}(\text{OH})$** .

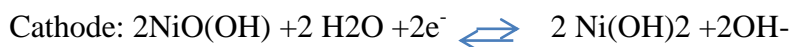
Electrolyte- KOH .

Separator- Polypropylene.

Representation: $\text{MH}_2 \mid \text{KOH} \mid \text{Ni}(\text{OH})_2, \text{NiO}(\text{OH})$

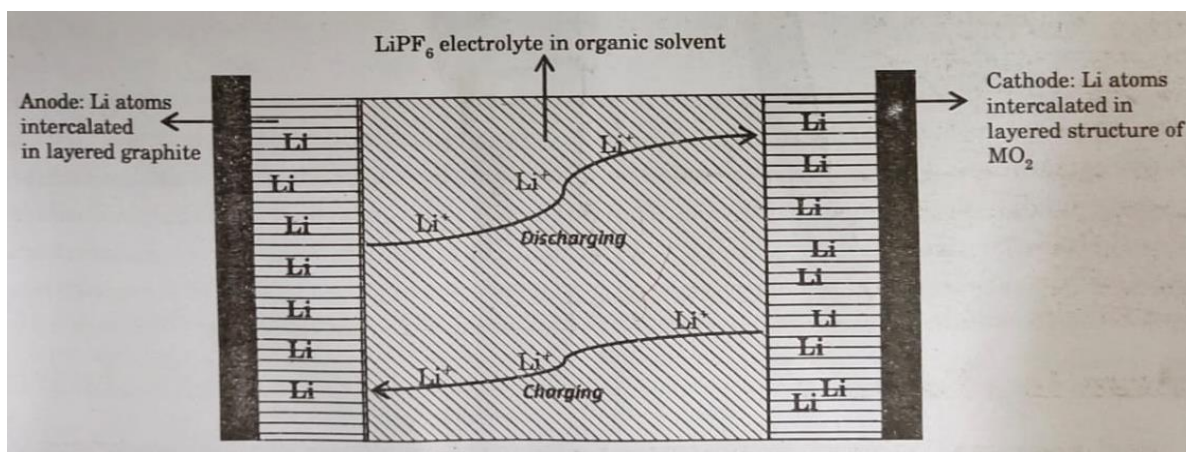


Working:



Applications: Used in cellular phones, camcorders and laptop computers.

2a. Lithium-ion battery



Construction:

Anode-Lithium intercalated graphite.

Cathode – Lithium metal oxide such as (LiCoO₂).

Electrolyte -A solution of lithium salt (LiPF₆) in organic solvent.

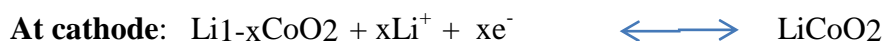
Separator- non-woven **polypropylene**.

Representation: *Li, C / LiPF₆, in organic solvent / LiCoO₂*

- It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers.
 - Lithium ions move between anode and cathode during discharging and charging process.
- Since

Both anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.

Working



Applications: Portable electronics, mobile phones, laptop, ipod etc.

a. **Primary Batteries:** A battery which cannot be recharged (because the cell reactions are irreversible)

i. e.g. Zn-MnO₂, Zn –Air , dry cell.

b. **Secondary Battery:** A battery which can be recharged (as the cell reactions are reversible) and also known as storage battery. e.g. Lead-acid battery, Li-ion battery

- c. **Reserve battery:** In this battery, one of the components is stored separately and used whenever required. e.g. Mg-AgCl battery where battery is activated by the addition of water. It is used in missiles and military weapon system.

$$2c. \quad E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$0.8 = \frac{0.059}{2} \log \frac{0.2}{x}$$

$$0.8 = 0.0295 \log \frac{0.2}{x}$$

$$0.8 = \log 0.2 - \log x$$

$$\log x = \log 0.2 - 0.8$$

$$= -0.6989 - 0.8$$

$$\log x = -1.499$$

$$x = \text{antilog of } (-1.499)$$

$$= 0.03M$$

3 a. Corrosion is the process of gradual degeneration of a metal/alloy from its surface due to chemical or electrochemical reaction with the surroundings.

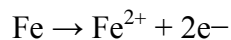
Electrochemical theory of corrosion:

According to this theory, corrosion is an electrochemical process and the reactions are similar to that in galvanic cells. At anode oxidation takes place liberating electrons which move to cathode where reduction occurs. A conducting medium is required over the surface of the metal for the movement of ions and for the completion of circuit between anode and cathode.

Eg. Rusting of iron

When a metal such as iron is exposed to corrosive environment, a large number of tiny galvanic cells with anodic and cathodic regions are formed.

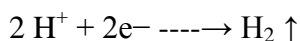
Reaction at anodic region: Since oxidation takes place at anode, iron is oxidised to ferrous (Fe^{2+}) ions with loss of electrons.



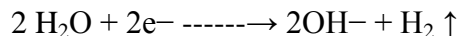
Reaction at cathodic region: Depending on the nature of environment possible reduction reactions that can take place at the cathode are:

1) Liberation of hydrogen: It takes place in the absence of oxygen.

i. In acidic medium, the reaction is,

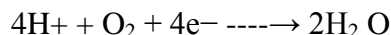


ii. In neutral or alkaline medium, the reaction is

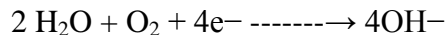


2) Absorption of oxygen: It takes place in the presence of oxygen.

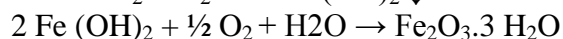
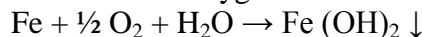
i. In acidic medium, the reaction is,



ii. In neutral or alkaline medium, the reaction is



Thus, Fe^{2+} ions formed at the anodic region move towards cathodic region whereas hydroxyl ions formed at cathode move towards anode. Fe^{2+} ions react with OH^- ions forming ferrous hydroxide which on further reaction with oxygen and water forms corrosion product (hydrated ferric oxide) or rust.



Rust

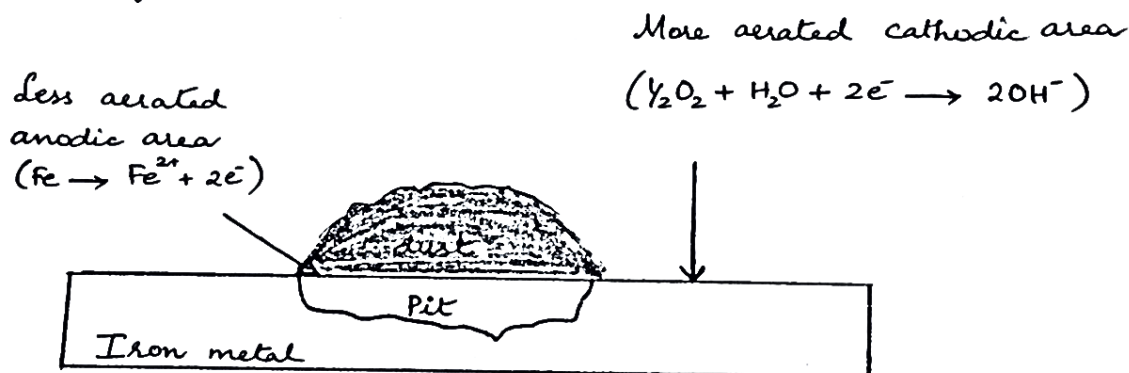
Since the layer of rust formed is highly porous, oxygen and moisture from the environment pierce deeper and increase the rate of corrosion.

3 b.

(i) Differential metal corrosion or Galvanic corrosion

This type of corrosion occurs when two dissimilar metals are in contact with each other and are exposed to a corrosive environment. The metal with lower electrode potential acts as anode and undergoes corrosion, whereas the metal with higher electrode potential acts as cathode and remains unaffected. Larger the potential difference between the two metals higher is the rate of corrosion.

(ii) **Pitting corrosion:** it is observed when dust particles get deposited on a metal surface. The portion covered by dust will be anodic (less oxygenated) and undergo corrosion, whereas the portion not covered by dust will be cathodic (more oxygenated) and remain unaffected. Formation of a small anodic area (dust covered part) and large cathodic area (exposed area), intensifies the rate of corrosion.



3c.

Metal finishing is defined as the modification of the surface properties of a metal by depositing a layer of another metal or a polymer or an oxide film. The technological importance of metal finishing are:

- To improve corrosion resistance

- To provide decorative appearance
- To improve chemical resistance
- To improve surface hardness
- To provide good thermal and electrical conductivity

4 a. **Polarisation** is defined as the change in electrode potential due to inadequate diffusion of metal ions from the bulk of electrolytic solution to the electrode. Polarisation occurs at anode also. Potential required to overcome polarisation of anode and cathode is called polarisation potential. If the rate of diffusion metal ions from the bulk of the solution towards the electrode is slow, there will be a decrease in electrode potential of the electrode according to Nernst equation,

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

Decomposition potential: The minimum external voltage that must be applied in order to carry out continuous electrolysis in an electrolytic cell is called decomposition potential (E_d). By extrapolating the curve in the plot of applied voltage against current flowing through the cell decomposition voltage is obtained.

$$E_d = E_{\text{back}} + \eta$$

Where, η is the over potential and E_{back} is the back EMF, which is the difference in potential of cathode and anode during electrolysis. Since this EMF opposes the applied potential, it is called back EMF.

For any system, knowing the salt being electrolysed, back EMF can be theoretically calculated. Hence, it is also called as theoretical decomposition potential.

Overvoltage: over potential can be defined as the excess potential that has to be applied above the theoretical decomposition potential to bring about continuous electrolysis. The difference between E_d and theoretical decomposition potential (E_{back}) is called over potential (η).

4b.

Electroless plating is the deposition of a thin layer of metal on a catalytically active surface from its salt solution in presence of a suitable reducing agent without using electric current. When the catalytically active surface is dipped in the bath, the reducing agent reduces metal ions to metal atoms, which gets deposited on the surface and the reducing agent itself gets oxidised.



Electroless plating of Copper

The article to be plated is degreased and etched by dipping in dil. H_2SO_4 . Electroless copper is deposited directly on iron, cobalt, nickel and other metals without any treatment in presence of reducing agents. However, insulators like plastics, glass etc. are catalytically activated by dipping in $SnCl_2$ containing HCl at $25^\circ C$ followed by $PdCl_2$. $SnCl_2$ reduces palladium ions on the surface of the object to palladium which catalyse the deposition reaction.

Composition of Plating bath solution:

Metal ion solution – Copper sulphate

Reducing agent – Formaldehyde

Buffer – Rochelle salt & sodium hydroxide

Complexing agent – EDTA

Temperature – 25°C

pH – 11

Reactions are:

At anode: $2 \text{HCHO} + 4\text{OH}^- \rightarrow 2\text{HCOO}^- + 2 \text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$

At cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

Overall reaction: $\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + 2\text{HCOO}^- + 2 \text{H}_2\text{O} + \text{H}_2$

Here formaldehyde is oxidised to formic acid in presence of strong alkali releasing two electrons which reduces Cu^{2+} to Cu. Copper deposition is thermodynamically more favourable in alkaline solutions. However, copper precipitates at elevated pH values. To overcome this difficulty, complexing agent EDTA is added to plating bath to maintain metal ion concentration in the solution. Formaldehyde and copper sulphate are added to the plating bath periodically as Cu^{2+} ions and HCHO are consumed in the reaction process.

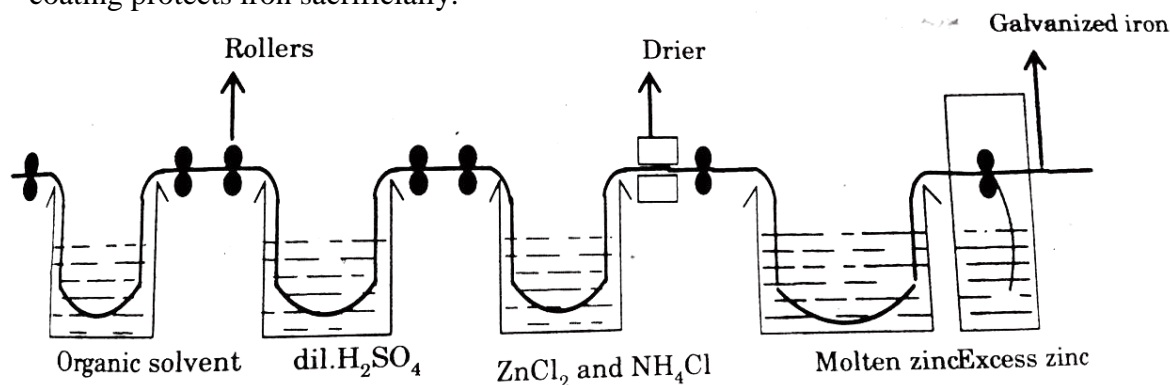
Applications: An important application is in the manufacture of double sided printed circuit boards (PCB's) where plating through holes is required.

4c. Galvanisation: the process by which iron/steel sheets are coated with zinc to protect them from corrosion is called galvanisation. The sheets thus obtained are called GI sheets.

Process:

- 1) The iron article is degreased by passing through organic solvents.
- 2) Then it is washed with dil. H_2SO_4 to remove rust and other impurities. This is called pickling.
- 3) Then it is treated with a mixture of aqueous solution of ZnCl_2 and NH_4Cl which acts as flux and then dried.
- 4) The article is finally dipped in a bath of molten zinc (430-470°C).
- 5) The article coated with zinc is taken out of the bath and passed through a pair of hot roller to remove excess Zn.

Zn being anodic to iron dissolves anodically, whereas iron (being cathodic) is protected from corrosion. Zn coating protects iron sacrificially.



Galvanizing

Applications:

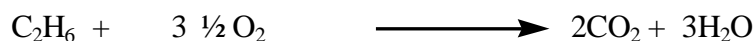
- It is widely used for the protection of iron from atmospheric corrosion in roofing sheets, wires, pipes, nails, bolts, screws etc.
- Galvanised ware is not useful for cooking or storing food as they form highly toxic compounds in presence of dilute acids.

5 a.

The rattling sound produced by shock waves in a petrol engine due to explosive combustion of fuel-air mixture at higher compression ratio.

Mechanism of knocking in chemical terms:

Under ideal conditions, when petrol sample has hydro carbons (like aromatic, branched, cyclic) can withstand high pressure, undergoes smooth and complete combustion by the spark produced in an engine. So there is no knocking. (Ideal case or normal case)

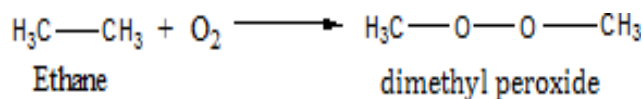


But, if hydrocarbon molecules (straight chain) present in the petrol cannot withstand the high pressure, undergoes incomplete combustion and forms unstable peroxides.

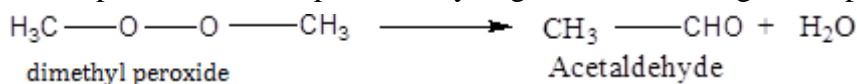
- These unstable peroxides decompose rapidly to give a number of gaseous compounds and increase the compression ratio beyond the limit.
- These products are **pre-ignited** (self-ignited i.e before spark produced) Due to this, petrol –air mixture suddenly burst into flames. This explosive combustion increases the pressure and leads to the production of **shock waves**.
- The shock waves dissipate its energy by hitting the walls of cylinder and piston. This causes a rattling sound referred to as **Knocking**.

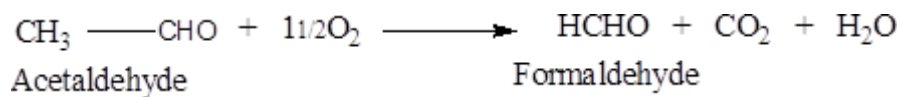
Under knocking conditions, the rate of combustion is very high. It involves following steps.

3. Oxygen combines with hydrocarbon molecule forming peroxides.



4. The peroxides decompose readily to give a number of gaseous products. For example,





Effects of knocking in petrol engine:

- Decreases the life of petrol engine
- Causes mechanical damage due to overheating.
- Consumption of petrol is more, results in less power output

5b. Mass of fuel = 0.96g Water equivalent of calorimeter = 385
 Mass of water = 3500g, Specific heat of water = 4.187 KJ/kg/K Rise in temperature = 2.7 °C, % of hydrogen in the fuel sample = 5%, Latent heat = 587 Cal/g

$$\text{GCV} = \frac{(w_1 + w_2) s t}{m}$$

$$= \frac{(3500 + 385) \times 2.7 \times 4.187}{0.96}$$

$$= 45749.5 \text{ KJ/Kg}$$

If latent heat has been given in 587 cal/g then latent

heat of steam = 587 x Specific heat of water

$$= 587 \times 4.187$$

$$= 2457 \text{ KJ/Kg}$$

$$\text{NCV} = \text{GCV} - (0.09 \% \text{ of H}_2 \text{ in fuel} \times \text{Latent heat of steam})$$

$$= 45749.5 - (0.09 \times 2.5 \times 2457)$$

$$= 45749.5 - 552.8$$

$$= 45196.6 \text{ KJ/Kg}$$

5c. Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

Methanol – Oxygen fuel cell

Construction:

Anode & cathode – Made up of porous nickel sheets impregnated with Pt/Ru electrocatalyst.

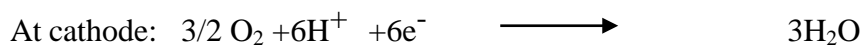
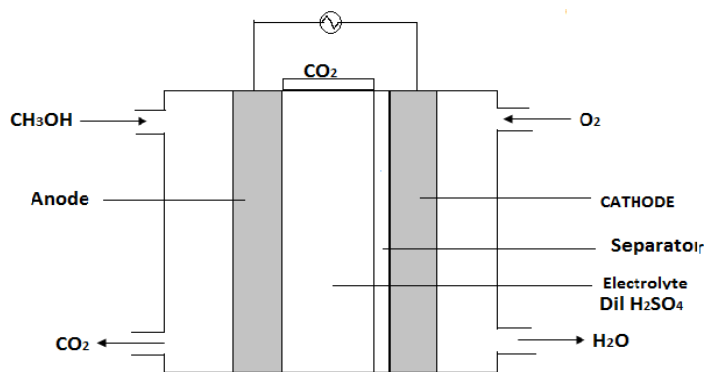
Fuel – Methanol

Oxidant – O₂

Electrolyte – Sulphuric acid(dilute)

Separator – Sulphonic acid polymer membrane.

Operating temperature – 25⁰C



A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and thereby prevents the oxidation of methanol at cathode. Methanol – H₂SO₄ mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

The advantage of acid electrolyte is that the CO₂, a product of the reaction, can be easily removed.

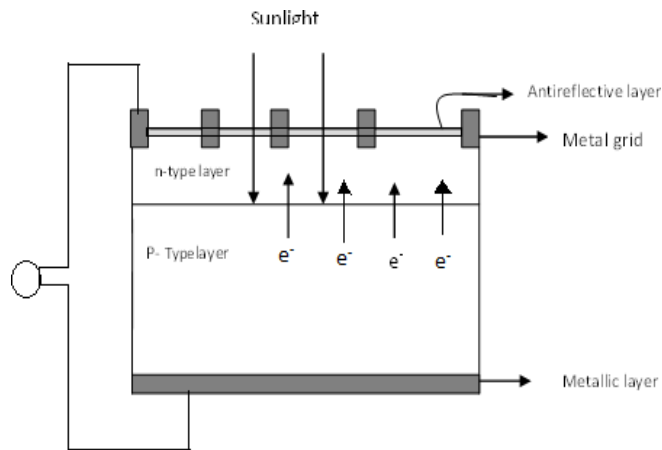
Applications – It is used in large-scale power production.

Military applications

6a.

Photovoltaic cells or solar cells are semiconductor devices which convert sunlight into electricity.

Construction of Photovoltaic cell: The solar cells or photovoltaic cells are made out of semiconductors which have the capacity to absorb light. When n-type and p-type semiconductor are brought together a semi-conductor diode is formed. A photovoltaic cell has two electrical contacts: 1) A metallic grid on top of n-type semiconductor which serves as a negative terminal. The top surface between grids is coated with anti-reflection layer to prevent the reflection of solar light. 2) A layer of noble metal at the bottom of p-type semiconductor serves as positive terminal. Both the terminals are connected to a battery.



Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy
h = Plank constant
 ν = frequency
c = speed of light
 λ = wavelength

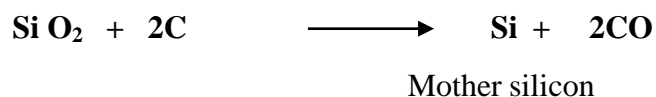
Working: when sunlight with their photons carrying energy $E=h\nu$ (h is the Plank's constant and ν is the frequency of radiation), falls on the p-n junction diode, electrons are ejected from p-type semiconductor forming electron-hole pairs. The electrons move to n-type end through p-n junction and the holes move to the p-type end. Since p-n junction allows only one way movement of electrons, they must flow through the external circuit to

recombine with holes present in p-side of semiconductor. This movement of electrons from n-side to p-side through the external circuit generates an electric current. Electrical energy obtained from a PV cell is directly proportional to the area of the cell exposed to light radiation and the intensity of light radiation which can eject electrons.

6b.

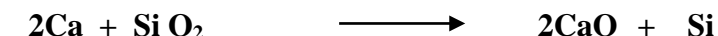
The Union Carbide process: This process involves the following steps:

Silica(Quartz) is treated with coal in an electric arc furnace

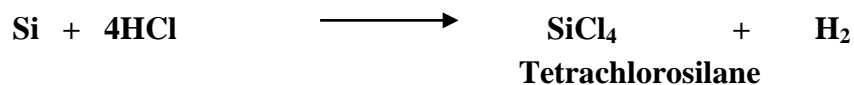
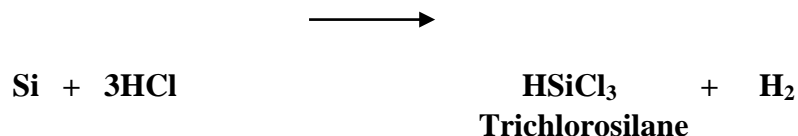


Carbon monoxide is further oxidized to carbon dioxide and released into the atmosphere.

In next step mother silicon is mixed with an oxygen and silica to remove the impurities such as Al, Ca and Mg. These impurities are removed in the form of slag (silicates) to get **Metallurgical grade silicon**

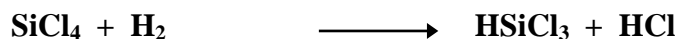


Metallurgical grade silicon is treated with dry HCl at 300⁰C to obtain trichlorosilane and tetrachlorosilane.



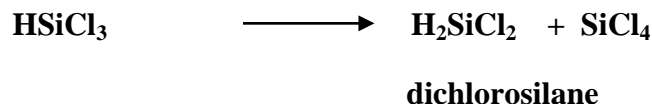
The trichlorosilane is separated by distillation.

Tetrachlorosilane is converted into trichlorosilane by **hydrogenating** in a reactor at 1000⁰ C.



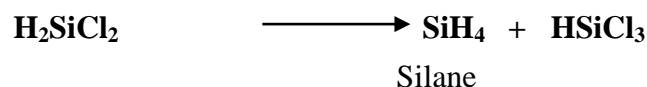
The purified trichlorosilane is passed through a ion exchange column filled with **quaternary ammonium ion exchange resin** acting as catalyst.

- **Trichlorosilane gets converted into dichlorosilane.**



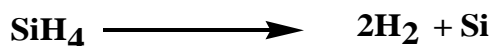
The products are separated by distillation, tetrachlorosilane is recycled to the hydrogen reactor and dichlorosilane is passed through a second ion exchange column filled with quaternary ammonium ion exchange resin.

- **Dichlorosilane is converted into silane.**



The above products are separated by distillation and trichlorosilane is recycled to the ion exchange column.

- **Silane** is further purified by distillation and then pyrolyzed (heated at high temperature) to produce solargrade silicon which is 99.99% pure.



The silicon obtained is further purified by zone refining

6c. (i) POWER ALCOHOL (gasohol)

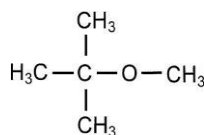
- This is alcohol-blended petrol.
- Gasohol is a blend of 15 – 85% of absolute ethanol and 85 – 15% of petrol by volume.
- Gasohol with 85% of absolute ethanol & 15% of petrol can be used with engine modification. Gasohol with 15% of absolute ethanol & 85% of petrol can be used without engine modification.
- Absolute alcohol is used in the preparation of Power alcohol to prevent phase separation.
- Alcohol contains higher percentage of oxygen than MTBE and hence brings about complete oxidation of petrol more effectively.
- Therefore power alcohol has better anti-knocking characteristics than unleaded petrol.

Advantages of power alcohol:

- Power output is higher than petrol
- Ethanol is better anti-knocking agent than MTBE.

(ii) Unleaded petrol:

In unleaded petrol, methyl-t-butyl ether (MTBE) and ethyl-t-butyl ether (ETBE) are used as anti-knocking agents.



MTBE has oxygen in its structure (in the form of ether group). This oxygen used for the complete combustion of the petrol, thus formation of peroxide compounds is minimized.

Advantages of unleaded petrol:

- Increases the efficiency of the engine.
- Helps in complete combustion of fuel hence, less air pollution

7a. Sources of lead pollution:

- Common source of lead poisoning is dust and chips from old paints.
- It also comes from smelting of metals, lead-acid battery manufacturing, and steel industries.

Ill effects:

- Once lead enters the body, it distributes throughout the blood and accumulates in the bones because of the similarity in sizes of Ca^{2+} and Pb^{2+} .
- Higher concentration of lead inhibits production of haemoglobin and cause anaemia.
- It can also affect the functioning of kidneys and permanent brain damage.

Control:

- Replacements of conventional lead based products by lead free products.
- Lead batteries to be dumped at a proper place.
- Eliminate lead contamination in drinking water by process such as reverse osmosis, distillation and filtration using carbon filters specially manufactured for lead removal.

7b. e-waste refers to electronic and electrical goods which can no longer be used. They contain hazardous and toxic materials which cannot be disposed off with other solid waste.

Sources:

- Mobile phones, batteries, telephones, switch, computer hardware, monitor, keyboard, TV's etc.
- Kitchen equipments (toasters, microwave ovens, refrigerator, washing machine etc.)

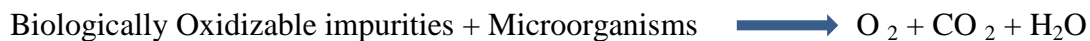
Disposal:

- The hierarchy in the disposal or treatment of e-waste encourages the reuse of original equipment as the first priority.
- Second is the re-manufacturing where the used products are disassembled, cleaned, repaired, reassembled and qualified for new or like-new equipments.
- Third is recycling of e-waste, which involves dis-mantling where hazardous and valuable components are separated.
- The last resort is disposal by incineration as Copper present in them acts as a catalyst for dioxin formation when flame-retardants are incinerated. Exposure to dioxin lead to cancer, diabetes etc.

7c. $V = 50 \text{ cm}^3$ $(x-y) = 11.5 \text{ cm}^3$ $N_{\text{K}_2\text{Cr}_2\text{O}_7} = 0.4 \text{ N}$

$$\begin{aligned} \therefore \text{COD value} &= \frac{8 \times (X-Y) \times (N) \text{FAS} \times 1000}{(V) \text{waste water}} \\ &= \frac{8 \times 11.5 \times 0.4 \times 1000}{50} \\ &= 736 \text{ mg of O}_2 / \text{ltr} \end{aligned}$$

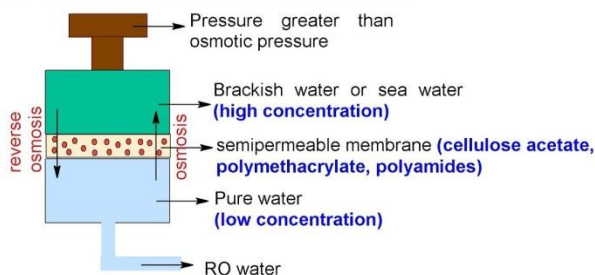
8a. Activated sludge is a water sample containing higher concentration of microorganisms like azobacter, bacillus etc. The water is mixed with proper quantity of activated sludge and the mixture is sent to aeration tank. During the process, microorganisms present in activated sludge attack on biologically oxidizable compounds of sewage and decompose them into CO_2 and H_2O . The effluent, after this treatment is passed to sedimentation tank (clarifier) where sludge is settled down. The clear effluent is sent to tertiary treatment. A part of sludge is used for further treatment and rest is disposed off.



8b. The process of removal of dissolved salts present in water is called desalination. This can be achieved by reverse osmosis method.

Reverse osmosis (R.O): Osmosis is a natural phenomenon in which solvent (water) molecules move from dilute solution to concentrated solution through a semi-permeable membrane. The minimum pressure which has to be applied on membrane to prevent osmosis is called osmotic pressure. In reverse osmosis, the water molecules are made to move in reverse direction that is from concentrated solution to dilute solution through a semi-permeable membrane by applying pressure greater than osmotic pressure. RO is used to convert sea water into potable water.

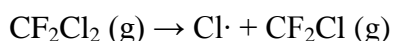
REVERSE OSMOSIS PROCESS



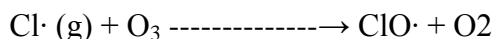
R.O unit consists of vessel, a semipermeable membrane made up of cellulose acetate and high pressure pump. When the salt water supplied with high pressure, water flow from salt water to fresh water. Fresh water is collect from fresh water outlet and salt water is discharged in to the environment.

8c. Depletion of Ozone layer:

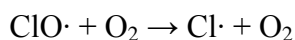
- A combination of low temperatures, elevated chlorine and bromine concentrations in the upper atmosphere are responsible for the gradual thinning of ozone layer.
- Ozone depleting substances include chlorofluorocarbons (CFC's) and volatile organic compounds (VOC's). CFC's or freons used as coolants in refrigeration and air conditioning are very stable on earth and slowly drift into stratosphere.
- They react with UV radiation to form chlorine free radical which is a potential ozone depleting species.



The chlorine free radicals then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.



Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.



The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFC'S are transporting radicals into the stratosphere and damaging the ozone layer.

9a. Colorimetry: This method is used for solutions which are themselves coloured or which gives colour with a suitable reagent. The colour Intensity is directly proportional to the concentration of the solution.

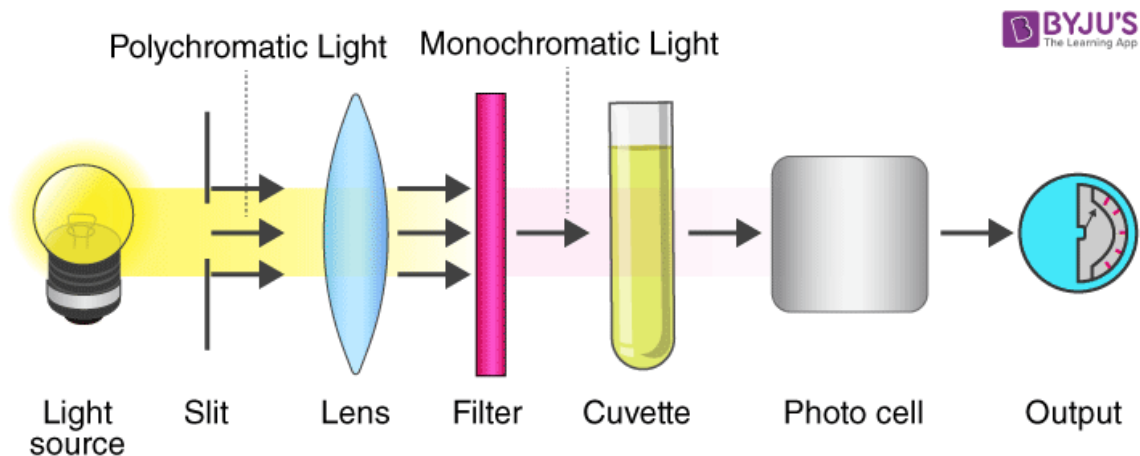
Theory: Beer's law states that the amount of light absorbed by a solution is proportional to the concentration of the solution. Lambert law states that the amount of light absorbed by a solution is proportional to the path length of the medium.

According to Beer-Lambert's law, when monochromatic light is passed through a solution, part of the light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and the path length of the light through the solution.

$$A = \epsilon C t$$

Instrumentation: Colorimeter made up of the following components.

- Tungsten lamp as the light source.
- A filter which provides the desired wavelength.
- A sample cell.
- A photocell detector.



Monochromatic light of suitable wavelength is allowed to fall on the sample cell. First, a blank solution is taken in the sample cell and placed in the path of light beam and its absorbance is adjusted to zero. Then the analyte solution is placed in the path of light and its absorbance is measured. A plot of absorbance versus standard concentrations of analyte is used to find the unknown concentration of analyte in the samples.

Applications:

- It is widely used in clinical laboratories for the analysis of glucose, creatine, urea etc.
- In soil testing laboratories for the analysis of pesticides, soil nutrients and plant nutrients.

9b. Potentiometry:

Theory: The measurement of e.m.f. to determine the concentration of ionic species in solution is referred to as potentiometry. The relation between electrode potential and metal ion concentration is given by the Nernst equation.

$$E = E_0 + \frac{0.0591}{n} \log [M^{n+}]$$

Instrumentation: It consists of

- A reference electrode which has a fixed potential and is independent of the concentration of the analyte solution. e.g., Calomel electrode.
- An indicator electrode whose potential depends on the concentration of the analyte solution. e.g., Platinum electrode.
- A device for measuring the potential.

A known volume of the analyte is taken in a beaker and its potential is determined by connecting the assembly to the potentiometer. The titrant is added in increments of 0.5 ml and the potential is measured each time. Near the equivalence point, there is a sharp increase in the potential. The end point is determined by plotting change in potential against volume of the titrant.

Eg. Redox titration of Ferrous Ammonium Sulphate against $K_2Cr_2O_7$.

9c. Fullerenes are a class of molecules made of only carbon atoms having a closed cage-like structure. Many numbers of fullerene molecules with different carbon atoms like C_{60} , C_{70} , C_{74} , C_{78} etc., have been prepared. C_{60} is the smallest, stable and abundant fullerene, obtained by usual preparation methods. C_{60} has a spherical shape and resembles a football and is commonly known as Bucky ball. Fullerenes are made up of pentagons and hexagons. Pentagons give the curvature required to form a closed structure. All fullerenes contain 12 pentagons and different numbers of hexagons. Each fullerene has $2(10+M)$ number of carbon atoms corresponding to 12 pentagons and M number of hexagons.

1. Single C_{60} molecule theoretically can take up a maximum of 60 hydrogen atoms.

Application- Hydrogen storage material for fuel cells. Electrode material in secondary batteries. Ex-Nickel Metal Hydride battery.

2. Each C_{60} molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

Application- Used as optical limiters. Optical limiters are used to protect materials from damage by intense incident light radiation.

10 a. Nano material refers to a material with at least one of its dimension (length, width or breadth) in nano scale.i.e 10⁻⁹m. And the size varies from 1-100nm. A nanometer is one billionth of a meter-approximately 100,000 times smaller than the diameter of a human hair.

SOL-GEL PROCESS

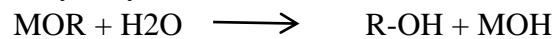
- In sol-gel process, either metal salt or alkoxide is used as precursor (starting material).
- It is mainly used in the synthesis of uniform nanoparticles of metal oxides.

Steps involved in synthesis

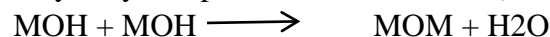
1. Preparation of Sol.
2. Conversion of Sol to Gel.
3. Aging of Gel.
4. Drying of the Gel (evaporation)
5. Heating at high temperature (calcination)

Step 1: Sol is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)

Step 2: Sol is further converted into a gel by hydrolysis and condensation of precursors.(adding acid or base as catalyst) Hydrolysis of alkoxides



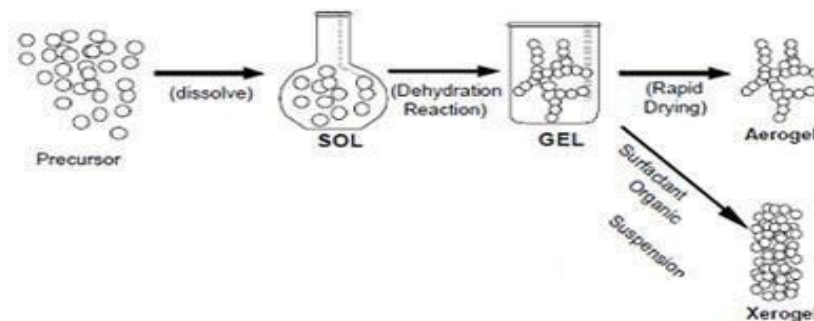
Condensation of hydrolysed species with each other (releases water)



Step 3: Aging (keeping for a known period of time) of colloid solutions takes place, i.e colloids can increase their particle size and grows into a sol-gel.

Step 4: Then the gel is dried by evaporation (solvent get evaporated)

Step 5: Calcinated (heating to high temperature) to produce nanoparticles.



10b. Graphene is a two dimensional crystalline allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice.

- It is a semi-metal with a small overlap between the valence and the conduction bands.
- Its carbon atoms are densely packed in a regular hexagonal pattern.
- The atoms are about 1.42 Å apart.
- Each carbon atom is bonded to three carbon atoms and is sp² hybridized.

Properties: 1. Very high electrical conductivity (One of the most useful properties of graphene because of a zero-overlap semimetal).

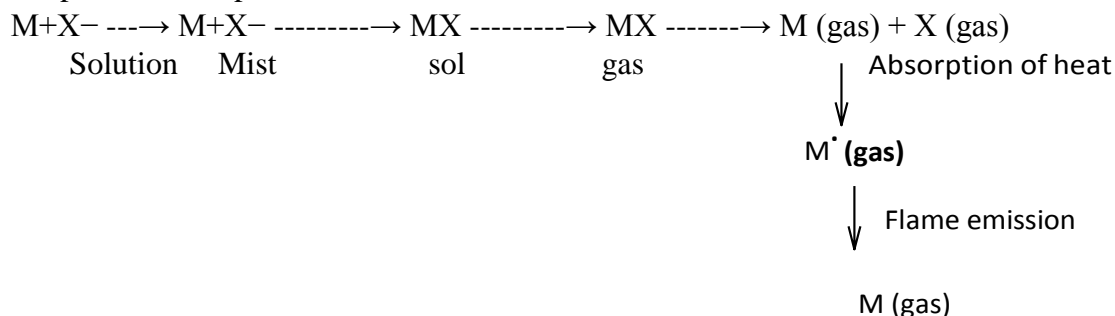
Applications: It is used in light-emitting diodes (LED), capacitors, field effect transistors (FETs)

2. It is the strongest material. So composite materials of graphene enhance the mechanical property.

Applications: Used in aerospace, building materials etc

10c. Theory: When the sample solution is aspirated into the flame, the solvent gets evaporated leaving behind the salt in the flame. The salt then turns into vapours of the metal, which dissociate to form atoms.

Evaporation vaporization dissociation



When monochromatic light of specific resonance wavelength is passed through the flame containing atoms, then part of light will be absorbed. The extent of absorption is proportional to the number of metal atoms in the flame or the concentration of the solution (Beer-Lamberts law). $A = \epsilon Ct$ Thus, from absorbance (A) value concentration (C) can be determined

Instrumentation: Atomic absorption spectrometer includes the following components.

1. Nebuliser: It creates a fine spray of the sample for introduction into the flame.
2. Atomiser (burner): Here the sample is burnt in the flame produced by fuel and oxidant combination. Solvent evaporates leaving behind a residue of neutral atoms.
3. Fuel and oxidant: They form an important part of the process. If the heat produced is not sufficient then the sample doesn't form neutral atoms. If the heat of burner is more, the sample molecules may ionize instead of forming atoms. Hence a proper combination of fuels and oxidant are to be used to produce recommended temperatures. Commonly used fuels are propane, hydrogen and acetylene and oxidant used is mostly air or oxygen.
4. Hollow cathode lamp: is mostly used as light source. The cathode of the lamp is coated with the metal of the analyte to be analysed.
5. Monochromator and Detector: Monochromator separates the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by the detector.
6. Recorder: records the intensity of the absorbed light.

A plot of absorbance versus standard concentration of analyte can be used to find the unknown concentration of analyte.

Applications:

- It is widely used for the determination of even trace amount of metals in solution.
- To estimate lead in petroleum products.

First/Second Semester B.E. Degree Examination, Aug./Sept.2020
Engineering Chemistry

Time: 3 hrs.

Max. Marks: 100

Note: Answer any FIVE full questions, choosing ONE full question from each module.

Module-1

- 1 a. Define Standard reduction potential and derive Nernst equation for single electrode potential. (06 Marks)
b. What is a Reference electrode? Explain the construction and working of a Calomel electrode. (07 Marks)
c. Define Cell Potential. Give the cell representation, cell reactions and calculate the potential of the cell consists of Li and Cu electrodes dipped in 0.1 M LiCl and 0.5M CuSO₄ solutions at 25°C. Given $E^{\circ}\text{Li} = -3.05\text{V}$ and $E^{\circ}\text{Cu} = 0.34\text{V}$. (07 Marks)

OR

- 2 a. Define Ion selective electrode. Explain the determination of pH using glass electrode. (06 Marks)
b. Derive an equation for potential of a concentration cell and calculate the potential of following cell at 25°C. Ag/AgNO₃ (0.005M) // AgNO₃ (0.5M)/Ag. (07 Marks)
c. Explain the construction and working of Li-ion cells. Mention its applications. (07 Marks)

Module-2

- 3 a. Briefly explain the effect of following factors on rate of corrosion :
i) The ratio of Anodic and Cathodic areas ii) Nature of corrosion product.
iii) pH of the medium. (06 Marks)
b. Define Corrosion of metals. Describe the electrochemical theory of rusting of iron. (07 Marks)
c. Define Electroless plating and explain electroless plating of copper. (07 Marks)

OR

- 4 a. Explain Electroplating of hard chromium and mention its applications. (06 Marks)
b. Discuss the following : i) Differential metal corrosion ii) Anodization of aluminum. (07 Marks)
c. Explain in brief : i) Sacrificial anode method ii) Decomposition potential. (07 Marks)

Module-3

- 5 a. Define Calorific value of a fuel and calculate the gross and net calorific value of a coal from the following data :
i) Mass of coal burnt = 0.85 gms.
ii) Water equivalent mass of copper calorimeter = 0.65kg.
iii) Mass of water taken in the copper calorimeter = 2.2kg.
iv) Rise in temperature of water = 3.0°C.
v) Percentage of H₂ in the coal = 3.2.
vi) Latent heat of steam = 2457.76 kJ/kg. (06 Marks)
b. Define Fuel cell and explain the construction and working CH₃OH – O₂ fuel cell. (07 Marks)
c. Describe the preparation of solar grade silicon by Union carbide process. (07 Marks)

OR

- 6 a. Explain the experimental determination of calorific value of a fuel using bomb calorimeter. (07 Marks)
b. What are Solar cells? Explain the construction and working of a Photo voltaic cell. (06 Marks)
c. Discuss : i) Knocking of petrol engine ii) Power alcohol. (07 Marks)

Module-4

- 7 a. Discuss the sources , effects and control measures of oxides of nitrogen. (06 Marks)
b. Explain the causes, effects and disposal methods of biomedical wastes. (07 Marks)
c. Explain Scale and Sludge formation in boilers. (07 Marks)

OR

- 8 a. Define BOD and COD. Calculate the COD of a wastewater if 25ml of which consumes 10.5ml of 0.02N $K_2Cr_2O_7$ for complete oxidation. (06 Marks)
b. Explain the softening of water by ion exchange method. (07 Marks)
c. Explain the following : i) Ozone depletions ii) Reverse osmosis. (07 Marks)

Module-5

- 9 a. Explain the theory and instrumentation of colorimetry. (07 Marks)
b. Discuss the theory of conductometric titration and explain the nature of graph for the following titrations :
i) Strong acid with strong base ii) Weak acid with strong base. (07 Marks)
c. Explain the synthesis of nanomaterials by Chemical Vapour Deposition method. (06 Marks)

OR

- 10 a. Explain Sol – gel method of synthesis of nanomaterials. (06 Marks)
b. Write a note on synthesis , properties and uses of Fullerenes. (07 Marks)
c. Explain 'Atomic Absorption Spectroscopy'. (07 Marks)

Answers of VTU question paper Aug/September 2020

1a. Single electrode potential: It is the potential developed at the junction of a metal and solution when a metal is in contact with its own ions due to loss or gain of electrons.

Nernst equation for single electrode potential:

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature. Consider a reversible electrode reaction,



Equilibrium constant for the above reaction is,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[M]}{[M^{n+}]} \dots\dots\dots (1)$$

According to thermodynamics, for a reversible process, equilibrium constant (K) is related to decrease in change in free energy ($-\Delta G$) as, by Vant Hoff equation.

$$\Delta G = -\Delta G^0 + RT \ln K_c \dots\dots\dots (2)$$

Where, ΔG^0 = Standard change in free energy
R = Universal gas constant
T = Temperature

Substituting 1 in 2

we have,

$$\Delta G = \Delta G^0 + RT \ln \frac{[M]}{[M^{n+}]} \dots\dots(3)$$

The decrease free energy ($-\Delta G$) for any reversible process is equal to the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\max} \dots\dots\dots(4)$$

In case of a Galvanic cell, W_{\max} = Electrical energy supplied by the cell

$$= [(\text{difference in potential between two electrodes}) \times (\text{total charge flowing through the cell})]$$

If 'n' moles of electrons are flowing from anode to cathode, then the total quantity of charges flowing through the cell is 'n' Faradays (nF).

$$\therefore W_{\max} = E_{\text{cell}} \times nF = nFE \dots\dots\dots(5)$$

By comparing equation 4 and 5,

$$-\Delta G = nFE \dots\dots\dots(6)$$

Under standard conditions,

$$-\Delta G^{\circ} = nFE^{\circ} \dots\dots\dots(7)$$

Substituting the values equation (6) and (7) in equation (3)

$$nFE = nFE^{\circ} - RT \ln K_c \dots\dots\dots(8)$$

Dividing throughout by nF and substituting for 'K',

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \dots\dots\dots(9)$$

$$E = E^{\circ} + 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$E = E^{\circ} - \left[\frac{2.303RT}{nF} [M] - \frac{2.303RT}{nF} \log [M^{n+}] \right] \dots\dots\dots(10)$$

In case of metal-metal ion electrode, as 'M' is solid metal, $[M] = 1$

$$\therefore E = E^{\circ} + \frac{2.303T}{nF} \log [M^{n+}]$$

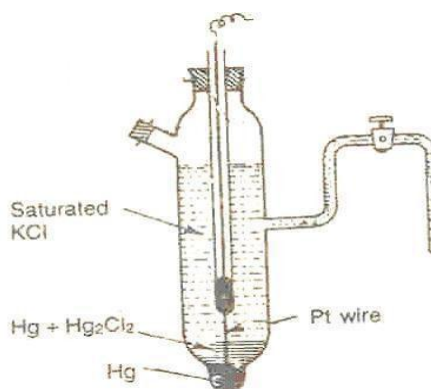
(R is a gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; T= temperature in absolute scale (298K); F is Faraday = $96,500 \text{ C mol}^{-1}$)

$$E = E^{\circ} + \frac{0.0591}{n} \log[M^{n+}] \quad \text{at 298 K}$$

1b. Reference electrodes are the electrodes whose potential is known and with reference to those, the electrode potential of any other electrode can be measured.

Construction and working of calomel electrode

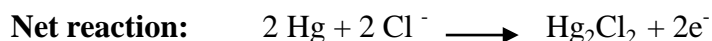
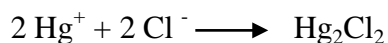
- Calomel electrode is a **Metal-metal salt electrode**
- A Metal-metal salt electrode consists of Mercury, Mercurous Chloride and a solution of KCl.
- Mercury is placed at the bottom of a glass tube.
- A paste of Mercury and Mercurous Chloride (calomel) is placed above the Mercury. The space above the paste is filled with a KCl solution of known concentration.
- A platinum wire is kept immersed into the mercury to obtain external electrical contact.
- It is internally connected through salt bridge.



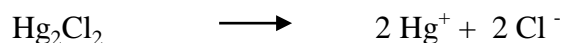
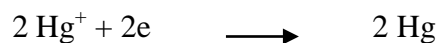
Calomel electrode can be represented as ,



The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.



When it is Cathode:-



1.c

Nickel-metal hydride battery:

Construction:

In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed.

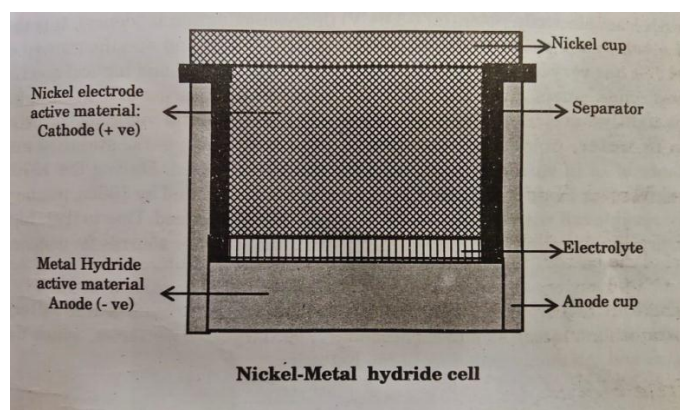
Anode – Porous nickel grid pasted with **metal hydride** (such as TiH_2 , VH_2 ,) and a hydrogen storage alloy (such as LaNi_5).

Cathode - Porous nickel grid pasted with **Ni(OH)_2 , NiO(OH)** .

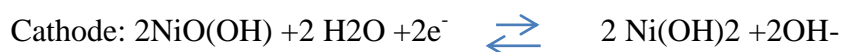
Electrolyte- KOH .

Separator- Polypropylene.

Representation : $\text{MH}_2 \mid \text{KOH} \mid \text{Ni(OH)}_2, \text{NiO(OH)}$



Working:



Uses: Used in cellular phones, camcorders and laptop computers.

2a. Ion selective electrodes are also called membrane electrodes or Ion sensitive electrodes. These are electrodes that will respond to certain specific ions present in a solution containing mixture of ions and the potential developed at the electrode is a function of concentration of these specific ions in the solution.

Determination of pH using glass electrode: The cell consists of a glass electrode as an indicator electrode and saturated calomel electrode as a reference electrode. The cell is immersed in a solution whose pH is to be determined. EMF of the cell is measured using potentiometer. Cell can be represented as:

Hg | Hg₂Cl₂ | KCl || solution of unknown pH | Glass | HCl (0.1M) | AgCl | Ag

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{g}} - E_{\text{SCE}}$$

$$E_{\text{cell}} = [E_{\text{G}}^0 - 0.0591\text{pH}] - E_{\text{SCE}}$$

$$0.0591\text{pH} = E_{\text{G}}^0 - E_{\text{cell}} - E_{\text{SCE}}$$

$$\text{pH} = \frac{E_{\text{G}}^0 - E_{\text{cell}} - E_{\text{SCE}}}{0.0591}$$

$$= \frac{E_{\text{G}}^0 - E_{\text{cell}} - 0.241}{0.0591}$$

$$2b. \quad E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$E_{\text{cell}} = \frac{0.059}{1} \log \frac{0.5}{0.005}$$

$$= 0.059 \log \frac{0.5}{0.005}$$

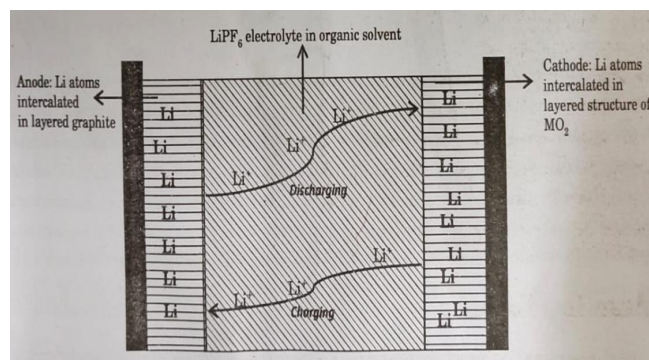
$$= 0.059 \log 0.5 - \log 0.005$$

$$= 0.059 \times (-0.301) - (-2.301)$$

$$= -0.0178 + 2.301$$

$$= 2.2832\text{V}$$

2c. Lithium-ion battery



Construction:

Anode-Lithium intercalated graphite.

Cathode – Lithium metal oxide such as (LiCoO₂).

Electrolyte -A solution of lithium salt (LiPF₆) in organic solvent.

Separator- non-woven **polypropylene**.

Representation: *Li, C / LiPF₆, in organic solvent / LiCoO₂*

- It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers.
- Lithium ions move between anode and cathode during discharging and charging process.
Since

Both anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.

Working

At Anode: $\text{Li}_x\text{C}_6 \rightleftharpoons x\text{Li}^+ + x\text{e}^- + 6\text{C}$

At cathode: $\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{LiCoO}_2$

Net Cell reaction: $\text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \rightleftharpoons 6\text{C} + \text{LiCoO}_2$

Applications: Portable electronics, mobile phones, laptop, ipod etc.

3 a. **Nature of corrosion product:**

- If the corrosion product is insoluble, stable and non-porous, then it acts as a protective film which prevents further corrosion.
- The film acts as a barrier between metal surface and the corrosive environment.
- On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

Example: Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of Cr₂O₃ on the surface.

Ratio of Anodic to cathodic areas:

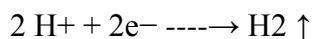
Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. When cathodic area is large, demand for electrons for reduction reaction is high. To meet this demand oxidation reaction occurs more intensely at anodic area.

For example, a broken coating of tin on iron surface, results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.

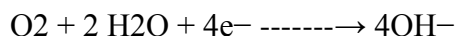
A broken coating of zinc on iron surface, results in less corrosion at the broken region. Iron is cathodic to zinc. Exposed region of iron acts as cathode with small area. Zinc acts as anode which has large area.

pH: the rate of corrosion increases with decrease in pH. Generally acids are more corrosive than neutral or alkaline solution.

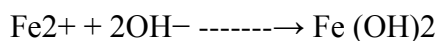
In acidic medium, the rate of corrosion depends upon the rate of evolution of hydrogen at cathode area. When pH < 4, rate of corrosion increases due to higher concentration of H⁺ ions.



If the pH is between 4 and 10, the rate of corrosion depends upon the availability of oxygen at cathode for reduction. Higher the concentration of O_2 , higher the rate of corrosion.



If pH is > 10 , then corrosion practically ceases due to formation of insoluble metal hydroxides on the surface of the metal.



3.b. Corrosion is the process of gradual degeneration of a metal/alloy from its surface due to chemical or electrochemical reaction with the surroundings.

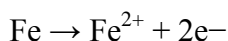
Electrochemical theory of corrosion:

According to this theory, corrosion is an electrochemical process and the reactions are similar to that in galvanic cells. At anode oxidation takes place liberating electrons which move to cathode where reduction occurs. A conducting medium is required over the surface of the metal for the movement of ions and for the completion of circuit between anode and cathode.

Eg. Rusting of iron

When a metal such as iron is exposed to corrosive environment, a large number of tiny galvanic cells with anodic and cathodic regions are formed.

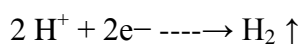
Reaction at anodic region: Since oxidation takes place at anode, iron is oxidised to ferrous (Fe^{2+}) ions with loss of electrons.



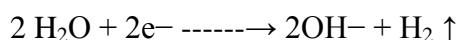
Reaction at cathodic region: Depending on the nature of environment possible reduction reactions that can take place at the cathode are:

1) Liberation of hydrogen: It takes place in the absence of oxygen.

i. In acidic medium, the reaction is,

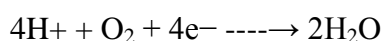


ii. In neutral or alkaline medium, the reaction is

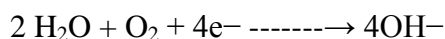


2) Absorption of oxygen: It takes place in the presence of oxygen.

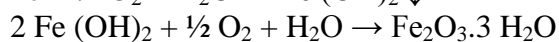
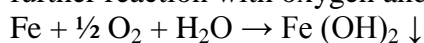
i. In acidic medium, the reaction is,



ii. In neutral or alkaline medium, the reaction is



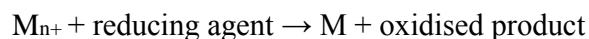
Thus, Fe^{2+} ions formed at the anodic region move towards cathodic region whereas hydroxyl ions formed at cathode move towards anode. Fe^{2+} ions react with OH^- ions forming ferrous hydroxide which on further reaction with oxygen and water forms corrosion product (hydrated ferric oxide) or rust.



Rust

Since the layer of rust formed is highly porous, oxygen and moisture from the environment pierce deeper and increase the rate of corrosion.

3.c. Electroless plating is the deposition of a thin layer of metal on a catalytically active surface from its salt solution in presence of a suitable reducing agent without using electric current. When the catalytically active surface is dipped in the bath, the reducing agent reduces metal ions to metal atoms, which gets deposited on the surface and the reducing agent itself gets oxidised.



Electroless plating of Copper

The article to be plated is degreased and etched by dipping in dil. H_2SO_4 . Electroless copper is deposited directly on iron, cobalt, nickel and other metals without any treatment in presence of reducing agents. However, insulators like plastics, glass etc. are catalytically activated by dipping in $SnCl_2$ containing HCl at $25^\circ C$ followed by $PdCl_2$. $SnCl_2$ reduces palladium ions on the surface of the object to palladium which catalyse the deposition reaction.

Composition of Plating bath solution:

Metal ion solution – Copper sulphate

Reducing agent – Formaldehyde

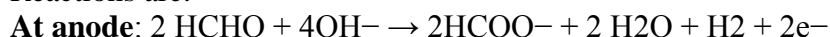
Buffer – Rochelle salt & sodium hydroxide

Complexing agent – EDTA

Temperature – $25^\circ C$

pH – 11

Reactions are:



Here formaldehyde is oxidised to formic acid in presence of strong alkali releasing two electrons which reduces Cu^{2+} to Cu . Copper deposition is thermodynamically more favourable in alkaline solutions. However, copper precipitates at elevated pH values. To overcome this difficulty, complexing agent EDTA is added to plating bath to maintain metal ion concentration in the solution. Formaldehyde and copper sulphate are added to the plating bath periodically as Cu^{2+} ions and $HCHO$ are consumed in the reaction process.

Applications: An important application is in the manufacture of double sided printed circuit boards (PCB's) where plating through holes is required.

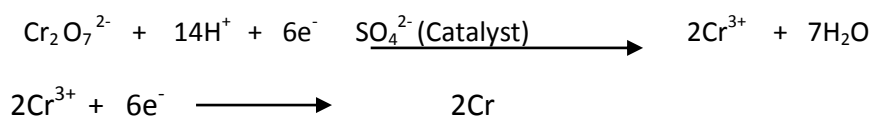
4.a. Electroplating is the process of electrolytic deposition of a metal on the surface of substrate; the substrate may be any metal, a polymer, a ceramic or a composite.

ELECTROPLATING OF CHROMIUM

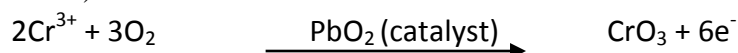
- The surface of the object is cleaned thoroughly. Oil and grease removed by organic solvent and then, treated with dilute H_2SO_4 to remove oxide layer.
- Finally, the surface is washed with distilled water. Then, chromium plating is done under the following conditions.

	Decorative Chromium Electroplating	Hard Chromium Electroplating
Plating bath composition	Chromic acid (H_2CrO_4) + H_2SO_4 in ratio 100 : 1	Chromic acid (H_2CrO_4) + H_2SO_4 in ratio 100 : 1
Operating temperature	45-60 °C	45-60 °C
Current density	100 – 200 mA cm^{-2}	200-400 mA cm^{-2}
Anode	Insoluble anode: Pb-Sn alloy coated with PbO_2 .	Insoluble anode: Pb-Sn alloy coated with PbO_2
Cathode	Object to be plated	Object to be plated
Anodic reaction	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
Cathodic reaction	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
Applications	1.Used in decorative coating in taps, handles, automobile bumpers, wheel rims 2. Used in corrosion resistant coating.	1. Cutting edges of milling machine 2. Hand guns, aircraft landing parts.
Thickness	0.25- 0.75micrometre	0.005-0.75 mm

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3⁺ state by a complex anodic reaction in the presence of sulphate ions. The Cr^{3+} then gets reduced to Cr on the substrate surface.



- For a good deposit, the Cr^{3+} concentration must be low. The PbO_2 oxidizes Cr^{3+} to Cr^{6+} , thus reduce (control) the concentration of Cr^{3+} .



In chromium plating we do not use chromium metal as anode due to the following reasons.

- If chromium dissolves at anode, there will be a high concentration of Cr^{3+} in solution. In such cases, a black,(bad, burnt) deposit is obtained.
- In acidic solutions, chromium may undergo passivation.

4.b. (i) Differential metal corrosion or Galvanic corrosion

This type of corrosion occurs when two dissimilar metals are in contact with each other and are exposed to a corrosive environment. The metal with lower electrode potential acts as anode and undergoes corrosion, whereas the metal with higher electrode potential acts as cathode and remains unaffected. Larger the potential difference between the two metals higher is the rate of corrosion.

(ii) Anodising of Aluminium

Anodising is the process of coating the metal with an oxide layer electrolytically to protect the metal from corrosion.

In anodisation of aluminium, clean, polished aluminium is taken as anode and immersed in an electrolytic cell containing 5-10% chromic acid. Inert electrodes like stainless steel or carbon is taken as the cathode. Temperature is maintained at 35°C and a suitable voltage is applied to get the desired thickness of oxide layer on aluminium. The aluminium oxide layer thus formed is porous. The pores are finally sealed by dipping in hot water to produce $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which occupies higher volume and thereby the pores are sealed. This non-porous protective layer prevents aluminium from corrosion. Metals such as Mg, Ti etc. can also be anodised to prevent corrosion.

At anode: $2\text{Al} \rightarrow 2\text{Al}^{3+} + 6\text{e}^-$

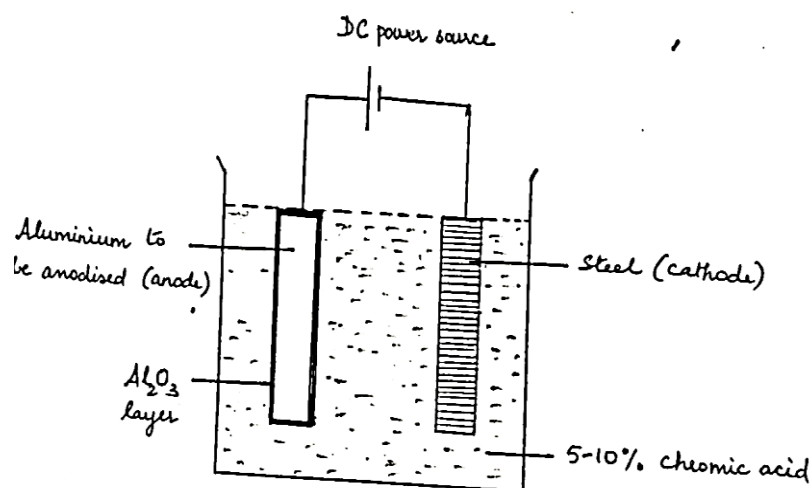
At cathode: $6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2$

$4\text{Al}^{3+} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$

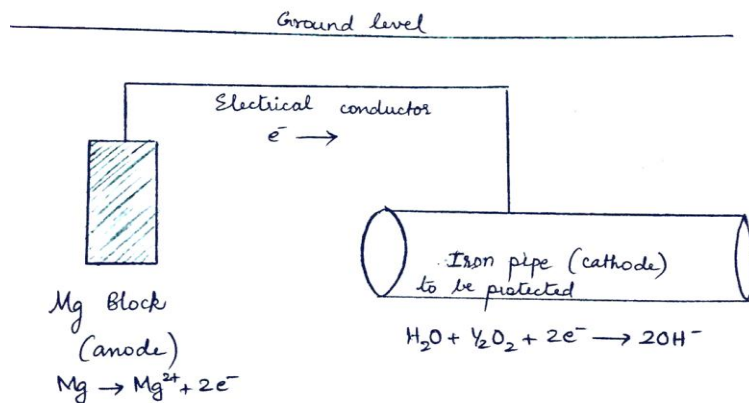
Advantages: Anodised aluminium is used in

- Various aircraft and automotive products due to its durability.
- Architectural and construction projects as they can withstand changes in weather.



4.c. (i) Sacrificial Anode Method: In this method, the metal to be protected (for example iron, steel etc) is connected to a more active anodic metal like magnesium or zinc. The anodic metal undergoes oxidation and sacrifice itself to provide electrons to the metal to be protected. Hence it is called sacrificial anode method. Once the sacrificial anodes are completely corroded, they should be replaced with fresh anodes.

This method is used to protect buried pipelines, ship hulls, buried oil storage tanks etc. where Zn or Mg blocks are connected to these to act as sacrificial anode.



(ii) Decomposition potential: The minimum external voltage that must be applied in order to carry out continuous electrolysis in an electrolytic cell is called decomposition potential (E_d). By extrapolating the curve in the plot of applied voltage against current flowing through the cell decomposition voltage is obtained.

$$E_d = E_{\text{back}} + \eta$$

Where, η is the over potential and E_{back} is the back EMF, which is the difference in potential of cathode and anode during electrolysis. Since this EMF opposes the applied potential, it is called back EMF.

For any system, knowing the salt being electrolysed, back EMF can be theoretically calculated. Hence, it is also called as theoretical decomposition potential.

5.a Mass of fuel = 0.85g Water equivalent of calorimeter = 0.65 Kg
 Mass of water = 2.2 Kg, Specific heat of water = 4.187 KJ/kg/K
 Rise in temperature = 3.0 C, % of hydrogen in the coal sample = 3.2%, Latent heat = 2457.76 KJ/Kg

$$\text{GCV} = \frac{(w_1 + w_2) s \Delta t}{m}$$

$$= \frac{(2.2 + 0.65) \times 3.0 \times 4.187}{0.00085}$$

$$= 42116.2 \quad \text{KJ/Kg}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - (0.09 \% \text{ of } H_2 \text{ in fuel} \times \text{Latent heat of steam}) \\ &= 42116.2 - (0.09 \times 3.2 \times 2457) \\ &= 42116.02 - 552.8 \\ &= 41563.4 \text{ KJ/Kg} \end{aligned}$$

5b. Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

Methanol – Oxygen fuel cell

Construction:

Anode & cathode – Made up of porous nickel sheets impregnated with Pt/Ru electrocatalyst.

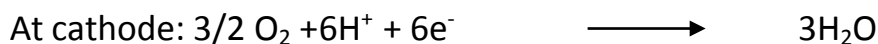
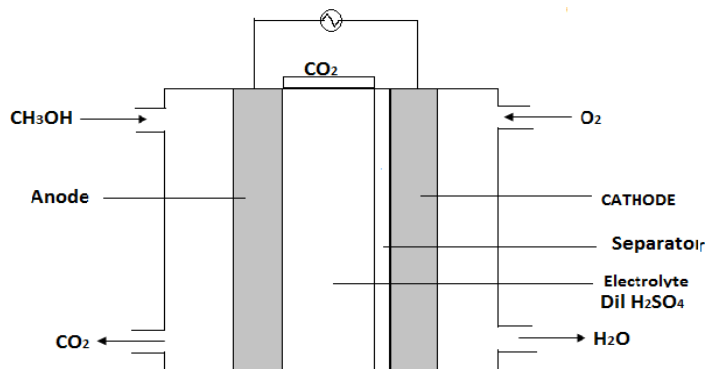
Fuel – Methanol

Oxidant – O₂

Electrolyte – Sulphuric acid (dilute)

Separator – Sulphonic acid polymer membrane.

Operating temperature – 25⁰C



A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and thereby prevents the oxidation of methanol at cathode. Methanol – H₂SO₄ mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

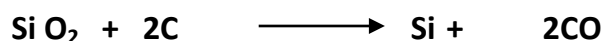
The advantage of acid electrolyte is that the CO₂, a product of the reaction, can be easily removed.

Applications - It is used in large-scale power production.

Military applications

5c. The Union Carbide process: This process involves the following steps:

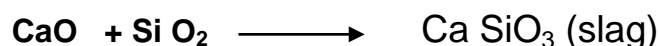
Silica (Quartz) is treated with coal in an electric arc furnace



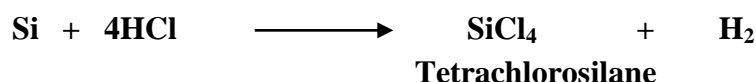
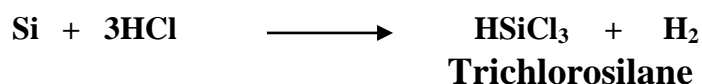
Mother silicon

Carbon monoxide is further oxidized to carbon dioxide and released into the atmosphere.

In next step mother silicon is mixed with an oxygen and silica to remove the impurities such as Al, Ca and Mg. These impurities are removed in the form of slag (silicates) to get **Metallurgical grade silicon**



Metallurgical grade silicon is treated with dry HCl at 300°C to obtain trichlorosilane and tetrachlorosilane.

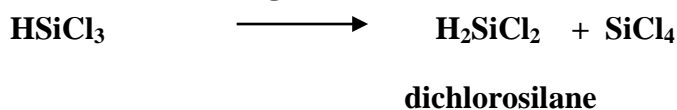


The trichlorosilane is separated by distillation. Tetrachlorosilane is converted into trichlorosilane by **hydrogenating** in a reactor at 1000°C.



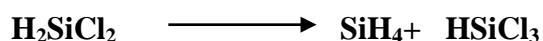
The purified trichlorosilane is passed through a ion exchange column filled with **quaternary ammonium ion exchange resin** acting as catalyst.

- **Trichlorosilane gets converted into dichlorosilane.**



The products are separated by distillation, tetrachlorosilane is recycled to the hydrogen reactor and dichlorosilane is passed through a second ion exchange column filled with quaternary ammonium ion exchange resin.

- **Dichlorosilane is converted into silane.**



Silane

The above products are separated by distillation and trichlorosilane is recycled to the ion exchange column.

- **Silane** is further purified by distillation and then pyrolyzed (heated at high temperature) to produce solargrade silicon which is 99.99% pure.

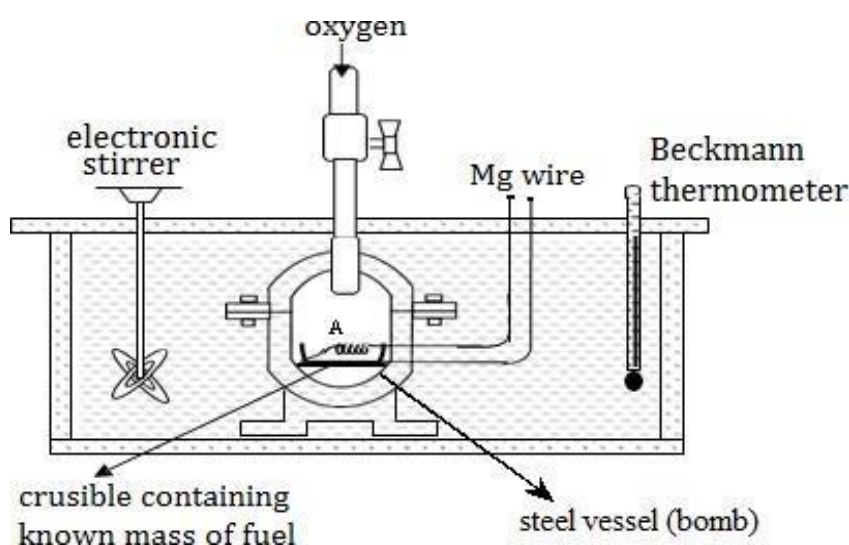


The silicon obtained is further purified by zone refining

6a.

Construction

- ❖ The bomb calorimeter (shown in the fig.) consists of a strong inner cylindrical steel vessel (bomb) with an airtight lid and an inlet for oxygen.



- ❖ The bomb has a crucible with a loop of wire. The ends of the wire project out and are connected to a source of electric current.
- ❖ The bomb is immersed in a rectangular copper vessel (calorimeter) of known weight and containing known volume of water, which is continuously stirred by mechanical stirrer.
- ❖ A Beckmann thermometer is introduced into the calorimeter to measure the temperature.

Working

- A known mass of water is taken in the calorimeter and is closed with the lid.
- The initial temperature of water is noted, $t_1^{\circ}\text{C}$
- A known mass of the fuel is taken in the crucible, inside the bomb.
- Oxygen is passed through the bomb.
- The ends of the wire are connected to an electric source so as to ignite the fuel.
- On passing an electric current through the ignition coil, the fuel gets ignited.
- The fuel burns liberating heat. Heat liberated is taken up by the water and calorimeter. The water is continuously stirred using the stirrer.
- The maximum temperature attained by the water, $t_2^{\circ}\text{C}$, is noted.

Observation and calculations:

$$\text{Gross calorific value} = \frac{(w_1 + w_2) s \Delta t}{m} \quad \text{kJ kg}^{-1}$$

where

w_1 = mass of water in the calorimeter, in kg

w_2 = water equivalent of the calorimeter, in kg

s = specific heat of water, in $\text{kJ kg}^{-1} \text{ } ^\circ\text{C}^{-1}$

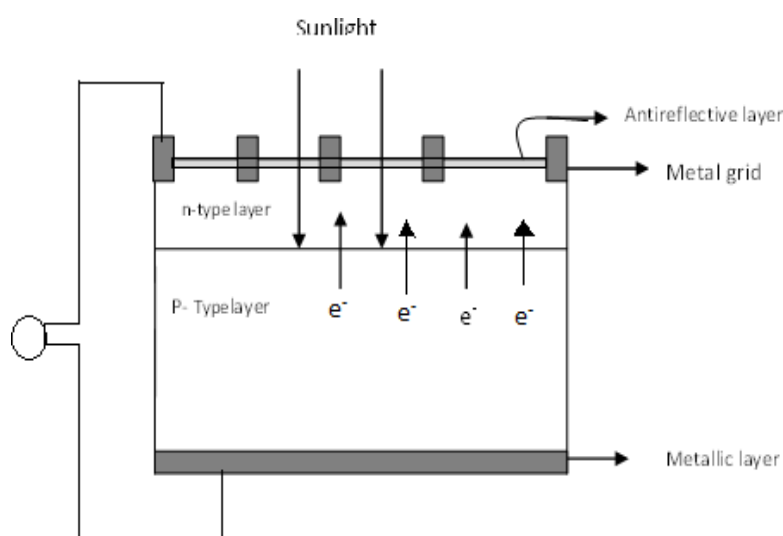
$\Delta t = t_2 - t_1$ = rise in temperature, in $^\circ\text{C}$

m = mass of the fuel, in kg

6b.

Photovoltaic cells or solar cells are semiconductor devices which convert sunlight into electricity.

Construction of Photovoltaic cell: The solar cells or photovoltaic cells are made out of semiconductors which have the capacity to absorb light. When n-type and p-type semiconductor are brought together a semi-conductor diode is formed. A photovoltaic cell has two electrical contacts: 1) A metallic grid on top of n-type semiconductor which serves as a negative terminal. The top surface between grids is coated with anti-reflection layer to prevent the reflection of solar light. 2) A layer of noble metal at the bottom of p-type semiconductor serves as positive terminal. Both the terminals are connected to a battery.



Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy
h = Planck constant
 ν = frequency
c = speed of light
 λ = wavelength

Working: when sunlight with their photons carrying energy $E=h\nu$ (h is the Plank's constant and ν is the frequency of radiation), falls on the p-n junction diode, electrons are ejected from p-type semiconductor forming electron-hole pairs. The electrons move to n-type end through p-n junction and the holes move to the p-type end. Since p-n junction allows only one way movement of electrons, they must flow through the external circuit to recombine with holes present in p-side of semiconductor. This movement of electrons from n-side to p-side through the external circuit generates an electric current. Electrical energy obtained from a PV cell is directly proportional to the area of the cell exposed to light radiation and the intensity of light radiation which can eject electrons.

6c.

(i) **The rattling sound produced by shock waves in a petrol engine due to explosive combustion of fuel-air mixture at higher compression ratio.**

Mechanism of knocking in chemical terms:

Under ideal conditions, when petrol sample has hydro carbons (like aromatic, branched, cyclic) can withstand high pressure, undergoes smooth and complete combustion by the spark produced in an engine. So there is no knocking. (Ideal case or normal case)

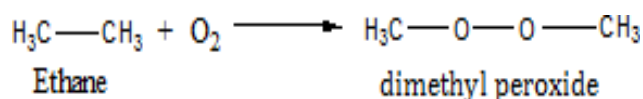


But, if hydrocarbon molecules (straight chain) present in the petrol cannot withstand the high pressure, undergoes incomplete combustion and forms unstable peroxides.

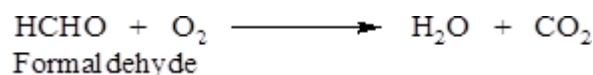
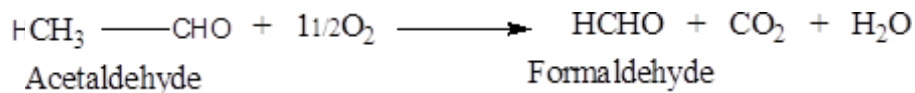
- These unstable peroxides decompose rapidly to give a number of gaseous compounds and increase the compression ratio beyond the limit.
- These products are **pre-ignited** (self-ignited i.e before spark produced) Due to this, petrol – air mixture suddenly burst into flames. This explosive combustion increases the pressure and leads to the production of **shock waves**.
- The shock waves dissipate its energy by hitting the walls of cylinder and piston. This causes a rattling sound referred to as **Knocking**.

Under knocking conditions, the rate of combustion is very high. It involves following steps.

Oxygen combines with hydrocarbon molecule forming peroxides.



The peroxides decompose readily to give a number of gaseous products. For example,



Effects of knocking in petrol engine:

- Decreases the life of petrol engine
- Causes mechanical damage due to overheating.
- Consumption of petrol is more, results in less power output

(ii) POWER ALCOHOL (gasohol)

- This is alcohol-blended petrol.
- Gasohol is a blend of 15 – 85% of absolute ethanol and 85 – 15% of petrol by volume.
- Gasohol with 85% of absolute ethanol & 15% of petrol can be used with engine modification. Gasohol with 15% of absolute ethanol & 85% of petrol can be used without engine modification.
- Absolute alcohol is used in the preparation of Power alcohol to prevent phase separation.
- Alcohol contains higher percentage of oxygen than MTBE and hence brings about complete oxidation of petrol more effectively.
- Therefore power alcohol has better anti-knocking characteristics than unleaded petrol.

Advantages of power alcohol:

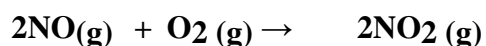
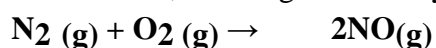
- Power output is higher than petrol
- Ethanol is better anti-knocking agent than MTBE.

7a.

OXIDES OF NITROGEN (NO_x): NO, NO₂ & N₂O are the common oxides of nitrogen

Source:

- N₂ & O₂ are the main constituents of air these gases don't react with each other at a normal temperature, **when lightning strikes**, they combine to form oxides of nitrogen.
- When fossil fuel is burnt, di nitrogen & di oxygen combine to yield NO & NO₂



- Nitrogen fixation , bacterial decay of nitrogenous compounds leads NO_x in atmosphere.
- From acid pickling plants

Ill effect:

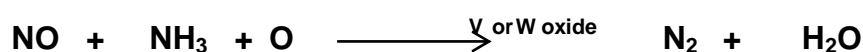
- Higher levels of NO_2 can cause damage to the human respiratory tract, respiratory infections & Asthma.
- It is unpleasant in odour and leads to irritation of eyes and even lung's congestion.
- Long- term exposure to high levels of nitrogen di oxygen can cause chronic disease.
- Formation of photochemical smog, which limits in visibility of road.
- Causes acid rain – NO_2 and N_2O_5 reacts with H_2O and O_3 to form HNO_3 .

Control:

- **Oxides of nitrogen & carbon monoxide** can be controlled by passing these gases through a catalyst converter containing **Pt-Rh** catalyst, which coverts these toxic gases to non-toxic nitrogen and carbon dioxide.



- Treatment of flue gas by injecting into NH_3 , powdered limestone or aluminum dioxide.
- Selective catalytic reduction at $300\text{--}400^\circ\text{C}$ by vanadium oxide or tungsten oxide as a catalyst.



7b.

BIO-MEDICAL WASTE:

Source: Biomedical waste is generated from hospitals, clinics, blood banks, animal house, animal research, labs, & veterinary institutions.

Characteristics:

- **BMW may be contaminated with pathogenic microbes, radioactive substance, heavy metals.**

-They can cause air pollution.

-The pathogens present in the waste can leach out & contaminate the ground water or surface water and cause water pollution.

-Land pollution is caused by final disposal of all BMW.

Disposal methods:

Generation → **segregation (packing in colour code polybags)** → **common storage point** → **transportation** → **incineration** → **disposal, recycling & landfill**

Incineration: This method involves burning of solid waste at high temperatures until the wastes are turned into ashes. But plastics cannot be burnt in this method.

Autoclave: Autoclaves are closed chamber that apply heat and pressure, sometimes steam over a period of time to sterilize (kill harmful bacteria, viruses, fungi etc) medical equipments.

Recycling: Recycling of resources.

7c.

Scale and Sludge formation: Water is heated under high pressure and temperatures inside the boilers which make the water to get evaporated in the form of steam.

As the boiling point of water is much less than that of many impurities, the impurities in water get concentrated inside the boiler. On reaching saturation point, impurities get precipitated out.

If the precipitates formed within the boiler are soft, loose and slimy, are called **sludges**. Whereas, if the precipitate is hard and strongly adhering on the inner walls of the boiler, it is known as **scale**.

SCALE: The hard deposits adhered to the inner surface of boilers which are difficult to remove is called scale. Scales are formed due to salts like $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 and silica which has low solubility.

1. Magnesium salts get hydrolysed at high temperature forming, a soft scale magnesium hydroxide precipitate.



2. Calcium bicarbonate on heating, produces calcium carbonate which has low solubility.



3. Solubility of CaSO_4 decreases with increase in boiler temperature. Thus get precipitated in the form of scale.

4. SiO_2 reacts with calcium and magnesium present in water to form silicates of Ca & Mg. These silicate form hard and glassy scale on inner surface of the boilers.

Problems caused by scale formation:

1. **Wastage of fuel.**-Scale is a bad conductor of heat. This leads to reduced rate of heat transfer from boiler to water and thereby leads to wastage of fuel.

2. **Cleaning expenses** - Scales must be removed regularly and this cleaning process is very much expensive.

3. **Boiler explosion.**-A coating is formed by scales on the inner surface of the boiler. On heating, metal gets heated faster than scale as metal is a very good conductor of heat resulting in expansion of metal. This results in cracking of scales and water inside the boiler percolates through cracks to reach hot metal and immediately becomes steam. Thus, there is a sudden increase in pressure on boilers walls which may be cracked and exploded.

4. **Decrease in efficiency**-Excessive scaling and sludge will cause clogging of boiler tubes. This choke them partially and thus reduce the efficiency of boiler.

Methods of removing scales

1. Using scraper or wire brush

2. By giving thermal shocks(heating the boiler and sudden cooling)

3. Chemical treatment (calcium carbonate scales can be removed with 5-10% HCl, calcium sulphate scales can be removed using EDTA)

SLUDGE: The loose collection of suspended solids in the cooler, less turbulent parts of the boiler and in the distribution pipes is called sludge. The major impurities which have more solubility in hot water than in cold water, form sludge. Example: CaCl_2 , MgSO_4 , MgCl_2 , MgCO_3

8a.

BOD: The amount of oxygen required for the oxidation of biologically oxidizable compounds (impurities) present in 1 liter of waste water over a period of five days at 20°C .

COD: It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds (impurities) present in 1 liter of waste water using strong oxidizing agent $\text{K}_2\text{Cr}_2\text{O}_7$.

$$V = 25 \text{ cm}^3 \quad (x-y) = 10.5 \text{ cm}^3 \quad N_{\text{K}_2\text{Cr}_2\text{O}_7} = 0.02 \text{ N}$$

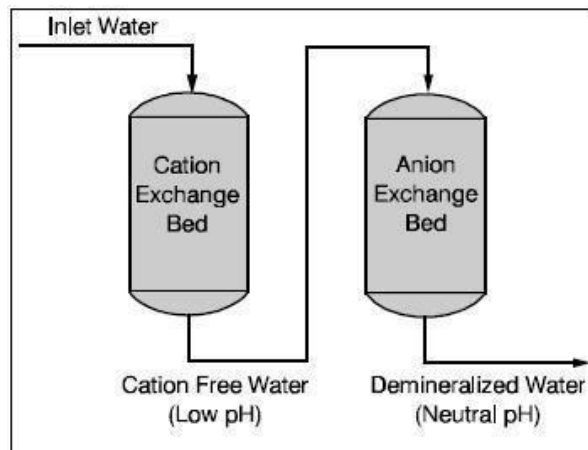
$$\begin{aligned}
 \therefore \text{COD value} &= \frac{8 \times (X - Y) \times (N) \text{FAS} \times 1000}{(V) \text{waste water}} \\
 &= \frac{8 \times 10.5 \times 0.02 \times 1000}{25} \\
 &= 67.5 \text{ mg of O}_2 \text{ / ltr}
 \end{aligned}$$

8b.

SOFTENING OF WATER BY ION EXCHANGE PROCESS:

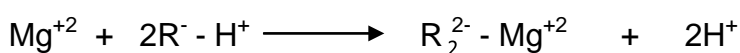
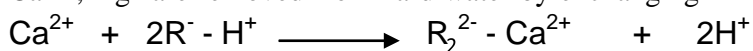
The process of removal of Ca, Mg, Fe salts and other metallic ions from water is called softening of water.

- Softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin.
- Ion exchange resins are high molecular weight, cross linked polymers with a porous structure.
- The functional groups which are attached to the chains are responsible for ion exchange properties.
 - **Cation exchange resins:** The resins containing acidic groups which are capable of exchanging H^+ ions for cations (Ca^{+2} or Mg^{+2}) present in water.
 - **Anion exchange resins:** The resins containing basic groups which are capable of exchanging OH^- ions for anions (Cl^- , SO_4^{2-} , HCO_3^-) present in water.

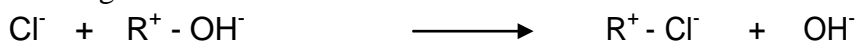


Process

◆ In this process, cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{+2} , Mg^{+2} are removed from hard water by exchanging H^+ ions as follows.



◆ Hard water is then passed through anion exchange resin where anions like Cl^- , SO_4^{2-} are exchanged with OH^- ions as follows.



The H^+ and OH^- ions released combine to form water molecule.

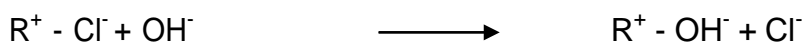
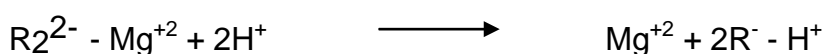
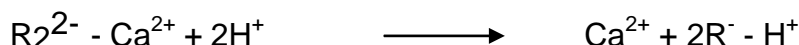
◆ Thus water coming out of two resin is free from metallic ions and called as ion exchanged water.

Regeneration:

When the resins lose their capacity to exchange ions, they should be regenerated. The process of regeneration is the reversal of the reaction taking place for ion exchange.

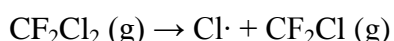
Cation exchange resin is regenerated by passing a solution of dil HCl or H_2SO_4 .

Anion exchange resin is regenerated by passing a solution of NH_4OH or NaOH respectively.

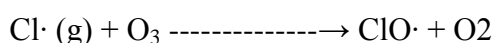


8c. (i) Depletion of Ozone layer:

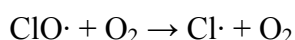
- A combination of low temperatures, elevated chlorine and bromine concentrations in the upper atmosphere are responsible for the gradual thinning of ozone layer.
- Ozone depleting substances include chlorofluorocarbons (CFC's) and volatile organic compounds (VOC's). CFC's or freons used as coolants in refrigeration and air conditioning are very stable on earth and slowly drift into stratosphere.
- They react with UV radiation to form chlorine free radical which is a potential ozone depleting species.



The chlorine free radicals then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.



Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

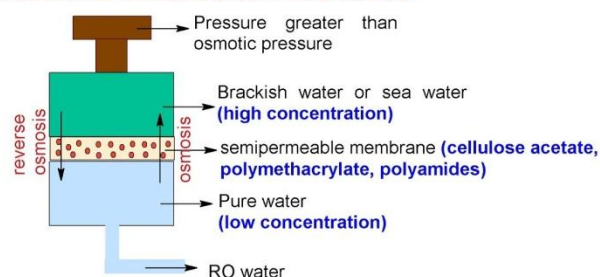


The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFC'S are transporting radicals into the stratosphere and damaging the ozone layer.

(ii) The process of removal of dissolved salts present in water is called desalination. This can be achieved by reverse osmosis method.

Reverse osmosis (R.O): Osmosis is a natural phenomenon in which solvent (water) molecules move from dilute solution to concentrated solution through a semi-permeable membrane. The minimum pressure which has to be applied on membrane to prevent osmosis is called osmotic pressure. In reverse osmosis, the water molecules are made to move in reverse direction that is from concentrated solution to dilute solution through a semi-permeable membrane by applying pressure greater than osmotic pressure. RO is used to convert sea water into potable water.

REVERSE OSMOSIS PROCESS



R.O unit consists of vessel, a semipermeable membrane made up of cellulose acetate and high pressure pump. When the salt water supplied with high pressure, water flow from salt water to fresh water. Fresh water is collect from fresh water outlet and salt water is discharged in to the environment.

9a.

Colorimetry: This method is used for solutions which are themselves coloured or which gives colour with a suitable reagent. The colour Intensity is directly proportional to the concentration of the solution.

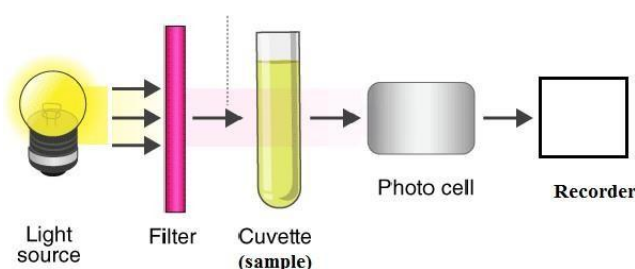
Theory: Beer's law states that the amount of light absorbed by a solution is proportional to the concentration of the solution. Lambert law states that the amount of light absorbed by a solution is proportional to the path length of the medium.

According to Beer-Lambert's law, when monochromatic light is passed through a solution, part of the light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and the path length of the light through the solution.

$$A = \epsilon C t$$

Instrumentation: Colorimeter made up of the following components.

- Tungsten lamp as the light source.
- A filter which provides the desired wavelength.
- A sample cell.
- A photocell detector.



Monochromatic light of suitable wavelength is allowed to fall on the sample cell. First, a blank solution is taken in the sample cell and placed in the path of light beam and its absorbance is adjusted to zero. Then the analyte solution is placed in the path of light and its absorbance is measured. A plot of absorbance versus standard concentrations of analyte is used to find the unknown concentration of analyte in the samples.

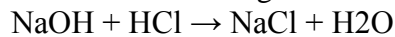
Applications:

- It is widely used in clinical laboratories for the analysis of glucose, creatine, urea etc.
- In soil testing laboratories for the analysis of pesticides, soil nutrients and plant nutrients.

9b.

1. Strong acid with strong base (HCl vs NaOH)

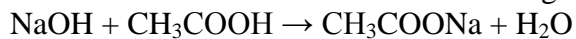
Consider the titration of strong acid HCl with a strong base NaOH.



On addition of NaOH, the conductance of the acid solution decreases gradually until the acid is completely neutralized. The conductance decreases, because the small and highly mobile H^+ ions in the acid is gradually replaced by heavier and less mobile Na^+ ions. Addition of base beyond the neutralization point leads to increase in the number of highly mobile OH^- ions and conductance increases sharply. A graph is plotted with conductance against the volume of NaOH. The point of intersection of two lines is the neutralization point.

2. Weak acid with strong base. (CH_3COOH vs NaOH)

Consider the titration of acetic acid with a strong base NaOH.



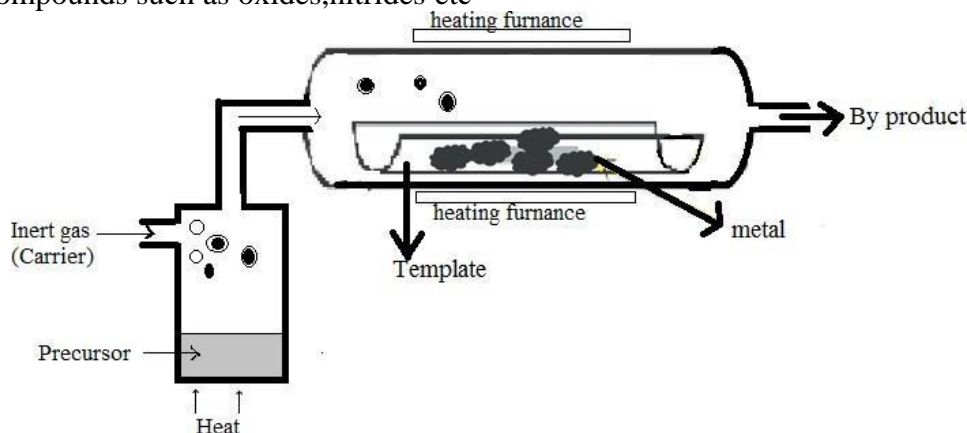
On addition of NaOH, the conductance of the weak acid solution increases until the acid is completely neutralized. This is because partially dissociating weak acid get converted to fully dissociating salt (sodium acetate). Addition of base

beyond the neutralization point leads to increase in the number of highly mobile OH^- ions and conductance increases sharply. A graph is plotted with conductance against the volume of NaOH. The point of intersection of two lines is the neutralization point.

9c.

CHEMICAL VAPOUR DEPOSITION:

- In CVD process, nanoparticles are synthesized from the gaseous phase by a chemical reaction or decomposition of precursors at high temperature.
- In this method precursor is vaporized and mixed with inert carrier gas like N_2 and mixture fed in to a reactor.
- Reactor is maintained at high temperature required for the reaction
- Precursors undergo reaction, producing a product which is deposited over the substrate.
- The by-products and leftovers from reactions are easily removed from the reaction chamber.
- Reaction is catalyzed by the catalyst present on the substrate.
- Precursors should be highly pure, stable at room temperature with sufficient volatility.
- Commonly used precursors are halides, carbonyls, hydrides of metal.
- In this method it is possible to produce almost any metal and nonmetallic material as well compounds such as oxides, nitrides etc



10 a. Nano material refers to a material with at least one of its dimension (length, width or breadth) in nano scale. i.e 10⁻⁹m. And the size varies from 1-100nm. A nanometer is one billionth of a meter- approximately 100,000 times smaller than the diameter of a human hair.

SOL-GEL PROCESS

- In sol-gel process, either metal salt or alkoxide is used as precursor (starting material).
- It is mainly used in the synthesis of uniform nanoparticles of metal oxides.

Steps involved in synthesis

- Preparation of Sol.
- Conversion of Sol to Gel.
- Aging of Gel.
- Drying of the Gel (evaporation)
- Heating at high temperature (calcination)

Step 1: Sol is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)

Step 2: Sol is further converted into a gel by hydrolysis and condensation of precursors (adding acid or base as catalyst) Hydrolysis of alkoxides



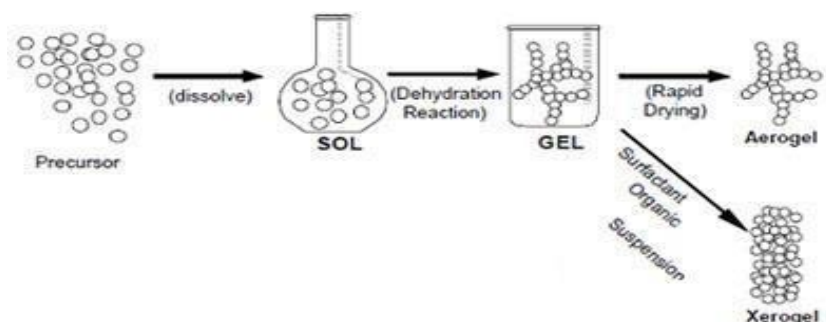
Condensation of hydrolysed species with each other (releases water)



Step 3: Aging (keeping for a known period of time) of colloid solutions takes place, i.e colloids can increase their particle size and grows into a sol-gel.

Step 4: Then the gel is dried by evaporation (solvent get evaporated)

Step 5: Calcinated (heating to high temperature) to produce nanoparticles.



10 b.

Fullerenes are class of molecules made of only carbon atoms having closed cage like structure. Many number of fullerene molecules with different carbon atoms like C₆₀, C₇₀, C₇₄, C₇₈ etc., have been prepared. C₆₀ is the smallest, stable and abundant fullerene, obtained by usual preparation methods. C₆₀ has spherical shape and resembles a football and commonly known as Bucky ball. Fullerenes are made up of pentagons and hexagons. Pentagons gives curvature required to form closed structure. All fullerenes contain 12 pentagons and different numbers of hexagons. Each fullerene has 2(10+M) number of carbon atoms corresponding to 12 pentagons and M number of hexagons.

Applications:

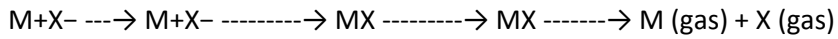
- Single C₆₀ molecule theoretically can take up maximum of 60 hydrogen atoms.
Application- Hydrogen storage material for fuel cells Electrode material in secondary batteries. Ex- Nickel Metal Hydride battery.
- Each C₆₀ molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

- Application- Used as optical limiters. Optical limiters are used to protect materials from damage, by intense incident light radiation.

10c.

Theory: When the sample solution is aspirated into the flame, the solvent gets evaporated leaving behind the salt in the flame. The salt then turns into vapours of the metal, which dissociate to form atoms.

Evaporation vaporization dissociation



Solution Mist

solid

gas

↓ Absorption of heat

M' (gas)

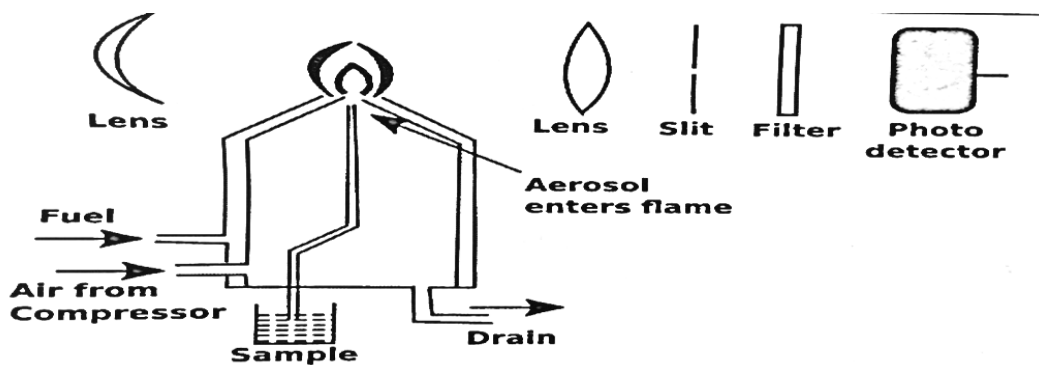
↓ Flame emission

M (gas)

When monochromatic light of specific resonance wavelength is passed through the flame containing atoms, then part of light will be absorbed. The extent of absorption is proportional to the number of metal atoms in the flame or the concentration of the solution (Beer-Lamberts law).

$A = \epsilon Ct$ Thus, from absorbance (A) value concentration (C) can be determined

Instrumentation: Atomic absorption spectrometer includes the following components.



1. Nebuliser: It creates a fine spray of the sample for introduction into the flame.
2. Atomiser (burner): Here the sample is burnt in the flame produced by fuel and oxidant combination. Solvent evaporates leaving behind a residue of neutral atoms.
3. Fuel and oxidant: They form an important part of the process. If the heat produced is not sufficient then the sample doesn't form neutral atoms. If the heat of burner is more, the sample molecules may ionize instead of forming atoms. Hence a proper combination of fuels and oxidant are to be used to produce recommended temperatures. Commonly used fuels are propane, hydrogen and acetylene and oxidant used is mostly air or oxygen.
4. Hollow cathode lamp: is mostly used as light source. The cathode of the lamp is coated with the metal of

the analyte to be analysed.

5. Monochromator and Detector: Monochromator separates the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by the detector.

6. Recorder: records the intensity of the absorbed light.

A plot of absorbance versus standard concentration of analyte can be used to find the unknown concentration of analyte.

Applications:

- It is widely used for the determination of even trace amount of metals in solution.
- To estimate lead in petroleum products.

CBCS SCHEME

21CHE12

JSN

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First Semester B.E./B.Tech. Degree Examination, Feb./Mar. 2022 Engineering Chemistry

Time: 3 hrs.

Max. Marks: 100

Note: Answer any FIVE full questions, choosing ONE full question from each module.

Module-1

- 1 a. What are Reference Electrodes? Explain the construction and working of Calomel Electrode. (07 Marks)
- b. Define Single Electrode Potential. Derive Nernst equation for Single Electrode Potential. (07 Marks)
- c. Explain the construction and working of Li-ion battery. Mention its applications. (06 Marks)

OR

- 2 a. Explain Primary, Secondary and Reserve batteries with an example. (06 Marks)
- b. Explain the experimental determination of pH by using glass electrode. (07 Marks)
- c. A cell consists of Copper rod dipped in 5M CuSO_4 solution and Iron rod dipped in 0.05 M FeSO_4 solution. Given $E_{\text{Cu}}^0 = +0.34\text{V}$ and $E_{\text{Fe}}^0 = -0.44\text{V}$. Write Cell representation, Cell reactions and calculate Emf of the cell. (07 Marks)

Module-2

- 3 a. Define Corrosion. Describe Electrochemical theory of corrosion by taking Iron as an example. (07 Marks)
- b. What is Cathodic Protection? Explain Sacrificial Anodic method and Impressed Current method of Cathodic protection. (07 Marks)
- c. What is Metal Finishing? Mention technological importance of Metal Finishing. (06 Marks)

OR

- 4 a. Explain the factors affecting the corrosion rate :
 - i) Ratio of anodic to cathodic areas.
 - ii) Nature of the corrosion product.
 - iii) pH.(06 Marks)
- b. What is Corrosion Penetration Rate? A piece of corroded plate was found in the submerged ocean vessel. It was estimated that the original area of the plate was 10 inch^2 and that approximately 2.6kg had corroded away during the submersion for a period of 10 years. Calculate Corrosion Penetration Rate (CPR) in terms of mpy and mmy. Given density (ρ) of iron = 7.9 g/dm^3
mpy $\rightarrow k = 534$
mmy $\rightarrow k = 87.6$. (07 Marks)
- c. What is Electroless Plating? Write the differences between Electroplating and Electroless plating. (07 Marks)

Module-3

- 5 a. What are Conducting Polymers? Explain the mechanism of conduction in Polyaniline. (07 Marks)
- b. Explain the synthesis, properties and applications of Poly Lactic Acid. (06 Marks)
- c. What are Nanomaterials? Explain the synthesis of Nanomaterials by Sol-gel process. (07 Marks)

OR

- 6 a. What are Polymer Composites? Explain the synthesis and applications of Kevlar fibre. (07 Marks)
 b. Explain any two size dependent properties of Nanomaterials. (06 Marks)
 c. Write a note on Fullerene and mention its applications. (07 Marks)

Module-4

- 7 a. What is Green Chemistry? Explain briefly any six basic principles of Green Chemistry. (07 Marks)
 b. Describe the production of hydrogen by Photocatalytic Water Splitting Method. (06 Marks)
 c. Explain the synthesis of Paracetamol by Conventional and Green Route Method. (07 Marks)

OR

- 8 a. Explain the impacts of Oxides of Nitrogen (NO_x) and Oxides of Sulfur (SO_x) on the Environment. (06 Marks)
 b. Explain the working of Photovoltaic cell, with a neat diagram. (07 Marks)
 c. Describe working of Methyl alcohol – Oxygen fuel cell [$\text{CH}_3\text{OH} - \text{O}_2$] with a neat diagram. Mention its applications. (07 Marks)

Module-5

- 9 a. Explain Theory, Instrumentation and Applications of Colorimeter. (07 Marks)
 b. Explain the principle of Volumetric analysis and requirement of Volumetric analysis. (06 Marks)
 c. Define Biological Oxygen demand and Chemical Oxygen demand. (3)
 25 ml of waste water required 18.0ml and 25.2ml of 0.1N FAS solution for sample and blank titration respectively. Calculate COD of the waste water sample. (07 Marks)

OR

- 10 a. Explain applications of Conductometry :
 i) Strong acid Vs Strong base. ii) Weak acid Vs Strong base. (07 Marks)
 b. Define the following units of Standard Solution :
 i) Normality ii) Molarity iii) PPM. (06 Marks)
 c. 25m^3 of hard water sample titrated against 0.01M EDTA solutions consumed 18.0 cm^3 of EDTA solution. 25cm^3 same sample of hard water was boiled, filtered and titrated against 0.01M EDTA solution consumed 12.0 cm^3 EDTA solution. Calculate Total, Permanent and Temporary hardness of the water sample. (07 Marks)

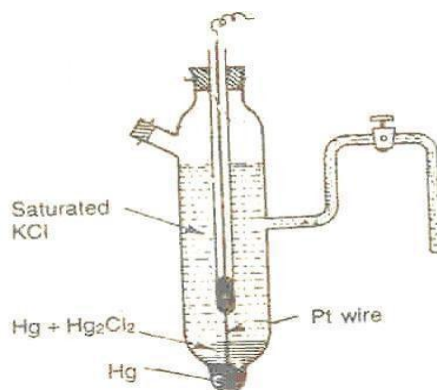
Answers for the VTU question paper Feb/Mar 2022

Module 1

1.a. Reference electrodes are the electrodes whose potential is known and with reference to those, the electrode potential of any other electrode can be measured.

Construction and working of calomel electrode

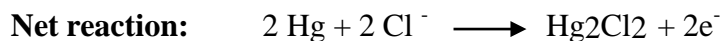
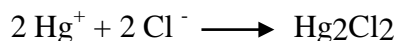
- Calomel electrode is a **Metal-metal salt electrode**
- A Metal-metal salt electrode consists of Mercury, Mercurous Chloride and a solution of KCl.
- Mercury is placed at the bottom of a glass tube.
- A paste of Mercury and Mercurous Chloride (calomel) is placed above the Mercury. The space above the paste is filled with a KCl solution of known concentration.
- A platinum wire is kept immersed into the mercury to obtain external electrical contact.
- It is internally connected through salt bridge.



Calomel electrode can be represented as ,



The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.



1.b. Nernst equation for single electrode potential:

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature.

Consider a reversible electrode reaction,



Equilibrium constant for the above reaction is,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[M]}{[M^{n+}]} \dots\dots\dots (1)$$

According to thermodynamics, for a reversible process, equilibrium constant (K) is related to decrease in change in free energy (- ΔG) as, by Vant Hoff equation.

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots(2)$$

Where, ΔG⁰ = Standard change in free energy

R = Universal gas constant

T = Temperature

Substituting 1 in 2

we have,

$$\Delta G = \Delta G^0 + RT \ln \frac{[M]}{[M^{n+}]} \dots\dots(3)$$

The decrease free energy (-ΔG) for any reversible process is equal to the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\max} \dots\dots\dots(4)$$

In case of a Galvanic cell, W_{\max} = Electrical energy supplied by the cell

$$= [(\text{difference in potential between two electrodes}) \times (\text{total charge flowing through the cell})]$$

If 'n' moles of electrons are flowing from anode to cathode, then the total quantity of charges flowing through the cell is 'n' Faradays (nF).

$$\therefore W_{\max} = E_{\text{cell}} \times nF = nFE \dots\dots\dots(5)$$

By comparing equation 4 and 5,

$$-\Delta G = nFE \dots\dots\dots(6) \text{ or } \Delta G = -nFE$$

Under standard conditions,

$$-\Delta G^\circ = nFE^\circ \text{ (7) or } \Delta G^\circ = -nFE$$

Substituting the values equation (6) and (7) in equation (3)

$$-nFE = -nFE^\circ + RT \ln K_c \text{ (8)}$$

Dividing throughout by $-nF$,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \text{ (9)}$$

$$E = E^\circ - 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \left\{ \frac{2.303RT}{nF} [M] - \frac{2.303RT}{nF} \log [M^{n+}] \right\}$$

In case of metal-metal ion electrode, as 'M' is solid metal, $[M] = 1$

$$\therefore E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

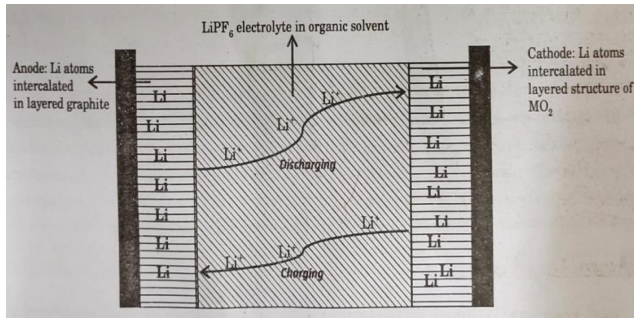
(R is a gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; T = temperature in absolute scale (298K);

F is Faraday = $96,500 \text{ C mol}^{-1}$)

$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \quad \text{at 298 K}$
--

1.c. Lithium-ion battery

Construction:



Anode-Lithium intercalated graphite.

Cathode – Lithium metal oxide such as (LiCoO₂).

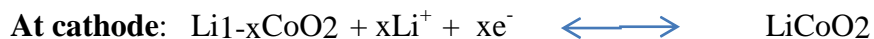
Electrolyte -A solution of lithium salt (LiPF₆) in organic solvent.

Separator- non-woven **polypropylene**.

Representation: *Li, C / LiPF₆, in organic solvent / LiCoO₂*

- It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers.
- Lithium ions move between anode and cathode during discharging and charging process. Since Both anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.

Working



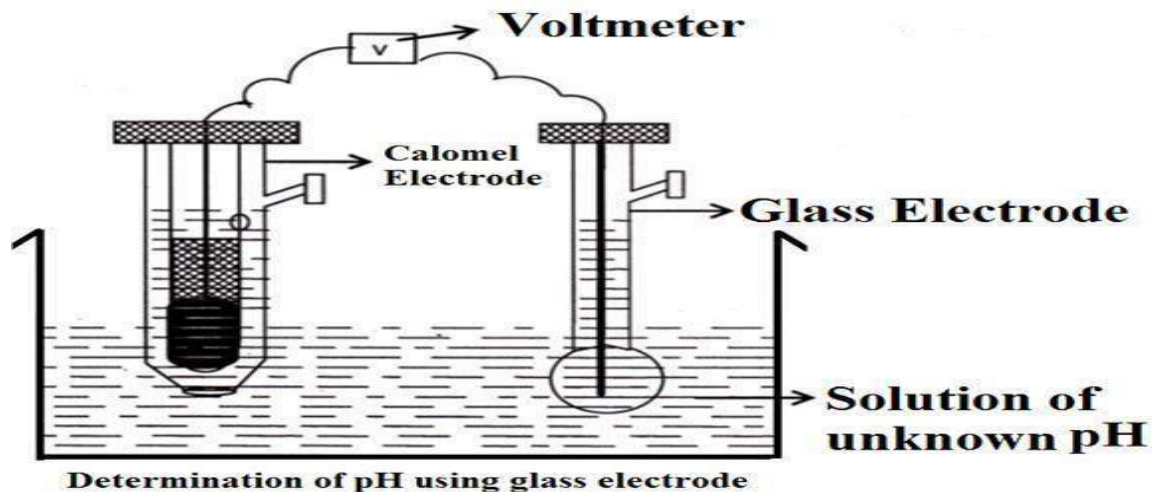
Applications: Portable electronics, mobile phones, laptop, ipod etc.

2.a.

- a) **Primary Batteries:** A battery which cannot be recharged(because the cell reactions are irreversible)
e.g. Zn-MnO₂, Zn –Air , dry cell.

- b) **Secondary Battery:** A battery which can be recharged (as the cell reactions are reversible) and also known as storage battery. e.g. Lead-acid battery, Li-ion battery
- c) **Reserve battery:** In this battery, one of the components is stored separately and used whenever required. e.g. Mg-AgCl battery where battery is activated by the addition of water. It is used in missiles and military weapon system.

2.b. Determination of pH using glass electrode:



- For pH determination Glass electrode is immersed in the solution whose pH is to be determined and it is combined with a reference electrode such as a calomel electrode (saturated) through a salt bridge.
- The cell assembly is represented as, $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^- || \text{Solution of unknown pH} | \text{glass} | 0.1\text{M HCl} | \text{Ag}^+ | \text{AgCl}$

Step 1:

The emf of the above cell, E_{cell} is measured using an electronic **voltmeter** or **pH meter**.

The emf of the cell is given by:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{cal}}$$

Since E_{cal} , E_{cell} is known, so E_{glass} can be evaluated.

The potential of glass electrode E_G is given by, $E_G = L^1 - 0.0591\text{pH}$

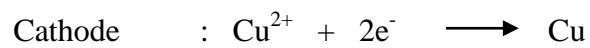
$$E_{\text{cell}} = E_G - E_{\text{cal}}, \quad E_{\text{cell}} = L' - 0.0591 \text{pH} - E_{\text{cal}}$$

$$\text{pH} = \frac{L' - E_{\text{cell}} - E_{\text{cal}}}{0.0591}$$

2.c. Solution :

Cell representation : $\text{Fe} \mid \text{Fe}^{2+}_{(0.05\text{M})} \parallel \text{Cu}^{2+}_{(5\text{M})} \mid \text{Cu}$

Cell reaction :



$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]}$$

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Fe}^{2+}/\text{Fe}}^0 \\ &= 0.34 - (-0.44) \end{aligned}$$

$$E_{\text{cell}}^0 = 0.78\text{V}$$

$$\begin{aligned} E_{\text{cell}} &= 0.78 + \frac{0.0591}{2} \log \frac{[5]}{[0.05]} \\ &= 0.78 + 0.0295 \log 10 \end{aligned}$$

$$E_{\text{cell}} = 0.78 + 0.0295 \times 1$$

$$E_{\text{cell}} = 0.8095 \text{ V}$$

Module 2

3.a. Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

Electrochemical Theory Of Corrosion: According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur.

A large number of tiny galvanic cells with anodic and cathodic regions are formed.

- Oxidation of metal takes place at the anodic region. e.g. $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
- The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.
- The electrons travel through the metal from the anodic region to cathodic region.

Reactions:

Reaction at anodic region: As mentioned above, oxidation of metal takes place at anode.

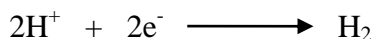


Reactions at cathodic region: At cathode, the reaction is either

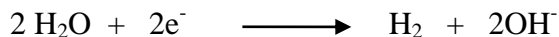
a) Liberation of hydrogen or b) absorption of oxygen.

A) **Liberation of hydrogen** (In the Absence of Oxygen)

In acidic medium the reaction is :

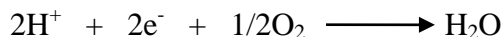


In neutral/alkaline medium, the reaction is:

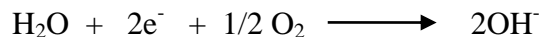


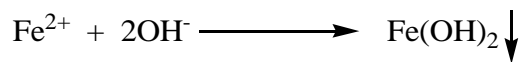
B) **Absorption of oxygen** (In the Presence Of Oxygen)

In acidic medium, the reaction is:



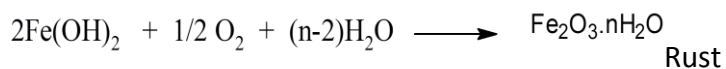
In neutral/alkaline medium, the reaction is :



Overall Reaction:

Ferrous hydroxide

Since the layer of rust formed is highly porous, oxygen and moisture from the environment pierce deeper and increase the rate of corrosion.

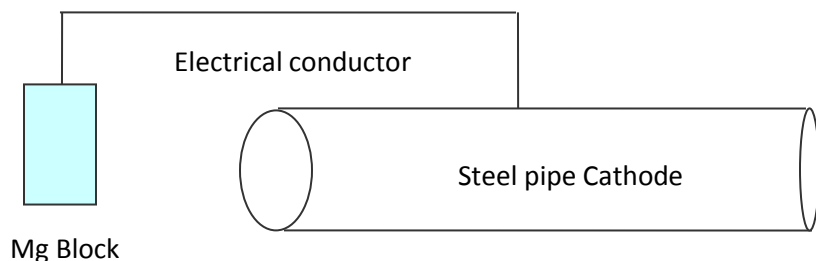


3.b. The process where metal to be protected is made cathode, by supplying electrons from an external source is called as cathodic protection.

There are two methods of cathodic protection

- a) Sacrificial anode method:
- b) Impressed current method

Sacrificial anode method:



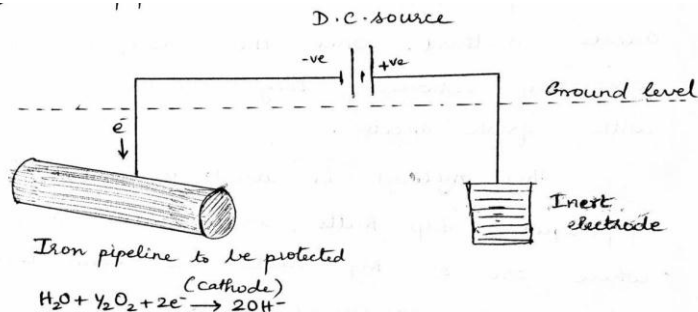
- In sacrificial anode method, the metal to be protected is connected to a more active metal.
- For example, when steel pipe is to be protected, it may be connected to a block of Mg or Zn. In such a situation, Mg or Zn act as anode and provide electrons to the steel pipe. Steel pipe acts as cathode and is unaffected. Here Mg or Zn which is anode undergoes sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

Other examples: Mg bars are fixed to the sides of ships to act as sacrificial anode.

Mg blocks are connected to buried pipe lines.

Impressed current method (impressed voltage method)

- In impressed current method, the electrons are supplied from the source of direct current. The metal to be protected made negative by connecting to the negative terminal of an external d.c. power supply.
- The positive terminal is connected to an inert electrode such as graphite.
- Potential greater than potential of anodic reaction is applied in the reverse direction to prevent anodic reaction.
- Under these conditions, the metal acts as cathode and hence does not undergo corrosion. The inert electrode acts as anode and it also does not undergo corrosion because it is inert.



3.c. Metal finishing is the process of surface modification of a metal by deposition of a layer of metal or by converting the surface layer metal into its oxide film.

ELECTROPLATING and ELECTROLESS PLATING are two important techniques of metal finishing.

Technological importance of metal finishing: Metal finishing is carried out to obtain technologically important surface properties. These properties are:

- A decorative appearance.
- An improved corrosion resistance.
- An improved heat resistance.
- Improved surface hardness. (An improved resistance to wear and tear, Abrasion.)
- Improved solder ability.
- Good thermal conductivity, electrical conductivity.
- Good optical reflectivity.

4 a. (i) Ratio of Anodic to cathodic areas:

Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. When cathodic area is large, demand for electrons for reduction reaction is high. To meet this demand oxidation reaction occurs more intensely at anodic area.

For example, a broken coating of tin on iron surface, results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.

A broken coating of zinc on iron surface, results in less corrosion at the broken region. Iron is cathodic to zinc. Exposed region of iron acts as cathode with small area. Zinc acts as anode which has large area.

(ii) Nature of corrosion product:

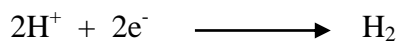
- If the corrosion product is insoluble, stable and non-porous, then it acts as a protective film which prevents further corrosion.
- The film acts as a barrier between metal surface and the corrosive environment.
- On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

Example: Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of Cr_2O_3 on the surface.

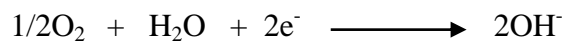
(iii) pH

The rate of corrosion increases with decrease in pH.

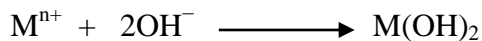
In acidic medium, rate of corrosion depends upon the rate of evolution of hydrogen at cathode area. When $\text{pH} < 4$, rate of corrosion increases due to higher concentration of H^+ ions



If the pH is in between 4-10, the rate of corrosion depends upon the availability of O_2 on the cathodic area for reduction.



If $\text{pH} > 10$, then the rate of corrosion is less (practically ceases) due to formation of insoluble metal hydroxide on the surface of metal.



4.b. To calculate CPR in mm/yr

	Given	CPR mm/yr
K		87.6
W	2.6 Kg	$2.6 \times 1000 \times 1000 \text{ mg}$
ρ	7.9 g/cm^3	7.9 g/cm^3
A	10 inch^2	$10 \times 2.54 \times 2.54 \text{ cm}^2$
t	10 years	$10 \times 365 \times 24 \text{ hrs}$

$$\text{CPR} = \frac{KW}{\rho X A t}$$

$$\text{CPR} = \frac{87.6 \times 2.6 \times 1000 \times 1000 \text{ mg}}{7.9 \text{ g/cm}^3 \times 10 \times 2.54 \times 2.54 \text{ cm}^2 \times 10 \times 365 \times 24}$$

$$\text{CPR} = 5.101 \text{ mm/yr}$$

To calculate CPR in mpy

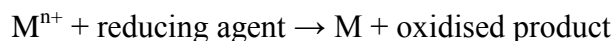
	Given	CPR in mpy
K		534
W	2.6 Kg	2.6x1000x1000 mg
ρ	7.9 g/cm ³	7.9 g/cm ³
A	10 inch ²	10 inch ²
t	10 years	10x365x24 hrs

$$\text{CPR} = \frac{KW}{\rho X A X t}$$

$$\text{CPR} = \frac{534 \times 2.6 \times 1000 \times 1000 \text{ mg}}{7.8 \text{ g/cm}^3 \times 10 \text{ inch}^2 \times 10 \times 365 \times 24}$$

$$\text{CPR} = 213.19 \text{ mpy}$$

4.c. Electroless plating is the deposition of a thin layer of metal on a catalytically active surface from its salt solution in presence of a suitable reducing agent without using electric current. When the catalytically active surface is dipped in the bath, the reducing agent reduces metal ions to metal atoms, which gets deposited on the surface and the reducing agent itself gets oxidised.



	Electroplating	Electroless plating
1	Requires electrical power source	Does not require electrical power source
2	Oxidation takes place at anode and reduction at cathode.	Both oxidation and reduction takes place at catalytically activated surface
3	Applicable only to conductors	Applicable for conductors, semiconductors and insulators
4	Not economical	Most economical
5	Give less uniform deposit on irregular shaped articles	Give more uniform coating on irregular shaped articles (due to better throwing power)
6	Holes cannot be plated	Holes can be plated
7	Does not require reducing agent	Requires reducing agent

Module 3

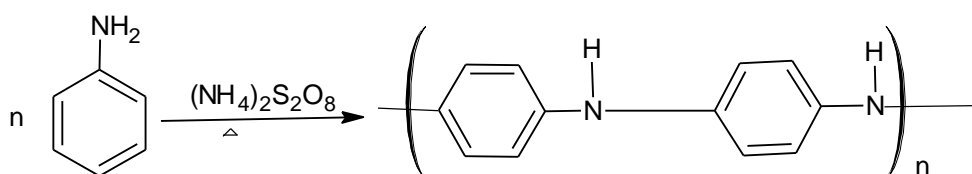
5a. Organic polymers having electrical conductivity in the order of a conductor are called as conducting polymers. They are also called as synthetic metals. Conducting polymers are generally produced by doping an oxidizing or a reducing agent into an organic polymer with conjugated back bone consisting of pi-electron system.

Examples: Conjugated polymers such as polypyrrole, polythiophene, polyaniline,

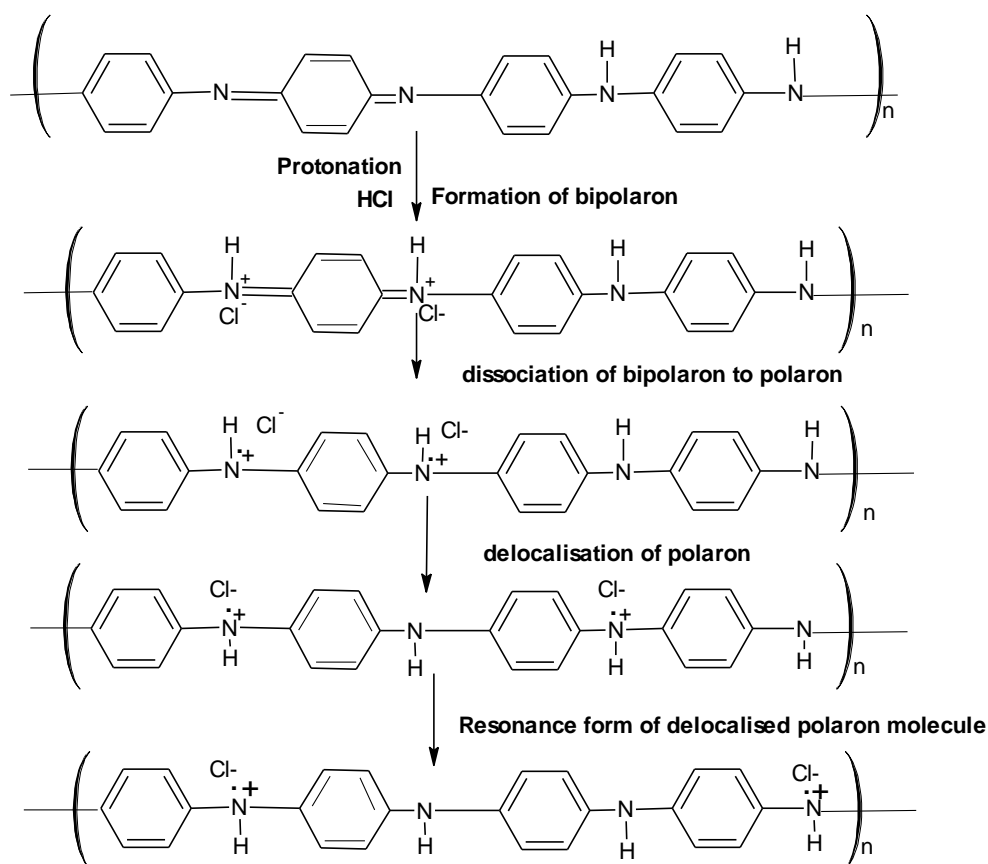
Mechanism of conduction in Polyaniline:

Polyaniline is obtained by the polymerisation of aniline dissolved in 1M HCl at 3-4°C in the presence of ammonium persulphate as an initiator.

General Reaction:



Mechanism:

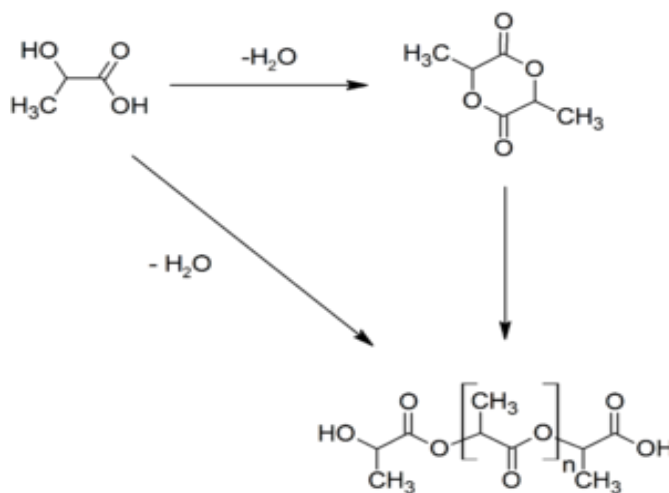


Applications:

1. One of the important applications of conducting aniline is its use as an electrode material for **rechargeable batteries**.
2. Polyaniline has also attracted considerable attention as an electrochemical transducer for **biosensors** which are used in clinical technology.
3. Polyaniline shows **electrochromic properties** which can be used to produce **smart windows** that absorb sunlight and control solar energy.

5.b. It is also known as poly(lactic acid) or polylactide (abbreviation PLA) is a thermoplastic polyester with backbone formula $(C_3H_4O_2)_n$, formally, obtained by condensation of lactic acid $C(CH_3)(OH)COOH$ with loss of water. It can also be prepared by ring-opening polymerization of lactide $[C(CH_3)HC(=O)O-]_2$, the cyclic dimer of the basic repeating unit.

PLA has become a popular material due to it being economically produced from renewable resources. But its widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in 3D printing.



Properties

- PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer
- Heat-resistant PLA can withstand temperatures of 110 °C.
- The high surface energy of PLA results in good printability, making it widely used in 3D printing
- PLA is soluble in a range of organic solvents

Applications of bio degradable polymer

Biodegradable polymers have been used with diverse applications such as:

- surgical sutures
- wound dressings
- enzyme immobilization
- controlled drug delivery and gene delivery

5c. nano material refers to a material with at least one of its dimension (length, width or breadth) in nano scale.i.e 10^{-9} m.

SOL-GEL PROCESS

- In sol-gel process, either **metal salt or alkoxide** is used as precursor (starting material).
- It is mainly used in the synthesis of uniform nanoparticles of **metal oxides**.

Steps involved in synthesis:

1. Preparation of Sol

2. Conversion of Sol to Gel.

3. Aging of Gel.

4. Drying of the Gel (evaporation)

5. Heating at high temperature (calcination)

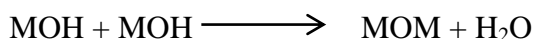
Step 1: Sol is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)

Step 2: Sol is further converted into a gel by hydrolysis and condensation of precursors.(adding acid or base as catalyst)

Hydrolysis of alkoxides



Condensation of hydrolysed species with each other (releases water)



Step 3: Aging (keeping for a known period of time) of colloid solutions takes place, i.e colloids can increase their particle size and grows into a sol-gel.

Step 4: Then the gel is dried by evaporation (solvent get evaporated)

Step 5: Calcinated (heating to high temperature) to produce nanoparticles.

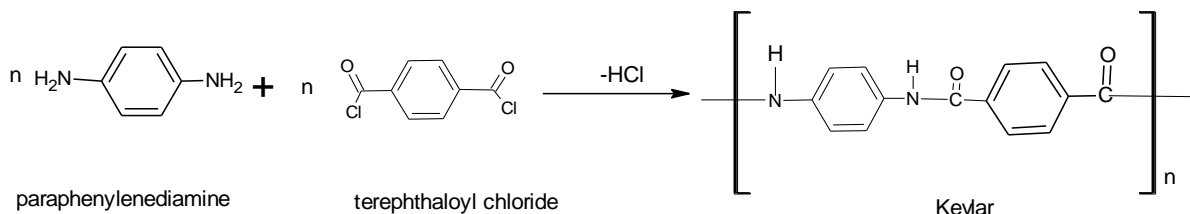
The particle size depends on concentration of precursor, rate of hydrolysis and condensation reactions and aging time. The nano particles obtained by this process have a size ranging from 1-100nm

6a.

A composite is a multiphase material made by the combination of two or more materials that exhibit specific properties. If any one of these material is polymer then it is known as polymer composite.

KEVLAR FIBRE:

- ❖ It is an aromatic polyamide (-CONH₂ Group) with the name poly(para phenylene terephthamide).
- ❖ It is prepared by the condensation reaction of para-phenylenediamine and terephthaloyl chloride.



Properties:

1. It has very light weight.
2. It has high strength and stiffness.
3. It has very good abrasion and corrosion resistance.

Applications:

- ❖ Used in the aircraft panels and Race cars.
- ❖ Used in bullet proof vests.
- ❖ Used in puncture resistant bicycle tyres.

6b. Surface area

- Some properties like **catalytic activity**, **gas adsorption** and **chemical reactivity** depend on the surface area of the material.
- When bulk material is subdivided into nanomaterial, the total volume of the material remains same, but the collective surface area is greatly increased. Due to increased surface area, the material becomes catalytically active or chemically reactive or gets good gas adsorption property.

Ex: **Bulk Gold** - Catalytically **inactive**, **Nano Gold** – Catalytically **active**

Electrical properties

- In bulk material electronic bands are continuous, due to overlapping of orbitals of billions of atoms, the material acts as conductor.
- But, in nanosize materials, very few atoms or molecules will be present, so electronic bands become separate.

- Hence, some metals which are good conductors in bulk become semiconductors and insulators as their size is decreased to nano level.

6c. Fullerenes are class of molecules made of only carbon atoms having closed cage like structure.

- Many number of fullerene molecules with different carbon atoms like C_{60} , C_{70} , C_{74} , C_{78} etc., have been prepared.
- C_{60} is the smallest, stable and abundant fullerene, obtained by usual preparation methods.
- C_{60} has **spherical** shape and resembles a football and commonly known as buck ball.
- Fullerenes are made up of pentagons and hexagons. Pentagons gives curvature required to form closed structure.
- All fullerenes contain **12 pentagons** and different numbers of hexagons.
- Each fullerene has **$2(10+M)$** number of carbon atoms corresponding to 12 pentagons and

M number of hexagons.

Properties and Application.

1. Single C_{60} molecule theoretically can take up maximum of 60 hydrogen atoms.

Application- Hydrogen storage material for fuel cells

Electrode material in secondary batteries. Ex- Nickel Metal Hydride battery.

2. Each C_{60} molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

Application-*Used as optical limiters. Optical limiters are used to protect materials from damage, by intense incident light radiation.*

Module 4

7a. GC is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

Principles Of Green Chemistry:

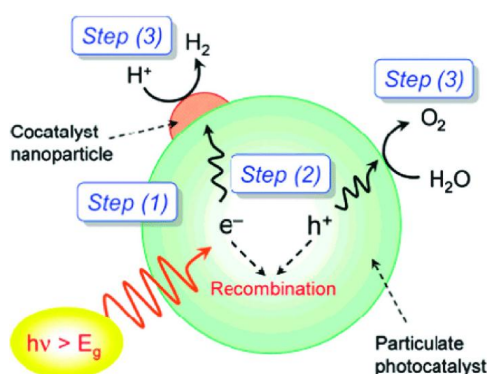
1. **Prevent waste:** It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Maximize atom economy:** Synthetic methods should be such that all the materials used in the process are converted into the final product.
3. **Design less hazardous chemical syntheses:** Synthetic methods should be designed to use and generate less toxic chemicals.
4. **Design safer chemicals and products:** Chemical products should be designed to affect their desired function while minimising their toxicity.

5. **Use safer solvents and reaction conditions:** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.
6. **Increase energy efficiency:** Energy requirements should be recognized and synthetic methods should be conducted at ambient temperature and pressure.

7b. Photo catalytic water splitting

Splitting of water to get hydrogen by using a photo catalyst and by using solar energy is called **Photo catalytic water splitting**. This process can be more efficient if the photo catalyst is directly suspended in water. So that the reaction takes place in one step.

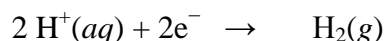
Working of Photo catalytic water splitting



The light energy excite an electron(e^-) in the catalyst and results in the production of hole (h^+). The produced hole (h^+) will react with the neighbouring water molecule to form hydrogen ions (H^+).



The H^+ ions combine to produce hydrogen at the surface of co catalyst using the electrons.



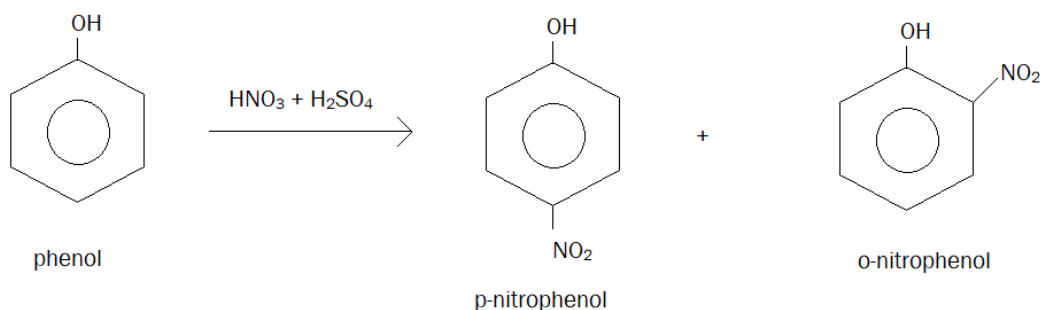
The produced hydrogen can be used as fuel in H_2 fuel cell. Photocatalyst and cocatalyst are directly kept in contact with water. There is a possibility of recombination of electron and hole resulting in decrease of efficiency. It is one of the drawbacks of Photo catalytic water splitting. But still it is used to produce hydrogen.

7c.

Synthesis of Paracetamol (Acetaminophen)

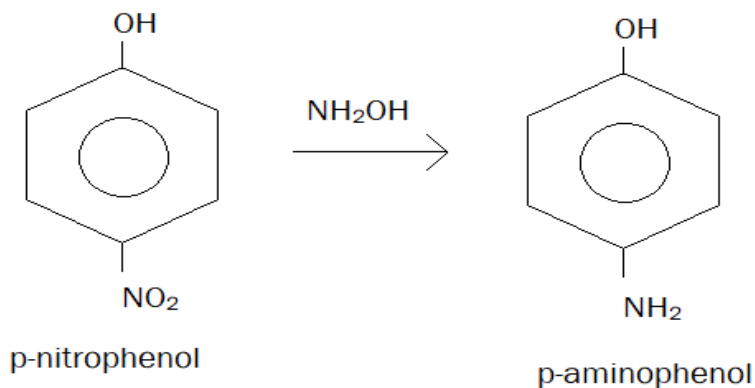
Traditional method for the production of paracetamol:

Step 1: Nitration reaction of phenol using nitrating mixture ($H_2SO_4 + HNO_3$), to form p-nitrophenol and o-nitrophenol.

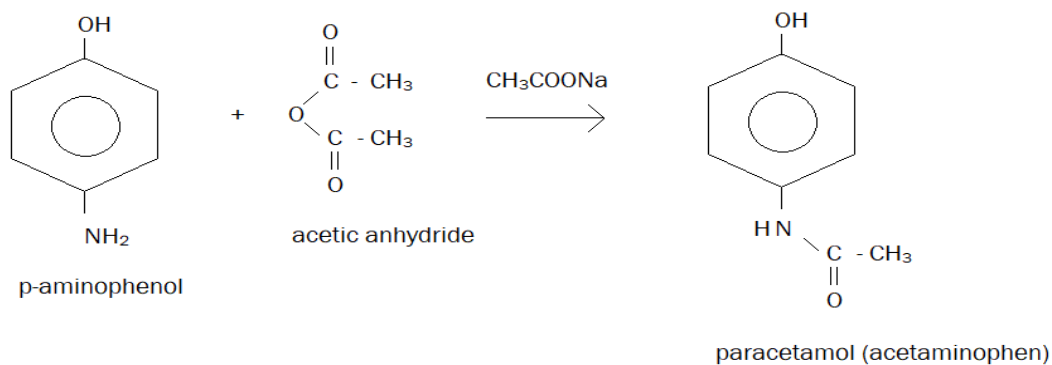


p-nitrophenol can be separated from o-nitrophenol by chromatographic methods and only p-nitrophenol is further used for the synthesis of paracetamol.

Step 2: p-nitrophenol is reduced to p-aminophenol using reducing agents such as hydroxylamine (NH_2OH)



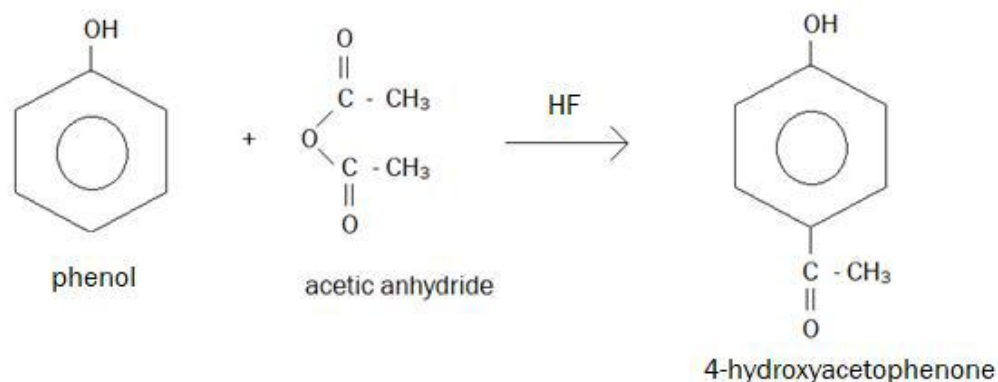
Step 3: Reaction of p-aminophenol with acetic anhydride in presence of sodium acetate (CH_3COONa) results in the formation of paracetamol.



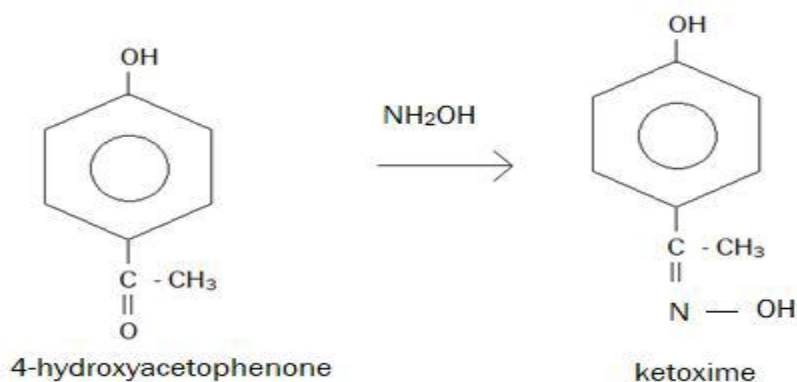
The % atom economy calculated for this synthesis is $\approx 36\%$

Green Synthesis of Paracetamol from Phenol

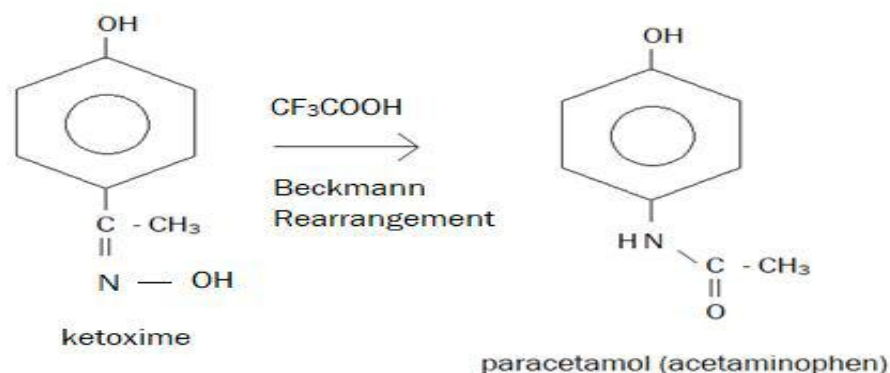
Step 1: Phenol reacts with acetic anhydride in the presence of strong acid like HF to undergo acylation reaction to produce 4-hydroxyacetophenone



Step 2: Reaction of aldehydes and ketones with hydroxylamine (NH_2OH) gives oximes. 4-hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.



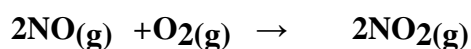
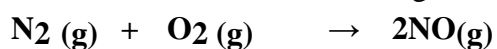
Step 3: Oximes in acidic medium (trifluoroacetic acid, CF_3COOH) undergoes Beckmann rearrangement to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.



The % atom economy calculated for this green synthesis $\approx 58\%$

8a. Sources:

- N_2 & O_2 are the main constituents of air these gases don't react with each other at a normal temperature, **when lightning strikes**, they combine to form oxides of nitrogen.
- When fossil fuel is burnt, nitrogen & oxygen combine to yield NO & NO_2



Ill effect:

- Higher levels of NO₂ can cause damage to the human respiratory tract, respiratory infections & Asthma.
- It is unpleasant in odour and leads to irritation of eyes and even lung's congestion.
- Long- term exposure to high levels of nitrogen di oxygen can cause chronic disease.
- Formation of photochemical smog, which limits in visibility of road.
- Causes acid rain – NO₂ reacts with H₂O and O₂ to form HNO₃. N₂O₅ forms acid upon reaction with water



OXIDES OF SULPHUR: (SO₂ and SO₃)

Source:

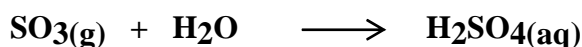
- Oxides of sulphur are produced when sulphur containing fossil fuel is burnt.
- They are also from Petroleum industries, oil refineries, sulphuric acid plants and nuclear power plants leads to sulphur dioxide and these further reacts with oxygen to give sulphur trioxide



- Decay of animal or plants also releases H₂S gas.

Ill effects:

- Cardiac , respiratory and pulmonary disease
- Eye irritation , throat troubles
- Acid rain : SO₃ and SO₂ formed in atmosphere can combine with water vapour forming H₂SO₄



- This causes Corrosion of metals, death of aquatic animals and effects the vegetation and fertility of the soil.
- It also reacts with marble leaving behind pitted and discolored surface.
- Damages plant cells/membranes & chlorophyll metabolism; leading to reduction of growth.

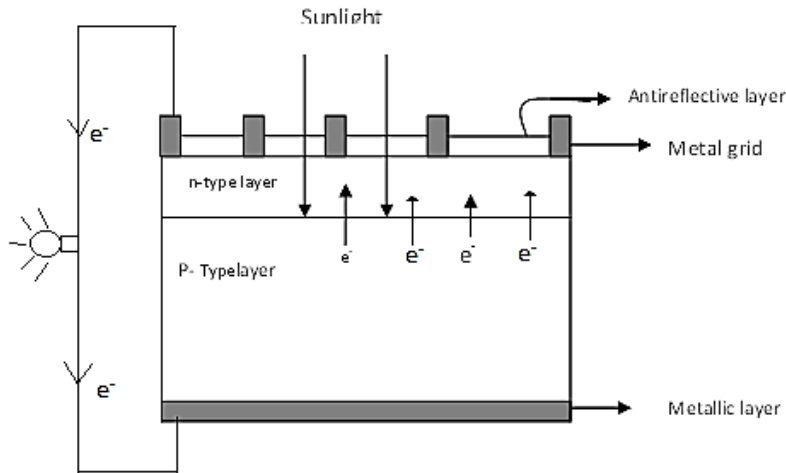
8b.

Photovoltaic cells are semiconductor device which convert solar energy into electrical energy.

Construction of Photovoltaic Cell:

- A typical silicon **PV cell** is composed of a n-type silicon on top of p-type silicon.
- Hence a p-n junction is formed between the two.

- A **metallic grid** forms one of the electrical contacts of the PV cell, over n-type semiconductor and coated with an **antireflective layer** (TiO₂) between the grid lines increase the amount of light transmitted to the semiconductor (prevent reflection of solar radiation).
- The other electrical contact is formed by a **layer of noble metal** (like silver) on the back of p-type semiconductor



Working of PV cell:

Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy
 h = Plank constant
 ν = frequency
 c = speed of light
 λ = wavelength

- When electromagnetic radiation (sunlight) is incident to the plane of solar cell, the photons are absorbed (which possess energy sufficient to overcome the barrier potential). That results in **drifting of electrons**. Thus electron-hole pairs are generated. The drifted electron will move from p- type semiconductor towards n-type through p-n junction to recombine with holes).
- Since p-n junction allows only one way movement of electrons, these electrons must flow through the external circuit to **recombine with holes**. This movement of electrons through the external circuit generates an electric current.

Applications of Photovoltaic Cells

The photovoltaic systems can be used to supply electricity for:

- telecommunication repeater stations
- water pumps
- navigational aids

8c. Methanol – Oxygen fuel cell

Construction:

Anode & Cathode – Made up of porous nickel sheets impregnated with Pt/Ru electrocatalysts

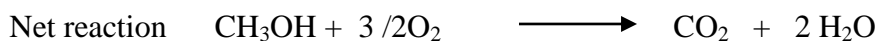
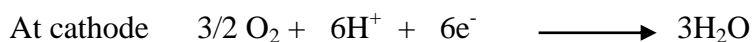
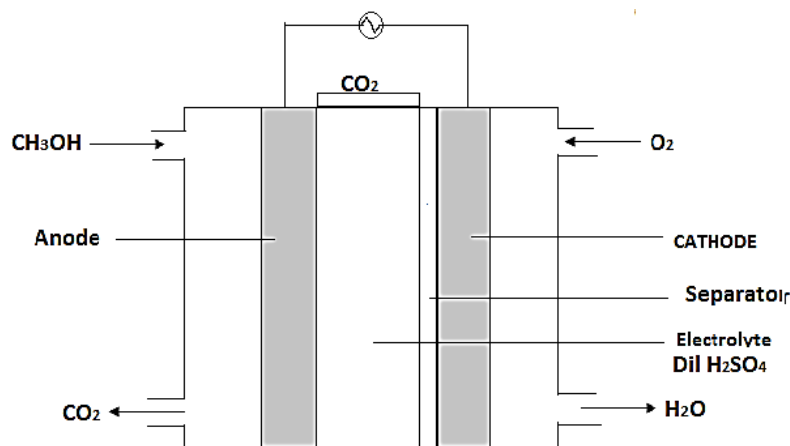
Fuel – Methanol

Oxidant – O_2

Electrolyte – Sulphuric acid(dilute)

Separator – Sulphonic acid polymer membrane.

Operating temperature – $25^{\circ}C$



A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and thereby prevents the oxidation of methanol at cathode. Methanol – H_2SO_4 mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

The advantage of acid electrolyte is that the CO_2 , a product of the reaction, can be easily removed.

Uses: It is used in large-scale power production. Military applications.

Module 5

9a. Colorimetry is used to determine the concentration of compounds in a solution. This method is used for solution which are themselves coloured or which gives colour with a suitable reagent. The intensity of colour is directly proportional to concentration of the solution.

Theory : This method is based on **Beer-Lamberts law**.

According to **Beer-Lamberts law**, when a monochromatic light is passed through a solution, part of light is absorbed by solution. The extent of absorption depends on the concentration of the solution and path length of the light through the solution.

$A = \epsilon \cdot c \cdot t$ Where, A = Absorbance

ϵ = molar extinction coefficient,

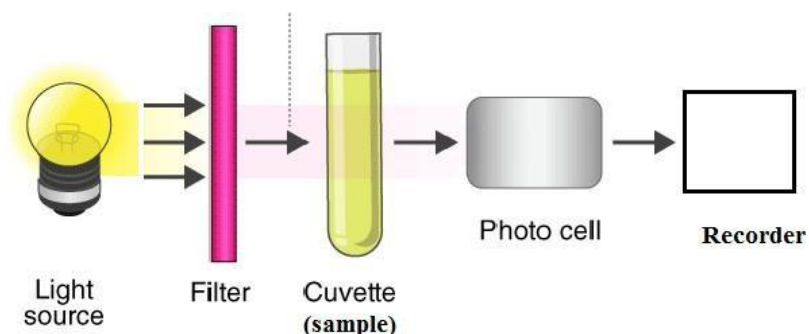
c = concentration of the solution;

t = path length & is constant for a given substance at a given wavelength.

If t, is kept constant, then, A directly proportional C. Hence a plot of absorbance against concentration gives a straight line.

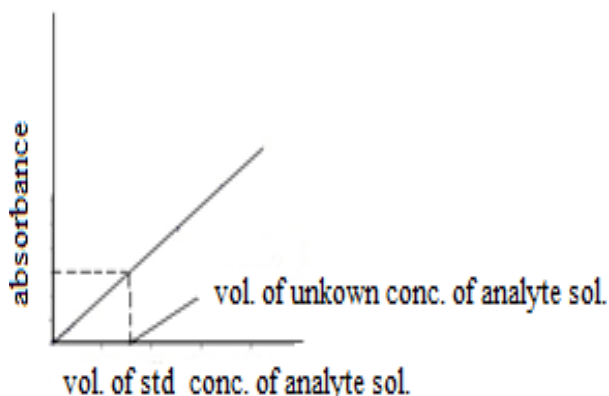
INSTRUMENTATION: Colorimeter are made of following components

- Light source.
- A filter which provides desired wavelength range.
- A sample cell.
- A photocell detector.
- Recorder.
- First, a blank solution is taken in the sample cell and monochromatic light of suitable wavelength is allowed to fall. Its absorbance is adjusted to zero.



- Then the different analyte solutions of known concentration are placed in sample cell one by one and its absorbance is noted.
- The absorbance for analyte solution of unknown concentration is noted.

- A plot of absorbance versus standard concentrations of analyte is used to find unknown concentration of analyte in the sample.



Application:

- Determination of the composition of colored complex
- Used in soil testing for analysis of soil and plant nutrients.

9b. Principles of Titrimetric Analysis

- Reagent called titrant or standard solution is added by means of a burette to the sample to be analysed called the titrand (analyte).
- Indicator is added to the analyte at the beginning of the titration.
- Towards the endpoint of the titration colour of the indicator changes.

Requirements of titrimetric analysis

- A device to measure the mass or volume of sample (e.g., pipette, graduated cylinder, volumetric flask, analytical balance etc).
- A device to measure the volume of the titrant added (i.e., burette).
- The titrant should be a standard solution (known concentration) which reacts with the analyte.
- The reaction should proceed to a stable and well defined equivalence point.
- The titrant's and sample's volume must be accurately known.

9c. BIOLOGICAL OXYGEN DEMAND:

The amount of oxygen required for the oxidation of biologically oxidizable compounds (impurities) present in 1 litre of waste water over a period of five days at 20°C

- Dissolved oxygen in water is determined by Winklers method.
- DO₁ is the Dissolved Oxygen of the sample in mg/ml at the start of the experiment (1st day)
- DO₂ is the Dissolved Oxygen of the sample in mg/ml after 5 days.

$$\text{BOD} = [\text{DO}_1 - \text{DO}_2] \text{ mg of oxygen/liter}$$

CHEMICAL OXYGEN DEMAND:

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds (impurities) present in 1 litre of waste water using a strong oxidizing agent like $\text{K}_2\text{Cr}_2\text{O}_7$.

$$\text{COD} = \frac{8 \times \text{NFAS} \times (x-y) \times 1000}{V}$$

$$= \frac{8 \times 0.1 \times (25.2-18) \times 1000}{25}$$

$$= 230.4 \text{ mg of oxygen/litre}$$

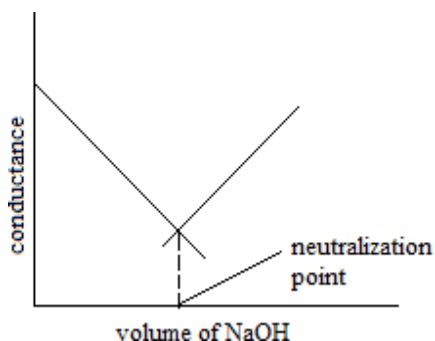
10a.

Conductometric titration: Strong acid v/s strong base (HCl v/s NaOH)

If the strong acid like HCl is titrated against a strong base such as NaOH, the conductance first decreases due to replacement of fast moving H^+ ions by slow moving Na^+ ions.

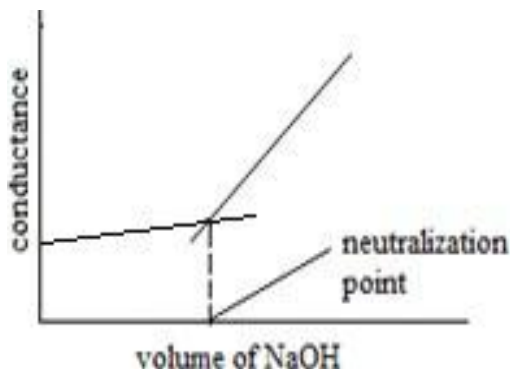


After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



Weak acid v/s Strong base (CH_3COOH v/s NaOH)

The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized (ions are more) and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH^- ions. Hence the conductance increases sharply.



10b. (i) Normality is defined as the number of gram equivalents of solute present in 1000 ml of solution. Normality is represented by the symbol 'N'.

$$\text{Normality (N)} = \frac{\text{Mass of solute} \times 1000}{\text{Equivalent mass of solute} \times \text{volume of solution}}$$

Molarity (M)

Molarity is the number of moles of solute present in 1000 ml or one litre of the solution. It is represented by the symbol 'M'.

Molar solution (Molarity = 1M)

A Molar solution contains one mole of solute in one litre (1000 ml) of the solution.

Formula

$$\text{Molarity, M} = \frac{\text{Mass of the solute} \times 1000}{\text{Molecular mass of the solute} \times \text{Volume of the solution}}$$

Parts per million (ppm)

It is a way of expressing very dilute concentrations of substances. Just as percentage means out of hundred, so parts per million or ppm means out of a million. Usually describes the concentration of something in water or soil.

(iii) One ppm is equivalent to 1 milligram of a substance per liter of water (mg/l) or 1 milligram of a substance per kilogram of soil (mg/kg).

$$\text{ppm} = \frac{\text{number of parts of the component} \times 10^6}{\text{total no. of parts of all components}}$$

or

$$\text{ppm} = \frac{\text{mass of the solute} \times 10^6}{\text{mass of the solution}}$$

10 c.

(i) *Total hardness*

1000ml of 1M EDTA = 100g of CaCO_3

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO_3

18ml of 0.01M EDTA = $\frac{100 \times 18 \times 0.01}{1000}$ g of CaCO_3
= 0.018g of CaCO_3

25ml of the water sample contains 0.00018g of CaCO_3

10^6 ml of the water sample contains $\frac{0.018 \times 10^6}{25}$ ppm of CaCO_3

Total hardness of the water sample = 720ppm of CaCO_3

(ii) *Permanent hardness*

1000ml of 1M EDTA = 100g of CaCO_3

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO_3

12.0ml of 0.01M EDTA = $\frac{100 \times 12 \times 0.01}{1000}$ g of CaCO_3
= 0.012g of CaCO_3

25ml of the water sample contains 0.012g of CaCO_3

10^6 ml of the water sample contains = $\frac{0.012 \times 10^6}{25}$ ppm of CaCO_3

= 480ppm of CaCO_3

Permanent hardness of the water sample = 480 ppm of CaCO_3

(i) *Carbonate hardness*

Carbonate hardness = 720-480 = 240ppm of CaCO_3

