

B.E.
First Semester Examination, May-2008
Chemistry (CH-101-E)

Note : Attempt any *FIVE* questions.

Q. 1. (a) Scale formation in boilers and its prevention.

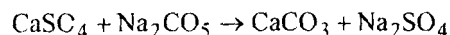
Ans. Scales are hard deposits, which stick family to inner surface of boiler. These are difficult to remove, each with hammer. In low pressure boiler, scale formation is due to decomposition of CaCO_3 & hydrolysis of MgCl_2 . whereas in high pressure boiler, it occur due to deposition of CaCO_4 & silica.

Prevention :

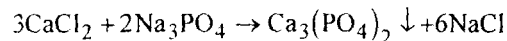
(a) External Method : This involves removal of scale forming impurities from water before feeding to the boiler some important method are L-S method, zeolite method etc.

(b) Interval Method : This involves addition of chemicals directly to water in boiler to remove scale forming sub. Which are not removed by external treatment. Some important methods are :

1. Carbonate Conditioning : Na_2CO_3 convert CaSO_4 present in water to CaCO_3 .



2. Phosphate Conditioning : In high p boiler, sodium phosphate convert CaCl_2 to $\text{Ca}_3(\text{PO}_4)_2$ which is a sludge



3. Calgon Conditioning : Scale forming salts are converted to soluble complexes by addition of collagen.

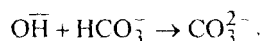
4. Colloidal Conditioning : In low P boilers, scale formation can be percentage by adding colloids like agar agar, terminal.

Q. 1. (b) Can alkalinity of water be due to simultaneous presence of OH^- , CO_3^{2-} and HCO_3^- ions?

Ans. Possible combination of ion causing alkalinity in water:

- (i) OH^- only (iv) $\text{OH}^- + \text{CO}_3^{2-}$
(ii) CO_3^{2-} only (v) $\text{CO}_3^{2-} + \text{HCO}_3^-$
(iii) HCO_3^- only.

Possibility of OH^- & HCO_3^- together is ruled out because they combine to give CO_3^{2-} ion.



Q. 1. (c) A standard hard water contains 15g of CaCO_3 per litre. 20ml of this required 25ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. The sample after boiling required 12 ml EDTA solution. Calculate the temporary and permanent hardness of the given water in

terms of ppm.

Ans. 11, (1000 ml of SHW) = 15g of CaCO_3 = 15000 mg of CaCO_3

$$1\text{ml} = \frac{15000}{1000} = 15\text{mg of } \text{CaCO}_2 \text{ equation}$$

25 ml of EDTA = 20 ml of SHW

$$= 20 \times 15\text{mg of } \text{CaCO}_3 = 300\text{mg of } \text{CaCO}_3$$

$$1\text{ ml of EDTA} = \frac{300}{25} \text{ mg of } \text{CaCO}_3$$

Total Hardness :

100 ml of head water = 18ml of EDTA

$$= 18 \times \frac{300}{2.5} \text{ mg of } \text{CaCO}_3$$

$$= 2160\text{mg of } \text{CaCO}_3$$

$$\text{Total hardness} = 2160 \text{ mg of } \text{CaCO}_3 = 2160 \text{ mg / L}$$

Permanent Hardness :

100 ml of boiled water = 12 ml of EDTA

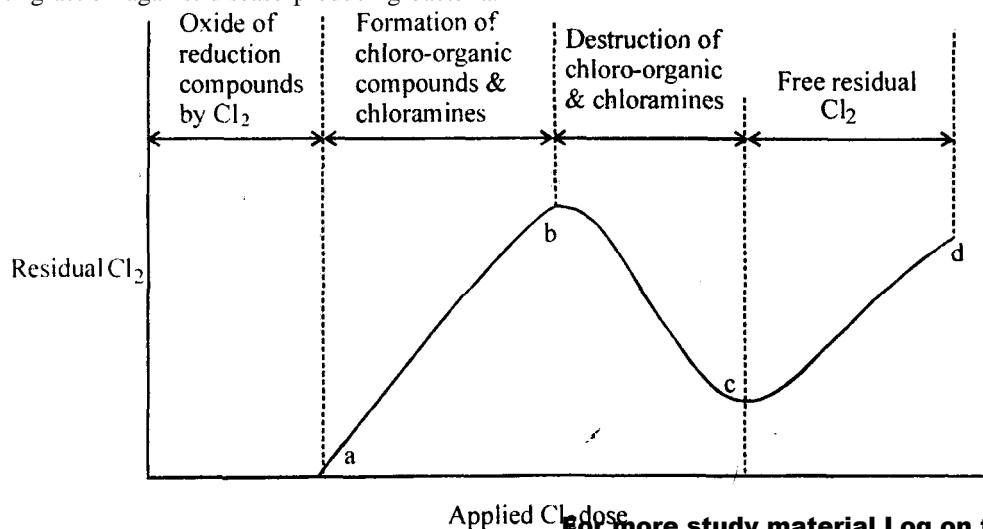
$$12 \times \frac{300}{25} \text{ mg of } \text{CaCO}_3$$

$$1000 \text{ ml of boiled water} = 12 \times \frac{300}{25} \times \frac{1000}{100} = 12 \times 12 \times 10 = 1440 \text{ mg of } \text{CaCO}_3$$

$$\text{Permanent hardness} = 1440 \text{ mg/L.}$$

Q. I. (d) Break-point chlorination and its importance.

Ans. Break point chlorination involves in addition of sufficient amount of chlorine to oxidise (a) Organic matters (b) Reducing substance (c) Free ammonia in raw water. Leaving behind free chlorine which processes disinfecting action against disease producing bacteria.



The addition of Cl_2 at dip/break point is called break point chlorination. At this point, free Cl_2 begins to appear.

Importance :

1. It oxidises completely organic compounds. NH_3 + other reducing compounds.

2. It remove colour in water.

3. It destroy disease producing bacteria.

4. Prevents growth of any weed in water.

Q. 2. (a) Explain the various units of hardness and **the relationship among them.**

Ans.

1. Parts Per Million (PPM) is the parts of CaCO_3 equivalent hardness per 10^6 part of water i.e.

1PPM -1 part of CaCO_3 in 10^6 party water.

2. Mtligemer Per Liter (Mg/L) is number of mgs of CaCO_3 equivalent hardness present per litre of water. $1 \text{ Mg/L} = 1 \text{ PPM}$.

3. Clarke's degree ($^\circ\text{Cl}$) is number of grains (1/7000 be) of CaCO_3 equivalent hardness per gallon (10eb) of water or it is part of CaCO_3 equivalent hardness per 70,000 parts of water.

$1^\circ\text{Cl} = 1$ part of CaCO_3 equivalent per 70,000 part of water.

4. Degree french ($^\circ\text{Fr}$) is part of CaCO_3 equivalent hardness per 10^5 parts of water.

$1^\circ\text{Fr} = 1$ part of CaCO_3 hardness equation per 10^5 parts of water.

Relationship:

$$1\text{PPM} = 1\text{mg/L} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl}.$$

Q. 2. (b) Name **the three gases dissolved in water responsible for causing corrosion.**

Ans. Gases responsible for corrosion are :

(i) Dissolved O_2 (ii) Dissolved CO_2 (iii) SO_3 .

Q. 2. (c) Name **the various internal methods used for treating boiler-feed water. Discuss in detail the phosphate-conditioning.**

Ans. Various internal methods are :

1. Colloidal conditioning.

2. Phosphate conditioning.

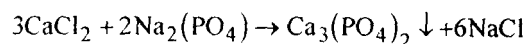
3. Carbonate conditioning.

4. Calgon conditioning.

5. Electrical conditioning.

6. Radioactive conditioning.

Phosphate Conditioning : In high P boilers, sodium phosphate added, react with hardware of water to form, non-adhered & easily removable sludge.



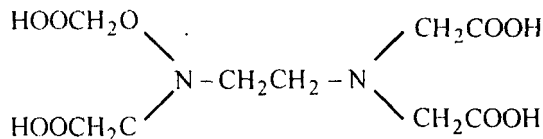
Main phosphate employed are :

(a) NaH_2PO_4 sodium dihydrogen phosphate (weakly alkaline).

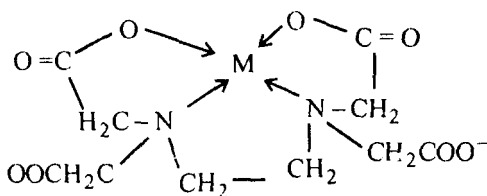
3. Na_3HPO_4 , trisodium phosphate (alkaline) works in acidic water.

Q. 2. (d) What is the principle of EDTA titration? Briefly discuss the estimation of hardness of water by EDTA method and the role of buffer solution used in it.

Ans. EDTA method is based on fact that bivalent hardness causing metal ion form complex with ecio-chrome block-T EBT as well as EDTA but EDTA complexes are more stable. EDTA has following structure.

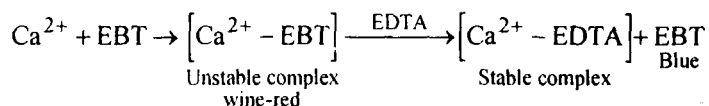


It forms stable complex with hardness producing metal ion.



Hard water is titrated against EDTA solution to form stable complex with $\text{Ca}^{2+} / \text{Mg}^{2+}$ ion in water is buffered as pH-9-10.

EBT form unstable wine red complex with $\text{Ca}^{2+} / \text{Mg}^{2+}$ at pH = 9-10



On addition of EDTA, free complexed $\text{Ca}^{2+} / \text{Mg}^{2+}$ form metal EDTA stable complex. Free indicator (EBT) shows blue colour is solution at pH = 9-10.

Estimation : Sample is treated with $\text{NH}_4\text{Cl}-\text{NH}_4\text{OH}$ buffer to maintain $\text{p}^{\text{H}} = 9-10$. Now small amount of indicator (EBT) is added which give wine red coloration to solution. This solution is titrated against EDTA, change in collocation is observed. End point will be wine red to blue. The litre value corresponds to total hardness.

Role of Buffer : Buffer is added to maintain the pH of solution to 9-10. These indicator works only at pH = 9 - 10.

Q. 3. (a) State Gibb's phase rule.

Ans. Phase rule may be stated as "Provided the equilibrium between any number of phase is not influenced by gravity or electrical or magnetic forces, or by surface action & only by temperature, pressure &

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concentration, the number of degree of freedom (F) of the system is related to number of component (C) & of phases (P) by phase rule equation,

$$F = C - P + 2$$

For any system at equilibrium at a definite temperature & pressure."

Q. 3. (b) Justify the statement "The Eutectic is a mixture and not a compound."

Ans. Eutectic system is a binary system of two sub, which are miscible in all proportion in liquid state, but do not react chemically. In eutectic system, two compound are completely miscible but do not for any inter-component compound. \therefore They remain immiscible in solid state & separate out as solid phase when the solution is cooled. Since there is no chemical interaction. \therefore it is not a compound, just a mixture.

Q. 3. (c) Differentiate between Metastable equilibrium and True equilibrium.

Ans. Metastable equilibrium is state of supersaturated solution in which the phase which is normally stable under the given condition does not form.

True equilibrium is one which system is always stable. This system will stay for a long period & will not disappear with slight change in condition.

Q.3. (d) Discuss the general phase diagram of two component system forming compound in the solid state with congruent m. point.

Ans. Let A & B be two components & AB a solid (stable) compound formed by chemical combination. This diagram is a combination of two eutectic system.

Along AC, solid A \rightleftharpoons liquid phase

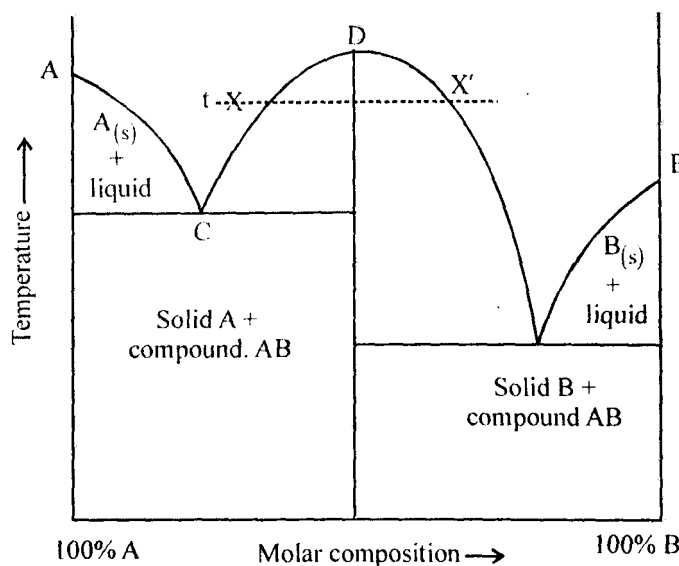
Along BE, B(s) \rightleftharpoons liquid phase

Along CDE, AB(s) \rightleftharpoons liquid phase

The point D of CDE curve is congruent m. Point of compound because solid & liquid phase have same composition at this point. This a two component become one component at point D because both solid & liquid has only one compound AB.

$$F = C - P + 1 = 1 - 2 + 1 = 0$$

D = invariant point.



There are two eutectic system.



$$F = C - P + 1 \quad (\text{at point C \& E})$$

$$= 2 - 3 + 1 = 0$$

System is invariant.

At a certain temperature t , liquid phase has two compositions $X + X$, in equilibrium with same solid AB. This means compound AB has two solubility at some temperature on left side of diagram A & AB are three & curve DC is usual depression in freezing point of compound AB on addition of A. Sky on right side, two component are B & AB & curve DE represent depression in freezing point of compound AB-on addition of B.

Example of such system are Zn Mg, Zn etc.

Q. 4. (a) Explain the Clausius-Clapeyron equation.

Ans. Two phases 1 & 2 are in equilibrium. Let $G_1 + G_2$ are molar gibbs free energy of phase 1 & 2 respectively. Since the system is in equilibrium, change in free energy is zero.

$$\Delta G_1 = G_2 - G_1 = 0 \quad \therefore \quad G_1 = G_2$$

A change in temperature will change free energy. Suppose temperature & pressure changes by dT & dP , free energy change will be same. Let free energy change by $dG_1 + dG_2$.

$$G_1 + dG_1 = dG_2 + dG_2$$

$$\therefore \quad dG_1 = dG_2$$

$$G = H - TS$$

$$= E + PV - TS$$

On differentiation

$$dG = dE + PdV + VdP - TdS - SdT$$

$$= q + VdP - TdS - SdT \quad \left[\because dE = q + w = q - PdV = q = dE + PdV \right]$$

$$= TdS + VdP - TdS - SdT \quad \dots(1) \left[dS = \frac{dq}{dT} \right]$$

$$dG_1 = V_1 dP - S_1 dT$$

$$dG_2 = V_2 dP - S_2 dT$$

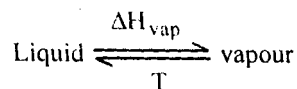
$$V_1 dP - S_1 dT = V_2 dP - S_2 dT$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta H}{T(V_2 - V_1)} \quad \dots(2) \left[\Delta S = \frac{\Delta H}{T} \right]$$

Clausius assumed certain specific cases.

Suppose system is of liquid & vapour equilibrium

$$\Delta H_{\text{vap}} = \text{Molar heat of vapourisation}$$



$$V_1 \rightleftharpoons V_2$$

At critical temperature $V_2 \gg V_1$

∴ $V_2 - V_1$ will be replaced by V_2

Equation (2) is modified by

$$\frac{dP}{dT} = \frac{\Delta H}{TV_2}$$

At low temperature vapour are treated as an ideal gas.

$$PV_2 = RT$$

$$V_2 = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H \cdot P}{RT^2}$$

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta H}{RT^2}$$

$$\frac{d_{\text{enp}}}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

Take integration,

$$\int \frac{d_{\text{enp}}}{dT} = \int \frac{\Delta H_{\text{vap}}}{RT^2}$$

$$\int d_{\text{enp}} = \frac{\Delta H_{\text{vap}}}{R} \int \frac{dP}{dT^2}$$

$$d_{\text{enp}} = \frac{\Delta H_{\text{vap}}}{R} \left[-\frac{1}{T} \right] + C$$

$$\log P = \frac{1}{2} \frac{\Delta H_{\text{vap}}}{2303R} \left[\frac{1}{T} \right] + C$$

If limits are P_1 , P_2 & T_1 , & T_2 , equation becomes,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Q. 4. (b) The free energy change (AG) accompanying a given process is -86kJ at 298 and -84kJ at

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308K. Calculate the change in enthalpy (ΔH) for the process at 303 K.

Ans.

$$G_1 = -86 \text{ kJ}, G_2 = -84 \text{ kJ},$$

$$T_1 = 298 \text{ K}, T_2 = 308 \text{ K}$$

$$T = 303 \text{ K}$$

$$\Delta G = \Delta H + T \left[\frac{d\Delta C}{dT} \right]_p \quad \dots(1)$$

$$\Delta G \text{ at } 303 = - \left[\frac{86 + 84}{2} \right] = -85 \text{ kJ}$$

$$\frac{d\Delta G}{dT} = - \frac{-84 - (-86)}{308 - 298} = \frac{2}{10} = 0.51 \text{ kJ K}^{-1}$$

Substitutes in equation (1)

$$-85 = \Delta H + 303 \times 0.5$$

$$\Delta H = -85 - 151.5 = -236.5 \text{ kJ}$$

$$\Delta H \text{ at } 303 \text{ K} = -236.5 \text{ kJ}.$$

Q. 4. (c) Give the application of Gibb's Helmholtz equation.

Ans. **Application :**

1. It tells that ultimate driving force in nature is entropy i.e. the drive towards disorder.
2. Either of two thermodynamic relations are useful in calculating the internal energy (E) & enthalpy (H).
3. It will dictate whether a process becomes more/less spontaneous as we change the temperature.

Q. 4. (d) Define Second law of Thermodynamics in different forms.

Ans. Some common statements of the law are as follows :

1. All spontaneous processes are thermodynamically irreversible.
2. Whenever a spontaneous process takes entropy of the universe.
3. It is impossible in a cyclic process to take heat from a cold body & convert it into work at the same time without transferring heat from a hot body to cold body (Kelvin statement).
4. It is impossible for a self-acting machine, unaided by an external agency, to convey heat from a body at a lower temperature to one at a higher temperature (Clausius statement).
5. It is impossible to convert heat completely into an equivalent amount of work without producing change elsewhere.

Q. 5. (a) Differentiate between addition polymers and condensation polymers.

Ans.

Addition polymerisation	Condensation polymerisation
1. Monomer involved are unsaturated.	1. Monomer has two/more functional groups.
2. No small molecules like H_2O , NH_3 get eliminated.	2. Elimination of small mol. like H_2O occurs.
3. It requires sunlight/UV radiation.	3. No such requirement is there.
4. Usually secondary van der Waals forces are present.	4. Formation of covalent bond makes them hard & rigid.

Q. 5. (b) Discuss the relation between structure of polymer and (i) Crystallinity (ii) Elasticity (iii) Strength.

Ans. Strength : The strength of polymer depends upon intermolecular force of attraction between molecule.

- * In straight chain/branched polymers, chains are held by weak Vanderwall forces, thus strength increases with increase in chain length. They show mechanical strength if chain length is 150-200 units.
- * The force can be greatly increased by presence of polar group like -COOH, -OH, -Cl, -F along the chain.
- * Shape of polymer greatly affects the strength. Straight chain benched polymer show slippage whereas cores-linked polymer are strong & tough, due to presence of strong covalent bond.

Crystallinity : The degree to which molecule of a polymer are arranged in orderly pattern w.r.t. each other is a measure of crystallinity. It impart denser packing of molecule, thereby increasing the intermolecular force of attraction. This accounts for highest sharper softening point, greater rigidity & strength as compared to amorphous polymer. In actual practice, many polymers consist of crystallites embedded in an amorphous matrix. In such polymer crystal its provide hardness & rigidity whereas amorphous matrix provide flexibility to polymer. Crystallisation tendency decreases by copolymerisation.

Elasticity : It is recoverence of original shape, after a deformation stress is released. The elastic deformation arise from fact that elastomer consist of long-chain molecular, having per rotating group, which assume, in the unstressed condition, a peculiar configuration of irregularly coiled & entangled shall. In stretched condition, polymers are in crystalline state which enhances force of attraction, thereby causing stiffening of material.

Q. 5. (c) Give in detail 'Polymer Composites.'

Ans. Polymer Composite : Polymers are mixed with some other polymer material. In order to incorporate additional properties to polymer. This mixture is called polymer composite. Some important polymers are :

1. Fibre Reinforced Plastic (FRP): The combination of polymeric substance with solid filler, is called FRP. The fillers are solid additives which modify the physical properties, particularly mechanical properties of basic polymer material. They improve : thermal stability, mechanical strength, insulating character, water resistance, hardness, rigidity etc.

The strength of plastic can be enhanced by reinforcing with high strength material like glass, graphite, boron etc. The choice of fibre depends on property to be improved. The common resin matrix used are polyester, phenolic resin, silicon resin etc., The mechanical strength depends on several factors like nature of fibre, fibre length nature of matrix e.g., strength of FRP increases with increase in fibre length. FRP are used in space-craft, aeroplane, motor-car etc.

2. Polymer Blend : A simple physical combination of two/more incompatible polymer is called a polymer blends. These chains are held by van der Waals forces. It, usually improve several property such as workability, resistance to abrasion, & impact some examples are ABS plastic, SAN polymer.

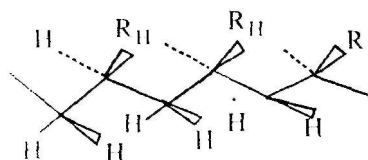
3. Polymer Alloy : It is compatible mixture of two/more polymer which interact chemically under specified set of conditions. Polymer have chemical interaction in presence of suitable compatibility, e.g., ABS-PC alloy.

Q. 5. (d) Explain the phenomenon of 'Tacticity.'

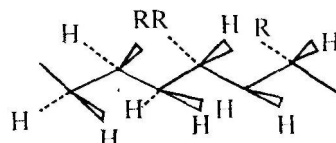
Ans. The orientation of monomeric units in polymer molecule can take place in orderly/disorderly with respect to main chain. This difference in chain affects their physical property.

1. The head to tail configuration, in which functional groups are on same side of chain, is called isotac-

tic polymer.

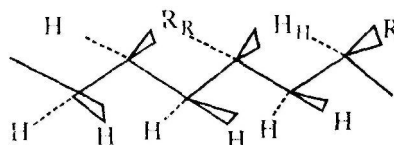


Isotactic



Atactic

2. If arrangement of functional groups are at random around the main-chain, it is called atactic e.g., polypropylene.
3. If arrangement of functional groups is in alternate fashion it is called syndiotactic polymer e.g. gutta peechea.



Q. 6. (a) What is Aniline point? Explain its significance.

Ans. Aniline point of an oil is defined as "the minimum equilibrium solution temperature for equal volume of aniline & oil sample. It gives indication of deteriorating of oil in contact with rubber sealing. Aromatic hydrocarbons usually have tendency to dissolve synthetic rubber. So low aromatic contents are always desirable.

Determination : It is determined by mixing equal volume of aniline & oil till a homogeneous solution is obtained. Solution is cooled till aniline & oil phase separate out. The temperature at which two phases separate out is called aniline point of the oil.

Q. 6. (b) Give a short **account of fluid-film lubrication and boundary lubrication.**

Ans. Fluid Film Lubrication : In this, moving/sliding surfaces are separated from each other by a thick film of fluid (1000 Å thick), so that direct surface-to-surface contact rarely occurs. The lubricant covers irregularities of surface & a thick layer is between. This reduces wear. Now the resistance to moving part is only due to internal resistance between the particles of lubricant. ∴ Lubricant should have minimum viscosity under working condition. It also should remain in place & separate the surfaces. This occurs in shafts running at a fair speed as well as bearings with not too high load. Delicate instruments, light machines like watches, clocks, guns are provided with this type of lubrication. Hydrocarbons are satisfactory lubricants: Hydrocarbons are blended with high chain polymers for better results.

Thin Film Lubrication/Boundary Lubrication : It is done when a continuous film of lubricant does not persist & direct metal-to-metal contact is possible. In such a case, a thin layer of oil is adsorbed by physical or chemical forces or both on a metallic surface. The load is carried by a layer of adsorbed lubricant on both metal surfaces. The coefficient of friction is 0.05-0.15.

Vegetable & animal oils possess properties of adsorption. Although fatty oils possess a great adhesive property than mineral oil, yet they tend to break down at high temperature. To improve oiliness, mineral oils are mixed with fatty acids. Graphite & MoS₂ either alone or in suspension are used for lubrication. High viscosity index, resistance to heat & oxidations, good oiliness, low pour point are good qualities of boundary lubrications.

Q. 6. (c) Explain the properties of lubricants.

Ans. Viscosity : is a property by virtue of which it offer resistance to its own film. It is important property of lubricating oil. If the viscosity is low, thin film can't be maintained, but if viscosity is high, excessive friction occurs.

The rate at which viscosity of oil changes with temperatures is known as viscosity index, viscosity of good oil should not change much.

Viscosity can be determined by Redwood viscometers.

2. Flash & Fire **Point** : Flash point is lowest temperature at which lubricant oil gives off sufficient vapour that ignites for a moment when a tiny flame is brought near to it. While fire point is lowest temperature at which vapours of oil burn continuously for at least 5 sec, when a tiny flame is brought near to it. Fire point is 5-40° higher than flash point. It is determined by Pensky Martens apparatus.

3. Oiliness : Of lubricant is measure of its capacity to stick on to surface of machine parts, under condition of heavy P or load, Mineral oil has got very poor oiliness while vegetable oil have good oiliness. In order to improve oiliness, mineral oil is blended with vegetable oil/fatty acid.

4. **Cloud & Pour Point**: When an oil is cooled slowly, the temperature at which it becomes cloudy/hazy is called cloud point while temperature at which it ceases to flow is called pour point. These are determined by pour point apparatus. Pressure of waxes raises the pour point.

5. **Aniline Point** : Is defined as "the minimum equilibrium solution temperature for equal volume of aniline & oil sample. It gives indication of deterioration of oil in contact with rubber sealing. Low aromatic contents are desirable.

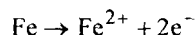
Q. 7. (a) Explain "Rusting of iron" with the help of electrochemical theory of corrosion.

Ans. Electrochemical corrosion involves flow of e^- current between the anodic & cathodic areas.

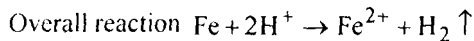
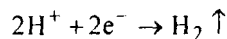
At anode $M \rightarrow M^{n+} + ne^-$

Cathode consumes e^- with either by (i) evolution of H_2 (ii) Absorption of oxygen.

(a) **Evolution** of H_2 : Occurs in acidic environment consider metal as Fe, at anode, dissolution of Fe occurs oxidation.



e^- flows through metal from anode to cathode where H^+ are eliminated as H_2 gas.



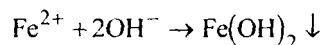
All metal ions above Fe in electrochemical series have tendency to get dissolved in acidic solution.

(b) Absorption of O_2 : Rusting of iron in neutral aqueous solution in presence of O_2 is an example of this corrosion. An iron oxide film develops cracks, anodic area gets created, rest part becomes cathode.

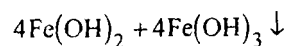
At anode $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

At cathode $O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

The Fe^{2+} & OH^- diffuse to give $Fe(OH)_2$



In enough O_2 is there, ferrous hydroxide oxidises to ferric hydroxide.



Q. 7. (b) Distinguish between Galvanizing and tinning process.

Ans.

Galvanisation	Tinning
1. The process of deposition of thin layer of Zn on Fe surface is called galvanisation.	1. Deposition of their layer of tin is called tinning.
2. Galvanisation can be done by dipping or by sherardising method.	2. There are no such method.
3. Iron does not rust even if Zn coating develops cracks.	3. If Sn coating develops cracks, Fe is no more protected.
4. Due to oxidation, Zn changes to $ZnCO_3$, $Zn(OH)_2$. This protects the exposed part.	4. Fe present in exposed part undergo oxidation in preference to tin & get rusted.

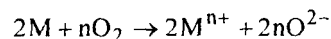
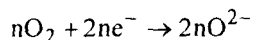
Q. 7. (c) What is Pilling-Bedworth rule? Explain it.

Ans. Pilling-Bedworth Rule : According to it an oxide layer is protective or non-porous, if volume of the oxide is at least as great as volume of metal from which it is formed, On otherhand. If volume of oxide is less than volume of metal, oxide layer is porous & non-protective. In alkali & alkaline earth metal, volume of oxide is less than volume of metal, consequently, it develops cracks on others hand, metal like Al form oxide whose volume is greater than volume of metal, hence corrosion is zero.

Q. 7. (d) Explain the mechanism of chemical-corrosion.

Ans. Chemical corrosion occurs by oxidation which occurs by direct action of oxygen at low/high temperature on metal in absence of moisture.

The reaction are,



Oxidation occurs on surface of metal & resulting metal oxide scale form barrier, that restrict further oxidation. For further oxidation either metal must diffuse outward or oxygen must diffuse inwards **through** metal. But outward diffusion is much more rapid than inward diffusion of O_2 since metal ions are smaller than oxygen ion : Consequently of much higher mobility.

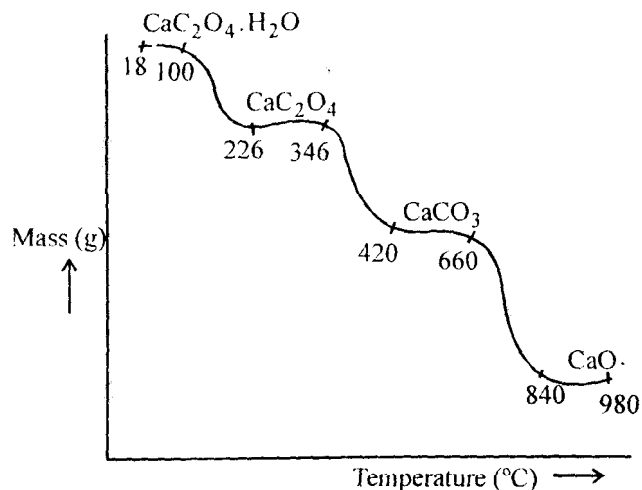
Q. 8. (a) What is thermogravimetric analysis? Describe briefly.

Ans. Thermogravimetric analyser involves the measurement of change of mass of system under examination with increase in temperatures. Preferably at linear rate. The information obtained is in form of thermogram which is a plot of mass (m) vs. temperature (T).

The apparatus used is called thermobalance. It can be manual/automatic. It consist of a sensitive recording balance (for accurately recording change in mass), a furnace (temperature increases linearly at predeter-

mined rate of 0.5 25°C7min from ambient to 1200°C/more), furnace controller, a recording device.

Principle : Thermogram consist of horizontal portions called plateaus & inflection. A plate an indicate consistency of mass & thus represent stable phase over temperature & inflection represents formation of intermediate compounds.



Take an example of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. It has three inflection & 4 plateaus. Inflection shows loss of H_2O , CO & CO_2 with increase in temperatures. Plateaus show stability of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, CaC_2O_4 , CaCO_3 & CaO compounds.

Some of important applications are :

1. In quantitative analysis.
2. In testing purity of sample.
3. In study of organic compounds.
4. In study of polymer.

Q. 8. (b) Explain laws of spectrophotometry.

Ans. Lambert's Law : According to law, rate of decrease of intensity of incident radiation w.r.t thickness of medium is proportional to intensity.

$$-\frac{dI}{dx} = KI \quad k = \text{absorption coefficient.}$$

$$-\frac{dI}{I} = kdx$$

I_0 Intensity of incident radiation

I = Intensity of transmitted radiation ,

$$-\int_{I_0}^I \frac{dI}{I} = -k \int_0^x dx$$

$$\left| \ln I \right|_{I_0}^I = -kx ; \ln \frac{I}{I_0} = -kx$$

$$2.303 \log \frac{I}{I_0} = -kx$$

$$\log \frac{I}{I_0} = \frac{-k}{2.303} \cdot x \quad x = -\Sigma x$$

Σ = Extinction coefficient.

Lambert Beer Law : According to this law, the rate of decrease of intensity of light w.r.t thickness of medium on passing through a solution is proportional to product of Intensity & concentration of solution.

$$-\frac{dI}{dx} = K.C.I \quad k = \text{molar absorption coefficient.}$$

$$\ln \frac{I}{I_0} = -k.c.x$$

$$\log \frac{I}{I_0} = -\frac{k}{2.303} \cdot c.x = -E.cx$$

E = Molar extinction coefficient

$$\frac{I}{I_0} = 10^{-Ecx}$$

$$\text{If } \frac{I}{I_0} = \frac{1}{10}, C = 1M, \text{ then } \epsilon = \frac{1}{x}.$$

$$\frac{I}{I_0} = T = \text{Transmittancy of solution.}$$

$$A = \log \frac{I_0}{I} = \text{absorption of solution}$$

$$\therefore A = -\log_{10} T$$

$$T = 10^{-A} = 10^{\epsilon'cx}.$$

Q. 8. (c) In conductometric titration, more concentrated solution is added from burette, why? What are the advantages of conductometric titrations over ordinary volumetric methods.

Ans. In order to obtain straight line graph, it is necessary to keep volume of solution constant during titration. This practically is not possible. It is tried to keep the volume change. \therefore the titrant used is kept about 10 times as concentrated as the solution to be titrated.

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Advantage:

1. Conductometric titration are more accurate.
2. They can be used for titrating coloured solution.
3. They can be employed even for titrating V dilute solution.
4. They can be used for titrating weak acids & weak bases.

Q. 8. (d) Differentiate between I.R. and U.V. spectroscopy.

Ans.

IR Spectroscopy	UV Spectroscopy
1. In IR spectroscopy, Infrared radiation are used.	1. In electronic speaker, ultraviolet radiation are used.
2. IR radiation carry out rotation & vibration.	2. It carry out transition among electron.
3. Change in dipole moment is must requirement.	3. No such requirement is there.
4. Vibrational motion never ceases i.e. it always has some energy/zero point energy.	4. This motion ceases at okelvin.