

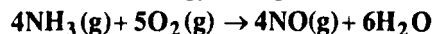
## B.E.

First Semester Examination, May-2009

### Chemistry (CH-101-E)

**Note :** Attempt any five questions. All questions carries equal marks.

**Q. 1. (a) Calculate the standard free energy change for the reaction**



The standard free energy of formation ( $\Delta G^\circ_f$ ) for  $\text{NH}_3(\text{g})$ ,  $\text{NO}(\text{g})$  are  $\text{H}_2\text{O}(\text{l})$  are -16.8, + 87.7, and - 237.2  $\text{kJ mol}^{-1}$  respectively.

Ans. A /Q

$$\left[ \frac{\partial (\Delta G)}{\partial T} \right]_p = \frac{(-84 \text{ kJ}) - (-86 \text{ kJ})}{308 \text{ K} - 298 \text{ K}}$$

$$= 0.2 \text{ kJ/K}$$

$\Delta G$  at 303 K may be taken as the average of values at 298 K & 303 K.

$$\Delta G \text{ at } 303\text{K} = \frac{(-86) + (-84)}{2}$$

$$= -85 \text{ kJ}$$

From Gibbs-Helmholtz equation :

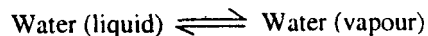
$$\Delta G = \Delta H + T \left[ \frac{\partial (\Delta G)}{\partial T} \right]_p$$

$$-85 \text{ kJ} = \Delta H + (303 \text{ K})(0.2 \text{ kJ/K})$$

$$\Delta H = -145.6 \text{ kJ} \quad \text{Ans.}$$

**Q. 1. (b) Derive Clausius-Clapeyron equation in its integrated form.**

**Ans. Clausius-Clapeyron Equation :** Let us consider  $\text{H}_2\text{O}$  in liquid & vapour phases & 2 phases equilibrium at constant temperature (T).



$$\frac{dP}{dT} = \frac{\Delta H V}{T(V_g - V_l)}$$

$$\therefore V_g - V_l = V_g \quad \text{since} \quad V_g \gg V_l$$

Thus,

$$\frac{dP}{dT} = \frac{\Delta H V}{T V_g}$$

Assuming

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

Hence, 
$$\frac{dP}{dT} = \frac{\Delta H_V}{T \Delta V} = P \frac{\Delta H_V}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_V}{R} \frac{dT}{T^2}$$

On integration, 
$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_V}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\lim \left( \frac{P_2}{P_1} \right) = - \frac{\Delta H_V}{R} \left[ \frac{1}{T} \right]_{T_1}^{T_2}$$

$$\lim \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_V}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

This is known as Clapeyron-Clausius equation.

**Q. 1. (c) Define the term Entropy. Explain its physical significance.**

**Ans. Entropy :** Entropy is a measure of the randomness or disorder of the molecules of the system. It is denoted by S

$$\Delta S = \frac{q_{rev}}{T}$$

In SI system,

$$EV = J/mol/K$$

In CGS system

$$eu = cal/mol/K$$

Thus

$$1 eu = 4.184 EV$$

**Significance :**

As

$$A = E - TS$$

$$dA = dE - TdS - SdT$$

$$dq = dE + W_{rev}$$

$$dS = \frac{dq}{T} \Rightarrow dq = TdS$$

$$TdS = dE + W_{rev}$$

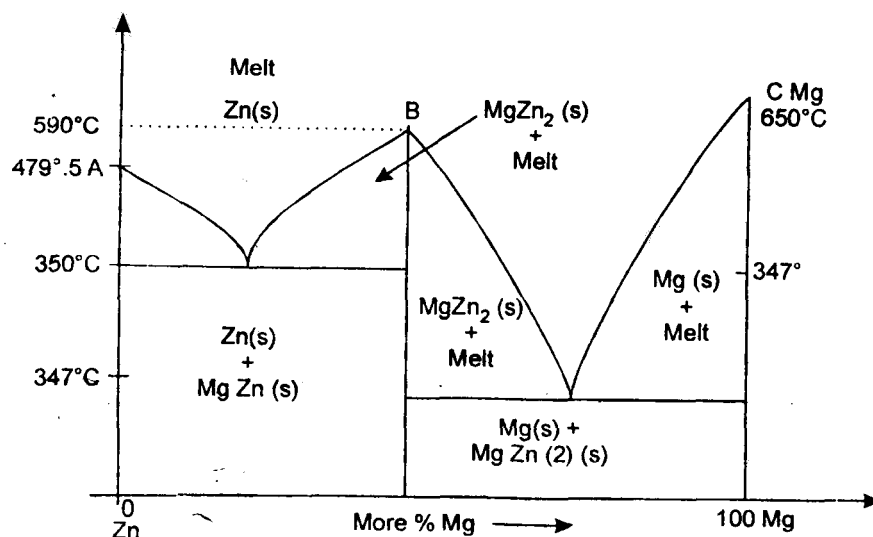
$\Rightarrow$

$$dE = TdS - W_{rev}$$

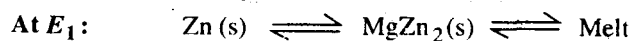
**Q. 2. (a) What do you understand by congruent and incongruent melting point ? Discuss Zn-Mg system in detail.**

**Ans. Zn-Mg System :** A compound is said to have Congruent Melting Point if it melts at a constant temperature to give a liquid having the same composition as that of the solid compound.

Zn-Mg system shows the formation of a congruent melting compound ( $MgZn_2$ ). A typical phase diagram is shown as :



First eutectic point  $E_1$

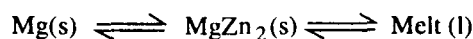


At  $E_1$ ,  $P=3$ ,  $C=2$

So

$$F = C - P + 1 \\ = 2 - 3 + 1 = 0$$

At  $E_2$ :  $\text{MgZn}_2 - \text{Mg}$  system

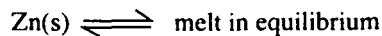


$C = 2$  viz.  $\text{MgZn}_2 + \text{Mg}$

$P = 3$  viz.  $\text{Mg(s)}$ ,  $\text{MgZn}_2(\text{s})$ , melt (l)

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

Curve  $AE_1$  represent



Curve  $LE_2$



Curve  $E_1$  &  $E_2$  has maxima at B ( $59^\circ\text{C}$ ), where liquid has the same composition as the solid in equilibrium.

Hence  $C=1$ , at B

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

Hence, congruent melting point is also Non-Variant point.

**Incongruent Melting Point** : Here, 2 components undergo chemical combination to form a new compound which is unstable.

Also called

- (i) peritectic      (ii) meritectic      or  
(i) transition      temperature.

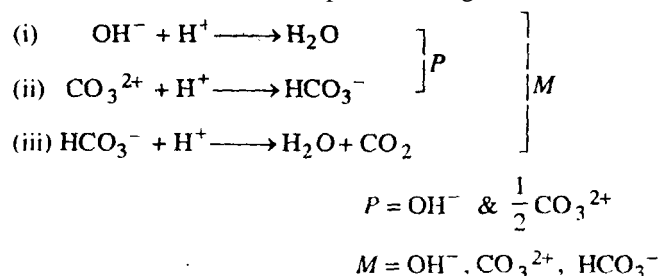
**Q. 2. (b) Justify the statement "The Eutectic is a mixture and not a compound."**

**Ans.** The eutectic mixture has a definite composition & a sharp melting point. In this respect, it resembles compound. However it is not a compound for the components are not present in stoichiometric proportions. Hence it is a mixture not a chemical compound.

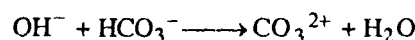
**Q. 3. (a) Define alkalinity. How is it determined ?**

**Ans.** By alkalinity of  $H_2O$ , we mean the total content of those substances in it which causes an increased hydroxide ion concentration  $[OH^-]$  upon dissolution due to hydrolysis.

The determination is based upon following reactions :



The possibility of  $OH^-$  &  $HCO_3^-$  together is ruled out, because of the fact that they combine instantaneously to form  $CO_3^{2-}$  ions.

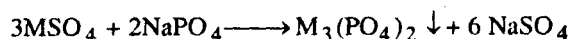
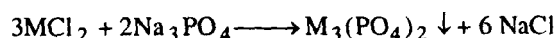


**Q. 3. (b) Write short note on :**

**(i) Phosphate conditioning**

**(ii) Calgon conditioning.**

**Ans. (i) Phosphate Conditioning :**

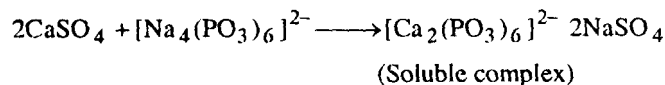
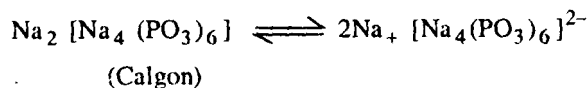


Where,  $M = Ca^{2+}, Mg^{2+}$

$$[PO_4^{3-}]^{2/3} / [SO_4^{2-}] > [Ca_3(PO_4)_2]^{2/3} / [CaSO_4]$$

Scale formation is avoided by adding sodium sulphate, which reacts with Mg & Ca salts forming non adherent & easily removable, soft sludge of Ca & Mg phosphate, the later than can be removed by blow down operation.

**(ii) Calgon Conditioning :** It involves in adding sodium hexa meta phosphate to boiled water to Prevent scale & sludge formation.



**Q. 3. (c)** A sample of water on analysis has been found to contain following in ppm :

$\text{Ca}(\text{HCO}_3)_2 = 10.5$ ,  $\text{Mg}(\text{HCO}_3)_2 = 12.5$ ,  $\text{CaCl}_2 = 8.2$ ,  $\text{MgSO}_4 = 2.6$

Calculate temporary and permanent hardness.

**Ans. Determination of Permanent Hardness :**

100 ml of boiled  $\text{H}_2\text{O} = 10 \text{ ml of EDTA}$

$= 10 \text{ mg of CaCO}_3 \text{ e.g., hardness}$

1000 ml of boiled  $\text{H}_2\text{O} = \frac{10}{100} \times 1000 = 100 \text{ mg of CaCO}_3 \text{ e.g., hardness}$

Hence

$\text{PH} = 100 \text{ rpm}$

**Determination of Temperature Hardness :**

Temperature Hardness = Total HD - PH

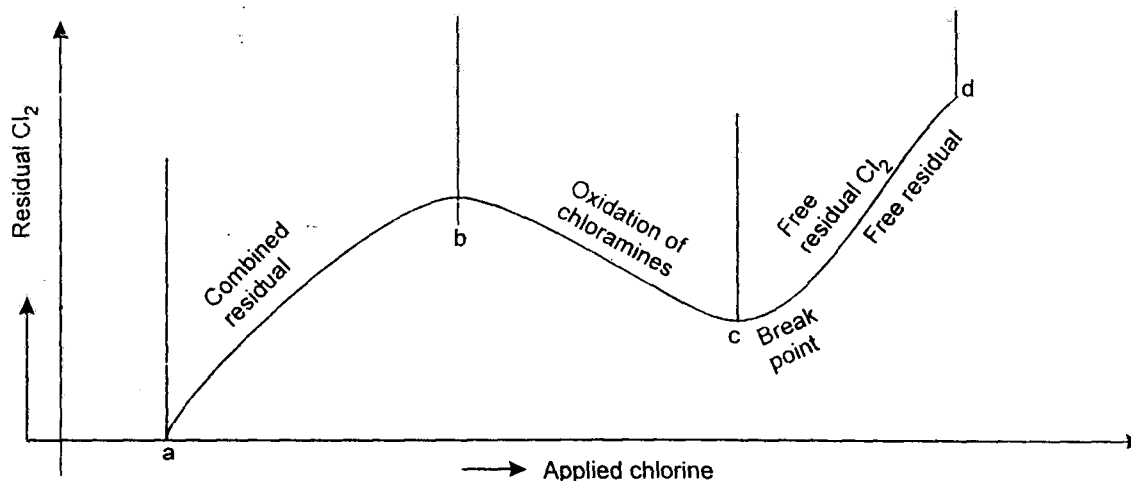
$= 350 - 100$

$= 250 \text{ rpm}$  **Ans.**

**Q. 4. (a) Write a short note on Break-point chlorination.**

**Ans.** It means chlorination of water to such an extent that living organism as well as other organic impurities as  $\text{H}_2\text{O}$  are destroyed.

It involves in addition of sufficient amount of chlorine to oxidise organic water, reducing substances and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfection action against pathogenic bacterias.



**Q. 4. (b) What are zeolites ? Describe the zeolite process for softening of water.**

**Ans. Zeolite/Permutit Process :** Zeolites are naturally occurring hydrated sodium aluminosilicate minerals capable of exchanging irreversibly its sodium ions for hardness producing ions in water.

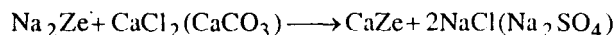
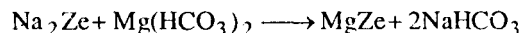
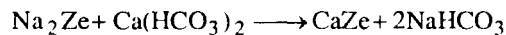
Zeolites are also known as permutits & in Greek it means boiling water stone.

Zeolites are of two types viz.

- (i) Natural
- (ii) Synthetic

**Softening Process :** For softening of  $\text{H}_2\text{O}$ , by zeolite process, hard water is percolated at a specified rate through a bed of zeolites, housed in a cylindrical unit.

Reactions taking place are :



Zeolite holds sodium ions loosely & can be simply represented as  $\text{Na}_2\text{Ze}$  where Ze represents insoluble radical framework.

**Q. 4. (c) How is reverse osmosis used for desalination of water ?**

**Ans.** If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move down from concentrated side to dilute side across the membrane. This is called reverse osmosis.

Semi-permeable membrane on this film of cellulose acetate, polymethyl acrylate & polyamide polymers is used. A pressure of the order of 15-40 kg/cm<sup>2</sup> is applied for water separation from its contaminations. This process is called distillation of water.

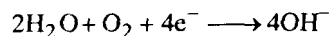
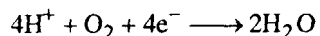
**Q. 5. (a) Describe the mechanism of electrochemical corrosion.**

**Ans. Electrochemical/Wet Corrosion :** It takes place mostly under wet/moist conditions through the formation of short-circuited galvanic cells. Wet corrosion is more common than dry one.

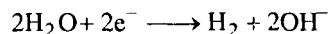
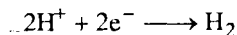
Electrochemical corrosion involves:

- (i) Separate 'anodic' and 'cathodic' parts/areas.
- (ii) Occurrence of oxidation.
- (iii) Non-metallic ions like  $\text{OH}^-$  or  $\text{O}^{2-}$
- (iv) Diffusion of metallic & non-metallic ions.

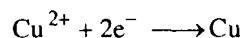
**(i) Oxygen Absorption:**



**(ii) Hydrogen Evolution :**



**(iii) Electroplating :**



Corrosion occurs at the anode, but products accumulate near the cathode.

**Q. 5. (b) Discuss the following :**

- (i) Sacrificial anodic protection
- (ii) Galvanic corrosion

**Ans. (i) Sacrificial Anodic Protection:** The metal structure can be saved from corrosion by connecting it with wire to a more active metal, so that all the corrosion is concentrated at the more active metal. As the more active metal is sacrificed in the process of saving metal from corrosion, hence it is known as sacrificial anode metals commonly used as sacrificial anodes are Zn, Al, Mg & their alloys. Zinc is used as sacrificial anode in good electrolytes such as sea water.

**(ii) Galvanic Corrosion :** It takes place when different metals are in contact & jointly exposed to corrosive atmosphere. The metal which is higher up in the electrochemical series, with more negative electrode potential will form anode & undergo corrosion.

In the Zn-Cu galvanic cell, Zn behaves as anode where oxidation & corrosion occurs & Cu behaves as cathode & is protected.

**Minimization :**

- (i) avoid galvanic couple
- (ii) provide an insulating material between metals.

**Q. 6. (a) Discuss the mechanism of hydrodynamic lubrication. Under what conditions are greases preferred to lubrication oil ?**

**Ans. Hydrodynamic Lubrication (Fluid Film Lubrication):**

In this, the movement/sliding surfaces are separated from each other by a bulk lubricant film. This bulk lubricant film prevents direct surface to surface contact so that the small peaks & valleys donot interlock.

This consequently reduces friction & prevents wear. Fluid film lubrication, the small friction is only due to the interval resistance between the particles of the lubricant moving over each other.

In such a system, friction depends on the thickness & the viscosity of the lubricant & the relative velocity & area of sliding surfaces.

$$\text{Coefficient of Friction} = \frac{F}{W}$$

Where,  $F$  = force required to causion motion.

$W$  = applied load.

**Lubricating Oil Applications:**

- (i) For lubricating ordinary machine parts.
- (ii) For lubricating clocks & sewing machines.
- (iii) Particularly suitable for light machinery.

**Grease Applications :**

- (i) Used in ball bearing which generates frictional heat.
- (ii) For aircraft applications at extreme heights.
- (iii) For lubricating caterpillar threads, tractors, water pumps etc.
- (iv) Used for equipment working at low speeds & high loads.
- (v) In bearings & gears that works at higher temperatures.

**Q. 6. (b) Why additives are used in lubricants ? Give some examples of additives.**

**Ans.**

**Lubricant Additives**

Additive	Typical Examples
(i) Antioxidant	aromatic amines, Hindered phenols etc.
(ii) Metal Deactivators	Amines, Sulfides or phosphites etc.
(iii) Antifoamant	Silicon polymers
(iv) Detergent	Magnesium phenolates, phosphates & sulfonates.
(v) Dispersant	Alkylsuccinimides, & polymeric alkylthiophosphonates.
(vi) Viscosity Modifier	Polymers and copolymers of olefins, alkylated styrenes, Methacrylates & butadiene.
(vii) Pour point depressant	Polyimethacrylates phenolic polymers & alkylated naphthalene
(viii) Seal swell agent	Aromatic hydrocarbons & organic phosphates.

**Q. 6. (c) What do you mean by purification of lubricant ? Discuss solvent refining.**

**Ans. Solvent Refining Method :** This method is used with the more fluid products, opening. A weighted sample is placed in a special glass bulb with a capillary opening. The glass bulb containing sample is inserted in one of the holes of an electrically heated small furnace maintained at approximately 550°C.

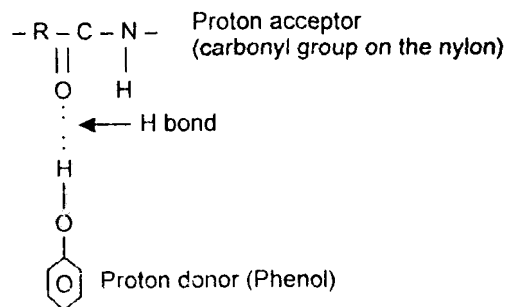
At this temperature, all volatile matter space escapes the bulb capillary leaving a residue that undergoes cracking & possible coke formation.

$$\% \text{ carbon residue} = \frac{\text{Weight of R in bulb}}{\text{Weight of original sample}} \times 100$$

**Q. 7. (a) Discuss in detail " The effect of structure on properties of polymer."**

**Ans. (i) Structural & Chemical Properties :**

**(a) Solubility & Swelling Behaviour:** The solution of a polymer in a solvent involves the diffusion of solvent into the polymer, so that later swells & finally disintegrates.



**(b) Chemical Reactivity :** PTFE is very stable & chemically inert as it contains only C-C & C-F bonds.

**(ii) Structure & Electrical Properties :**

(i) In non polar polymers, only electronic polarization is responsible for dielectric constant.

(ii) In polar polymers, both electronic as well as dipole polarization contributes towards overall dielectric constant.

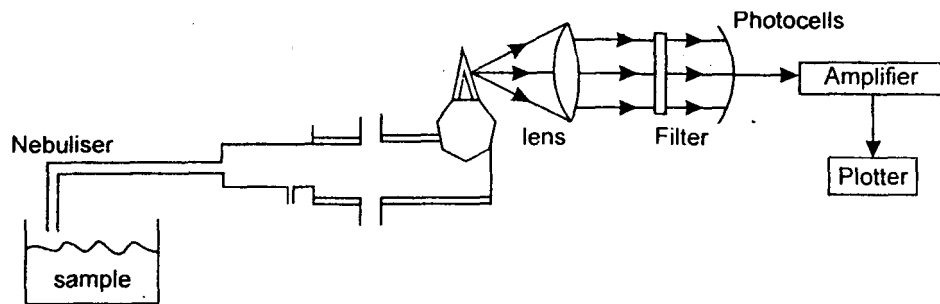


**Q. 8. (a) Discuss the principle and working of a flame photometer.**

**Ans. Flame Photometer:** Characteristic colours imparted to the flame by the emission of radiation by the alkali metals excited in flame is the basis of flame emission spectroscopy (FES). FES was formerly referred as flame photometry.

**Working :** Air at a given pressure is passed into an atomiser & the suction thus produced draws a solution of the samples into the atomiser. Air is mixed with it in mixing chamber & this mixture is passed into the burner, along with the fuel gas.

**Applications :** Primarily used for the analysis of those elements which have an easily excited flame spectrum of sufficient intensity for detection of photocell.



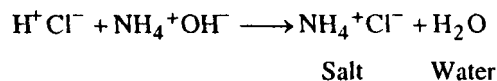
**Flame photometry**

**Q. 8. (b) Define conductometric titration. Discuss conductometric titration of strong acid with weak base.**

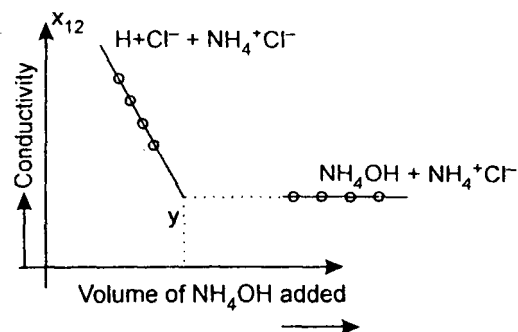
**Ans. Conductometric Titration :**

It is a method of volumetric analysis is based on the change in conductance of the solution, at the end point.

Titration of strong acid (HCl) with weak base (NH<sub>4</sub>OH)



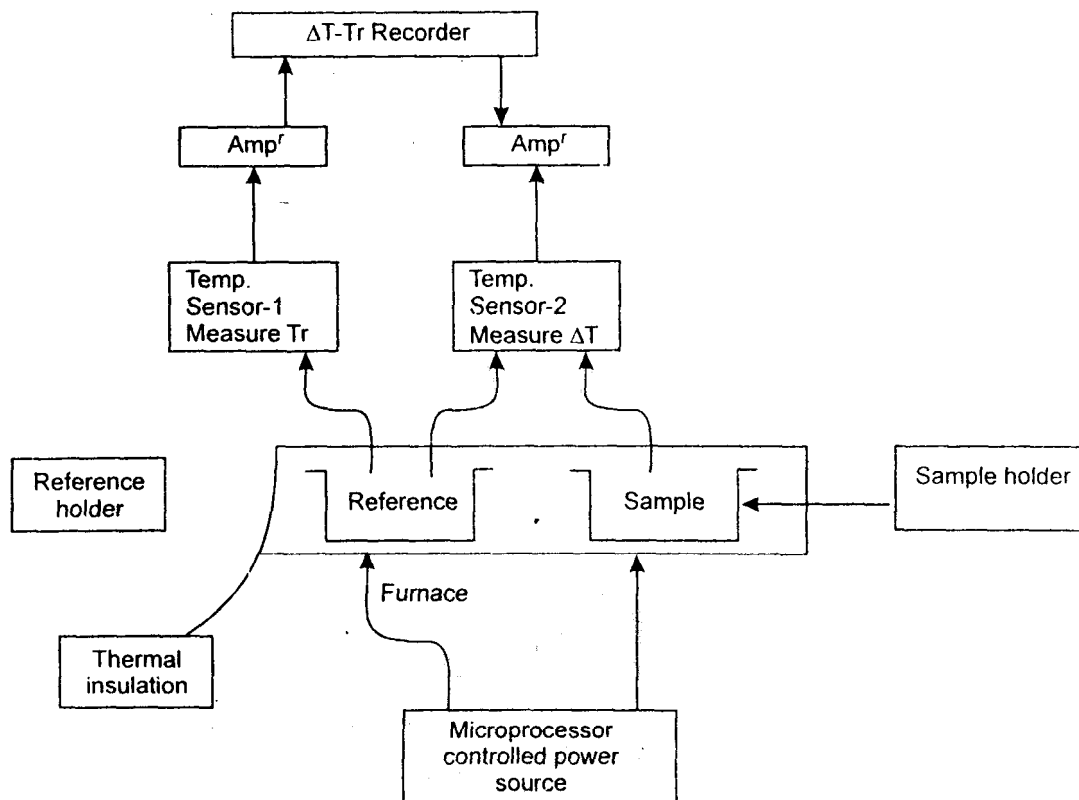
When ammonium hydroxide (NH<sub>4</sub><sup>+</sup>OH<sup>-</sup>) is added to hydrochloric (HCl), the conductivity decreases along xy because of the replacement of the fast moving H<sup>+</sup> ions by slow moving NH<sub>4</sub><sup>+</sup> ions.



**Q. 8. (c) Write a short note on Differential Thermal Analysis (DTA).**

**Ans. DTA : Differential Thermal Analysis (DTA)**

DTA employs a similar type of furnace heating programmer & recording devices as employed in TGA. But the furnace in DTA contains 2 chambers which are identical & symmetrically located & are connected with temperature sensor:



**B.D. of DTA Apparatus**