Dr.Pusalkar Notes **ELECTROCHEMISTRY** S.Y.B.Sc

Q.1) What is electrochemistry? Distinguish between electrolytic cells and galvanic cells

Ans: A branch of physical chemistry which deals with the study of interrelation between chemical changes and electricity is called electrochemistry

Electrolytic cell	**Electrochemical cell**
a)It converts electrical energy to chemical energy	**a)** It converts chemical energy to electrical energy.
b)An electric current drives a non-spontaneous reaction.	b) A spontaneous chemical reaction generates electric current.
c) Oxidation occurs at positive electrode.	c) Oxidation occurs at negative electrode
d)Reduction occurs at negative electrode	d) Reduction occurs at positive electrode

Q.2) Define the following terms:

i) Cell ii) Electrochemical cell iii)Anode iv) Cathode
v) Oxidation vi) Reduction vii) Redox reaction viii) oxidizing agent
ix) reducing agent x) Electrolysis xi) emf xii) single electrode potential xiii) oxidation potential xiv)Reduction potential
xv) Standard oxidation potential xvi) Standard reduction potential
xvii) Reference electrode xviii)Standard hydrogen electrode
xix) emf series

Ans:

<u>i)Cell</u>:A device consisting of two electrodes in contact with an electrolyte which convert chemical energy to electrical energy or vice-versa.

ii)<u>Electrochemical cell</u>: The cell which converts chemical energy to electrical energy and vice versa is called an electrochemical cell.

iii) Anode: It is defined as the electrode at which oxidation occurs as electrons are lost by some species.

iv)Cathode: It is defined as the electrode at which reduction occurs as electrons are gained by some species.

v)Oxidation: The process in which an atom or an ion loses electrons is called oxidation.

vi)Reduction: The process in which an atom or an ion gains electrons is called reduction.

vii) Redox reaction: The chemical reactions in which oxidation and reduction occur simultaneously are called redox reactions

viii)Oxidising agent: A species which oxides others and itself gets reduced by gain of electrons is called an oxidizing agent.

ix)Reducing agent: A species which reduces others and itself gets oxidised by loss of electrons is called a reducing agent

x) Electrolysis: It is defined as a process in which electric current is used to bring about a chemical reaction or a process in which electrical energy is converted to chemical energy.

xi)E.M.F: The potential difference between the electrodes corresponding to an external flow of electrons from left hand side electrode(anode) to right hand side electrode(cathode)measured across the terminals of the cell in an open circuit **i.e.** when no current flows in the circuit is called emf of the cell.

xii)Single Electrode Potential: A difference of electrical potential developed between the metal electrode and its surrounding salt solution **at equilibrium** is called single electrode potential.

xii)Oxidation potential: A difference of electrical potential developed at an electrode **due to oxidation** when a metal electrode is in contact with its own electrolytic solution at equilibrium is called oxidation potential.

xiv)Reduction Potential: A difference of electrical potential developed at an electrode **due to reduction** when a metal electrode is in contact with its own electrolytic solution at equilibrium.

xv)Standard Oxidation Potential: A difference of electrical potential potential developed at an electrode due to oxidation when a metal or a gas at partial pressure of 1 atm. is placed in a solution of its own ions at unit activity and measured at **298K** is called standard oxidation potential.

xvi)<u>Standard Reduction Potential</u>: A difference of electrical potential developed at an electrode due to reduction when a metal or a gas at partial pressure of one atm. is in contact with a solution of its own ions at unit activity and measured at **298K** is called standard reduction potential.

xvii)<u>Reference electrode:</u> An electrode whose potential is arbitrarily taken as zero or is exactly known.

xviii)<u>Standard hydrogen electrode:</u>An electrode in which pure and dry hydrogen gas at one atmosphere is bubbled over the surface of platinised platinum kept immersed in solution of 1M H^+ ions and whose potential is arbitrarily fixed as zero volts at 298 K is called standard hydrogen electrode.

xix)<u>E.m.f. series:</u>The arrangement of the electrodes(**as half cells**) in the decreasing order of their standard reduction potential measured w.r.t. hydrogen gas electrode at **298K** is called **e.m.f. series**

Q.3)What are reversible and irreversible cells? Explain with a suitable example

Ans:A reversible cell is a cell in which the driving and opposing force differ infinitesimally small amount from each other and the the chemical change taking place in it can be reversed by applying an external force infinitesimally greater than the emf of the cell. A reversible cell should satisfy the following conditions:

i)When the external emf of the cell is infinitesimally greater than the emf of the cell, then current should flow through the cell and the cell reaction of the cell should get reversed.

Ii) When the external emf of the cell is infinitesimally less than the emf of the cell, then current should flow from the cell.

iii) When the external emf of the cell is exactly equal to the emf of the cell, then no current should flow through the cell.

Example: **Daniel cell** is a reversible cell.

The reaction of the Daniel cell is

$$\mathbf{Zn + Cu^{2+} \longleftrightarrow Zn^{2+} + Cu}$$

The cell reaction can be adjusted to forward or reverse direction by adjusting the external emf of the cell.

Any cell which does not satisfy the condition of reversibility is an irreversible cell

Consider the following cell set up by dipping copper and zinc electrodes in a solution of sulphuric acid .When the cell operates, the following reaction take place

$$\mathbf{Zn + 2H^+ \longrightarrow Zn^{2+} + H_2}$$

When this cell is connected to an external emf which is slightly greater than the emf of the cell, the following reaction occurs

$$\mathbf{Cu + 2H^+ \longrightarrow Cu^{2+} + H_2}$$

Thus the first reacton is not reversed than that of the second.Hence it is an irreversible cell

Q.4) Distinguish between reversible cell and irreversible cell

Ans:

	Reversible cells	**Irreversible cells**
1)	Cell reaction is reversible	1) Cell reaction is irrreversible
2)	Emf is generated by the cell reaction of its own	2) An external potential greater than the cell emf is required for the cell reaction to occur
3)	Cell reaction occurs only when the two electrodes are connected externally.	3) Cell reaction may occur even if the two electrodes are not connected externally
4)	It is a galvanic cell	4) It is an electrolytic cell.

Q.5) What are reversible electrodes? Give a brief account of the various reversible electrodes with suitable examples.

Ans: The electrodes of a reversible cell are called reversible electrodes.The various types of reversible electrodes are as follows

The various types of electrodes are as follows:

i)Gas electrode: It consist of a gas bubbled around an inert metal like platinised platinumdipped in a solution containing ions to which the gas is reversible.The gas gets **adsorbed** on the inert metal and an equilibrium is established between the gas and its own ions in the solution.

The potential of the gas electrode depends on the pressure of the gas, the concentration of the solution and the pressure.

Sr.No.	**Name of the gas electrode**	**Representation**	**Reduction reaction**

1	Hydrogen gas electrode	$HCl \mid H_{2(g)} \mid Pt$ **(a =1) 1 atm**	$H^+ + e^- \rightarrow 1/2H_{2(g)}$
2	Oxygen gas electrode	$OH^- \mid O_{2(g)} \mid Pt$ **(a=1) 1atm**	$\mathbf{1/2O_{2(g)} + H_2O + 2e^- \rightarrow 2OH^-}$
3	Chlorine gas electrode	$Cl^- \mid Cl_{2(g)} \mid Pt$ **(a=1) 1atm**	$\mathbf{½\ Cl_{2(g)} + e^- \rightarrow Cl^-}$

ii)**<u>Metal-Metal ion electrode</u>**: It consist of a metal rod in contact with a solution of its own ion or ions(cations), with which the electrode is reversible. The potential of this electrode depends on the concentration of the metal ions in the solution and the temperature.

General representation : $M\ M^{n+}aq|(c_1\ M)$

General electrode reaction: $M \xrightarrow{\quad} M^{n+} + ne^-$

Electrode representation	**Electrode reaction**
i) $Zn(s) \mid Zn^{2+}(aq)$	$Zn \longrightarrow Zn^{2+} + 2e^-$
ii) $Cu(s) \mid Cu^{2+}(aq)$	$Cu \longrightarrow Cu^{2+} + 2e^-$

iii)<u>Metal –Metal sparingly salt electrode</u>: This type of electrode consist of a metal in contact with one of the sparingly soluble salts and a solution containing a negative ion of the salt.The electrode involves a reversible reaction between the metal and the negative ion to form sparingly soluble salt with the liberation of electrons.

Electrode representation	**Electrode reaction**
1) $Ag(s) \mid AgCl(s) \mid KCl\ aq$ (c_1M)	$Ag(s) + Cl^- \longrightarrow AgCl(s) + e^-$
2) $Hg \mid Hg_2Cl_2(s) \mid KCl\ aq$ (c_1M)	$Hg(l) + Cl^- \longrightarrow 1/2\ Hg_2Cl_2(s) + e^-$
3) $Pb(s) \mid PbSO_4(s) \mid H_2SO_4\ aq$ (c_1M)	$Pb(s) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$

iv) **<u>Redox electrodes</u>**.This type of electrodes consists of an inert metal like platinum in contact with an aqueous solution of the salt of an element in different oxidation state. The potential of this electrode depends on the ration of the activities of the metal into in different oxidation state

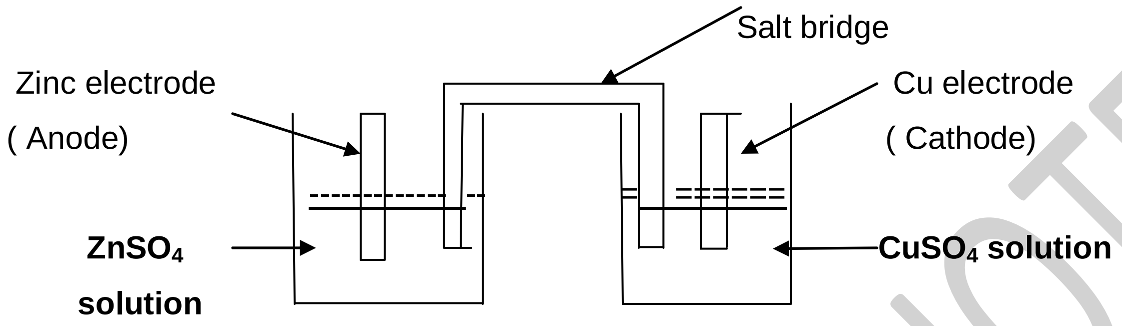
Redox electrode	$Fe^{3+}{}_{\mathbf{aq}} \mid Fe^{2+}{}_{\mathbf{aq}} \mid Pt$	$Fe^{3+}(aq)+e^- \longrightarrow Fe^{2+}(aq)$
	$Sn^{4+}{}_{\mathbf{aq}} \mid Sn^{2+}{}_{\mathbf{aq}} \mid Pt$	$Sn^{4+}(aq)+ 2e^- \longrightarrow Sn^{2+}aq)$

Q.6)Describe the construction and working of a Daniel cell .

Ans.

Principle:It is a chemical cell which spontaneously converts chemical energy into electrical energy.

Labelled diagram:



Daniel cell

Construction :

It consists of two half cells .One half cell consists of 1M aqueous solution of **$ZnSO_4$** placed in a beaker inside which a zinc rod is imersed.The other half cell consists of 1M aqueous solution of **$CuSO_4$** placed in a beaker inside which a copper rod is immersed. The two solutions externally are in contact by a metallic wire while internally are in contact by means of a KCl salt bridge as shown in the figure.

Formulation $Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu$

Working : The daniel cell with salt bridge works as soon as the salt bridge is introduced into the circuit. The electrons flow from Zn to Cu & is indicated by a deflection in the galvanometer placed in the circuit. Zn dissolves at one electrode to form Zn^{2+} ions leaving behind electrons. As a result, it becomes negatively charge and acts as negative electrode(anode)

$$Zn_{(S)} \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{oxidation}$$

The electrons travel from Zn to Cu through the metallic wire and are accepted by the Cu^{2+} ions from $CuSO_4$ solution and gets deposited at Cu electrode.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu_{(S)} \quad \text{reduction}$$

Net cell reaction : $Zn_{(S)} + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu_{(S)}$

Observations:

I) At **298K**, the e.m.f.of the Daniel cell is **1.1 volts** when the concentration of $ZnSO_4$ & $CuSO_4$ solutions used are one molar each.

ii) During the operation of the cell, mass of copper rod increases due to deposition of copper at cathode and the concentration of the Cu^{2+} ions decreases.

III) During the operation of the cell, mass of zinc rod decreases due to its tendency to undergo oxidation to form Zn^{2+} ions.As a result,the concentration of the Zn^{2+} ions increases in the solution.

The e. m. f. of the cell depends upon

i) **Temperature**

ii) **Concentration** of **$CuSO_4$** and **$ZnSO_4$ solution.**

At **298K**, the e.m.f.of the Daniel cell is **1.1 volts** when the concentration of $ZnSO_4$ & $CuSO_4$ solutions used are one molar each.

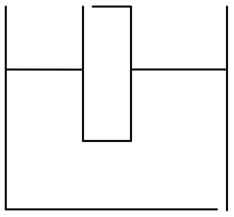
Q.7)Discuss Nernst theory of single electrode potential.

Ans.

Nernst Theory of Single Electrode Potential: Nernst theory helps to explain the concept of electrode potential. It states that when all metals and hydrogen gas are in contact with a solution containing its own ions, then the following processes occur at the electrode:

De-electronation: The metal shows a peculiar tendency of passing into the solution as +ve ions thereby leaving electrons on the surface of the metal. As a result, the solution acquires a positive charge while the metal acquires a negative charge.This results in the formation of electrical double layer across the surface of the metal.This tendency of the metal is called **solution pressure of the metal**. This property is also exhibited by the hydrogen gas. The extent of this type of behaviour varies from metal to metal.

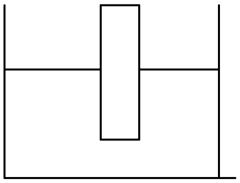
Reaction : $M \longrightarrow M^{n+} + ne^-$ **Oxidation**



As electrons are given out, the process is also called **de-electronation.**

Electronation: The tendency of the metal to send positive ions into its own salt solution is opposed by the reverse tendency of the metal ions in solution to accept the electrons from the metal surface. This tendency is called **osmotic pressure of the metal ions of the solution**.As a result, the metal acquires +ve charge while solution acquires -ve charge.The attraction between opposite charges results in the formation of electrical double layer across the surface of the metal. The metal ions by accepting electrons get deposited as metal atoms on the surface of the metal.

$$\mathbf{M^{n+} + ne^- \longrightarrow M} \qquad \textbf{Reduction}$$



The osmotic pressure changes from one ion to another and varies with the concentration of the solution. Thus the two pressures (**P_s** & **P_o**) oppose each other and reach an equilibrium. When these opposing pressures at equilibrium are unequal, one of the pressure predominates and gives rise to electrode potential.

Magnitude and Nature of Single Electrode Potential: The magnitude is dependent on the relative magnitudes of the solution pressure of the metal (P_s) and osmotic pressure of the cations involved (P_0)

i) If **$P_s > P_0$** , then oxidation reaction takes place rapidly at that electrode. The solution acquires a +ve charge while metal acquires a negative charge, e.g **Zn/Zn^{2+}** electrode, Cd/Cd^{2+} and alkali metal in their solution of their own salts.

ii) If **$P_s < P_0$** ,then reduction occurs rapidly at that electrode. The metal acquires positve charge and thus acts as positive electrode, e.g. Cu^{2+} / Cu, Ag^{+1} / Ag etc.

iii) If **Ps = Po** then neither electronation nor de-electronation takes place at that electrode. The metal do not acquire any charge. Such an electrode is called null electrode.

Q.8) Describe the construction and working of a primary reference electrode.

Ans. The primary reference electrode is the hydrogen gas electrode

<u>Hydrogen gas electrode</u> : It is a primary reference electrode in which pure and dry hydrogen gas at one atmosphere is bubbled over the surface of platinised platinum kept immersed in HCl solution of unit activity and whose potential is arbitrarily fixed as **zero volts** at **298 K**.

<u>Labelled diagram:</u>

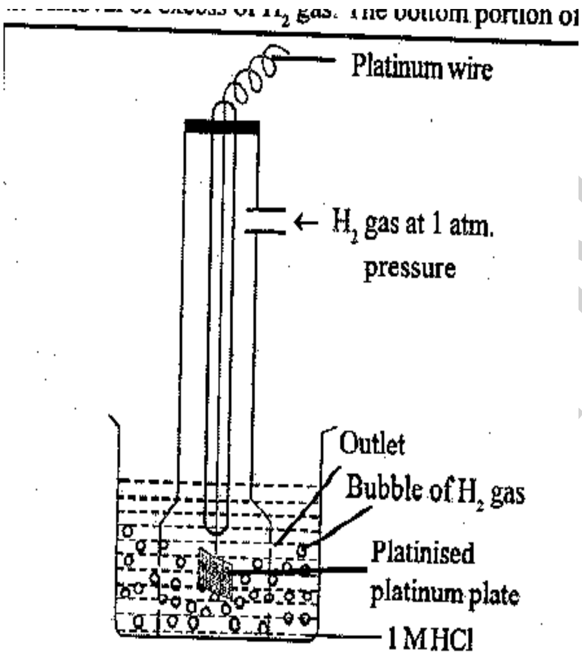


Fig. 4.10 Standard hydrogen electrode

<u>Construction</u> : It consist of a **platinum foil** coated with platinum black to **adsorb H_2 gas**. A platinum wire is connected to this platinum foil. This platinum wire is sealed in a glass tube and is used to make electrical contact with outer surface. A glass jacket, having inlet at top and number of outlets at the bottom, surrounds the platinum foil and the glass tube. This whole assembly is placed in a vessel containing a solution of **1MHCl**.

<u>Working</u>:When **pure and dry H_2 gas** at **one atm. pressure** is bubbled through the solution, part of H_2 gas is adsorbed on surface of platinum black while the remaining gas escapes through the holes of glass jacket. An equilibrium is set up between adsorbed H_2 gas and H^+ ions in the solution within 10 minutes. H_2 enters into the solution as positive ions leaving behind electrons on the platinum electrode.Thus the platinum electrode becomes negatively charge and a potential is developed on it. This **potential** developed is very less and is therefore arbitrary taken as **zero volts** at **298K**.

<u>Reaction</u> $2\,H^+\,(1M) + 2\,e^- \longrightarrow H_2(g, 1atm)$ **(reduction half reaction** $E^0 = 0.0000V$
at cathode)

$$\mathbf{H_2(g,\ 1\ atm)} \xrightarrow{\qquad\qquad} 2\ \mathbf{H^{+}\ (1M)} \quad \mathbf{+} \quad \mathbf{2\ e^{-}}$$
(oxidation half reaction E^{0}= 0.0000V **at anode)**

Representation $\quad$ **H^{+}(1M) | H_2 (g, 1 atm) | Pt**

Application of SHE:

It is used to find the standard potentials of other electrodes. For example, consider the determination of standard potential of Zn/Zn^{2+} electrode.The cell set up is as follows

Zn | Zn^{2+} (1 M) || H^{+}(1M) | H_2(g,1 atm) | Pt

The emf of the above cell from the potentiometer is found to be 0.763V.As the potential of the hydrogen gas electrod is 0.0000V, therefore the potential of the zinc electrode is obtained from the following equation

$$E^{0}cell = E^{0}_{SHE} - E^{0}_{Zn}$$

$$0.763V = 0 - E^{0}_{Zn}$$

Therefore $\quad E^{0}_{Zn} = -0.763V$

Q.9) Give the demerits of hydrogen gas electrode.

Demerits:

1)It is very difficult to maintain the pressure of H_2 gas at one atm.

2) Any impurity in H_2 gas disturbs the equilibrium set up and poisons the platinum plate.Thus it is difficult to obtain a highly pure H_2 gas.

3) Bubbling of H_2 gas through HCl solution causes evaporation of water thereby increasing the concentration of HCl solution.

4)The electrode is complicated and cumbersome to carry and therefore it is not portable.

10)Why is the standard hydrogen electrode assigned zero electrode potential?

Ans.

i)A standard hydrogen electrode is a gas electrode which consist of a platinised platinum plate dipped in **IM HCl** solution over which pure and dry H_2 gas at **1 atmospheric pressure** is bubbled.

ii) When dry H_2 gas at 1 atm pressure is bubbled over platinum plate, very few molecules are **adsorbed** on platinum plate. The adsorbed molecules dissociate to produce H^{+} ions which enter the solution leaving electrons on platinum plate.

iii) An electrical double layer is set up between electrons on platinum plate and H^{+} ions in solution which gives rise to a potential.

iv) As very few H^+ ions are obtained by hydrogen gas dissociation therefore the potential developed across the electrode is very less and is arbitrarily taken as zero volts at 298K.

Q.11) Describe the construction and working of the calomel electrode.

Ans.

Principle: It is called secondary reference electrode as its potential is determined w.r.t. std. H_2 gas electrode.

Labeled diagram:

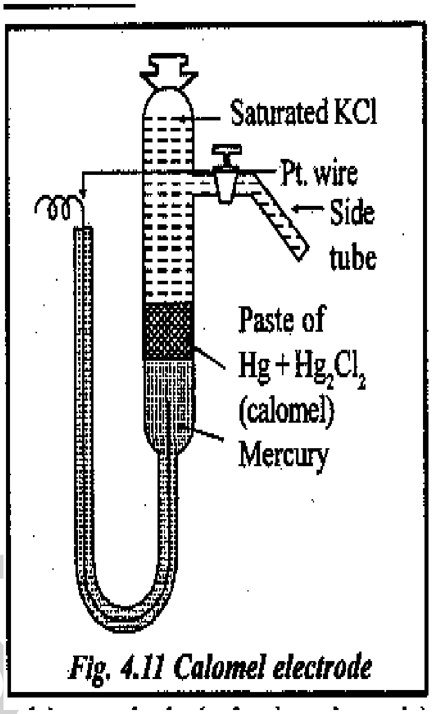


Fig. 4.11 Calomel electrode

Construction:It consists of a tubular glass vessel having a bent tube(B) at the bottom and a side arm in the middle for insertion in the desired solution.At the bottom lies mercury which is covered with a paste of **mercury and mercurous chloride**(calomel).A platinum wire is sealed in the mercury through the bent tube. The remaining portion of the vessel is filled with **KCl solution(either of 1N, O.1N or saturated)**.The side tube is closed by a glass wool plug and dipped in solution of other electrode.

Formulation: **KCl(sat) | Hg_2Cl_2(s) | Hg (l)**

<u>Electrode reactions</u>:

At anode : $2Hg_{(l)} + 2Cl^{-}(sat) \longrightarrow Hg_2Cl_2(s) + 2e^{-}$ **oxidation**

At cathode: $Hg_2Cl_2(s) + 2e^{-} \longrightarrow 2Hg(l) + 2Cl^{-(}sat)$ **reduction**

<u>Application</u> Consider the determination of oxidation potential of zinc electrode using saturated calomel electrode. The cell is represented as follows

$$Zn \mid ZnSO_4 \parallel KCl\ (satd) \mid Hg_2Cl_2 \mid Hg$$

The **e.m.f.** of the above cell is determined with the help of the **potentiometer**.The reduction potential of the saturated calomel electrode is **0.242 volts** at **298K**.Thus by substracting the value of e.m.f of the cell from 0.242, the reduction potential of zinc electrode is obtained.

$$\underset{Zn/Zn2+}{E_{oxidation}} = 0.242 - E_{cell}$$

The potential of the calomel electrode depends upon the concentration of KCl solution used. Following table gives the values of std. oxidation potentials for different concentrations of KCl solution used.

(measured at **298K)**.

Conc. of KCl	**0.1N**	**1N**	**Saturated**
$E_{oxidation}$	**-0.334V**	**-0.280V**	**-0.242V**
$E_{reduction}$	**+0.334V**	**+0.280V**	**+0.242V**

12) Give the merits of secondary reference electrode.

Ans:**<u>Merits:</u>**

i) It is easy to construct and transport and convenient to handle.

ii)Its potential is highly reproducible and remains constant.

ii) No separate salt bridge is required for its combination with other electrode

Q.13) Derive Nernst equation for emf of a cell.

Ans) Consider the following reversible reaction occurring in the galvanic cell

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant of the reaction is given by

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{I}$$

Let E be the emf produced by the cell reaction. If ΔG is the free energy change of the reaction and n is the number of electrons involved in the reaction, then

$$\mathbf{\Delta G = -nFE_{Cell}} \qquad \text{II}$$

Under standard conditions, standard free energy change ΔG^0 is given by

$$\mathbf{\Delta G^0 = -nFE^0_{cell}} \qquad \text{III}$$

According to Vant Hoff reaction isotherm,

$$\mathbf{\Delta G = \Delta G^0 + RTlnK}$$

Substitution of equn I, II and III in the above equation, we get

$$-nFE_{Cell} = -nFE^0_{cell} + RTln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Dividing throughout by **–nF** we get,

$$E_{Cell} = E^0_{cell} - \frac{RT}{nF} ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Converting to natural log, we get

$$\mathbf{E_{Cell} = E^0_{cell} - \frac{2.303RT}{nF} log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

When T= 298K, F=96500C R=8.314$JK^{-1}mol^{-1}$, then the expression $\frac{2.303RT}{F} = 0.0592$

Therefore $\mathbf{E_{Cell} = E^0_{cell} - \frac{0.0592}{n} log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b}}$ **Equation V**

Equation V is the Nernst expression for the emf of the cell.

Q.14) Write an informative note on glass electrode.

Ans: A **glass electrode** is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. It is an important part of the instrumentation for chemical analysis and physico-chemical studies.

The most common glass electrode is the pH-electrode. Only a few chalcogenide glasselectrodes are sensitive to double-charged ions, like Pb^{2+}, Cd^{2+} and some others.

There are two main glass-forming systems:

- **silicate** matrix based on molecular network of silicon dioxide (SiO_2) with additions of other metal oxides, such as Na, K, Li, Al, B, Ca, etc.
- **chalcogenide** matrix based on molecular network of AsS, AsSe, AsTe.

Diagram:

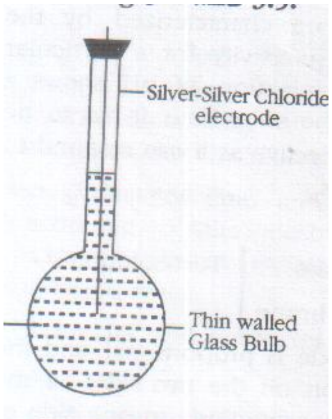


Fig. 3.4 Glass electrode

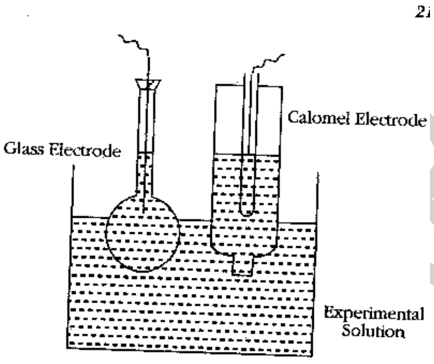


Fig. 3 : Glass and Calomel Electrode System

Construction:

A glass electrode consists of a long glass tube with a thin walled glass bulb at one end. Special glass (Corning glass containing 22% Na2O, 6% CaO and 72%SiO2) of low melting point and high electrical conductance is used for the purpose. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and a Ag/AgCl electrode (as internal reference electrode) is immersed into the solution and connected by a platinum wire for electrical contact. The electrode is represented

Ag | AgCl | 0.1NHCl | glass membrane | Test solution

Working: The glass electrode is combined with the calomel electrode and the emf of the cell set up is measured.If the value of E^0 is known, then the pH of the test solution can be determined.The E^0 value of the electrode is determined by using buffer solutions of pH = 4 and pH= 9.2

Cell representation

Ag - AgCl | 0.1NHCl | glass membrane | Test solution || KCl(satd) | Hg_2Cl_2(s)-Hg(l)

The emf of the cell is determined specially designed electronic circuits.The emf of the cell is given by

$$E_{cell} = \underset{cathode}{E_{reduction}} -- \underset{anode}{E_{reduction}}$$

$$= E_{cal} -- E_{glass}$$

The electrode potential of the glass electrode is given by the expression

$$E_{Glass} = E^0_{Glass} -- 0.0592pH$$

Advantages of glass electrode:

(i) Glass electrode can be employed in the presence of strong oxidizing or reducing substances and metal ions.

(ii) It is not poisoned easily.

(iii) Accurate results are obtained between pH range 1-9. However, by using special glass electrodes, pH 1-13 can be measured.

(iv) It is simple to operated, can be used in portable instruments and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

Limitations of glass electrode:

(i) In strongly acidic solutions of pH<1, the salt effect due to anions is observed.

(ii) It can be used upto a pH of 13 but being sensitive to Na+ ions above a pH of 9, the linear relationship between glass electrode altered. So an alkaline error is introduced beyond a pH of 9, which should be taken into consideration.

(**iii)**It does not function properly in some organic solvents like pure alcohol.

Q.15) How will you determine ΔG, ΔH and ΔS of a cell reaction by emf measurement:- Under what conditions the cell becomes hot or cold?

Ans:

(1) Free energy change (ΔG):- Whenever a reversible galvanic cell operates, a chemical reaction takes place in the cell and decrease in free energy of cell reaction appears in the form of electrical work. i.e. electrical energy is produced by the decrease in free energy of cell reaction. But electrical work done = nFE volt-coulombs or Joules

Where n is number of valence electrons involved in the cell reaction, F is known as Faraday (1F =

96500 coulombs) and E is the emf in volts of a reversible cell.

Now decrease in free energy = Electrical work

$$\therefore\ -\Delta G = nFE \quad \text{or} \quad \Delta G = -\,nFE \ \text{ Joules} \quad \rightarrow (1)$$

The negative sign indicates the spontaneity of cell reaction. A reaction can proceed spontaneously only if $\Delta G < 0$ (i.e $E > 0$).

(2) **Enthalpy change (ΔH):-** The emf of a cell changes with temperature and concentrations of the materials of cell. According to Gibbs-Helmholtz equation, the decrease in free energy of the system at constant pressure is given by the relation:

$$\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_P \quad \rightarrow (2)$$

Substituting $\Delta G = -\,nFE$ in equation (2)

$$\therefore -\,nFE = \Delta H + T\left(\frac{d(-nFE)}{dT}\right)_P$$

$$\therefore -\,nFE = \Delta H - nFT\left(\frac{dE}{dT}\right)_P$$

$$\therefore\ \Delta H = -\,nF\left[E - T\left(\frac{dE}{dT}\right)_P\right] \ \text{ Joules} \quad \rightarrow (3)$$

The term $(dE/dT)_p$ is known as temperature coefficient of emf. It is defined as change in emf per degree change in temperature. If E_1 and E_2 are emf values of cell at temperatures T_1 and T_2, them the temperature coefficient of emf $(dE/dT)_p$ is given by the relation:

$$\left(\frac{dE}{dT}\right)_P = \frac{E_2 - E_1}{T_2 - T_1} \ \text{ Volt per degree.}$$

(3) **Entropy change (ΔS):-** The Gibbs free energy change is given by the relation

$$\Delta G = \Delta H - T\Delta S \qquad \therefore\ T\Delta S = \Delta H - \Delta G$$

$$\therefore T\Delta S = -\,nFE - T\left(\frac{dE}{dT}\right)_P - (-nFE) \quad \therefore \Delta S = nF\left(\frac{dE}{dT}\right)_P \ \text{ Joules/degree} \rightarrow (4)$$

Conditions for a cell becoming hot or cold

1)If **dE/dT** is greater than **zero**, then electrical energy obtained will be greater than the heat of reaction..In such a case, the the cell absorbs energy from the surroundings during its operation.Thus the cell is said to become cold.

2) If **$dE/dT < 0$**, then heat of reaction will be greater than the electrical work produced.In such a case, the heat energy will be given to the surroundings which will increase the temperature of the cell.The cell is said to become hot.

3) If **$dE/dT = 0$**, then electrical work done will be equal to the enthalpy change of the reaction.Thus the cell neither becomes hot nor becomes cold during its operation.

Q.16) Explain the term concentration cell.

Ans: The cell in which the emf arises due to free energy change that accompanies the transfer of matter from one compartment to other due to difference in concentration of the electrode or electrolyte of same type is called concentration cell.

They are of two types:

i) **Electrode concentration cells**: In this type, the two electrodes of different activities are immersed into a single electrolytic solution.

Example Gas concentration cell **Pt, H_2(g| P_1atm)| HCl(a=x) H_2(g,P_2 atm**) ($P_2 > P_1$)

Amalgam concentration cell: **Cd(Hg) a_1| $CdCl_2$ | Cd(Hg) a_2 $a_2 > a_1$**

ii) **Electrolyte concentration cells**: In this type, the the two electrodes are of same activity but the electrolytes are of different activities.The emf arises due to difference in concentration of the two electrolytes by the transfer of matter.They are of two types

a) **Electrolyte concentration cells with transference**

Pt | H_2(g, 1 atm)| HCl | HCl| H_2(g, 1atm)| Pt (a_2>a_1)

a_1 a_2

b) **Electrolyte concentration cells without transference**

Ag| $AgNO_3$|| $AgNO_3$| Ag

a_1 a_2

Expression for emf of an electrolytic concentration cell **with transference** reversible to cation is given by

$$E_{cell} = t_- \frac{2.303RT}{nF} \log \frac{a_2}{a_1}$$

where **t_-** is the transport number of anion

Expression for emf of an electrolytic concentration cell **without transference** reversible to cation is given by

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{a_2}{a_1}$$

Q.17) Distinguish between chemical cell and concentration cell

Ans:

	Chemical cell	**Concentration cell**
1	Emf arises due to chemical reaction of the cell	1) Emf arises due to difference in concentration of the electrode or electrolyte
2	Two electrodes are different	2) Two electrodes or electrolytes used are same
3	The emf of the cell depends upon the electrodes and the activities of the ions involved	3) The emf of the cell depends only upon the activities of the electrode/el;ectrolyte involved.
4	E^0_{cell} is not zero	E^0_{cell} is zero

Q.18) Obtain a relation between equilibrium constant and standard emf of the cell

Ans: The standard free energy change for a chemical cell is related with the standard emf of the cell by the relation

$$\Delta G^0 = - nFE^0_{cell} \qquad \text{Equation I}$$

Consider the following reversible reaction occurring in the galvanic cell

$$\mathbf{aA + bB \rightleftharpoons cC + dD}$$

The equilibrium constant of the reaction is given by

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{Equation - I}$$

According to Vant Hoff reaction isotherm,

$$\Delta G = \Delta G^0 + RT\ln K$$

For a reaction at equilibrium, $\Delta G = 0$

Therefore $\Delta G^0 = - RT\ln K$ Equation- II

Substituting equn I in equn II, we get

$$- nFE^0_{cell} = - RT\ln K$$

$$nFE^0_{cell} = RT\ln K$$

Therefore $E^0_{cell} = \frac{RT\ln K}{nF}$

Converting to natural log, we get

$$\mathbf{E^0_{cell} = \frac{2.303RT}{nF} \log_{10} K}$$

When T= 298K, F=96500C R=8.314JK^{-1}mol^{-1}, then the expression $\frac{2.303RT}{F} = 0.0592$

Therefore $\mathbf{E^0_{cell} = \frac{0.0592}{n} \log_{10} K}$

IONIC EQUILIBRIA

Q.1) Obtain an expression for dissociation constant of a weak acid.

Ans:

Consider a weak acid HA which exist in the following equilibria in aqueous solution

$$HA + H_2O \Longleftrightarrow H_3O^+ + A^-$$

By law of mass action

$$K = \frac{[H_3O^+][A-]}{[HA][H_2O]}$$ where K is equilibrium constant

As water is in excess, **$[H_2O] = \text{constant}$**

$$\therefore \quad K\,(\text{constant}) = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{[H_3O^+][A-]}{[HA]}$$

where **K_a** is **dissociation constant** of weak acid

Q.2)Derive Ostwald's dilution law.

OR

Show that the degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration or directly proportional to square root of its dilution.

Ans .Consider the dissociation of a weak electrolyte BA as shown below. Let α be its degree of dissociation and let one mole of the weak electrolyte be dissolved in V dm^3 of the solution.

	$BA \Longleftrightarrow$	B^+ +	A^-
Moles at start	1	0	0
Moles at equilibrium	$1-\alpha$	α	α
Moles at equilibrium/dm^3	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

By law of mass action

$$K = \frac{[B^+][A-]}{[BA]}$$

where **K** = equilibrium constant

$$K = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}}$$

$$K = \frac{\alpha^2}{1-\alpha} \cdot \frac{1}{V}$$

For a weak electrolyte, α is very small compared to 1 and hence $1 - \alpha \approx 1$

$$\therefore \quad K = \frac{\alpha^2}{V}.$$

$= \alpha^2 .c$ (because **$c = 1/V$** where c is the initial concentration of the solution

$$\therefore \alpha = \sqrt{K/c}$$

$$\text{or} \quad \alpha = \sqrt{K.V}$$

Thus the degree of dissociation of a weak electrolyte is **inversely proportional** to **square root of its concentration** or **directly proportional** to **square root of its dilution**.

Q.3) Derive Ostwald's dilution law for a weak acid.

OR

Show that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to square root of its dilution.

Ans .Consider the dissociation of a weak acid HA as shown below. Let α be its degree of dissociation and let **one mole** of the weak acid be dissolved in **V dm^3** of the solution.

	HA	$\Longleftrightarrow$ H^+	$+$ A^-
Moles at start	**1**	**0**	**0**
Moles at equilibrium	**$1 - \alpha$**	α	α
Moles at equilibrium/dm^3	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

By law of mass action

$$K_a = \frac{[H^+][A-]}{[HA]}$$

where K_a = dissociation constant of a weak acid.

$$K = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1--\alpha}{V}} = \frac{\alpha^2}{1--\alpha} \cdot \frac{1}{V}$$

For a weak electrolyte, α is very small compared to 1 and hence $1 - \alpha \approx 1$

$$\therefore \quad K_a = \frac{\alpha^2}{V} .$$

$= \alpha^2 .c$ (because $c = 1/V$ where c is the initial concentration of the solution

$$\therefore \alpha = \sqrt{K_a /c}$$

$$\text{or} \quad \alpha = \sqrt{K_a .V}$$

Thus the degree of dissociation of a weak acid is **inversely proportional** to **square root of its concentration** or **directly proportional** to **square root of its dilution**.

Q.4) Derive Ostwald's dilution law for a weak base.

OR

Show that the degree of dissociation of a weak base is inversely proportional to the square root of its concentration or directly proportional to square root of its dilution.

Ans .Consider the dissociation of a weak base **BOH** as shown below. Let α be its degree of dissociation and let **one mole** of the weak acid be dissolved in **V dm^3** of the solution.

$$BOH \Longleftrightarrow B^+ + OH^-$$

	BOH	B^+	OH^-
Moles at start	**1**	**0**	**0**
Moles at equilibrium	**$1--\alpha$**	α	α

Moles at equilibrium/dm^3 $\quad \frac{1-\alpha}{V} \qquad \frac{\alpha}{V} \qquad \frac{\alpha}{V}$

By law of mass action

$$K_b = \frac{[B^+]\,[A^-]}{[BOH]}$$

where **K_b** = dissociation constant of a weak acid.

$$K_b = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1-\alpha} \cdot \frac{1}{V}$$

For a weak base, α is very small compared to 1 and hence $1 - \alpha \approx 1$

$$\therefore \quad K_b = \frac{\alpha^2}{V}.$$

$= \alpha^2 .c$ (because **$c = 1/V$** where c is the initial concentration of the solution

$$\therefore \alpha = \sqrt{K_b /c}$$

$$\text{or} \quad \alpha = \sqrt{K_b .V}$$

Thus the degree of dissociation of a weak base is **inversely proportional** to **square root of its concentration** or **directly proportional** to **square root of its dilution**.

Q.5) Define pH and pOH. Obtain a relation between them.

Ans. pH : It is defined as the **negative logarithm** to the **base10** of the molar **hydrogen ion concentration.**

pOH: It is defined as the **negative logarithm** to the **base 10** of the molar **hydroxyl ion concentration.**

By definition, **$pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$**

The ionic product of water K_w is given by

$$K_w = [H^+]\,[OH^-]$$

At 298K $K_w = 1 \times 10^{-14}$

$$\therefore \quad 1 \times 10^{-14} = [H^+][OH^-]$$

Taking $\log_{10}$ on both sides, we get

$$\log_{10}(1 \times 10^{-14}) = \log_{10}[H^+] + \log_{10}[OH^-]$$

Introducing negative sign on both sides, we get

$$-\log_{10}(1 \times 10^{-14}) = (-\log_{10}[H^+]) + (-\log_{10}[OH^-])$$

$$-(-14 \log_{10}10) = pH + pOH$$

$$\therefore \quad 14 = pH + pOH$$

Q.6) Derive an expression for ionic product of water or ionization constant of water.
Ans.

Pure water being a weak electrolyte, undergoes dissociation as follows :

$$H_2O + H_2O \Longleftrightarrow H_3O^+ + OH^-$$

In simplified form, the above equation can be written as

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

By law of mass action

$$K = \frac{[H^+]\,[OH-]}{[H_2O]}$$

As water is in excess, $[H_2O]$ = constant

$$K(\text{ constant }) = [H^+]\,[OH-]$$

$K_w = [H^+]\,[OH-]$ where K_w is called ionic product of water

<u>Ionic product of water:</u> It is defined as the product of molar concentrations of hydrogen and hydroxyl ions in pure water or in any neutral aqueous solution at a given temperature

Q.7 **What are buffer solutions? Explain the mechanism of buffer action of acidic and basic buffers.**

Ans. Solutions which resist a change in their pH values when kept for a long time or even when small amount of strong acid or alkali are added to them, are called buffer solutions.

<u>Mechanism of acidic buffer:</u>

An acidic buffer is prepared by mixing equimolar amounts of weak acid and a slat of weak acid and strong base. Eg. consider an acidic buffer obtained by mixing acetic acid and sodium acetate

$$CH_3COOH \qquad CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Acetic acid, being a weak acid, ionizes to a less extent while sodium acetate , being a strong electrolyte, ionizes completely. When a small amount of HCl is added to it, the added H^+ ions combines with acetate ions to form acetic acid molecules. Thus the pH of the buffer remains unchanged.

$$HCl \rightarrow H^+ + Cl^-$$

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

Thus phenomenon is called reverse basicity due to acetate ions. On addition of small amount of strong base like NaOH, the following reactions occur

$$NaOH \rightarrow Na^+ + OH^-$$

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

$$\underline{CH_3COOH \qquad CH_3COO^- + H^+}$$

$$CH_3COOH + OH^- \qquad CH_3COO^- + H_2O$$

The combination of H^+ of CH_3COOH with OH^- disturbs the equilibrium position of acetic acid. Therefore to maintain its Ka constant it dissociates to a greater extent. Thus the OH^- ions combine with acetic acid thereby maintaining the pH of the buffer. This phenomenon is called reverse acidity due to acetic acid.

	Mechanism of basic buffer: Basic buffer is prepared by mixing equimolar amount of weak base and a salt of a weak base and strong acid. Eg. consider the basic buffer obtained by mixing ammonium hydroxide and ammonium chloride $\mathbf{NH_4OH \qquad NH_4^+ + OH^-}$ $\mathbf{NH_4Cl \longrightarrow NH_4^+ + Cl^-}$ NH_4OH, being a weak base, ionizes to a less extent while NH_4Cl being a strong electrolyte ionizes almost completely. When a small amount of strong acid like HCl is added, the H^+ ions combines with OH^- to form un-dissociated water molecules. However, to maintain Ka constant, NH_4OH dissociates more thus removing H^+ ions. $\mathbf{HCl \longrightarrow H^+ + Cl^-}$ $\mathbf{H^+ + OH^- \longrightarrow H_2O}$ $\mathbf{NH_4OH \qquad NH_4^+ + OH^-}$ $\mathbf{NH_4OH + H^+ \qquad NH_4^+ + H_2O}$ On addition of a small amount of a strong base, the following reaction occurs. $\mathbf{NaOH \longrightarrow Na^+ + OH^-}$ $\mathbf{NH_4^+ + OH^- \longrightarrow NH_4OH}$ Thus the OH^- ions are removed by NH_4^+ ions thereby maintaining the pH constant. This is called reserved acidity due to NH_4^+ ions.
Q.8	**Derive the Henderson's equation for acidic and basic buffer.**
Ans.	**Henderson's equation for acidic buffer**: Consider an acidic buffer obtained by mixing weak acid HA and salt of weak acid and strong base. The acid, being weak ionizes to a less extent while the salt ionizes almost completely. $HA \qquad H^+ + A^-$ $BA \rightarrow B^+ + A^-$ By law of mass action, the dissociation constant Ka of weak acid HA is given by: Therefore,

As the acid is weakly ionized and its dissociation is further supported by A^- ions, therefore [HA] = [acid], similarly [A^-] = [salt]

Therefore,

Taking $-\log_{10}$ on both sides we get

But,
$P^H = -\log_{10}[H^+]$ and $pKa = -\log_{10}Ka$

Therefore,

The above equation is Henderson's equation for acidic buffer.

Henderson's equation for basic buffer:
Consider a basic buffer obtained by mixing base BOH and a salt of weak base and strong acid BA
$BOH \quad B^+ + OH^-$
$BA \rightarrow B^+ + A^-$
By law of mass action, the dissociation constant Kb of weak base is given by:

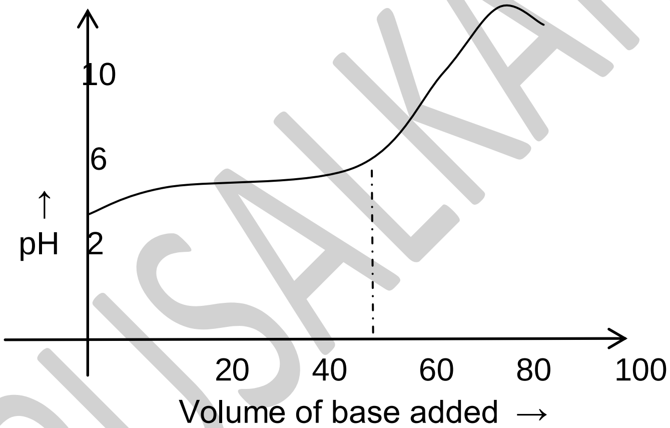
Therefore ,

As the base is weakly dissociated and its dissociation being further supported by B^+ ions, therefore , [BOH] = [Base] and [B^+] = [salt]

Therefore ,

Taking $-\log_{10}$ on both sides we get

But,
p^{OH} – $\log_{10}^{[OH]}$ and $pK_b = -\log_{10}K_b$
Therefore,

	Now, pH + pOH = 14 Therefore, pH = 14 – pOH = 14 – {pKb + log ([salt]/[base])} Therefore, pH = 14 – pKb – log ([salt]/[base])
Q..9	**Write a note on Buffer capacity**
Ans.	i) Buffer capacity: The magnitude of the buffer action is determined by its capacity. It is defined as the amount of strong acid or strong base required to produce a change in the pH of the buffer by one unit. ie where db is the small amount of acid or base added to produce a change in pH equal to dpH. An indication of the buffer capacity of any acid base system can thus be obtained directly from pH neutralization curve. It is a plot of pH against volume of NaOH added.  Consider the neutralization of 0.1M CH_3COOH eith 0.1M NaOH. Initially , the pH is low. With successive addition of 1 ml NaOH, the pH increases. At the same time, the amount of salt formed also increases. At the equivalence point, the pH suddenly rises. At that point, [salt]=[acid] and hence according to Henderson's equation **pH = pKa for acid buffer** **pOH = pKb for basic buffer** at this point, the slope d(pH)/db is the smallest and hence the buffer capacity is maximum. However, if the ratio of acid to salt is increased or decreased ten fold, ie. 10 :1 or 12 : 1 then according to Henderson's equation of acid buffer, pH = pKa + $\log_{10}$([salt]/[acid]), the pH ranges to pKa+1 or pKa -1 respectively. If the pH lies

	within the range pKa±1 the buffer capacity is appreciable, but outside this range it falls off to such an extent as to be of no practical use. It follows therefore that a given acid or base buffer has useful buffer section over the range, pH = pKa ± 1 for acid buffer and pOH = pKb ± 1 for basic buffer To prepare an acidic or basic buffer of desired pH, the acid or base selected should have pKa or pKb values near to the required pH. The pH of a buffer solution is determined by the ratio of concentrations of the salt and acid and not by their amounts. However the buffer capacity at a given pH does depend upon the actual concentration.