

n 1 . constant for the reaction

Q8

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with the conversion of chemical energy into electrical energy.

A device in which chemical energy is converted into electrical energy is called electrochemical cell or Galvanic cell or Voltaic cell. The basis of such cells is an oxidation — reduction reaction. Oxidation is the process in which electrons are removed from atoms to form ions. Reduction is the process of addition of electron takes place.

Features of electrochemical cell:

1. Electrochemical cell is constructed by joining two single electrodes. A **single electrode** is a metal rod dipping in its own ions. Oxidation and reduction take place in these separate vessels. Transference of electrons takes place through outer conducting wire. The energy so released appears in the form of electricity.

2. The single electrode at which oxidation takes place is called oxidation half cell and is called anode or -ve electrode. The oxidation half cell reaction can be represented as



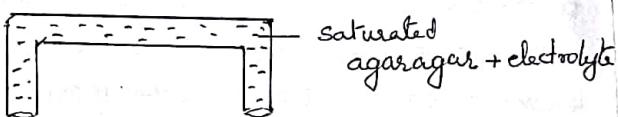
3. The electrode at which reduction takes place is called reduction half cell and is called cathode or +ve electrode. The reduction half cell reaction can be represented as



4. The electrode has a tendency to lose or gain electrons when it is dipped in its own solution. Thus a potential difference arises across the boundary between the metal rod and the solution. This potential difference is called **single electrode potential**. Single electrode potential is either **oxidation potential** if oxidation takes place at the metal rod or **reduction potential** if reduction occurs at the half cell. Single electrode potential is represented as $E_M^{n+}/_M$, where M^{n+} is the oxidized form and M is the reduced form of the metal.

5. **Liquid junction potential:** The two solutions in two half cells are different and the ions in them have different charges and mobilities and their capacity to carry current may be different. There exists a potential difference across the boundaries of two liquids in contact with each other called liquid junction potential.

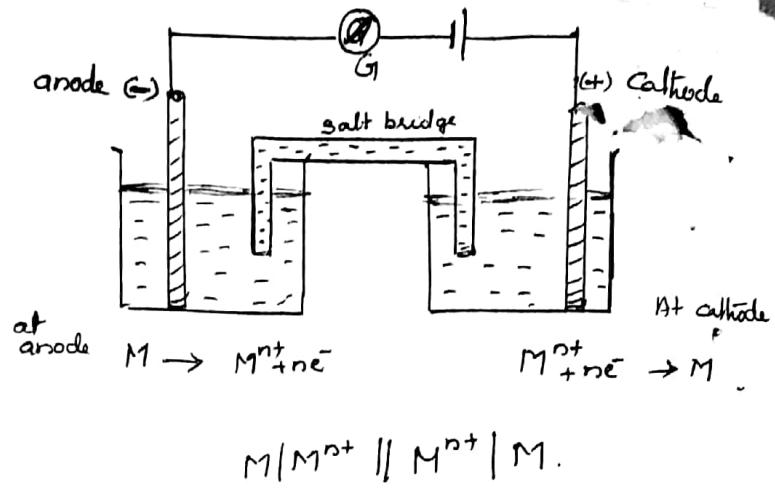
6. **Salt bridge:** Salt bridge is a device used to eliminate or minimize the liquid junction potential. To construct a salt bridge, a hot solution of agar agar is saturated with a strong electrolyte such as KCl , K_2SO_4 or KNO_3 .



The hot solution is sucked into a narrow U-shaped glass tube and cooled. On cooling the gel solidifies preventing the electrolyte from mixing with the solution in the cell.

The main functions of salt bridge are (1) To connect the two solutions in two half cells (2) to complete the electrical circuit of the cell and (3) It eliminates the liquid junction potential. The high concentration of salt in salt bridge provides good conductivity of ions between the half cells and decreases the potential difference at the liquid junction.

An electrochemical cell is constructed by joining two single electrodes externally through a conducting wire to a galvanometer and a key and the two solutions are connected internally by means of salt bridge. Electrons flow from anode to cathode through external wire, generating the electric current. The ions move internally through the salt bridge. The potential difference between the two electrodes is the driving force for this electron flow. This driving force is called electromotive force 'emf' of the cell represented as E_{cell} .



The deflection of the needle in galvanometer indicates the direction in which electron is flowing. A cell is represented by writing the anode half cell on the left side and cathode on the right side. The two half cells are separated by a parallel line (||) which represents the salt bridge as: $M | M^{n+}(c) || M^{n+}(c) | M$ (where C is the concentration of solution in the half cell) E_{cell} can be calculated as : $E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode}$

Cell reaction is represented as :

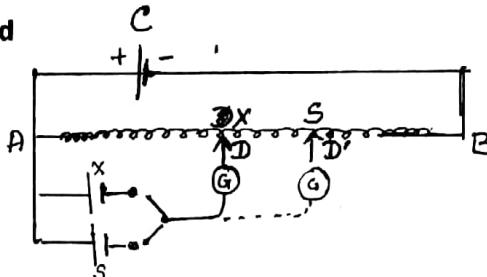


EMF measurement- The Poggendorff potentiometric method

A storage cell 'C' is connected across the conductor AB (potentiometer wire). The cell 'X' whose emf to be measured is connected to A through a galvanometer G and to a contact D which can be moved along AB. The position of D is adjusted by moving through the wire AB until no current flows through the galvanometer. The potential due to storage cell 'C' is then exactly balanced by the emf of the experimental cell 'X'. It is E_x . By means of a two way switch a standard cell whose emf E_s is accurately known is then connected. The contact is adjusted for null deflection in galvanometer so that

$$\frac{E_x}{E_s} = \frac{\text{Resistance of AD}}{\text{Resistance of AD'}} = \frac{\text{Length AD}}{\text{Length AD'}}$$

Thus emf of experimental cell E_x can be calculated by knowing the E_s of standard cell.



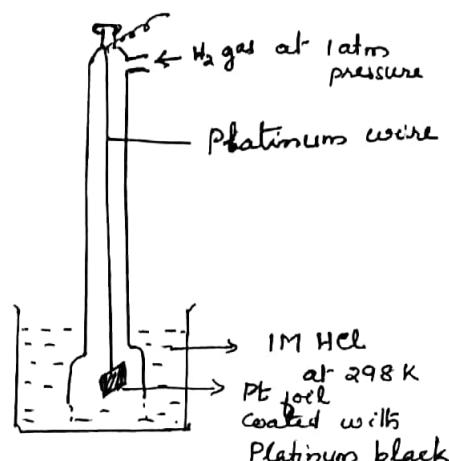
Reference electrodes. Single electrode potential of a half cell is measured by combining it with a reference electrode to give a complete cell. By arbitrarily fixing the potential of reference electrode as zero, the potential of various other single electrodes can be determined using $E_{cell} = E_R - E_L$. Thus from E_{cell} and single electrode potential of reference electrode (E_R or E_L), the single electrode potential of other electrode can be calculated.

Standard electrode potential : The single electrode potential when measured under standard conditions such as the temperature 298K, 1atm pressure for a 1M solution is called standard electrode potential denoted by $E^\circ_{\text{M}^+/\text{M}}$.

Standard hydrogen electrode (SHE)

is a primary standard reference electrode

Standard hydrogen electrode consists of a platinum wire sealed in a glass tube. Platinum foil coated with platinum black is attached to one end of the platinum wire. This wire is dipped in an aqueous solution of 1M hydrochloric acid. Hydrogen gas at 1atm is constantly bubbled through the solution at 298K.



The electrode potential of hydrogen electrode is taken as zero under standard conditions such as 1M HCl, 1atm and 298K.

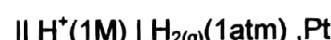
Electrode reactions

Representation of hydrogen electrode

When it acts as anode(oxidation): $\text{H}_{(g)} \rightarrow 2 \text{H}^+ + 2\text{e}^-$,



When it acts as cathode(reduction): $2 \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{(g)}$,

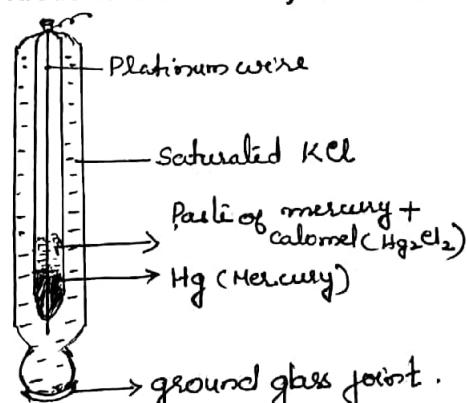


When it is attached to other half cells, the direction of flow of current indicates whether oxidation or reduction takes place at the unknown electrode. As per IUPAC , if reduction occurs at an electrode , then +ve sign is given to electrode potential and - ve sign is given in the case of oxidation.

It is difficult to maintain the concentration of H^+ as 1M and keeping the pressure at 1atm. Hence secondary reference electrodes are also used. Saturated calomel electrode is a secondary reference electrode.

Saturated Calomel Electrode (SCE)

Saturated calomel electrode consists of a platinum wire dipping in mercury taken in a narrow glass tube. A paste of mercury saturated with calomel (mercurous chloride Hg_2Cl_2) is placed above mercury .



A saturated solution of KCl with calomel(Hg_2Cl_2)

is filled in the outer tube. The potassium chloride solution in the outer tube serves as salt bridge. This compact form of calomel can directly be dipped into the solution of the other electrode. Connection between the two solutions occurs at ground glass joint. The representation of the electrode and cell reactions are

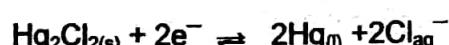
when anode : $\text{Hg}_{(l)}, \text{Hg}_2\text{Cl}_{2(s)} \mid \text{KCl} \parallel$

and when cathode : $\parallel \text{KCl} \mid \text{Hg}_{(l)}, \text{Hg}_2\text{Cl}_{2(s)}$

cell reaction $2\text{Hg}_{(l)} + 2\text{Cl}_{\text{aq}}^- \rightarrow \text{Hg}_2\text{Cl}_{2(s)} + 2\text{e}^-$

$\text{Hg}_2\text{Cl}_{2(s)} + 2\text{e}^- \rightarrow 2\text{Hg}_{(l)} + 2\text{Cl}_{\text{aq}}^-$

The over all reaction is given as



Nernst equation for this electrode is $E_{\text{el}} = E^\circ - 2.303RT \log \frac{[\text{Hg}][\text{Cl}^-]}{[\text{Hg}_2\text{Cl}_2]}$ or $E_{\text{el}} = E^\circ - 2.303RT \log \text{Cl}^-$

i.e. The saturated calomel electrode is reversible w.r.t. to Cl^- ions (since $[\text{Hg}]$ and $[\text{Hg}_2\text{Cl}_2] = 1$)

Electrochemical series or Activity series.

An arrangement of elements or electrodes in the increasing order of their standard reduction called Electrochemical series or electromotive force series or activity series.

Element	Electrode	Electrode reaction	Standard reduction potential E^0 Volts
Li	$\text{Li}^+ \text{Li}$	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
K	$\text{K}^+ \text{K}$	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
			,
			,
Al	$\text{Al}^{3+} \text{Al}$	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} \text{Zn}$	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
			,
			,
H ₂	$2\text{H}^+ \text{H}_2$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
Ag	$\text{Ag}^+ \text{Ag}$	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
			,
			,
			,
F ₂	$\text{F}_{2(g)} 2\text{F}^-$	$\text{F}_{2(g)} + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87

Negative sign shows the negative tendency of the electrode to get reduced.

The Nernst Equation for a single electrode potential

If 'n' is the number of electrons liberated or taken up at an electrode in the cell, then nF faraday of electricity will be generated in the complete cell reaction. If the emf of cell is denoted by E, The electrical energy produced by the cell is nFE volts.

The electrical work done by the cell = free energy of the cell $\Delta G = -nFE_{el}$ ———(1)

The minus sign indicates that the free energy of the cell decreases as the work is done by the cell.

If the reaction occurring at an electrode is $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}_{(s)}$ ———(2)

Equilibrium constant K for the electrode reaction is $K = \frac{[\text{M}]}{[\text{M}^{n+}]}$ ———(3)

Relation connecting K and ΔG is given by the Van't Hoff's equation as

$$\Delta G = \Delta G^0 + 2.303RT \log K$$
 ———(4)

Substituting (1) and (3) in (4) we get

$$-nFE_{el} = -nFE_{el}^0 + 2.303RT \log \frac{[\text{M}]}{[\text{M}^{n+}]}$$
 ———(5)

$$\text{Dividing by } -nF, \text{ eqn becomes } E_{el} = E_{el}^0 - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]}$$
 ———(6)

The above eqn is the Nernst eqn for single electrode potential. Since $[\text{M}] = 1$, eqn can also be written in the form

$$E_{el} = E_{el}^0 + \frac{2.303RT}{nF} \log [\text{M}^{n+}]$$
 ———(7),

$$\text{At } T = 298\text{K (25}^\circ\text{C}), \text{ substituting } R = 8.314\text{J K}^{-1} \text{ mol}^{-1}, F = 96500\text{C, } E_{el} = E_{el}^0 + \frac{0.05916}{n} \log [\text{M}^{n+}]$$
 ———(8)

of reversible electrodes :

1. Metal ion electrodes: This consists of a metal rod dipping in a solution of the same metal ion.

e.g. Zn rod in $ZnSO_4$ solution represented as $Zn|Zn^{2+}$ or a copper rod in $CuSO_4$ solution which is represented as $Cu|Cu^{2+}$ or in general $M|M^+$ and electrode reaction is $M \rightarrow M^{n+} + ne^-$

2. Gas electrodes: A gas at a given pressure acts as electrode. ex. (a) **Hydrogen electrode :** Electrode consists of Hydrogen gas at a given pressure is bubbling through hydrochloric acid solution. For electrical contact Pt metal is inserted. Electrode is represented as $Pt, H_{2(g)} | H^+$

Hydrogen electrode is used to determine the pH value of an unknown solution. For this, the solution whose pH is to be determined is taken in a vessel and a Pt electrode is dipped in it. Hydrogen gas at 1atm pressure is passed through the solution.



$$\text{Nernst eqn is } E_{el} = E_{el}^0 - \frac{2.303RT}{F} \log \frac{1}{[H^+]} = \frac{2.303RT \log [H^+]}{F} \quad (E^0_{H+/H2} = 0)$$

$$= -0.0592 \text{ pH at } 25^\circ\text{C}$$

The above half cell is connected with saturated calomel electrode to form a complete cell and e.m.f of cell is determined .



$$\text{The e.m.f cell } E_{cell} = E_{right} - E_{left} = 0.2422V + 0.0592 \text{ pH} \quad (E_{\text{saturated calomel}} = 0.2422V)$$

$$\text{Or } pH = \frac{E_{cell} - 0.2422V}{0.0592V}$$

(b) Chlorine electrode

Chlorine gas at a given pressure is bubbled into HCl solution, represented as $Pt, Cl_{2(g)} | Cl^-$



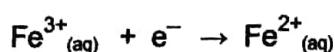
$$\text{Electrode potential by Nernst eqn is } E_{el} = E_{el}^0 - \frac{2.303RT}{F} \log \frac{[Cl^-]}{[Cl_2]} = \frac{2.303RT \log [Cl^-]}{F}$$

Electrode is reversible with respect to chloride ion.

3. Metal – insoluble metal salt electrodes. Consists of a metal rod dipping in a sparingly soluble salt of the same metal and a solution of a soluble salt of the same anion

For example , calomel electrode (for details refer back)

4. Oxidation –reduction electrodes. Constructed by dipping Pt rod in solution of same substance in two different oxidation state such as Fe^{2+} and Fe^{3+} , or Sn^{2+} and Sn^{4+} or Ce^{3+} and Ce^{4+} ions.



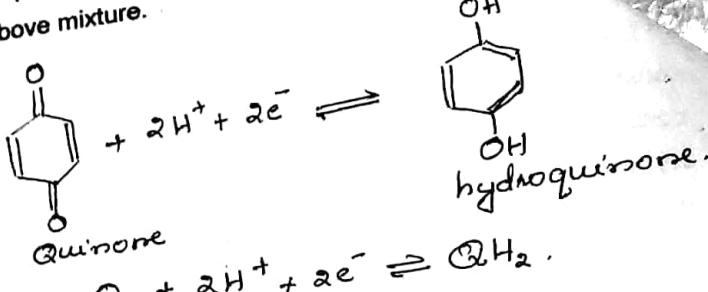
Oxidized state $+ ne^- \rightarrow$ reduced state.

$$\text{Electrode potential is } E_{el} = E_{el}^0 - \frac{2.303RT}{nF} \log \frac{[\text{reduced state}]}{[\text{oxidized state}]}$$

The potential at the electrode arises from tendency of the ions in one oxidation state to change into other more stable state.

Quinhydrone electrode is a slightly different oxidation-reduction electrode which is sensitive to solution. Quinhydrone is equi molar solid mixture of quinone and hydroquinone. The electrode can be represented as Pt, Q, $\text{QH}_2 \text{ | H}^+ \text{ (aq)}$

$$E_a = E^\circ_a + \frac{2.303RT}{2F} \log \frac{[Q][\text{H}^+]^2}{[\text{QH}_2]}$$

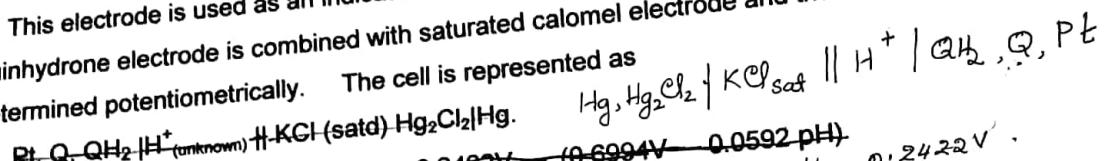


$$E_a = E^\circ_a + \frac{2.303RT}{F} \log \text{H}^+$$

$$\text{or } E_a = E^\circ_a - \frac{2.303RT}{F} \text{ pH}$$

$$\text{Or } E_a = 0.6994V - \frac{2.303RT}{F} \text{ pH} = 0.6994V - 0.0592 \text{ pH at } 25^\circ\text{C} \quad (E^\circ_a = 0.6994V)$$

This electrode is used as an indicator electrode. For determining pH of an unknown solution, quinhydrone electrode is combined with saturated calomel electrode and the e.m.f of the complete cell is determined potentiometrically. The cell is represented as



$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{quinhydrone}} = 0.2422V - (0.6994V - 0.0592 \text{ pH})$$

$$E_{\text{cell}} = E_{\text{Hg}_2\text{Cl}_2/\text{Hg}} - E_{\text{calomel}} = 0.6994V - 0.0592 \text{ pH} - 0.2422V$$

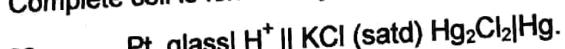
$$\text{Or } \text{pH} = \frac{E_{\text{cell}} + 0.6994V - 0.2422V}{0.0592} = \frac{0.6994V - E_{\text{cell}} - 0.2422V}{0.0592}$$

5. Glass electrode: A glass electrode is made of a special glass of low melting point and high electrical conductivity. It is blown in the form of a bulb. A solution of 0.1M HCl is taken in the bulb. A Platinum wire is dipped in this solution for electrical contact. A difference of potential exists at the interface between glass and solution containing H^+ ions. The magnitude of this difference of potential for a given glass varies with the concentration of H^+ ions at 25°C .

Electrode potential of glass electrode is

$$E_G = E^\circ_G - 0.0592 \text{ pH}$$

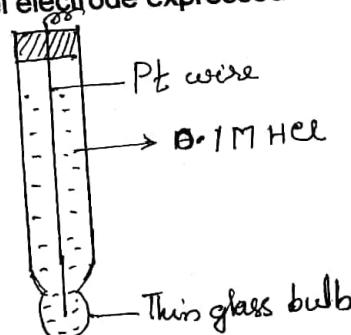
Complete cell is formed by connecting it with a reference electrode, usually a calomel electrode expressed as



$$\text{The e.m.f of cell is given by } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$E_{\text{cell}} = 0.2422V - [E^\circ_G - 0.0592 \text{ pH}]$$

$$\text{pH} = \frac{0.2422V - E_{\text{cell}} + E^\circ_G}{0.0592V}$$



All glass electrode do not have same value of E°_G because this depends on the pH of solution init, the thickness of glass and kind of glass material. This variation is known as asymmetry potential. Therefore each glass electrode must be standardized by measuring its E°_G by using a standard solution of known

electrodes :

A glass electrode consists of a metal rod dipping in a solution of the same metal ion. The solution which is

constructed by glass is called glass electrode. Potassium hydrogen phthalate solution is a common standard for the calibration of glass electrode.

Electrode is used as the 'internal reference electrode'.

Advantages: It is simple to operate, hence used in chemical, industrial, agricultural and biological laboratories. Very little volume of solution is required for measuring pH. Glass electrode is nearest to universal pH electrode.

6. Amalgam electrodes: Solution of metal in mercury is called amalgam. Highly reactive metals can be used safely as electrodes by amalgamation. sodium amalgam and Zn amalgam electrodes are examples.

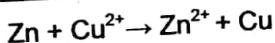
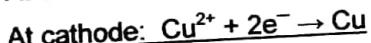
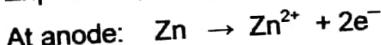
Classification of electrochemical cells.

Two different types of cells are present.(1). Chemical cells and (2) concentration cells.

(1) Chemical cells : In these cells two electrodes of two different metals with a liquid junction is present. liquid junction is eliminated by a salt bridge. Electrical energy is produced by the chemical reaction taking place in the cell.

Daniell cell is a very good example. It consists of (1) oxidation half cell in which a Zn rod is dipped in ZnSO₄ solution(say 1M) (2) Reduction half cell consists of Cu rod dipped in CuSO₄ solution(say 1M).

The two solutions are separated by a salt bridge. Cell and cell reactions are represented as



Zn rod gradually dissolves in ZnSO₄ solution

Cu²⁺ get deposited as copper at cathode.

emf of cell is 1.1V

Nernst equation for the cell

Nernst equation for single electrodes are

$$E_R = E_{\text{Cu}^{2+}/\text{Cu}} = E^0_{\text{Cu}^{2+}/\text{Cu}} + \frac{2.303RT}{2F} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}]}$$

$$E_L = E_{\text{Zn}^{2+}/\text{Zn}} = E^0_{\text{Zn}^{2+}/\text{Zn}} + \frac{2.303RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}]}$$

$$E_{\text{cell}} = E_R - E_L = E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}} + \frac{2.303RT}{2F} \left[\frac{\log [\text{Cu}^{2+}]}{[\text{Cu}]} - \frac{\log [\text{Zn}^{2+}]}{[\text{Zn}]} \right]$$

$$\text{Or } E_{\text{cell}} = E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}} + \frac{2.303RT}{2F} \frac{\log [\text{Cu}^{2+}]}{[\text{Cu}]} \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

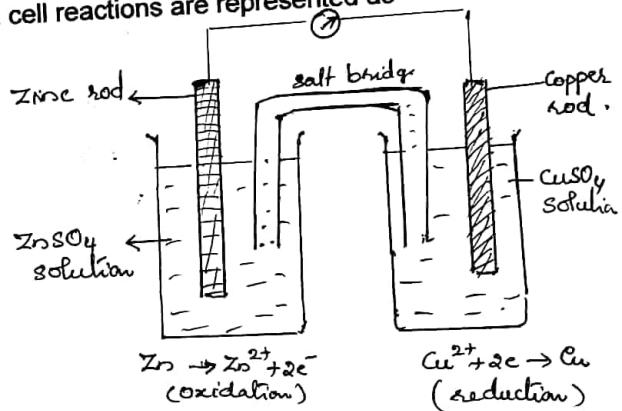
Similarly in general, for any cell reaction



the Nernst equation can be written as

$$E_{\text{cell}} = E^0_R - E^0_L + \frac{2.303RT}{nF} \log \frac{[\text{A}]^a [\text{B}]^b}{[\text{C}]^c [\text{D}]^d}$$

(log [reactants] / [products])



8

(2) Concentration cells: These cells are made up of two half cells having identical electrolytes but the concentrations of ions or electrodes are different. Electrical energy arises from transfer of matter from a solution of higher concentration to region of lower concentration.

Concentration cells are of two types. 1. Electrode concentration cells 2. Electrolyte concentration cell.

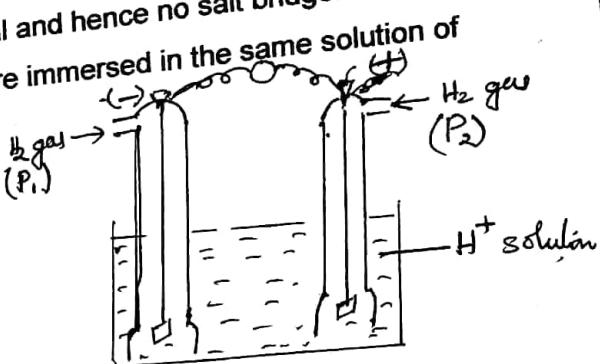
Electrode concentration cells: In these cells, two electrodes of same type but different concentrations are dipping in the same solution. There is no liquid junction potential and hence no salt bridge.

Two hydrogen electrodes at different gas pressures P_1 and P_2 are immersed in the same solution of hydrogen ions (HCl solution) form an Electrode concentration cell.

Pt, $H_{2(g)}$ (P_1) | H^{+} aq (say HCl) | $H_{2(g)}$ (P_2), Pt

Cell reaction: LHE(at anode) $H_{2(g)}$ (P_1) $\leftrightarrow 2H^{+} + 2e^{-}$
 RHE(at cathode) $2H^{+} + 2e^{-} \leftrightarrow H_{2(g)}$ (P_2)
 $H_{2(g)}$ (P_1) $\leftrightarrow H_{2(g)}$ (P_2)

Over all reaction



Thus reaction is independent of the concentration of solution.

The Nernst equation may derive as follows:

When a metal electrode is dipped in its own solution, then a potential (E) is developed which depends on the concentrations of electrodes

According to Nernst eqn, single electrode potentials of RHE and LHE are given by:

single electrode potential of cathode $E_{right} = E_{right}^0 - \frac{2.303RT}{2F} \log(P_2)$

$$\text{single electrode potential of anode } E_{left} = E_{left}^0 - \frac{2.303RT}{2F} \log(P_1)$$

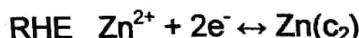
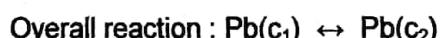
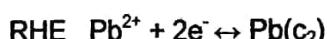
$$\begin{aligned} \text{EMF of cell} &= E_{right} - E_{left} = \left\{ E_{right}^0 - \frac{2.303RT}{2F} \log(P_2) - (E_{left}^0 - \frac{2.303RT}{2F} \log(P_1)) \right\} \\ &= (E_{right}^0 - E_{left}^0) + \frac{2.303RT}{2F} \log \frac{(P_1)}{(P_2)} \end{aligned}$$

Since $E_{right}^0 - E_{left}^0 = 0$ (same electrode)

$$E_{cell} = \frac{2.303RT}{2F} \log \frac{(P_1)}{(P_2)}$$

$$E_{cell} = \frac{0.0591}{2F} \log \frac{(P_1)}{(P_2)} = 0.02955 \log \frac{(P_1)}{(P_2)} \text{ at } 25^\circ C$$

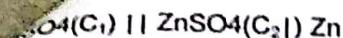
Another example of electrode concentration cell is that of amalgam with two different concentration of the same metal



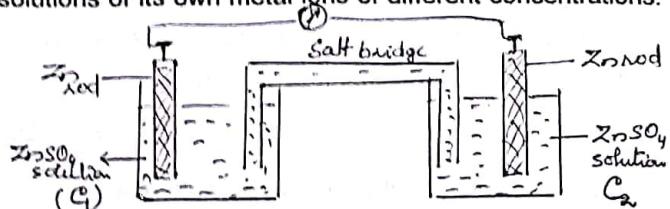
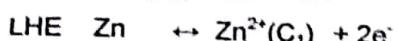
$$\text{EMF of cell } E_{cell} = \frac{0.0591}{2F} \log \frac{(C_1)}{(C_2)} = 0.02955 \log \frac{(C_1)}{(C_2)} \text{ at } 25^\circ C$$

Concentration cells.

Two electrodes of same metal are dipping in solutions of its own metal ions of different concentrations.



reactions



According to Nernst eqn, reduction potentials of RHE and LHE are given by:

$$\text{single electrode potential of cathode } E_{\text{right}} = E_{\text{right}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}]}{(\text{C}_2)}$$

$$\text{single electrode potential of anode } E_{\text{left}} = E_{\text{left}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}]}{(\text{C}_1)}$$

$$\begin{aligned} \text{EMF of cell} &= E_{\text{right}} - E_{\text{left}} = \{ E_{\text{right}}^0 + \frac{2.303RT}{nF} \log (\text{C}_2) \} - \{ E_{\text{left}}^0 + \frac{2.303RT}{nF} \log (\text{C}_1) \} \\ &= (E_{\text{right}}^0 - E_{\text{left}}^0) + \frac{2.303RT}{nF} \log \frac{(\text{C}_2)}{(\text{C}_1)} \end{aligned}$$

Since $E_{\text{right}}^0 - E_{\text{left}}^0 = 0$ (same electrode)

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{(\text{C}_2)}{(\text{C}_1)}$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{(\text{C}_2)}{(\text{C}_1)} = \frac{0.02955}{n} \log \frac{(\text{C}_2)}{(\text{C}_1)} \text{ at } 25^\circ\text{C}$$

Polarization: Electrode potential is given by $E_{\text{el}} = E_{\text{el}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{2+}]}$

The actual emf produced from cell is less than the theoretical value. The cell is said to be polarized. There are two reasons for cell polarization. (1) concentration polarization and (2). Electrode polarization

Concentration polarization: When current is drawn from the cell, metal ions begin to be discharged at the cathode and there will be fall in concentration of ions in the vicinity of the metal electrode. The potential of electrode will decrease. Similarly at anode, metal will begin to dissolve giving M^{2+} ions. Hence concentration of M^{2+} ion in the vicinity of metal electrode increases and the potential of the electrode would increase. Under such conditions, the electrode is said to be polarized. Polarization is a process when there is a variation of electrode potential occur due to decrease in diffusion of ions from bulk of the electrolyte to vicinity of electrode. Polarized cell develops smaller potential than theoretically predicted value.

Polarization depends on the size of electrode, concentration of electrolyte, temperature etc. polarization effects can be decreased by stirring the solution, increasing the temperature and taking low concentration of electrolyte in cell.

Overshoot or electrode polarization: In gas electrode cells, the gases evolved during cell reaction form a layer around electrode. This prevents the ions in solution from coming in contact with the metal electrode. The reaction slows down and drop in emf results. This difference between the potential of an electrode at which gas evolution occurs and the theoretical reversible potential of the electrode is called overshoot.

Applications of emf measurements.

1. Equilibrium constant of the cell reaction.

For any cell reaction $aA + bB \rightarrow cC + dD$

The equilibrium constant K is given by

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

Nernst equation for the cell can be written as

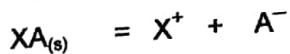
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{nF}{2.303RT} \log K$$

$$\text{at equilibrium } E_{\text{cell}} = 0, \text{ Therefore } 0 = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log K$$

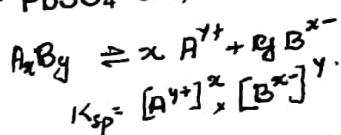
$$\text{or } \log K = \frac{nFE_{\text{cell}}^0}{2.303RT} \quad \text{or } K = \text{anti log } \frac{nFE_{\text{cell}}^0}{2.303RT}$$

2. Determination of solubility of sparingly soluble salts (an application of concentration cells):

In a saturated solution of a sparingly soluble salt (like AgCl, AgI or PbSO₄ etc) there exist an equilibrium as



The equilibrium constant $K = \frac{[X^+][A^-]}{[XA_{(s)}]}$; Equilibrium constant for cell reaction K = solubility product K_{sp}



Since $[XA_{(s)}] = 1$, solubility product is given by $K_{sp} = [X^+][A^-]$

$K_{sp} = [X^+][A^-] = sxs = s^2$, therefore Solubility $s = \sqrt{K_{sp}}$

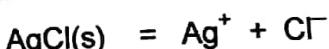
For a cell, $nFE^0 = 2.303RT \log K$ or $\log K_{sp} = \frac{nFE^0}{2.303RT}$

Solubility of sparingly soluble salt can be calculated by measuring e.m.f of a concentration cell containing the salt under consideration. For ex: for AgCl, following cell may be constructed



For which the half cell reactions are: RHE $\text{AgCl}(s) + e^- = \text{Ag} + \text{Cl}^-$
LHE $\text{Ag} = \text{Ag}^+ + e^-$

Overall reaction



The values of E_R^0 and E_L^0 are taken from table. For Ag- AgCl electrode E_R^0 is 0.2225V and for Ag electrode E_L^0 is 0.7991V. Therefore $E_{\text{cell}}^0 = E_R^0 - E_L^0 = 0.2225 - 0.7991 = -0.5766\text{V}$

Equilibrium constant for cell reaction K = solubility product K_{sp}
 $nFE_{\text{cell}}^0 = 2.303RT \log K$ or $\log K_{sp} = \frac{nFE_{\text{cell}}^0}{2.303RT}$

$$\frac{nFE_{\text{cell}}^0}{2.303RT} = \frac{1 \times 96500 \times (-0.5766\text{V})}{2.303 \times 8.314 \times 298} = -9.7517$$

$$\text{Therefore } K_{sp} = \text{antilog}(-9.7517) = 1.771 \times 10^{-10}$$

$$\text{Solubility } s = \sqrt{1.771 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ mol L}^{-1}$$

, cells are galvanic cells in which chemical energy of fuels is directly converted into electrical energy. Hydrogen – Oxygen fuel cell is an example.

consists of two electrodes made of porous

white coated with a catalyst like Pt or Ag or

a metal oxide. The electrodes are placed in

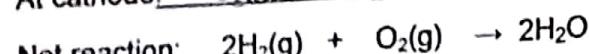
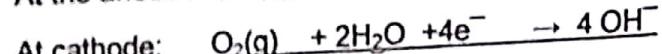
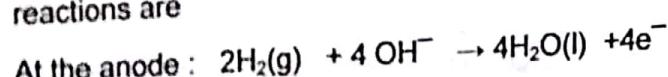
25% KOH solution. Oxygen and hydrogen

gases usually under 50 atm pressure are

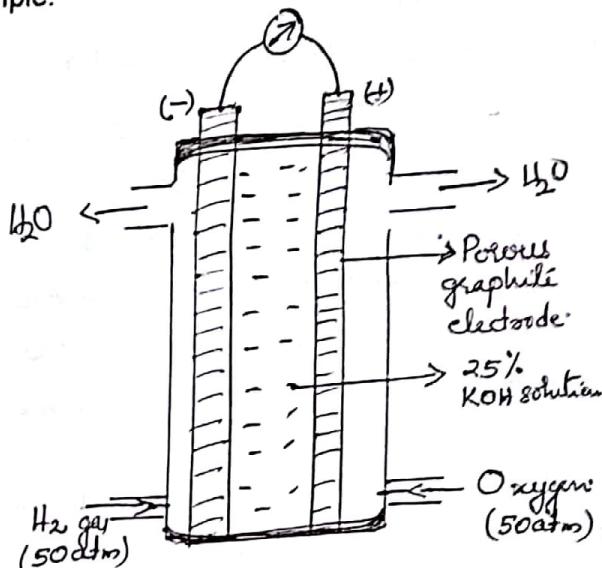
passed continuously through porous

electrode into the electrolyte. The electrode

reactions are



$$E_{\text{cell}} = E_{\text{R}}^{\circ} - E_{\text{L}}^{\circ} = 0.48 + 0.83 = 1.23\text{V}$$



Merits

The byproduct water can be condensed and reused. 75% of chemical energy can be converted into electrical energy. This fuel cell is used as auxiliary energy source in space vehicles, submarines etc. Fuel cells are light, compact and easy to operate. The main advantage would be the elimination of air pollutants such as CO, SO₂, NO_x etc. Fuels used are easily available at low cost. Fuel cell technology would bring revolution in the area of energy production.

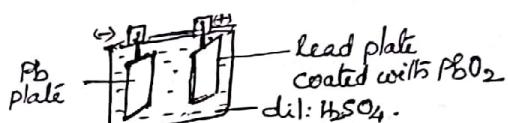
Commercial cells: are of two types (1). Primary cells (2). Secondary cells.

Commercial cells: are of two types (1). Primary cells (2). Secondary cells.

(1). Primary cells: In Primary cells the reaction occur only once and cannot be recharged. Ex: Torch or dry cell or transistor cells.

(2). Secondary cells: Reversible chemical reactions take place in secondary cells. They can be recharged. It is a device in which electrical energy is stored in the form of chemical energy which may be drawn out at will. Hence they are also called storage cells.

Ex: Lead-acid battery, nicad cell, lithium ion cell etc.

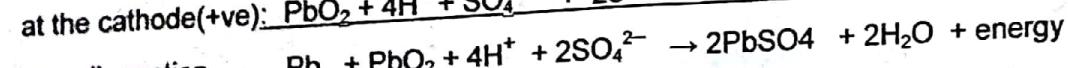
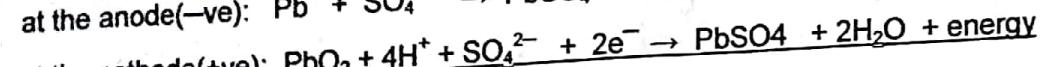
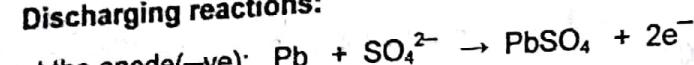


The Lead-acid storage cell

Cell consists of Lead anode and lead dioxide as the cathode. A number of lead plates and lead dioxide plates are arranged alternately, each is separated by thin fiber glass sheets. The whole arrangement is suspended in dilute sulphuric acid taken in a plastic or hard rubber vessel.

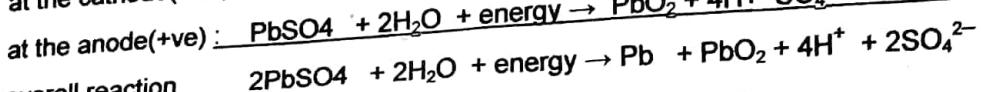
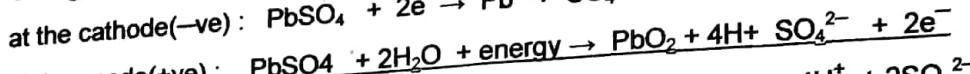
When operating the cell is said to be discharging

Discharging reactions:



Thus Pb, PbO₂ and H₂SO₄ are consumed during discharging. Since water is produced, the acid in cell becomes more and more dilute and cell becomes weaker and weaker. Reverse reaction takes place during charging.

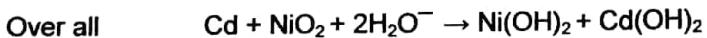
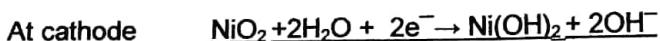
Charging reactions:



All reactants regain their original state and the cell is ready to use.

During discharging the cell behaves as a voltaic cell and during charging the cell behaves as electrolytic cell. e.m.f cell is about 2V. In medium vehicles such as cars, a 12V battery consisting of six such cells connected in series and in heavy vehicles a 24V battery consists of 12 such cells connected in series are used.

'nicad' cell (nickel-cadmium cell): It consists of cadmium anode and nickel dioxide cathode and an alkaline electrolyte. The reaction during discharging :

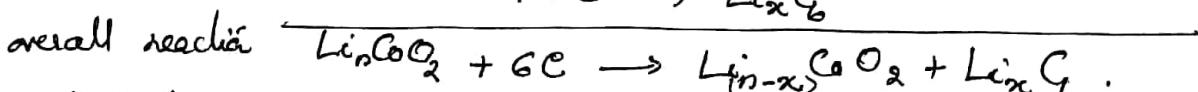
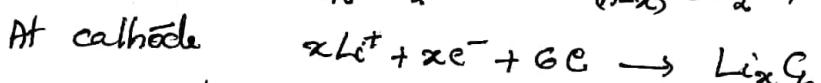
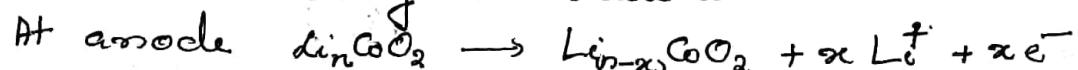


Cell potential is 1.4V. It has longer life than lead storage cell. It is commonly used in calculators, mobile phones, cameras and flashes.

For photovoltaic cell and Solar cells- refer notes under solid state chemistry.

Lithium ion batteries.

Problems: It consists of porous graphite cathode and lithium cobalt oxide or lithium iron phosphate or lithium manganese oxide cathode. Cell reaction using cobalt oxide is



Potential of cell is 3.7V.

produces high voltage and current density.

It has a 'charging memory' which means, the capacity of cell may decrease if it is recharged before it is completely discharged.

Calculate the emf of a Zn electrode if the concentration of ZnSO_4 is 0.1 M at a temperature of 30°C . $E_{\text{Zn}}^\circ = -0.76\text{ V}$.

Ans: Nernst equation of Zn electrode is

$$E_{\text{el}} = E_{\text{el}}^\circ + \frac{2.303RT}{2F} \log [\text{Zn}^{2+}] .$$

$$R = 8.314 \text{ J K}^{-1} \quad T = 273 + 30 = 303 \text{ K} \quad F = 96500 \text{ C}$$

$$\therefore E_{\text{el}} = -0.76\text{ V} + \frac{2.303 \times 8.314 \text{ J K}^{-1} \times 303 \text{ K}}{2 \times 96500} \log(0.1) .$$

$$= -0.79\text{ V} .$$

2. Calculate the emf of a Cu electrode if the concentration of CuSO_4 is 2 M at a temperature of 25°C . $E_{\text{Cu}}^\circ = +0.34\text{ V}$.

Nernst equation for single electrode is

$$E_{\text{el}} = E_{\text{el}}^\circ + \frac{2.303RT}{2F} \log [\text{Cu}^{2+}] .$$

$$\therefore E_{\text{el}} = E_{\text{Cu}}^\circ + \frac{2.303 \times 8.314 \times 298}{2F} \log [2] .$$

$$= +0.34 + \frac{0.0592}{2} \log(2) .$$

$$= 0.3489\text{ V} .$$

3. Calculate the emf of the following cell at 25°C .



Nernst equation for a cell.

$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{2.303RT}{2F} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]} .$$

$$T = 298 . \quad \begin{array}{c} \text{[cathode]} \\ \hline \text{[anode]} \end{array}$$

$$= 1.54\text{ V} + \frac{0.0592}{2} \log \frac{(0.002)^2}{0.2} .$$

$$= 1.54\text{ V} + 0.0296\text{ V} \log [2 \times 10^{-4} - 2 \times 10^{-5}] .$$
~~$$= 1.54\text{ V} + 0.0296\text{ V} \log 2 \times 10^{-5} .$$~~

$$= 1.54\text{ V} + 0.0296\text{ V} (\log 2 - 5 \log 10) .$$

$$= 1.54\text{ V} - 0.139\text{ V} .$$

$$= 1.401\text{ V} .$$

4. Two copper rods are placed in CuSO_4 solutions of concentration 0.1 M and 0.01 M separately to form a cell. Give the cell notation and calculate the emf of cell at 298 K.

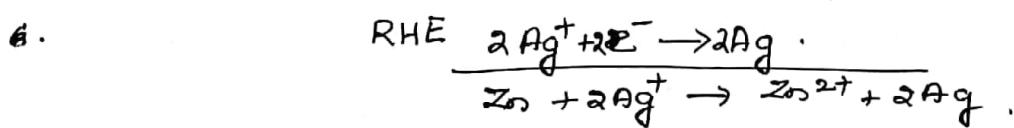
Cell notation at
25°C



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{2.303RT}{2F} \log \frac{[\text{cathode}]}{[\text{anode}]}$$
$$= \frac{0.0592}{2} \log \frac{0.1}{0.01} = 0.0296 \text{ V} \log 10 = \underline{\underline{0.0296}}$$

5. Calculate the emf of the cell and write down the cell
AgI reaction if Zn and Ag electrodes are dipped in
respective solutions. Also find out the standard
emf of the cell, given that $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.76\text{V}$ and
 $E_{\text{Ag}^+/\text{Ag}}^{\circ} = -0.8\text{V}$ at 25°C .

Ans Std reduction potential of $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$ and
 $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.8\text{V}$ since $E_{\text{Ag}^+/\text{Ag}}^{\circ} > E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$, Ag electrode is called
cell notation $\text{Zn}_{(s)} | \text{Zn}^{2+} \parallel \text{Ag}^+ | \text{Ag}_{(s)}$.



Stand EMF of cell $E_{\text{cell}} = E_R^{\circ} - E_L^{\circ} = 0.84 - (-0.76\text{V})$
 $= \underline{\underline{1.56\text{V}}}$

6. Calculate the equilibrium constant for the Daniell cell at
 25°C . $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$ $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34\text{V}$.

At eqm. $E_{\text{cell}}^{\circ} = \frac{2.303RT}{2F} \log K$. $\therefore \log K = \frac{2F E_{\text{cell}}^{\circ}}{2.303RT}$.

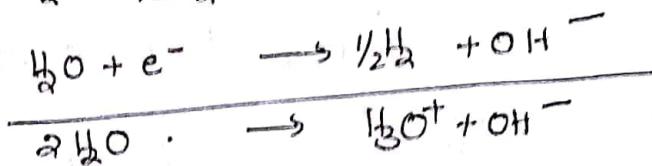
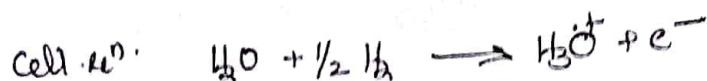
at 25°C $= \frac{0.592}{2} \log K = 0.296 \text{ V} \log K$.

$$\therefore \log K = \frac{(E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ})}{0.296 \text{ V}} = \frac{1.1}{0.296} = 37.23$$

$$\therefore K = \text{anti log } 37.23 = \underline{\underline{1.697 \times 10^{37}}}$$

calculate the equilibrium constant for the reaction
 $\text{anode: } \text{H}_2 + 2\text{OH}^- - 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C

standard reduction potential at 25°C is -0.8277 .



$$\log K_e = \frac{nFE_{\text{cell}}^\circ}{2.303RT}, \text{ at } 25^\circ\text{C} \rightarrow E_{\text{cell}}^\circ$$

$$\text{At } 25^\circ\text{C} \quad \log K_e = \frac{0.0296V}{0.0592} E_{\text{cell}}^\circ = \frac{0.0296V}{0.0592} \times -0.8277$$

$$= -$$

$$E_{\text{cell}}^\circ = 0.0592 \log K_e$$

$$\frac{-0.8277}{0.0592} = \log K_e$$

$$-13.9814 = \log K_e$$

$$\therefore K_e = \text{anti log } (-13.9814)$$

$$= \underline{\underline{9.58 \times 10^{-13}}}$$

$$\text{If } \log a = b \\ \text{then } a = 10^b$$

8. The potential of hydrogen gas electrode in a solution of an acid of unknown strengths is 0.29V at 298K . calculate the pH of acid solution.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - 0.0592\text{V}(\log H^+)$$

$$= E_{\text{cell}}^\circ + 0.0592\text{V pH}$$

$$\therefore \text{pH} = \frac{E_{\text{cell}}}{0.0592\text{V}} = \frac{0.29}{0.0592} = \underline{\underline{4.9}}$$

9. Find out the pH of a solution of quinhydrone half-cell which is coupled with std calomel electrode. The emf of combined cell was 0.123 V at 25°C. $E_{\text{cal}} = 0.2415 \text{ V}$ and $E_{\text{Q/H}_2}^{\circ} = 0.6990 \text{ V}$.

$$E_{\text{cell}} = E_R - E_L = E_{\text{Q/H}_2}^{\circ} - E_{\text{cal}} = 0.6990 - 0.2415$$

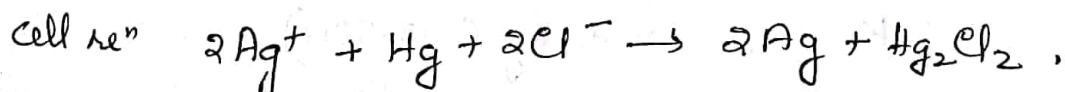
$$\text{Quinhydrone} = E_{\text{Q}}^{\circ} - \frac{2.303RT}{nF} \text{ pH}$$

$$= 0.6990 - 0.0592 \text{ V pH}$$

$$\therefore 0.123 \text{ V} = (0.6990 - 0.0592) + 0.2415$$

$$\therefore \text{pH} = \frac{0.6990 - 0.2415 - 0.123}{0.0592} = 5.65$$

10. EMF of cell : SCE || AgCl(satd) | Ag at 298 K was found to be 0.2621 V. What is the solubility of AgCl at this temperature? E° of SCE = $\frac{0.2415}{2.415} \text{ V}$ and E° for $\text{Ag}^+/\text{Ag} = 0.799 \text{ V}$



$$E_{\text{cell}} = (E_R^{\circ} - E_L^{\circ}) + \frac{0.0592}{2} \log [\text{Ag}^+]^2$$

$$0.2621 \text{ V} = (0.7991 - 0.2415) + 0.0592 \text{ V} \log [\text{Ag}^+]$$

$$\therefore \log [\text{Ag}] = \frac{-2.955}{0.0592} = -5$$

$$\therefore [\text{Ag}] = 10^{-5} \text{ mol L}^{-2}$$

$$K_{\text{sp}} = [\text{Ag}][\text{Cl}^-] = (10^{-5})^2 = \underline{\underline{10^{-10}}} \text{ mol}^2 \text{ L}^{-2}$$