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Department of Chemistry

ONLINE STUDY RESOURCE GE-T4: SEC-A

For Detailed Discussion Contact Any Faculty Member Electronically

ELECTROCHEMISTRY

Objectives

- Electrochemical cells

- EMF

- Measurement of EMF

- Relation between EMF & free energy change of cell reaction

- Electrode potential with reference to H-electrode

- Electrodes

- Determination of pH

- Different types of cells

Electrochemical Cell & Galvanic Cell:

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes, which are joined by a salt bridge. Electrochemical cell is of two types.
(a) Electrolytic Cell
(b) Galvanic Cell or Voltaic Cell

Electrolytic Cell: It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

Galvanic Cell: The device used to convert the chemical energy produced on a red-ox reaction into electrical energy is called an electrochemical cell or simply a chemical cell. These are also called galvanic cells or voltaic cell after the names of Luigi Galvanic and Alessandro Volta who were first to perform experiments on the conversion of chemical energy into electrical energy.

In electrochemical cell, a spontaneous red-ox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy. An indirect red-ox reaction is such that reduction and oxidation processes are carried out in two separate vessels called half-cells.

Daniel Cell: It consists of two half-cells. The left hand half-cell contains a zinc metal electrode dipped in $ZnSo_4$ solution. The half-cell on the right hand side consists of Cu metal electrode in a solution of $CuSo_4$. A salt bridge that prevents the mechanical mixing of the solution joins the half-cells.
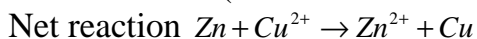
When the zinc and copper electrodes are joined by a wire the following observation are made.
(a) There is flow of electric current through the external circuit.
(b) The Zn rod loses its mass while copper rod gains in the mass.
(c) The concentration of $ZnSo_4$ solution increases while the concentration of $CuSo_4$ solution decreases.
(d) The solutions in both the compartments remain electrically neutral.

During the passages of electric current through external circuit, electrons flow from zinc electrode to the copper electrode. At the zinc electrode, zinc metal is oxidized to zinc ions, which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they

are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode.

Cell Reaction

$Zn \rightarrow Zn^{2+} + 2e$ (Oxidation So anode)

$Cu^{2+} + 2e \rightarrow Cu$ (Reduction So cathode)

Net reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

At the zinc rod, oxidation occurs. So it is the anode of the cell and negatively charged.

Electrode Sign : The sign of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells.
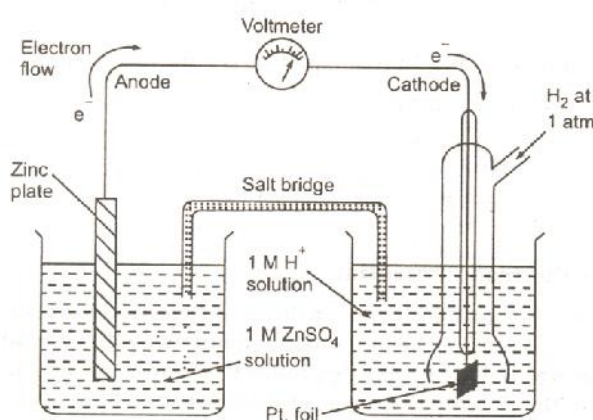
Salt bridge and its function:
Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions neither involved in any electrochemical change nor do they react chemically with the electrolytes in two half-cells. Generally salts like KCl, KNO_3, and K_2SO_4 etc. are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and solution thus formed is filled in the U-tube. On cooling the solution set in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimize diffusion effects.
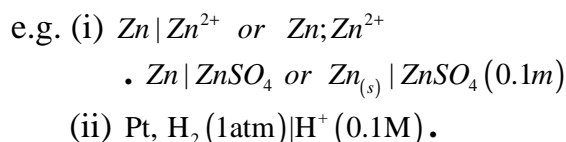
Function of salt bridge:
(a) It connects the solutions of two half cells and complete the cell circuit.
(b) It prevents transference or diffusion of the solutions from one half cell to the other.

(c) It keeps the solutions in the two half-cells, electrically neutral. In anodic half-cell, positive ions pass into solution and there shall be accumulation of extra positive charge in the solution around the anode, which will prevent flow of electrons from anode. Similarly in the cathodic half cell accumulate around cathode due to deposition of positive ions by reduction. To neutralize these ions, sufficient numbers of positive and negative ions are provided by salt bridge. Thus salt bridge maintains electrical neutrality of the solution.

(d) It prevents liquid-liquid junction potential i.e. the potential difference which arises between two solutions when contact with each other.

Representation of Electrochemical Cell (Galvanic Cell)
(a) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.
(b) The anode of the cell is represented by writing metal or solid phase and then the metal ion present in the electrolytic cell. Both are separated by a vertical line or a semicolon. For example

e.g. (i) $Zn \mid Zn^{2+}$ or $Zn; Zn^{2+}$

$\quad \bullet$ $Zn \mid ZnSO_4$ or $Zn_{(s)} \mid ZnSO_4 (0.1m)$

$\quad$ (ii) $Pt, H_2 (1atm) \mid H^+ (0.1M)$.

(c) The cathode of the cell is represented by writing the cat-ion of the electrolyte first and then the metal. Both are separated by a vertical line or semicolon.

$Cu^{2+} \mid Cu$ or $Cu^{2+}; Cu$ or $Cu^{2+} (1m) \mid Cu$.

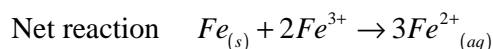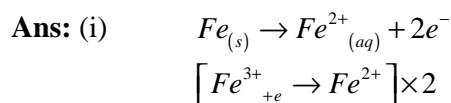For gaseous electrode e.g. $Cl^- (1m) \mid Cl_2 (1atm), P \mid$

(d) The salt bridge which separates the two half cells is indicated by two parallel vertical line. For example the Daniel cell can be represented as
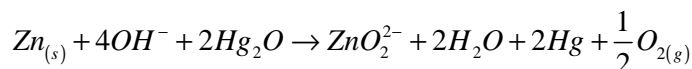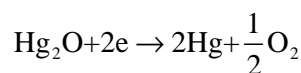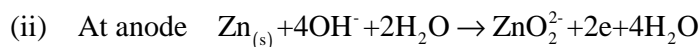
$Zn_{(s)} \mid ZnSo_{4(aq)} \parallel CuSO_{4(aq)} \mid Cu_{(s)}$

$\quad$ Anode   Salt bridge   Cathode

Q. **Write down the reactions at the following two electrodes as well as the total cell reactions.**
(i) $Fe \mid Fe^{2+} \parallel Fe^{2+} - Fe^{3+} \mid P+$
(ii) $Zn \mid ZnO_2^{2-}, OH^- \parallel Hg_2O_{(s)} \mid Hg$

Ans: (i) $\quad Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

$\quad\quad\quad \left[Fe^{3+}_{+e} \rightarrow Fe^{2+} \right] \times 2$

$\quad\quad$ _____

Net reaction $\quad Fe_{(s)} + 2Fe^{3+} \rightarrow 3Fe^{2+}_{(aq)}$

(ii) At anode $Zn_{(s)} + 4OH^- + 2H_2O \rightarrow ZnO_2^{2-} + 2e + 4H_2O$

$$Hg_2O + 2e \rightarrow 2Hg + \frac{1}{2}O_2$$

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$$Zn_{(s)} + 4OH^- + 2Hg_2O \rightarrow ZnO_2^{2-} + 2H_2O + 2Hg + \frac{1}{2}O_{2(g)}$$

Q. Write the cell reactions and electrode half-reactions for the following cells:

(a) $P + | K_3\left[Fe(CN)_6\right]_{(aq)}, K_4\left[Fe(CN)_6\right]_{(aq)} \parallel CvCl_{3(aq)} | Cv$

Ans: At anode $\left[\left[Fe(CN)_6\right]^{4-} \rightarrow \left[Fe(CN)_6\right]^{3-} + e\right] \times 3$

At cathode $Cr^{3+} + 3e \rightarrow Cr_{(s)}$

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$$Cr^{3+}_{(aq)} + 3\left[Fe(CN)_6\right]^{4-} \rightarrow 3\left[Fe(CN)_6\right]^{3-} + Cr_{(s)}$$

Q. $Cd \mid CdCl_{2(aq)} \parallel HNO_{3(aq)} \mid H_{2(g)}, P+$

Ans: $Cd_{(s)} \rightarrow Cd^{2+} + 2e$

$2H^+ + 2e \rightarrow H_{2(g)}$

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$$Cd_{(s)} + 2H^+_{(aq)} \rightarrow Cd^{2+}_{(aq)} + H_{2(g)}$$

Q. $Zn \mid ZnSO_{4(aq)} \parallel AgNO_{3(aq)} \mid Ag$

Ans: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$

$\left[Ag^+_{(aq)} + e \rightarrow Ag_{(s)}\right] \times 2$

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$$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Q. $Cu \mid Cu^{2+}_{(aq)} \parallel Mn^{2+}_{(aq)}, H^+_{(aq)} \mid MnO_{2(s)}, P+$

Ans: $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e$

$MnO_{2(s)} + 4H^+ + 2e \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(e)}$

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$$Cu_{(s)} + MnO_{2(s)} + 4H^+ \rightarrow Cu^{2+}_{(aq)} + Mn^{2+}_{(aq)} + 2H_2O$$

Q. $Pt_0 \mid Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \parallel Sn^{4+}_{(aq)}, Sn^{2+}_{(aq)} \mid Pt$

Ans: $\left[Fe^{2+} \rightarrow Fe^{3+} + e\right] \times 2$

$$Sn^{4+} + 2e \rightarrow Sn^{2+}$$

$$2Fe^{2+} + Sn^{4+} \rightarrow 2Fe^{3+} + Sn^{2+}$$

Q. $Pt, Cl_{2(g)} \mid HCl_{(aq)} \parallel K_2Cr_2O_{4(aq)}, Ag_2CrO_{4(s)} \mid Ag$

Ans: $2Cl^-_{(aq)} \rightarrow Cl_2 + 2e$

$$Ag_2CrO_4 + 2e \rightarrow 2Ag_{(s)} + CrO_4^{2-}{}_{(aq)}$$
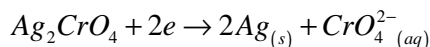
Electrode Potential

When a metal is placed in a solution of its ions the metal acquires either a positive or negative change with respect to the solution due to this. A definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.
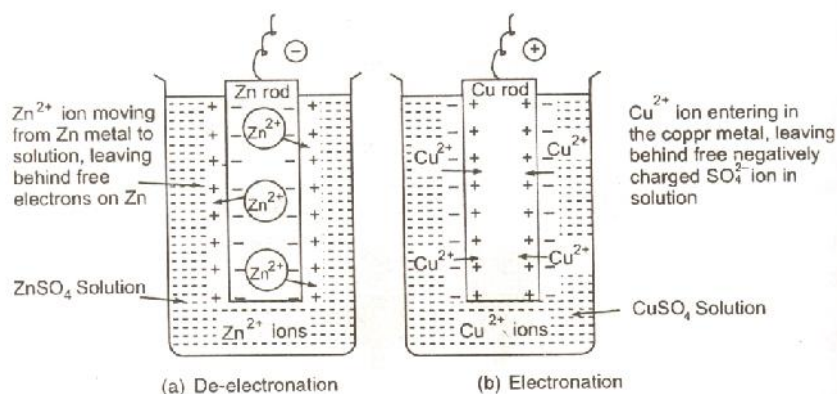
Fig. 6.3   Electrode potential.

For example when a plate of zinc placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to the solution and thus a potential difference is set up between zinc plate and solution. This potential difference is termed electrode potential of zinc. Similarly when copper is placed in a solution having Cu^{2+} ions it becomes positively charged with respect to the solution. A potential is setup between the copper plate and the solution. The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution.

The development of negative charge (as on Zn plate) or positive charge (as on Cu plate) can be explained as follows.

When a metal rod is dipped in its salt solution, two charges occur.
(a) Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode..
(b) Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

Definition: The electrical potential difference setup between the metal and its ions in the solution is called electrode potential or the electrode potential may be simply defined as the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.

The electrode potential is further termed as oxidation potential if oxidation takes place at the electrode with respect to standard hydrogen electrode and is called reduction potential.

If in the half-cell, the metal rod is suspended in a solution of one molar concentration and the temperature is kept at 298K, the electrode potential is called standard electrode potential, represented usually by E^0.

Measurement of Electrode Potential
The absolute value of the electrode potential of a single electrode (called single electrode potential) can not be determined because oxidation half reaction or reduction half reaction cannot takes place. It can only be measured by using some electrode as the reference electrode. The reference electrode used is the standard or normal hydrogen electrode (SHE or NHE). So the electrode potential of a given electrode is measured by connecting a standard hydrogen electrode through a salt bridge. The e.m.f of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter.

In the standard hydrogen gas electrode, hydrogen gas at atmospheric pressure is passed into 1M HCl at 298K in which a foil of platinum coated with platinum black (finely divided platinum) remains immersed. The electrode is usually represented as

$Pt, H_{2(g)} \mid H^+ (1m)$
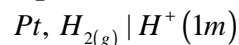
Example: Determination of standard electrode potential of Zn/Zn^{2+} electrode.

A cell comprising of a Zn electrode immersed in 1m $ZnSO_4$ solutions and standard hydrogen is setup and connected to it through a salt bridge. Both the electrodes are connected with a voltmeter as shown in figure.

H₂ gas at 1 atm
Glass envelope
Platinum wire
Platinum foil covered with platinum black
1 MH⁺ solution at 298 K
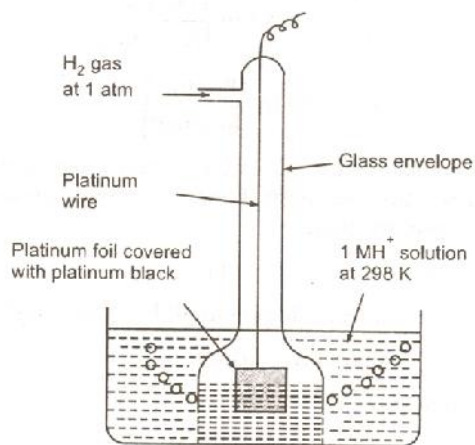
Fig. 6.4 Normal hydrogen electrode.

FIGURE (Normal hydrogen electrode)

Effect of Electrolytic Concentration and temperature on the electrode potential:
(Nernst Equation)

Consider a general reaction $M^{n+}_{(aq)} + ne \rightarrow M_{(s)}$

According to Law of Mass Action
According to Vant Hoff's reaction isotherm

$$\Delta G = \Delta \overset{0}{G} + RT \ln Q$$

$$\Delta G = \Delta \overset{0}{G} + RT \ln \frac{\left[M_{(s)} \right]}{\left[M^{n+}_{(aq)} \right]}$$

As $\left[M_{(s)} \right] = 1$

So $\Delta G = \Delta G^0 + RT \ln \dfrac{1}{\left[M^{n+}_{(aq)} \right]}$

Since in a reversible reaction, the electrical energy produced at the expense of the free energy change i.e $-\Delta G = nFE$, $\Delta G^o = -nFE^o$, where E and E^o are standard electrode potential.

F – Faraday's of electricity = 96500 coulombs

n – number of electrons involved in the cell reaction

So $-nFE = -nFE^0 + RT \ln \dfrac{1}{\left[M_{(aq)}^{n+}\right]}$

or, $E = E^0 - \dfrac{RT}{nF} \ln \dfrac{1}{\left[M^{n+}\right]}$

$E = E^0 \dfrac{-2.303RT}{nF} \log \dfrac{1}{\left[M^{n+}\right]}$

At 25^0C, T = 298K, F = 96500 coulomb, R = 8.314 $JK^{-1}mole^{-1}$

$E = E^0 - \dfrac{0.0591}{n} \log \dfrac{1}{\left[M^{n+}\right]}$

Electrochemical Series

By measuring the potential of various electrodes again at standard hydrogen electrode (SHE), a series of standard electrode potential has been established. When the electrodes (metals and non metals) in contact with their ions are arranged on the basis of the values of their standard reduction potential or standard oxidation potential, the resulting series is called the electrochemical or electromotive or activity series of the elements.

By international convention, the standard potential of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathode towards SHE. Those with positive E^o values for reduction half reactions do in fact act as cathode vs SHE while those with negative E^o values of reduction half reactions behave instead as anodes vs SHE.

Application of Electrochemical Series

1. Calculate the standard EMF of the cell: to be discussed under determination of e.m.f
2. To predict anode or cathode:
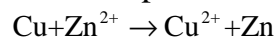   An electrode with higher oxidation potential (lower reduction potential) is taken as cathode.
   Example: $E^o_{Zn^{2+}/Zn}$ =-0.76 - Anode
   E^0Cu^{2+}/Cu=0.34V - Cathode
3. To test the feasibility of a reaction:
   For example, let us consider the reaction
   $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$
   Given $\quad E^0Cu^{2+}/Cu = 0.34V$
   $\quad\quad\quad\; E^0Zn^{2+}/Zn = -0.76V$

For the above reaction to take place, Cu has to lose electron and Zinc has to gain electron and this is only feasible only if oxidation potential of is more that that of Zinc. But from the electrochemical series it has been found that oxidation potential of Zn (0.76V) is more than that of Cu (-0.34V). So the above reaction is not feasible.

4. To predict the reactivity of the elements
   (To compare the relative activities of metal)
   Greater the oxidation potential of a metal, more easily it can lose electrons and hence greater is it is reactivity. As a result, a metal with greater oxidation potential can displace with lower oxidation potential from their salt solution. For example Zn can displace Cu from it is salt solution.
   Similarly the metals which are above hydrogen in electrochemical series can displace hydrogen from mineral acids.

Cell Potential or EMF of a cell
Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). One of the electrodes must have a higher electrode potential (higher tendency to lose electrons) than the other electrode. As a result of this potential difference, the electrons flow from an electrode at a higher potential to the electrode at a lower potential. The difference between the electrode potentials of the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage.

The EMF of the cell or cell potential can be calculated from the values of electrode potential of the two half cells constituting the cell.
(i) When oxidation potential of anode and cathode are taken into account
$$E^o{}_{cell} = E^o{}_{anode} - E^o{}_{cathode}$$
(ii) When reduction potential of cathode and anode are taken into account
$$E^o{}_{cell} = E^o{}_{cathode} - E^o{}_{anode} \, .$$

Effect of Electrolytic concentration and temperature EMF of a cell (Nernst equation)
The electrode potential and the EMF of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potential with concentration of ions in solution can be obtained from thermodynamic considerations.
For a general reaction
aA+bB $\rightleftharpoons$ mM+nN occurring in the cell. According to Gibbs reaction isotherm, the Gibbs free energy change is given by
  G= G^0+RT in Q

or $\Delta G = \Delta G^0 + RT \; in \; \dfrac{[M]^m [N]^n}{[A]^a [B]^b}$ -------- (1)

The decrease in free energy of a chemical reaction appears as electrical energy in an electrochemical cell.

The electrical energy produced in a cell is given by nFE_{cell} and nFE^0_{cell}.

So $-\Delta G = nFE_{cell}$ and $-\Delta G^0 = nFE^0_{cell}$

Putting these values in equation (1)

$$-nFE_{cell} = -nFE^0_{cell} + RT \, 1n \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} 1n \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$E_{cell} = E^0_{cell} \frac{-2.303RT}{nF} \log \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad \text{-------------- (2)}$$

The equation is known as Nernst equation.

At 25^0C,

$T = 298K$, $R = 8.314 JK^{-1}mole^{-1}$ $F = 96500$coulaub

Equation (2) reduces to

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

Relation between Electrical energy and enthalpy of a cell reaction (Temperature dependence of EMF)

According to Gibbs Heimholtz equation

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

but $\Delta G = -nFE_{cell}$

$$\left[\frac{\partial(\Delta G)}{\partial T} \right]_p = -nF \left(\frac{\partial E_{cell}}{\partial T} \right)_p$$

or, $E_{cell} = \frac{-\Delta H}{nF} + T \left(\frac{\partial E_{cell}}{\partial T} \right)_p$

$\left(\frac{\partial E_{cell}}{\partial T} \right)_p$ is known as temperature coefficient of EMF of the cell.

(i) If $\left(\frac{\partial E_{cell}}{\partial T} \right)_p = 0$, the electrical energy will be equal to enthalpy of the reaction.

(ii) If $\left(\frac{\partial E_{cell}}{\partial T} \right)_p > 0$, then EMF of the cell, then electrical energy increases with rise in

temperature and the additional energy will be supplied to the cell by surrounding and if that is not possible the temperature of the cell fall during its working.

(iii) If $\left(\frac{\partial E_{cell}}{\partial T} \right)_p$ is <0, then electrical energy will be less than the enthalpy of the reaction.

The EMF of the cell Cd, CdCl₂. 2.5 H₂) (solid) || AgCl₍ₛ₎. Ag, in which the cell reaction is
$Cd_{(s)} + 2AgCl_{(s)} \rightleftharpoons CdCl_2 \cdot \frac{5}{2}H_2O + 2Ag_{(s)}$ **is 0.6753V at 25⁰C and 0.6915V at 0⁰C.**
Calculate the free energy change, ΔH and ΔG of the reaction at 25⁰C.

Ans: The cell reaction requires 2 electrons, so
n = 2
$$\Delta G = -nFE = -2 \times 96500 \times 0.6753$$
$$= 130332.9 \ J$$
$$= -130.33 \ KJ$$

$$E = \frac{-\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$$

In this case, EMF decreases with increase in temperature i.e
$\left(\dfrac{\partial E}{\partial T}\right)_p$ is negative thus
$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{-(0.6915 - 0.6753)}{25K}$$
$$= -0.00065 \ VK^{-1} \text{ at atm pressure}$$
$$0.6753V = \frac{\Delta H}{2 \times 96500} + 298\left(-0.00065 VK^{-1}\right)$$
$$\Delta H = -167717 = -167.72 \ KJ$$
Again $\Delta S = \dfrac{\Delta H - \Delta G}{T} = -123.8 \ JK^{-1}$

Determination of Equilibrium Constant from EMF
$$-\Delta G^0 = RT \ln K = nFE^0_{cell}$$

$$E = \frac{2.303RT}{nF} \log K \ \frac{-2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At 25⁰C $E = \dfrac{0.0591}{n} \log K - \dfrac{0.0591}{n} \log \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$

Q. Calculate the equilibrium constant of the reaction $2Ag^+ + Zn \rightleftharpoons 2Ag + Zn^{+2}$ occurring in the Zinc Silver cell at 25⁰C when $\left[Zn^{2+}\right] = 0.10M$ and $\left[Ag^+\right] = 10M$ EMF of the cell is found to be 1.62 volt.

Ans: $E = \dfrac{0.0591}{n} \log K \dfrac{-0.0591}{n} \log \dfrac{\left[Zn^{2+}\right]}{\left[Ag^+\right]^2}$

$$1.62 = \frac{0.0591}{2} \log K \frac{-0.0591}{2} \log \frac{0.10}{(10)^2}$$

or, $K = 8.128 \times 10^{52}$

Q. Consider the electrochemical cell Fe, $Fe^{2+}(0.1M) \mid Cd^{2+}(0.001M)Cd$

(a)   **Write the cell reaction**

(b)   **Calculate the EMF of the cell** $E^0 Cd^{2+}/Cd = -0.40V$
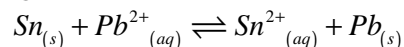
(c)   **Calculate equilibrium constant** $E^0 Fe^{2+}/Fe = -0.448V$

Ans: Std. EMF = 0.091V

$$\log K = \frac{nFE^0}{2.303RH} = 0.643$$

K = 4.39d

Q. What ratio of Pb^{2+}/Sn^{2+} **concentration is needed to reverse the following reaction?**

$Sn_{(s)} + Pb^{2+}_{(aq)} \rightleftharpoons Sn^{2+}_{(aq)} + Pb_{(s)}$

$E^0 Sn^{2+}/Sn = 0.136V \quad E^0 Pb^{2+}/Pb = -0.126V$

$$E^0_{cell} = E^0 Pb^{2+}/Pb - E^0 Sn^{2+}/Sn$$

Ans: $= -0.126 + 0.136$

        $= 0.01V$

$$E_{cell} = E^0_{cell} \frac{-0.0591}{2} \log \frac{[Sn^{2+}]}{[Pb^{2+}]}$$

At equilibrium $E_{cell} = 0$

So $0 = 0.01 + \frac{0.0591}{2} \log \frac{[Pb^{2+}]}{[Sn^{2+}]}$

$$\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.458$$

Thus till $\dfrac{[Pb^{2+}]}{[Sn^{2+}]} > 0.458$, cell reaction exists and it will be reversed when $\dfrac{[Sn^{2+}]}{[Pb^{2+}]} < 0.458$

Determination of ΔG^0, ΔS^0 and ΔH^0 of a cell reaction

We know $\Delta G = -nFE^0$

Differentiating the above equation

$$\left[\frac{\partial(\Delta G^0)}{\partial T}\right]_p = -nF\left[\frac{\partial E^0}{\partial T}\right]_p$$

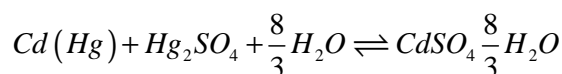As $-\Delta S^0 = \left[\frac{\partial(\Delta G^0)}{\partial T}\right]_p$

So $\Delta S^0 = nF\left[\frac{\partial E^0}{\partial T}\right]_p$

Again $\Delta H^0 = \Delta G^0 + T\Delta S^0$

$$= -nFE^0 + nFT\left(\frac{\partial E^0}{\partial T}\right)_p$$

$$\Delta H^0 = -nFE^0 + nFT\left(\frac{\partial E^0}{\partial T}\right)_p$$

Q. The EMF of the standard Weston cell written as Cd(Hg), $CdSO_4, \frac{8}{3}H_2O_{(s)} \| CdSO_{4(sat)}, Hg_2SO_4, Hg$ in which the cell reaction

$$Cd(Hg) + Hg_2SO_4 + \frac{8}{3}H_2O \rightleftharpoons CdSO_4\frac{8}{3}H_2O$$

is 1.0185 V at 25⁰C. Calculate $\Delta G^0, \Delta S^0$ and ΔH^0 for the reaction if $\left(\frac{\partial E^0}{\partial T}\right)_p$ for the cell

is $5 \times 10^{-5} VK^{-1}$

Ans: $\Delta G^0 = -nFE^0 = -196531.93$

$$= 196.53 \ KJ$$

$$\Delta S^0 = nF\left(\frac{\partial E^0}{\partial T}\right)_p = 2 \times 96500 \times 5 \times 10^{-5}$$

$$= 9.65 \ JK^{-1}$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0$$
$$= -193656 J = -193.656 \ KJ \ .$$
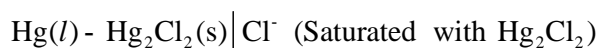
Calomel Half Cell

Introduction

Because of the experimental difficulty involved in the preparation and use of standard hydrogen electrode (SHE), secondary reference electrodes have been composed with the former and widely used. Amongst these, there are calomel electrode which is extensively used as reference electrode.
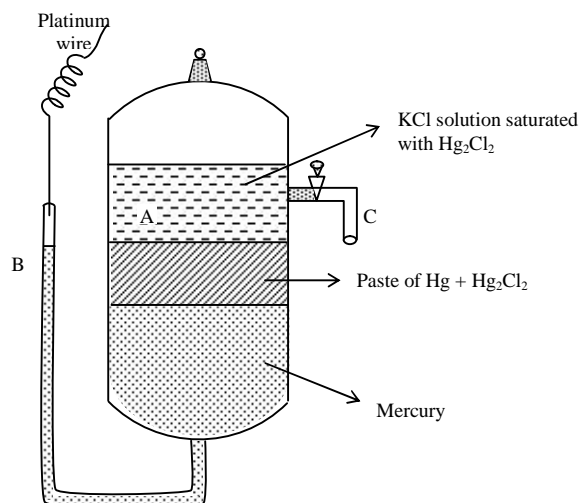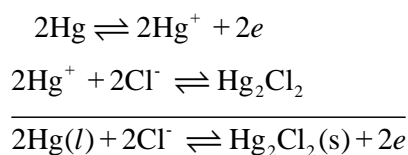
Construction

The electrode consists of a glass vessel A to which one side arm B is attached for making electrical contact and another arm C for insertion of any desired solution into the bottom of A. A Pt-wire is sealed into the bottom of A over which are placed in turn a layer of specially purified mercury and paste of mercury and calomel and then the appropriate KCl solution saturated with calomel was filled into the cell.
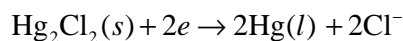
Representation

$$\text{Hg}(l) - \text{Hg}_2\text{Cl}_2(s) \mid \text{Cl}^- \ (\text{Saturated with Hg}_2\text{Cl}_2)$$

Reaction

$$2\text{Hg} \rightleftharpoons 2\text{Hg}^+ + 2e$$

$$2\text{Hg}^+ + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2$$

$$\overline{2\text{Hg}(l) + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2(s) + 2e}$$

Expression of Potential

Let the actual process occurring at the electrode be reduction, then the electrode reaction will be

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

Then the electrode potential will be given by

$$E_{\text{red}} = E^0_{\text{Hg}_2\text{Cl}_2 \to \text{Hg}} - \frac{RT}{2\Im} \ln \frac{a^2_{\text{Hg}(l)} \times a_{\text{Cl}^-}^2}{a_{\text{Hg}_2\text{Cl}_2(s)}}$$

$$= E^0_{\text{Hg}_2\text{Cl}_2 \to \text{Hg}} - \frac{RT}{2\Im} \ln a_{\text{Cl}^-}^2$$

$$= E^0_{\text{Hg}_2\text{Cl}_2 \to \text{Hg}} - \frac{RT}{\Im} \ln a_{\text{Cl}^-}$$

Discussion

(1) Electrode potential depends upon the activity of KCl solution used, usually three standard calomel electrode are used in the laboratory with reduction potential,

Concentratiof KCl	Saturated	1.0 N	0.1 N
Electrode Potential (reduction)	0.2415V	0.2800V	0.3338 V

(2) If $a_{Cl^-} = 1$ then $E_{red} = E^0_{Hg_2Cl_2 \to Hg} \Rightarrow$ standard calomel potential. Because of the experimental difficulties in the preparation of H_2 - half Cell, calomel half cell is extensively used as reference half cell. As it is standard and not primary standard H_2 half cell it is called secondary standard half cell.

(3) It can be easily prepared and can attain reversibility readily. Hence it is extensively used over H_2 electrode.

Hydrogen Half Cell

Construction

A solution containing H^+ is taken in a pyrex vessel provided with lid. Though the lid a pt-wire is introduced which carry a pt-foil coated with pt-black and kept immersed in solution, pure H_2 gas at pressure P is continuously bubbled so that the pt-black and the solution are saturated and equilibrium is reached. Guard tube is fitted to ensure that external atmospheric gases do not diffuse in the system. Temperature is maintained constant by placing it in a thermostat.

Representation

Pt, $H_2(g, P$ - atm$)\big|H^+$
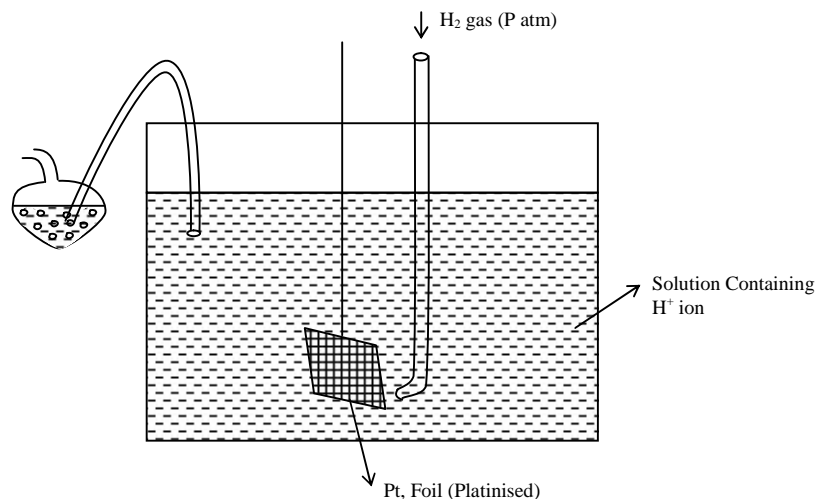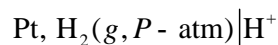
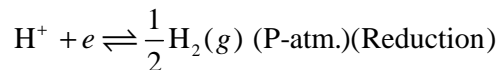*Reaction*

The actual reaction for hydrogen half cell is

$$H^+ + e \rightleftharpoons \frac{1}{2}H_2(g) \text{ (P-atm.)(Reduction)}$$

Expression of potential

From Nernst equation we get,

The reduction potential $E_{red} = E^0_{H^+ \to H_2} - \dfrac{RT}{1.\Im} \ln \dfrac{a^{1/2}_{H_2(g)}}{a_{H^+}}$

$$= E^0_{H^+ \to H_2} - \frac{RT}{\Im} \ln a^{1/2}_{H_2} + \frac{RT}{\Im} \ln a_{H^+}$$

$$= E^0_{H^+ \to H_2} - \frac{RT}{2\Im} \ln a_{H_2} + \frac{RT}{\Im} \ln a_{H^+}$$

$$= E^0_{H^+ \to H_2} - \frac{RT}{2\Im} \ln P_{H_2} + \frac{RT}{\Im} \ln a_{H^+}$$

(P_{H_2} Pressure at which H_2 gas is passed)

Discussion

(1) The hydrogen half cell potential depends on a) temperature b) activity of H^+ ion   c) pressure at which H_2 gas is passed.

(2) If H_2 gas at one atmosphere pressure is kept in constant with a solution containing H^+ ion of unit activity then it is called standard or normal hydrogen electrode half cell (SHE).

$$\text{Here } E_{H_2} = E^0 \quad \because a_{H^+} = 1 \text{ and } P_{H_2} = 1$$

Then E^0 is called standard hydrogen electrode potential (SHEP).

By convention this potential E^0 is arbitrarily taken a zero at all temperature.

Thus for

$$\left. \begin{array}{c} Pt, H_2(g) \\ p = 1\,atm \end{array} \right| H^+(a_{H^+} = 1) \ , \ E = E_{H_2} = 0 \text{ volt.}$$

(3) Thus

$$E = -\frac{RT}{2\Im} \ln P_{H_2} - \frac{RT \times 2.303}{\Im} p_H$$

So P^H of the solution can be ascertained by measuring the HEP.
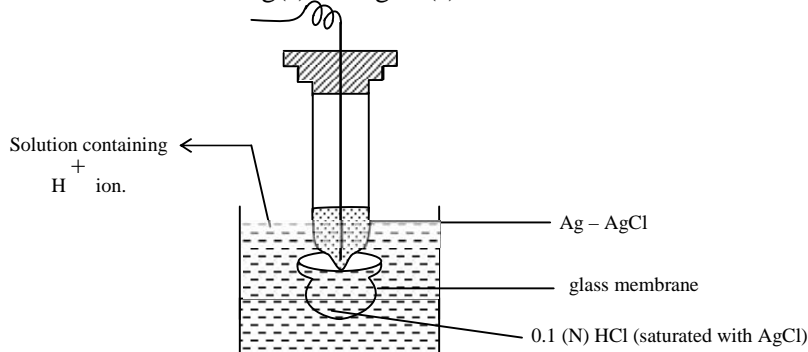
Membrane on Glass Half Cell

Introduction:

This is the most reproducible of all electrodes that is why it is widely used.

Construction:

The glass half cell consists of a specially prepared soft glass globe of thin (< 0.2 mm) membrane containing a dilute solution (say 0.1 m) of HCl or solution of HOAc containing KCl in which is immersed Ag(s) — AgCl (s) electrode.

Representation:

Ag (s)	AgCl (s)	0.1 (M) HCl (or HOAc +KCl) Saturated with AgCl	Glass	Solution Containing H $^+$ ion

Principle of development of potential:

Ag(s) - AgCl(s) $|$ Cl $^-$ consists one half cell. More over Haber and others calculated that when a tin glass membrane separates to two solution of different pH, a difference of potential is developed across the membrane. The combined potential of the Ag – AgCl and that of membrane is actually the glass half cell potential.

Expression of potential:

Thus $x_{\text{glass}} = x_{\substack{\text{internal} \\ \text{electrode}}} + x_{\text{assymmetric}} - \dfrac{RT}{\text{Á}} 2.303 \left(pH_{HCl} + pH_{Soln.} \right)$

So the magnitude of this glass membrane potential depends on the difference in pH of the two solutions. If the pH of these solution be kept constant and that of the other is varied, then the potential of the glass half cell follows the relation.

$$E_{\text{Glass}} = E^{\circ}_{\text{Glass}} - \dfrac{RT}{\text{Á}} \ln a_{H^+} \quad \text{when } x^{\circ}_{g} = x_{\substack{\text{internal} \\ \text{electrode}}} + x_{\text{assymetric}}$$

due to nature to Glass and

difference in thickness of glass

$$= E^{\circ}_{glass} + \frac{RT}{\acute{A}} \,' \, 2.303 pH.$$

Discussion:

(1) If $a_{H^+} = 1$ (i.e. $p_H = 0$), the $x = x^{\circ}_{glass}$

(2) The potential depends on a_{H^+} (i.e. pH) of the solution in which it is dipped.

(3) Thus it can be used for determination of pH of the solution.

(4) The electrode can function in the same way as a hydrogen electrode.

Determination of pH

The glass half cell is dipped into the experimental solution.   This is coupled with a reference half cell say a calomel half cell by means of a salt bridge to eliminate liquid junction potential. Resulting cell is represented as

Ag (s)	AgCl (s)	0.1 (N) HCl Saturated with AgCl	Glass	Solution Containing H$^+$ ion	Reference Calomel half cell
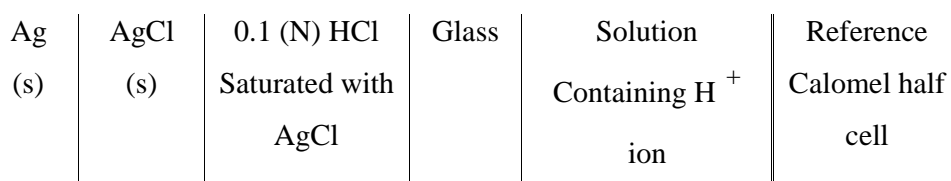
The expression of emf of a cell:

$$E_{Cell} = E_{Glass} + E_{Calomel(reduction)} \qquad \text{where } E_{Glass} = \text{emf of glass}$$

$$= E^{0}_{Glass} + 2.303 \frac{RT}{\acute{A}} pH + E_{Calomel(reduction)}$$

So measuring the e.m.f. of the cell and knowing the value of E^{0}_{Glass} (using a buffer of known pH) and $E_{calomel(reduction)}$ we can calculate pH.

In practice, the assembly of glass half cell is first used with a solution of known pH (say, pH_1) and its e.m.f E_1 is measured.   This solution is then substituted with the experimental solution of pH_2 and its e.g. E_2 is then measured.

Then

$$E_1 = E^{0}_{Glass} + 2.303 \frac{RT}{\acute{A}} pH_1 + E_{Calomel}$$

$$E_2 = E^{0}_{Glass} + 2.303 \frac{RT}{\acute{A}} pH_2 + E_{Calomel}$$

$$\backslash \ E_1 - E_2 = 2.303 \frac{RT}{\acute{A}} \left(pH_1 - pH_2 \right)$$

So measuring E_1 and E_2 and knowing pH_1, we can calculate pH_2.

Advantages:

The advantages of this electrode are

    (1) It can be used in any solution not being affected by oxidizing or reducing agent or unsaturated organic compound.

    (2) It is not easily poisoned.

    (3) A small quantity of solution is sufficient.

    (4) The value is reproducible (reliable)

    (5) Temperature coefficient is very small.

Hence it is most widely used for different pH.

Limitations:

    (1) It cannot be used in strong alkaline solution $(pH > 8.5)$ where glass is attacked by alkaline solution.

    (2) It is not used where $pH^3 \ 10$. Presence of various cations particularly Na^+ leads to appreciable errors. However special glasses (e.g. alkaline earth) have been developed with which good results are obtained up to $pH = 13 - 14$

    (3) Because of high integral resistance [about $(10 - 1000) \times 10^6$ ohm] ordinary potentiometer cannot be used to measure the emf, so the emf of the cell is measured with an electronic voltmeter or quadrant electrometers.

Precaution of glass half cell:

    (1) Glass must have low melting point i.e. soft.

    (2) Glass bulbs must be of thin walled.

   (3) Glass electrode must have high electrical conductivity.

Quinhydrone Electrode

Quinhydrone is an equimolecular compound of quinone and hydroquinone (H_2Q) associated through hydrogen bonding.
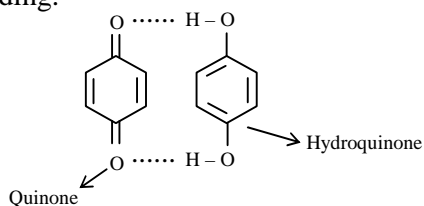
Consequently there is decrease in the co-association of this compound with water making it sparingly soluble. So when a punch of quinhydrone is immersed in solution; the solution is made saturated. This remains in equilibrium with the solid compound. But in aqueous solution it breaks into equimolecular proportion of Quinone and hydroquinone such that $\dfrac{a_Q}{a_{H_2Q}} = 1$ which establishes the equilibrium.
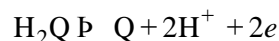
$$Q + 2H^+ + 2e \rightleftharpoons H_2Q$$
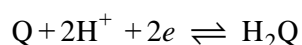
This is a redox system. Now if an inert electrode like Pt or Au is dipped in it, a redox half cell is formed. This is **represented** as,

$$\text{Pt} \left| \begin{array}{l} \text{Solution saturated with, } H^+ \\ \text{Quinhydrone} \end{array} \right.$$
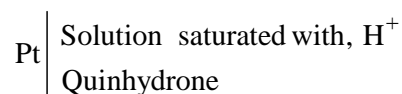
Reaction: Actual reaction occurring in the electrode is

$$H_2Q \,Þ\; Q + 2H^+ + 2e$$

Expression of potential: Now for reduction reaction

$$Q + 2H^+ + 2e \,®\; H_2Q$$
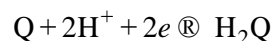
The corresponding reduction potential of quinhydrone half cell is

$$E_{red} = E^0_{Q® H_2Q} - \frac{RT}{2Á} \ln \frac{a_{H_2Q}}{a_Q \,´\, a_{H^+}^2}$$

$$= E^0_{Q ® H_2Q} + \frac{RT}{2Á} \ln a_{H^+}^2 \quad \left[\text{since} \frac{a_Q}{a_{H_2Q}} = 1 \right]$$

$$= E^0_{Q® H_2Q} + \frac{RT}{Á} \ln a_{H^+}$$

$$= E^0_{Q® H_2Q} + \left(\frac{RT}{Á} ´\, 2.303\,pH \right) = E^0_{Q® H_2Q} - \frac{RT}{Á} ´\, 2.303\ pH$$

Discussion:

(1) The quinhydrone half cell potential depends only on the activity of H^+ ions or pH of the solution. Consequently this quinhydrone half cell can be used to determine the pH of a solution.

(2) When $a_{H^+} = 1$, i.e. $pH = 0$, $E = E^0_{red}$ Þ Standard quinhydrone

electrode potential

Determination of pH

The experimental solution whose pH is to be measured is taken in a beaker. A pinch of quinhydrone (which is equimolar mixture of compound quinone $C_6H_4O_2$ and Hydroquinone $C_6H_4(OH)_2$ are held together by hydrogen bonding. Consequently there is decrease in co-association) is added to it, with stirring to ensure saturation. Then a bright Pt wire (or foil) is suspended in the solution. In solution quinhydrone breaks up to equimolecular proportion of quinone and hydroquinone such that
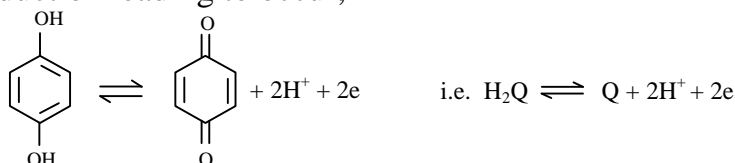
$$a_Q = a_{H_2Q}$$

Thus we have both quinine (Q) and reduction product of hydroquinone (H_2Q) present together in solution, containing H^+ ions. Consequently the following oxidation and reduction leading to occur,

i.e. $H_2Q \rightleftharpoons Q + 2H^+ + 2e$

This indeed a redox system, so the immersed Pt wire records a potential. Evidently a redox half cell known as quinhydrone half cell is set up, Pt | quinhydrone, H^+ of experimental solution. Thus H_2Q electrode is then coupled a saturated calomel electrode, so as to be a complete cell. The liquid junction potential is eliminated by means of a suitable salt bridge. In this combination H_2Q acts as the Å ve electrode. Hence the complete cell is represented as

$Hg | HgCl_2(s) |$ saturated KCl solution $\| Q, H_2Q$ (Saturated) experimental solution $|$ Pt
As reduction takes place at cathode hence,

$$Q + 2H^+ + 2e \ \text{Þ} \ H_2Q$$
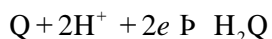
Reduction potential $E_{red} = E^0_{Q \circledR H_2Q} - \dfrac{RT}{\acute{A}} \acute{} 2.303\, pH$. As the calomel electrode acts as the $-$ ve electrode and consequently involved oxidation types of reduction, its potential will be $E_{calomel\,(ox)}$, hence the net e.m.f.

$$E_{cell} = (E_+) - (E_-) = E^0_{Q \circledR H_2Q} - 0.059\, pH - E_{calomel\,(reduction)}$$

$$pH = \dfrac{-E_{cell} + E^0_{Q \circledR H_2Q} - E_{calomel\,(reduction)}}{0.059}$$ E_{cell} is measured experimentally while

$E_{calomel}$ and $E^0_{Q \circledR H_2Q}$ can be obtained from standard reduction potential table. Hence pH can be calculated.

Advantages:

1) It is simple and easier to set up.
2) It does not require constant attention.
3) Equilibrium is quickly attained, hence it is not so time consuming.
4) A small quantity of solution is needed.
5) Air need not be eliminated.
6) It can be used in presence of a) heavy ions b) unsaturated substances.

Limitations:

i) In alkaline medium hydroquinone undergoes aerial oxidation to form phenonide ion. Hence it cannot be used in alkaline medium. So it is not of such a general use as H_2- electrode.

ii) It is found that when, $pH < 7.8$ the half cell potential is positive.

   $pH > 7.8$ the half cell potential is negative

   $pH = 7.8$ the half cell potential is zero.

iii) It cannot be used if any other redox system is present in experimental solution.

iv) It cannot be used in solution of very high activity of ions.

Amalgam Half Cell
Definition:

In some cases of metal metal ion electrodes the pure metal is too active, we have to them in aqueous solution of their ions. As such they are used in the form of their mercury amalgam, hence often called amalgam electrode.

Representation: This is represented as,

$$Na(Hg)_x \big| Na^+$$

$$Cd(Hg)_x \big| Cd^{++}$$
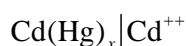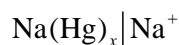
Reaction: The actual reaction occurring in the half cell is

$$Na\,(Hg)_x \;\text{®}\; Na^+ + e$$

$$Cd\,(Hg)_x \;\text{®}\; Cd^{++} + 2e.$$

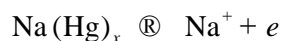**Expression of potential:** Now for reduction form $Cd^{2+} + 2e \;\text{®}\; Cd(Hg)_x$

Hence, $\quad E_{red} = E^0_{Cd^{2+}\,\text{®}\,Cd} \; - \; \dfrac{RT}{2\acute{A}} \ln \dfrac{a_{Cd(Hg)_x}}{a_{Cd^{2+}}}$

$$= E^0_{Cd^{2+}\,\text{®}\,Cd} \; - \; \dfrac{RT}{2\acute{A}} \ln a_{Cd(Hg)_x} + \dfrac{RT}{2\acute{A}} \ln a_{Cd^{+2}}$$

$a_{Cd(Hg)_x}$ is the activity of metallic Cd in mercury – a constant.

$$E_{red} = \acute{e}\grave{e} E^0_{Cd^{2+}\,\text{®}\,Cd} \; - \; \dfrac{RT}{2\acute{A}} \ln a_{Cd(Hg)_x} \grave{u}\acute{u} + \dfrac{RT}{2\acute{A}} \ln a_{Cd^{+2}}$$

$$= E^0_{Amalgam} + \dfrac{RT}{2\acute{A}} \ln a_{Cd^{2+}}$$

Discussion:

(a)

(i) EMF depends on a_{M^+} as well as an $a_{M(Hg)x}$

(ii) For fixed amalgam activity, $E_{red} = E^0_{amalgam} + \dfrac{RT}{2\acute{A}} \ln a_{Cd^{2+}}$ – which is analogous to the electrode potential of M^{+n}/M half cell from this determination of activity of metal in amalgam is possible.

(iii) Amalgam of metal are more active than mercury behaves essentially as the do the pure metals, the only difference being that the activity of the metals is lowered (from unity) by dilution with Hg.

(b) Some metals like alkali metals (Na, K etc) and alkaline earth metals (Ca) are too reactive to be used as pure metals in aqueous solution. Hence amalgamation is carried out to reduce the activity.

(c) Since by convention activity of pure metal is unity, so there is no scope of alternation of the activity of the metal (and consequently the corresponding half cell potential can not be changed). This is utilized in the construction of electrode concentration cell (by amalgamation).

(d) Amalgam electrode are readily reversible.

(e) Equilibrium is attained much more quickly in comparison to the corresponding pure metal.

(f) Some metals which can easily be contaminated with full of impurities, give rise to erratic potential, but amalgamation removes these impurities so as to give good results.

Chemical Cells/Weston-Cadmium Cell

Construction and Fig:

The cell is prepared in a H-shaped vessel – one arm containing the electrode, 12.5% cadmium amalgam and the other arm containing mercury in contact with a paste Hg and mercurous sulphate. The whole vessel is then filled up with saturated solution of $CdSO_4$. Some crystals of $3CdSO_4, 8H_2O$ being added over the negative electrode. The vessel is then sealed. The electrodes are connected to the external circuit through two Pt wires sealed at the bottom of the electrodes.
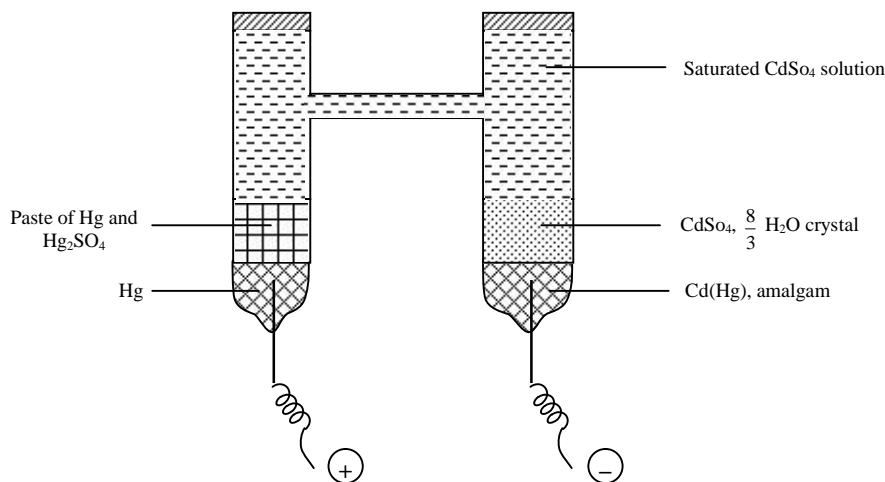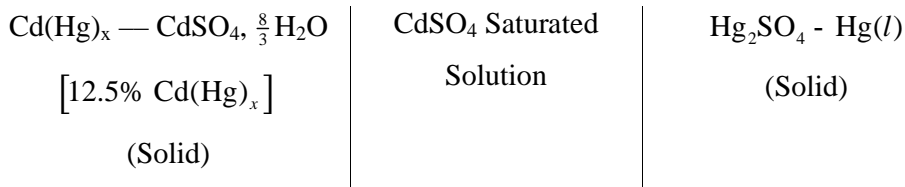

Its electrode potential is measured by comparison with potential difference across a standard known resistance carrying an absolutely known current.
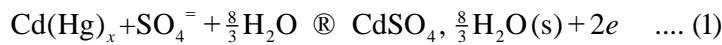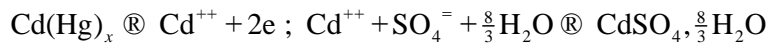
(say Ag – accumulator).

Depiction:

Since in combination $\left[Cd(Hg)_x\right]$ acts as the negative half cell, hence the cell is depicted as follows:-

Cd(Hg)$_x$ — CdSO$_4$, $\frac{8}{3}$H$_2$O $\left[12.5\%\ Cd(Hg)_x\right]$ (Solid)	CdSO$_4$ Saturated Solution	Hg$_2$SO$_4$ - Hg(l) (Solid)

Reaction: At the negative electrode oxidation reaction occurs:

$$Cd(Hg)_x \circledR\ Cd^{++} + 2e\ ;\ Cd^{++} + SO_4^{=} + \tfrac{8}{3}H_2O\ \circledR\ CdSO_4, \tfrac{8}{3}H_2O$$

$$Cd(Hg)_x + SO_4^{=} + \tfrac{8}{3}H_2O\ \circledR\ CdSO_4, \tfrac{8}{3}H_2O(s) + 2e\quad ....\ (1)$$

At the positive electrode reduction reaction occurs.

$$Hg_2SO_4(s) + 2e\ \circledR\ 2Hg(l) + SO_4^{=}\qquad ....(2)$$
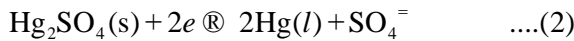
Adding (1) and (2) we get redox (chemical) reaction of the cell.

$$Cd(Hg)_x + \tfrac{8}{3}H_2O(l) + Hg_2SO_4(s)\ \circledR\ CdSO_4, \tfrac{8}{3}H_2O(s) + 2Hg(l)$$
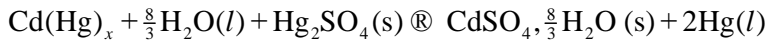
Thus when the cell generates current (i.e. discharges) the above redox (chemical) reaction proceeds with the cell.

Electrode potential of the Cell:

Electrode potential at the negative electrode is

$$E_{Ox} = E^0_{Cd(Hg)_x \circledR\ CdSO_4, \frac{8}{3}H_2O} - \frac{RT}{2\acute{A}}\ln\frac{a_{CdSO_4, \frac{8}{3}H_2O(s)}}{a_{Cd(Hg)_x}\ a_{SO_4^=}.a_{H_2O}}$$

$$= E^0_{Cd(Hg)_x \circledR\ CdSO_4.\frac{8}{3}H_2O} - \frac{RT}{2\acute{A}}\ln\frac{1}{a_{Cd(Hg)_x}.a_{SO_4^=}}\quad [\text{Since } a_{CdSO_4,\frac{8}{3}H_2O(s)} = a_{H_2O} = 1]$$

In reduction form

$$E_{red} = -\left[E^0_{Cd(Hg)_x \circledR\ CdSO_4.\frac{8}{3}H_2O} - \frac{RT}{2\acute{A}}\ln\frac{1}{a_{Cd(Hg)_x}.a_{SO_4^=}}\right]$$

Electrode potential of the positive half cell is

$$E_{red} = E^0_{Hg_2SO_4 \circledR\ Hg} - \frac{RT}{2\acute{A}}\ln\frac{a^2_{Hg(l)}{}'\ a_{SO_4^=}}{a_{Hg_2SO_4(s)}}$$

$$= E^0_{Hg_2SO_4 \circledR Hg} - \frac{RT}{2\acute{A}} \ln a_{SO_4^=} \qquad [\text{Since } a_{Hg(l)} = 1 \text{ and } a_{Hg_2SO_4(s)} = 1]$$

Hence total emf of the cell is

$$E_{cell} = (E_{reduction})_{right} - (E_{reduction})_{left}$$

$$= E^0_{cell} - \frac{RT}{2\acute{A}} \ln a_{SO_4^=} - \frac{RT}{2\acute{A}} \ln \frac{1}{a_{Cd(Hg)_x} \cdot a_{SO_4^=}}$$

$$E_{cell} = E^0_{cell} - \left[\frac{RT}{2\acute{A}} \ln a_{SO_4^=} + \frac{RT}{2\acute{A}} \ln \frac{1}{a_{Cd(Hg)_x} \,\acute{}\, a_{SO_4^=}} \right]$$

$$= E^0_{Cell} - \frac{RT}{2\acute{A}} \ln \frac{a_{SO_4^=}}{a_{Cd(Hg)_x} \,\acute{}\, a_{SO_4^=}}$$

$$= E^0_{Cell} - \frac{RT}{2\acute{A}} \ln \frac{1}{a_{Cd(Hg)_x}}$$

Discussion:

(i) The cell e.m.f depends on the activity of the amalgam. For an amalgam of fixed composition e.g. 12.5% possesses a definite potential depending on the working temperature.

(ii) (a) High reproducibility of e.m.f. e.g. $E = 1.01845$ volt at $20°C$

(b) Emf remains constant for long time.

(c) The temperature coefficient of this cell is very small, $\dfrac{dE}{dt} = -0.00004$ volt degree^{-1}

Hence it is mostly used as the standard cell in measurement of e.m.f.

(iii) The cell is reversible. It is not subjected to a permanent damage due to passage of current through it.

(iv) Unsaturated Weston cell is the cell in which is similar to the saturated Weston cell, except that the electrolyte is a solution of $CdSO_4 \dfrac{8}{3} H_2O$ is omitted and the electrolyte is a solution of $CdSO_4$ saturated the electrolyte in this cell is unsaturated.

Application of EMF Measurement

(1) To ascertain the change in thermodynamic function

(a) To measure ΔG : If E be the emf of a cell supplying a quantity of electricity Q, then the electrical energy is EQ. With each equivalent of reactant involved is associated one faraday, $\Im$ of electricity. If n equivalent of reaction occurs, electrical energy produced $= n\Im E$

Again according to Helmholtz, "the decrease in free energy of the process is equal to the electrical energy obtained from a Galvanic Cell"

So, $-\Delta G = n\,\acute{A}\,E$

or, $\Delta G = -\,n\,\acute{A}\,E$

So, as 'n' and '$\Im$' is known, measuring e.m.f (E) of the cell we can measure $'\Delta g'$.

(b) To measure ΔH : From Gibbs-Helmholtz equation we know that,

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

So, $-\,n\,\acute{A}\,E = \Delta H + T(-\,n\,\acute{A})\dfrac{\P E}{\P T}$

or, $\Delta H = n\,\acute{A}\left[T\,\dfrac{\P E}{\P T} - E\right]$

But $\dfrac{\P E}{\P T} = \dfrac{\Delta E}{\Delta T} = \dfrac{E - E^1}{T - T^1}$

So measuring E at constant temperature T and the temperature coefficient of the cell $\dfrac{\partial E}{\partial T}$ we can measure ΔH.

(c) **To measure** ΔS :

Again we know that, $\Delta S = -\left[\dfrac{\P}{\P T}(\Delta G)\right]_P$

$\therefore \; \Delta S = n\,\acute{A}.\dfrac{\P E}{\P T}$

So, as 'n' and '$\Im$' is known, measuring temperature coefficient $\dfrac{\partial E}{\partial T}$, we can calculate ΔS.

(2) To ascertain the equilibrium constant of a reversible chemical reaction:

Let us consider a reversible chemical reaction

$$n_1 A + n_2 B + \cdots\cdots \rightleftharpoons n_3 D + n_4 E + \cdots\cdots$$
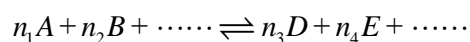
The equilibrium constant of this reaction is related to the standard free energy change of the process as $-RT \ln K_{(eq)} = \Delta G^0 \quad \cdots(1)$

But standard free energy change is related to the standard e.m.f of the cell as,

$$\Delta G^0 = -n\acute{A}E^0 \qquad ...(2)$$

From (1) and (2) we have

$$-RT \ln K_{(eq)} = \Delta G^0 = -n\acute{A}E^0$$

$$\text{or,} \quad \log K_{(eq)} = \frac{n\acute{A}E^0}{RT \acute{} 2.303}$$

$$\text{or,} \quad K_{(eq)} = 10^{\frac{n\acute{A}E^0}{RT \acute{} 2.303}}$$

So knowing E^0 and the temperature we can calculate the equilibrium constant.

(3) To ascertain the valency of an ion:

Let we construct an electrolyte concentration cell without transference such that the activity of the metal ion of the left hand electrode is 10 times greater than that of the right hand electrode.

The cell is given by $M \left| \begin{matrix} M^{+n} \\ (a) \end{matrix} \right| \left| \begin{matrix} M^{+n} \\ (a/10) \end{matrix} \right| M$

So e.m.f of the left hand electrode is

$$E_1 = E^0 - \frac{0.059}{n} \log a_1 \qquad \cdots(1)$$

So e.m.f of the right hand electrode is

$$E_2 = E^0 - \frac{0.059}{n} \log \frac{a}{10} \qquad \cdots(2)$$

Subtracting, [Where n is the valency of ion]

$$E_2 - E_1 = \frac{0.059}{n} \log \frac{a}{a/10}$$

$$= \frac{0.059}{n} \log 10$$

$$= \frac{0.059}{n}$$
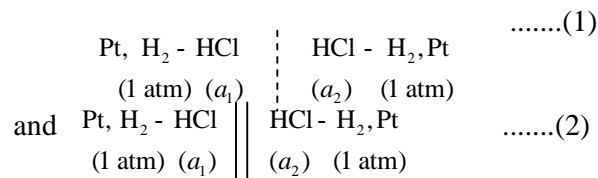
$$\text{or, } E = \frac{0.059}{n}$$

$$\text{or, } n = \frac{0.059}{E} \text{ (at 25°C)}$$

So measuring e.m.f. of the cell we can measure the valency (n) of the metal at a definite temperature.

(4) Determination of transport number:

Transport number can be measured by measuring the emf of a concentration cell with and without transference.

Let we construct the following two concentration cells of which one is with transference and another is without transference, in which liquid junction potential is eliminated by salt bridge.

$$
\text{Pt, } H_2 - HCl \quad \vdots \quad HCl - H_2, Pt \qquad \text{.......(1)}
$$
$$
\text{(1 atm) } (a_1) \quad \vdots \quad (a_2) \quad \text{(1 atm)}
$$
$$
\text{and} \quad \text{Pt, } H_2 - HCl \,\Vert\, HCl - H_2, Pt \qquad \text{.......(2)}
$$
$$
\text{(1 atm) } (a_1) \,\Vert\, (a_2) \quad \text{(1 atm)}
$$

The e.m.f of (1) is given by

$$
E = 2t_- \frac{RT}{n\acute{A}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \text{........(3)}
$$

The e.m.f of (2) is given by

$$
E\cent = \frac{RT}{n\acute{A}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \text{.......(4)}
$$

Hence $(3) \div (4) \Rightarrow$

$$
\frac{E}{E\cent} = 2t_-
$$

$$
\text{or, } t_- = \frac{E}{2E\cent} \quad \text{and} \quad t_+ = (1 - t_-)
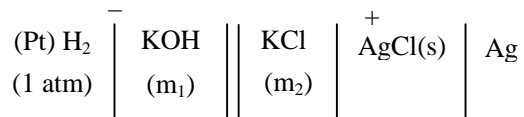$$

So measuring e.m.f of the two we can measure the transport number.

(5) Determination of ionic product of water:

Construction: A solution containing H^+ ion is taken in a pyrex vessel provided with lid. Through the lid a Pt wire is introduced which carry a Pt foil coated with Pt black and kept immersed in solution, pure H_2 gas at pressure P is continuously bubbled so that the Pt black and the solution are saturated and at equilibrium. Guard tube is fitted to ensure that external atmospheric gases do not diffuse in the system. The temperature is maintained constant by placing it in a thermostat.

The half cell is then coupled with $Ag - AgCl(s)/Cl^-$ electrode and the liquid junction potential is eliminated by means of a suitable salt bridge.
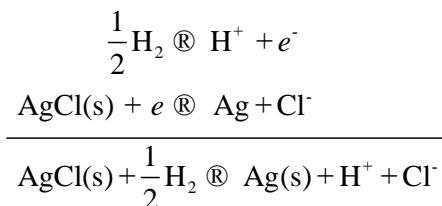
Depiction: The cell is depicted as follows

$$\text{(Pt) H}_2 \overset{-}{\Big|} \begin{matrix}\text{KOH}\\(\text{m}_1)\end{matrix} \Big|\Big| \begin{matrix}\text{KCl}\\(\text{m}_2)\end{matrix} \Big| \overset{+}{\text{AgCl(s)}} \Big| \text{Ag}$$
(1 atm)

Reaction: Since in this cell Ag - AgCl(s) is the positive electrode, and H_2 - H^+ is the negative electrode. Hence oxidation occurs in the negative electrode.

$$\frac{1}{2}H_2 \ \text{®} \ H^+ + e \qquad\qquad ...... (1)$$

and reduction occurs in the positive electrode

$$AgCl(s) + e \ \text{®} \ Ag + Cl^- \quad ......(2)$$

So total reaction is obtained by adding (1) and (2)

$$\frac{1}{2}H_2 \ \text{®} \ H^+ + e^-$$
$$\underline{AgCl(s) + e \ \text{®} \ Ag + Cl^-}$$
$$AgCl(s) + \frac{1}{2}H_2 \ \text{®} \ Ag(s) + H^+ + Cl^-$$

Expression of EMF:

So that its e.m.f

$$E = E^0 - \frac{RT}{\text{Á}} \ln \frac{a_{Ag(s)} \cdot a_{H^+} \cdot a_{Cl^-}}{a_{AgCl(s)} \cdot a_{H_2}^{\frac{1}{2}}}$$

$$= E^0 - \frac{RT}{\text{Á}} \ln a_{H^+} \cdot a_{Cl^-} \quad [\text{ since } a_{Ag(s)} = a_{AgCl(s)} = a_{H_2(g)} = 1]$$

$$= E^0 - \frac{RT}{\text{Á}} \ln \frac{a_{H^+} \cdot a_{OH^-} \cdot a_{Cl^-}}{a_{OH^-}}$$

$$= E^0 - \frac{RT}{\text{Á}} \ln \frac{kw \cdot a_{Cl^-}}{a_{OH^-}}$$

$$= E^0 - \frac{RT}{\text{Á}} \ln kw - \frac{RT}{\text{Á}} \ln \frac{m_{Cl^-}}{m_{OH^-}} - \frac{RT}{\text{Á}} \ln \frac{g_{Cl^-}}{g_{OH^-}}$$

$$\text{or, } \left[E - E^0 + \frac{RT}{\text{Á}} \ln \frac{m_{Cl^-}}{m_{OH^-}} \right] = - \frac{RT}{\text{Á}} \ln kw - \frac{RT}{\text{Á}} \ln \frac{g_{Cl^-}}{g_{OH^-}}$$

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$$= -\frac{RT}{\mathcal{F}}\ln kw - \frac{RT}{\mathcal{F}}2.303\left(\log g_{Cl^-} - \log g_{OH^-}\right)$$

$$= -\frac{RT}{\mathcal{F}}\ln kw - \frac{RT}{\mathcal{F}} \times 2.303\left(-A Z_{Cl^-}^2 \sqrt{i_2} + A Z_{OH^-}^2 \sqrt{i_1}\right)$$

$$= -\frac{RT}{\mathcal{F}}\ln kw + \frac{RT}{\mathcal{F}} \times 2.303 \times A\left(\sqrt{i_2} - \sqrt{i_1}\right) \quad ......(A)$$

$$\left[\because Z_{Cl^-} = Z_{OH^-} = 1\right]$$

The value of E^0 is 0.2224 volts at $25°C$

The e.m.f of the cell is measured using various dilute solutions of KCl and KOH i.e. with different low values of m_{Cl^-} and m_{OH^-}. The left hand side of the equation (A) is then plotted against the difference of square root of the ionic strength of the KCl and KOH solution used. The curve on extrapolation to infinite dilution of the solution i.e. zero ionic strength (where, $g_{Cl^-} = g_{OH^-}$ = unity) gives the value of $-\frac{RT}{\mathcal{F}}\ln kw$.

The value of the kw was thus found to be 1.008×10^{-14} at $25°C$

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