Electrochemistry

oxidation → Reaction which involve addition of O_2 or removal of hydrogen

⇒ Loss of electrons $M \rightarrow M^{n+} + ne^-$

⇒ Increase in oxidation number

Reduction ⇒ Gain of electron $M^+ + e^- \rightarrow M$

⇒ Decrease in oxidation number

oxidising agent ⇒ substance which can accept electron and itself reduced.

Reducing agen ⇒ Substance which can donate electron and itself ~~redu~~oxidised

Redox Reaction ⇒ Reaction involving simultaneous oxidation and reduction.

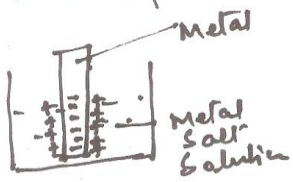
$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

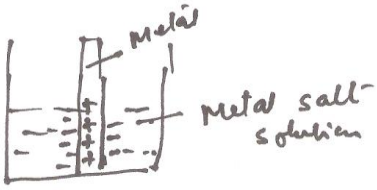
$Zn(s) \longrightarrow Zn^{2+}(aq)$ oxidation

$Cu^{2+}(aq) \longrightarrow Cu(s)$ Reduction

Single Electrode and Electrode potential

When a metal is in contact with a solution of its own ions, then either oxidation or reduction of metal occurs. Because of this negative or positive charge is developed on the metal which attracts positively or negatively charged free ions present in the solution. This leads to the formation of a layer of negative ions or positive ions around the metal. Because of the formation of this layer (Helmholtz electrical double layer), a potential difference is set up between the metal and the solution. Then the metal is called electrode and develop potential is electrode potential.





If oxidation of metal occurs then the potential is oxidation electrode potential and if reduction of metal occurs, potential is reduction electrode potential.

Thus

The tendency of an electrode to loose or gain electrons when it is in contact of its own ions in solution, is called electrode potential.

oxidation electrode potential ⟹ Tendency of lose electron
reduction electrode potential ⟹ Tendency to gain electrons

oxidation electrode potential is reverse of reduction electrode potention. For example

If oxidation potential of any ~~react~~ electrode is −1.5 volts then its reduction potential will be +1.5 volts.

<u>Standard Electrode potential</u> -

When ~~an electrode~~ a metal is dipped in 1 M solution of its own ions at 25°C, the developed potential is known as standard electrode potential.

The absolute value of ~~a single~~ the electrode potential of a single electrode can not be measured directly. ~~But in~~ The difference of potential between two electrodes can be measured. Therefore for measuring electrode potential of a single electrode, it is attached with a reference electrode and potential difference is measured.

Reference electrode is the electrode of known electrode potential. Examples, Standard hydrogen electrode (SHE) and calomel electrode.

The electrode potential of different metals are arranged in electrochemical series.

Nerst Equation

The effect of concentration and Temperature on electrode potential can be explain by Nerst equation. Nerst equation for the reaction

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$ is given as

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

From Nerst equation it is clear that

(a) E increases as $[M^{n+}]$ is increased

(b) E decreases as temperature is increased.

Type of electrode

① Metal - Metal ion electrode –

A metal rode dipped in solution of its own ions such as in case of Daniell cell

Zn rod dipped in solution of $ZnSO_4$

Cu rod dipped in solution of $CuSO_4$

Electrode reaction

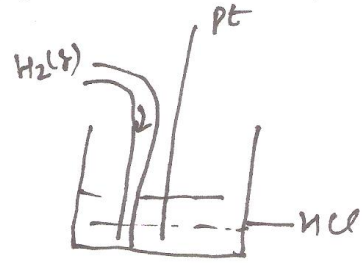
$$M^{z+}(aq) + ze^- \rightarrow M(s)$$

The electrode is reversible to M^+ ions.

Representation $M(s), M^{z+}(aq)$

② Gas electrode –

(a) Hydrogen electrode – Hydrogen gas bubbling in a solution of an acid (HCl) forms an electrode of this type.



$$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$

The electrode reversible to $[H^+]$

Pt is used to make electrical contact in the circuit.

Representation $Pt : H_2(g), H^+(aq)$

(b) Chlorine electrode → chlorine gas bubbled into a solution of hydrochloric acid. $Pt : Cl_2(g), Cl^-(aq)$

$$\frac{1}{2} Cl_2(g) + e^- \rightarrow Cl^-(aq)$$

Electrode is reversible to $[Cl^-]$

(c) Oxygen electrode – oxygen gas at a given pressure is bubbled through a solution containing OH^- ions

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$$

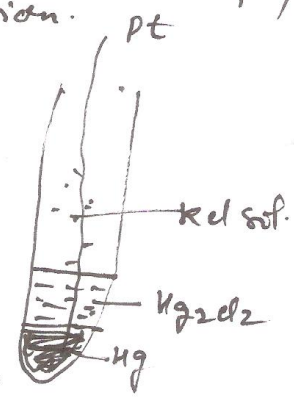
But since, the equilibrium between O_2 gas and OH^- ions in solution can not be established quickly, so O_2 electrode does not behave as reversible electrode.

③ Metal-Insoluble Metal salt Electrode –

Electrode consisting of a metal and ~~in~~ sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion present in the sparingly soluble salt. Example(a) calomel electrode consisting of $Hg(l)$, $Hg_2Cl_2(s)$ and KCl solution.

represented as

$$Pt, Hg(l), Hg_2Cl_2(s) : KCl$$



Electrode reaction

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$

therefore the electrode is reversible to $Cl^-(aq)$.

(b) Ag|AgCl electrode. which is consisting a silver wire coated with AgCl and dipped in KCl solution

$$Ag, AgCl(s) : Cl^-(aq)$$

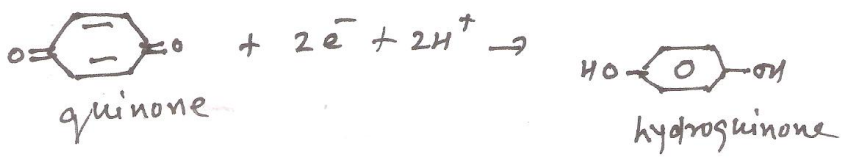
The electrode is reversible to Cl^- ~~(aq)~~ ion

(4) <u>oxidation-reduction electrode</u> - This is an electrode in which potential is developed from the presence of ions of the same substance in two difference, ~~pt~~ oxidation states. Example. Solution containing Fe^{2+} and Fe^{3+} ions. In this type of electrode Pt is wire is dipped in solution for electrical contacts.

$Pt, Fe^{2+}, Fe^{3+}(aq)$

Another example.

quinhydrone electrode - which consist of a Pt wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equimolar amount

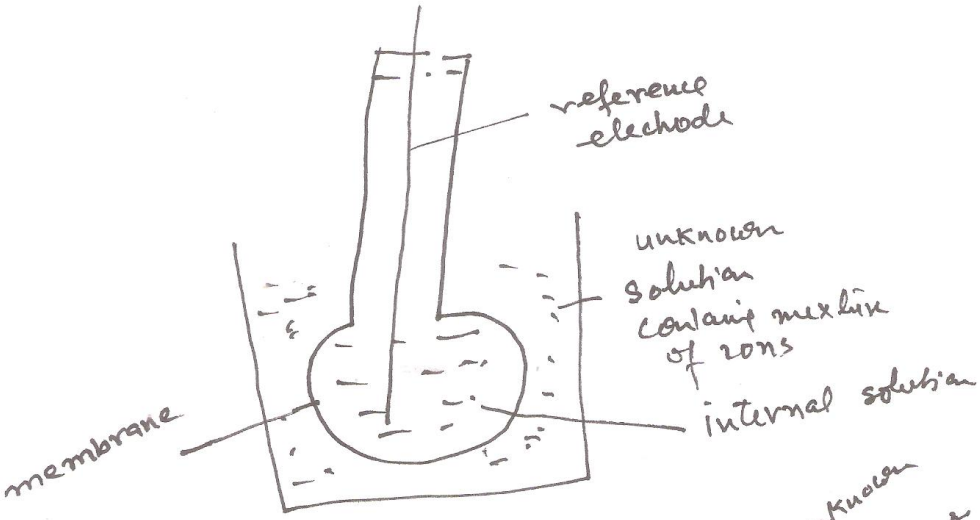


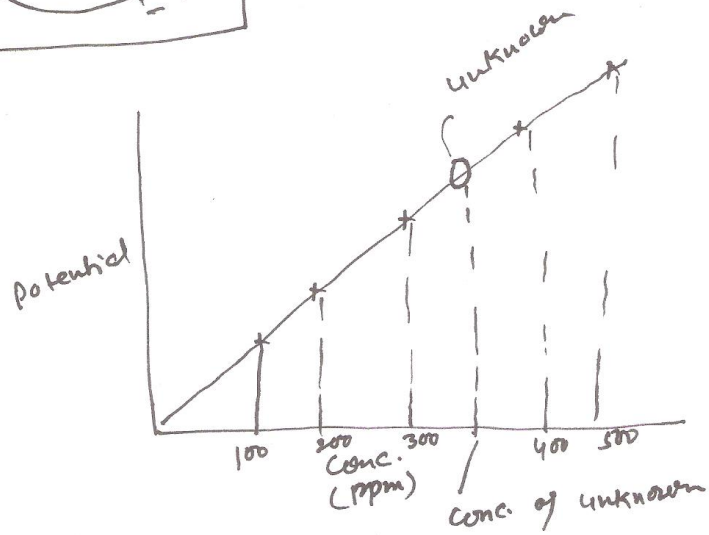
Representation $Pt, Q, QH_2 : H^+(aq)$

the electrode is reversible to H^+ ions.

(5) Reference Electrode - The electrode whose electrode potential is known and used to measure the potential of unknown single electrode. Example standard hydrogen electrode (SHE) having electrode potential zero and saturated calomel electrode having electrode potential ~~0.2420~~ 0.2422 volt.

⑥ <u>Ion selective electrode</u> - Ion selective electrodes have the ability to respond to certain specific ions (in a mixture of ions) and develop a potential. The potential developed is a measure of the concentration of the species of interest. These electrodes use a membrane which is sensitive to a particular ion.





Measurement of concentration of M^{n+} in a solution using ion-selective electrode.

Reference electrode 1	Solution to be analysed $[M^{n+}] = c_1$	Membrane	Internal sol. $[M^{n+}] = c_2$	Reference electrode 2

The membrane potential

$$E_{M^{n+}} = \frac{RT}{nF} \ln \frac{c_2}{c_1}$$

Measurement of concentration of M^{n+} in a solution using ion-selective membrane electrode

Reference electrode 1	Solution to be analysed $[M^{n+}] = C_1$	Membrane	Internal standard solution $[M^{n+}] = C_2$	Reference electrode 2

The membrane potential is given by the equation

$$E_{M^{n+}} = \frac{RT}{nF} \ln \frac{C_2}{C_1} \quad \text{—— (I)}$$

Suppose reference electrode act as anode and membrane electrode as cathode

$$\therefore \quad E_{cell} = E_{M^{n+}} - \Delta E_{reference} \quad \text{—— (II)}$$

Here $\Delta E_{reference} = 0$ when identical reference electrode are used

Since $[C_2]$ is known therefore it is constant

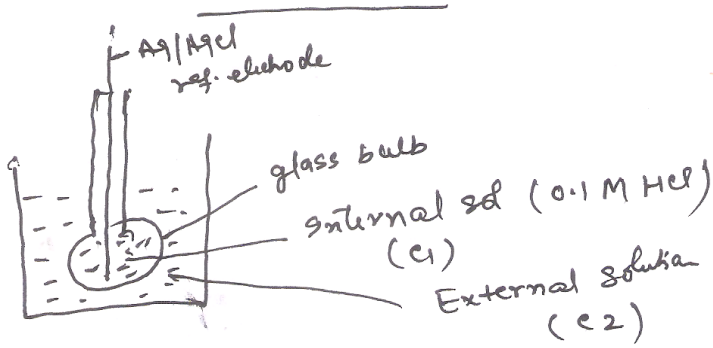
So from (II)

$$E_{cell} = \text{Constant} - \frac{RT}{nF} \ln C_1$$

Thus cell potential depend on the selectivity of membrane for the ion to be analysed and conc. of ion to be analysed.

~~Applicati~~

Glass electrode



Boundary potential $E_b = \frac{RT}{nF} \ln \frac{c_1}{c_2}$

As $c_1 = 0.1$ M HCl

$$E_b = \text{Constant} - \frac{RT}{nF} \ln c_2$$

$$E_b = L - \frac{RT}{nF} \ln c_2 \quad \text{——— (1)}$$

When $c_1 = c_2 \Rightarrow E_b$ should be zero

But during practice it is observed that even at $c_1 = c_2$, a small potential is developed. This potential is called asymmetric potential ($E_{ass.}$)

Thus The potential of the glass electrode (E_G) is given by

$$E_G = E_b + E_{Ag|AgCl} + E_{ass.}$$

$$= -\frac{RT}{nF} \ln c_2 + L + E_{Ag|Ag} + E_{ass.}$$

$$= E^0_G - \frac{RT}{nF} \ln c_2 \quad \text{where } E^0_G = (L + E_{Ag|AgCl} + E_{ass})$$

$$E_G = E^0_G - \frac{RT}{nF} \ln [H^+]$$

$$\boxed{E_G = E^0_G + .0591\, pH} \quad \text{at } 25^\circ C$$

Electrochemical cell

Galvanic cell

conversion of chemical energy to electrical energy

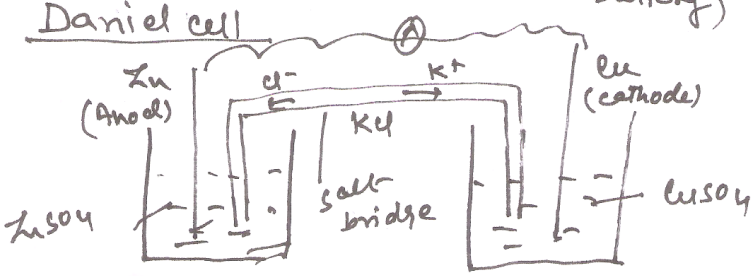
(Dry cell, Daniell cell

Electrolytic cell

Electrical energy from an external source is used to bring about chemical change.

(charging of Lead storage battery)

Daniel cell



At Anode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (oxidation

At cathode $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (Reduction)

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

(complete cell reaction)

Representation

$$Zn | ZnSO_4(aq) || CuSO_4(aq) | Cu$$

$$Zn | Zn^{2+} || Cu^{2+} | Cu$$

oxidation E_L ~~oxi~~ (Reduction E_R

EMF of the cell $= E_R - E_L = E_{reduction} - E_{oxidation}$

$$\boxed{E_{cell} = E_{cathod} - E_{anode}}$$

Electrical energy in a Galvanic cell

Electrical energy produced by the cell = nFE

The electrical energy of a cell is originates from decrease in free energy ($-\Delta G$) of the cell reaction.

Thus $-\Delta G = nFE$

Application of EMF

① Feasibility of reaction –

emf is positive → Feasible reaction

emf is negative – Non feasible

② EMF and equilibrium Constant –

If the standard EMF (E^0) of a cell is known, equilibrium constant can be determined using the relation

$$-\Delta G = RT \ln K_{eq.}$$

$$nFE^0 = RT \ln K_{eq.}$$

$$\boxed{\log K_{eq.} = \frac{nFE^0}{2.303RT}}$$

③ Solubility product and EMF

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$ ~~Ksp = L~~

The solubility product ~~Ksp = nFE°~~

$$K_{sp} = [M^+][X^-]$$

The above reaction is the cell reaction of the following cell

$$M, M^+X^- (sol.sol.) \mid MX(s), M$$

RHE $\quad MX(s) + e^- \rightarrow M + X^-$

LHE $\quad M \rightarrow M^+ + e^-$

overall reaction

$$MX(s) \rightleftharpoons M^+ + X^-$$

$$E^0 = E^0_R - E^0_L$$

the value of E^0_R and E^0_L are taken by electrochemical series.

Knowing the value of E^0 for the cell and using

$$\Delta G^0 = -nFE^0 \quad \text{and}$$

$$-\Delta G^0 = 2.303\,RT \log K_{sp}$$

$$nFE^0 = 2.303\,RT \log K_{sp}$$

$$E^0 = \frac{2.303\,RT}{nF} \log K_{sp}$$

$$\boxed{E^0 = \frac{0.0591}{n} \log K_{sp}}$$

Thus K_{sp} can be calculated from known value of E^0.

(4) Determination of pH – The potential of a hydrogen electrode in contact with a sol. of H^+ involve the reaction $H^+ + e^- \rightarrow \frac{1}{2} H_2(g)$

By Nernst equation $E_{el} = E^0_{el} + \frac{2.303RT}{F} \log[H^+]$

$E^0_{el} = 0$ so

$$E_{el} = \frac{2.303RT}{F} \log[H^+]$$

$$E_{el} = -0.0591\, pH \quad \text{at } 25^\circ c$$

~~EMF of~~ Potential of hydrogen electrode can be determined by adding it with reference electrode (calomel)

$Pt, H_2 (1\ atm), H^+ (c = unknown) \,||\, KCl$ (sat. sol.) $Hg_2Cl_2(s), Hg(l)$

$$EMF = E_R - E_L = 0.2422 - (-0.0591\, pH)$$

$$0.0591\, pH = E - 0.2422$$

$$\boxed{pH = \frac{E - 0.2422}{.0591}}$$

(5) Determination of pH by using a

(5) Measurement of pH using glass electrode

For measurement of pH, the glass electrode is immersed in the solution, whose pH is to be determined. It is the combined with a reference saturated calomel electrode. The cell assembly is represented as.

$$Ag \mid AgCl(s) \mid 0.1\,M\ HCl \mid Glass \mid \text{solution of unknown pH} \parallel \text{saturated Calomel electrode}$$

$$E_{cell} = E_R - E_L$$

$$E_{cell} = E_{ref.} - E_G$$

$$E_{cell} = E_{ref} - E^0_G - 0.0591\,pH$$

$$\boxed{pH = \frac{(E_{ref} - E^0_G) - E_{cell}}{0.0591}}$$

$$\boxed{pH = \frac{(0.2422 - E^0_G) - E_{cell}}{0.0591}}$$

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Determination of pH by quinhydrone electrode

$$C_6H_4O_2 + 2H^+ 2e^- \rightarrow C_6H_6O_2$$
(Q) (QH2)

$$E_{el} = E^0_{el} - \frac{2.303RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2}$$

$$= E^0_{el} + \frac{2.303}{2F} \log \frac{[Q][H^+]^2}{[QH_2]}$$

$$= E^0_{el} + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{F} \log [H^+]$$

$$E_{el} = E^0_{el} + \frac{2.303RT}{2F}$$

$$\boxed{E_{el} = E^0_{el} - 0.0591\, pH}$$

The standard electrode potential of the quinhydron electrode, $E^0_{el} = 0.0699$ V

$$E^0_{el} = 0.6996 - .0591\, pH$$

Hg $Hg_2Cl_2(s)$ KCl(sat) || H^+(unknown) Q, QH_2, Pt

$$E = E_R - E_L$$

$$= .6996 - 0.0591\, pH - .2422$$

$$\boxed{pH = \frac{0.6996 - 0.2422 - E}{0.0591}}$$