1.1 Important Terminologies

Current

Flow of electrons through any conducting material is known as the current.

Oxidation:

The tendency to lose electrons

Reduction:

The tendency to gain electrons

Electrode:

When a metal rod is dipped in its salt solution, it develops a positive or negative potential. This assembly is called as an electrode.

Anode:

The electrode at which oxidation occurs is called as anode.

Cathode:

The electrode at which reduction occurs is known as cathode.

The electrochemical cell consists of two conductors called electrodes that are immersed in an electrolyte and are connected externally by means of a metal conductor.

Electrolysis:

The process that occurs in the electrochemical cell is called as electrolysis.

It is the breakdown of electrolyte into ions by electricity.

Half cell: Electrochemical cell:

A part of a cell containing electrode dipped in an electrolytic solution is called as a half cell.

Oxidation half cell:

The electrode where oxidation takes place i.e. where electrons are lost.

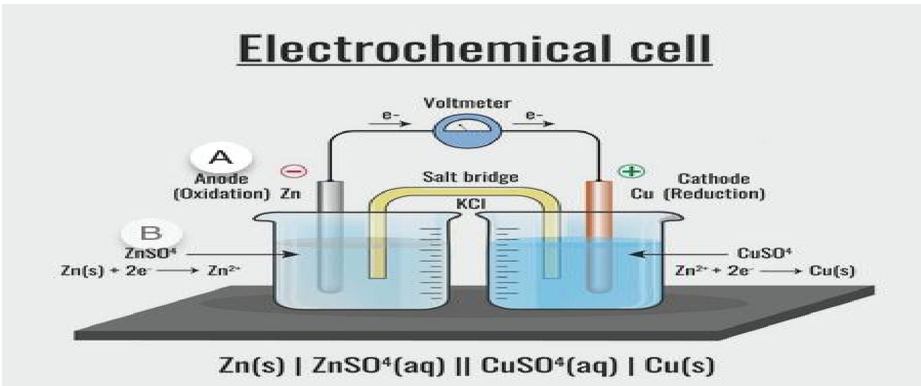
Reduction half cell:

The electrode where reduction takes place i.e. where electrons are gained.

The combination of two single electrodes or two half cell constitute a cell.

Electro-chemical cell

Daniell cell (galvanic cell)



- Consist of two electrodes. One zinc immersed in $ZnSO_4$ Soln. And the other copper immersed in $CuSO_4$ soln. Separated by porous portion (barrier).

- The reactions at electrodes:

(1) At anode: (oxidation)

$Zn \rightarrow Zn^{+2} + Ze^{-}$ $\qquad E^{o}_{ox} = 0.76$ V.

(2) At cathode: (Reduction)

$Cu^{+2} + 2e^{-} \rightarrow Cu$ $\qquad E^{o}_{red} = 0.34$ V.

$E^{o}_{cell} = [E^{o}_{cathode} - E^{o}_{anode}]$

$E^{o}_{cell} = 0.34 - (-0.76) = 1.1$ volt.

The over all reaction:

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu \quad E^{o}_{cell} = 1.1\ V$$

Cell notation : ترميز الخلية $\qquad$ A / At // C^{+} / C

Anode / anode ion // cathode ion / cathode

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

- Since Zn^{+2} ion increase and Cu^{+2} ions decrease as it precipitated at cathode so salt bridge of Na_2SO_4, KCl, KNO3, and K2SO4 used to allow metal ions to poses from one solution to the other to balance the charge of the solution that allow the reaction to continue.

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, KNO3, and K2SO4 etc. are used.

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.

problem:

Calculate the single electrode potential for Cu metal in contact with 0.1µ

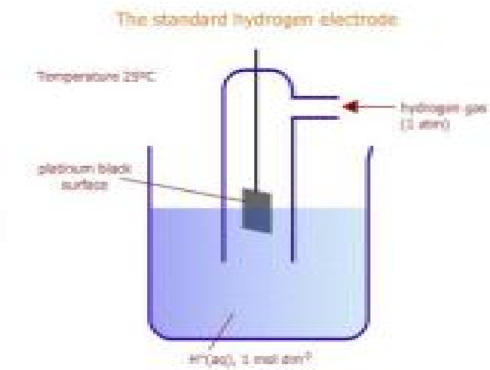
$Cu^{+2} + 2e \rightarrow Cu$ $\qquad E^0_{red}$ For Cu = 0.34 Volt ?

$$E = E^0 + \frac{0.0591}{n} \log \frac{oxidized}{reduced}$$

$$= 0.34 + \frac{0.0591}{2} \log 0.1$$

Reference Electrode

[1] Primary reference electrode (hydrogen electrode) :



It's primary electrode consist of (pt) immersed in H^+ ion and placed in glass tube containing hydrogen gas (p = 1 atm).

$$\frac{1}{2} H_2 \rightarrow H^+ + \bar{e}$$

$$e^o = Zero$$

$$e = e^o + \frac{0.0591}{n} \log \frac{H^+}{H_2}$$

$$e = zero + \frac{0.0591}{1} \log H^+$$

$$e = -0.0591 \text{ pH}$$

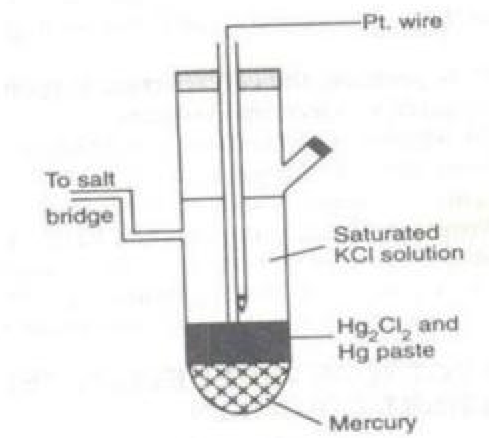
This electrode can be connected with any element to measure its E^o_{ox} or E^o_{red}.

Exercise: If the electrode pot = 3v calculate the pH of hydrogen electrode.

[2] Secondary reference electrode:

Calomel electrode:

Saturated Calomel Electrode:



Calomel electrode

- Consist of vessel glass. Hg is in contact with soln. of KCl saturated with Hg_2Cl_2.

- Hg and Hg_2Cl_2 must be pure to give good result.

- Pt wire is fused in glass tube.

$$Hg_2Cl_2 + 2\bar{e} \rightarrow 2Hg + 2Cl^-$$

$$Cl_2 + 2\bar{e} \rightarrow 2Cl^-$$

$$e = e^o + \frac{0.059}{2} \log \frac{1}{Cl^{-2}}$$

$$E = 0.242 - 0.591 \log Cl^-$$

Concentration Cell

Two types:

(1) The cell contains identical electrodes immersed in two solutions of different concentration.

$$M / M^+_{(C1)} \; / M^+_{(C_2)} \; / M$$

Where $C_2 > C_1$

$$E = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

(2) Electrodes of different conc. immersed in the same solution. .

$$Zn - Hg(C_1) \ / \ ZnSO_4 \ / \ Zn - Hg(C_2)$$

- The electrodes are amalagm Zn alloy with different ratio of Zn and Hg.

$$E = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

Determination of PH & POH

$PH = - \log [H^+]$

$POH = - \log [OH^-]$

PH + POH = 14

(1) For strong acid:

Calculate the PH for 0.3M (H_2SO_4) and 0.3 N H_2SO_4.

0.3 M

$PH = - \log [H^+]$ $\quad$ PH = - log (0.3 x 2) = - log (0.6)

0.3 N

$PH = - \log [H^+] = - \log [0.3]$

Calculate the pH for 0.1N or 0.1M NaOH

$POH = - \log [OH^-]$

$- \log [0.1] = 1$

PH + POH = 14

PH = 14 – 1 = 13

Calculate the PH for 0.05M $Ca(OH)_2$

POH = –log (0.05 x 2) = 1

PH = 14 – 1 = 13

To calculate the PH for weak acid and weak base:

CH3COOH   CH3COO⁻ + H+

C (1 - α)   Cα   Cα

Calculate the PH and POH for 0.1 CH_3COOH

Ka = 10^{-5}

$[H^+] = C\alpha$

$$\alpha = \sqrt{\frac{Ka}{C}} \quad (1) \qquad = \sqrt{\frac{10^{-5}}{0.1}} \qquad (2)$$

$\alpha = 10^{-2}$

$$[H+] = 0.1 \times 10^{-2} = 10^{-3} \qquad (3)$$

PH = – log $[10^{-3}]$ = 3

POH=14-3=11

Problem

For the following cell:

Zn / Zn^{2+} // H^+ (aq) / H_2 (1 atm) / Pt

(1.0 M) $E°(Zn/Zn^{2+})$ = 0.76 V

Example

If the measured potential is 0.26 V and the pressure of the hydrogen gas is 1 atm, what is the pH of the solution in the cathode compartment?

Using the Nernst equation:

$E\_cell = E°\_cell + (0.0591/n) * \log((\text{cathode ion concentration}) / (\text{anode ion concentration}))$

$E\_cell = 0 - (-0.76) + (0.0591 / 2) * \log([H^+]^2 / [Zn^{2+}])$

$0.26 = 0.76 + 0.0591 \log[H^+]$

$0.26 - 0.76 = 0.0591 \log[H^+]$