

Nernst equation

For electrochemical cell, the free energy of the reaction (ΔG)

$$\Delta G = -nEF$$

$n \rightarrow$ number of electrons.

F = Faraday constant (96500)

E = E.M.F.

$$\text{Since } \Delta G = \Delta G^0 - RT \ln Q$$

$$Q \Rightarrow \frac{[\text{product}]}{[\text{reactant}]} \text{ or } \frac{[\text{reduced}]}{[\text{oxidized}]}$$

ΔG^0 = Change in standard free energy التغير في الطاقة الحرة الأولية

$$\therefore -nEF = -nE^0F + RT \ln Q$$

$$-E = -E^0 + \frac{RT}{nF} \ln Q$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{oxidized}]}{[\text{reduced}]}$$

at $T = 298\text{K}$, $F = 96500$, $R = 8.314$, $\ln = 2.3 \log$

$$E = E^0 + \frac{0.059}{n} \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

or
$$E = E^0 - \frac{0.059}{n} \log \frac{[\text{product}]}{[\text{reactant}]}$$

electrode potential standard electrode potential

$$E = E^0 + \frac{0.059}{n} \log \frac{\text{oxidized}}{\text{reduced}}$$

electrode potential:

When metal is in contact with a solution of its own ions at 25°C it may undergo oxidation reaction or reduction reaction

Single Electrode Potential

Definition:

Single electrode potential is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

The tendency of a metallic electrode to lose electrons is known as oxidation potential and the tendency of an electrode to gain electrons is known as reduction potential.

It is impossible to measure absolute value of single electrode potential because neither oxidation nor reduction takes place independently. It is possible to measure the potential difference between two electrodes with the help of the potentiometer. In other words, we can only measure electrode potential with reference to a reference electrode.

Standard Electrode Potential

Definition

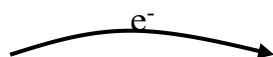
Standard electrode potential is the tendency of a metallic electrode to lose or gain electrons when in contact with 1M concentration of its own salt solution at 25°C.

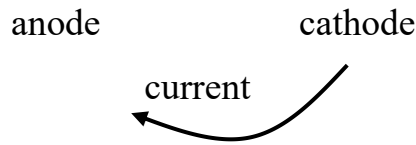
Note $\Delta G = -nEF$

↓

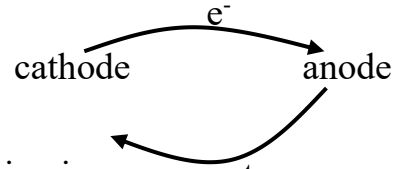
$$\Delta G = -ve \qquad \therefore E = +ve$$

This means that the reaction is spontaneous and electrons transfer from anode to cathode but current transfer from cathode to anode





$\Delta G = +ve$
 $E = -ve$



This means that the reaction is non-spontaneous
 and electrons transfer from cathode to anode but
 current transfer from anode to cathode

Note:

$$E_{A/A^+} = E_{ox} \qquad E_{A^+/A} = E_{Red}$$

For the same element

$$E_{A/A^+} (oxi) = - E_{A^+/A} (red.)$$

E_{ox} = higher positive..... reducing agent

E_{red} = higher positive..... oxidizing agent

At equilibrium $E_{cell} = 0$

$$E_{cell}^{\circ} = \frac{0.059}{n} \log \frac{oxidized}{reduced} = \frac{0.059}{n} \log Keq$$

Cell Notation:

Anode / anode ion // Cathode ion / cathode

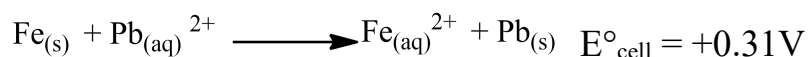
For cell

$$emf = (e^{\circ} cathode - e^{\circ} anode) + \frac{0.0591}{n} \log \frac{cathodeion}{anodeion}$$

reduction

Problem 1:

Given the following in formation



E°_{ox} (e°_{anod}) = + 0.44 V, what is the standard potential of the other half reaction?

$$E^\circ_{\text{cell}} = e^\circ_{\text{cathode}} - e^\circ_{\text{anode}}$$

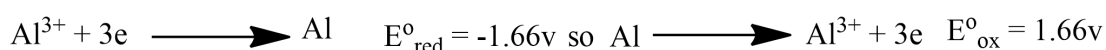
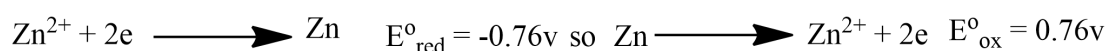
$$0.31 = E^\circ_{\text{red}} - (-0.44)$$

$$E^\circ_{\text{red}} = -0.13 \text{ V}$$

Problem 2:

Knowing that the standard reduction of silver, copper, zinc and aluminum are 0.8, 0.34, -0.76, -1.66 v respectively

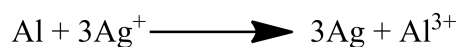
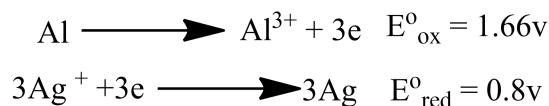
- Which is the stronger oxidizing agent and a stronger reducing agent?
- Evaluate the standard cell potential for these pairs (Al, Ag) and (Zn, Cu) write the equation for the cells reactions.
- What is the potential of each cell when the ions conc. are 0.1 M



- The metal ion with the most positive E°_{red} is the stronger oxidizing agent and the metal ion with the most positive E°_{ox} is the stronger reducing, so Ag^+ is the most oxidizing agent and Al^{3+} is the most reducing agent.

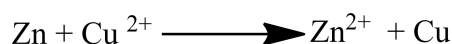
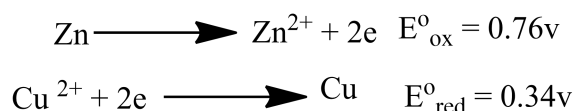
- $E^\circ_{\text{cell}} = e^\circ_{\text{cathode}} - e^\circ_{\text{anode}}$

For (Al, Ag) cell



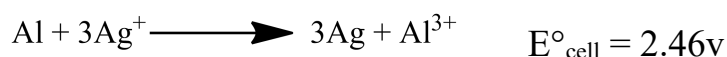
$$E^\circ_{\text{cell}} = 0.8 - (-1.66) = 2.46\text{v}$$

For (Zn, Cu) cell



$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.1\text{v}$$

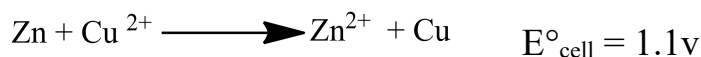
c) $E_{\text{cell}} = E^\circ_{\text{cell}} + (0.059 / n) \log (\text{oxidized} / \text{reduced})$



$$E_{\text{cell}} = 2.46 + (0.059 / 3) \log [0.1]^3 / (0.1)$$

$$E_{\text{cell}} = 2.42 \text{ v}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} + (0.059 / n) \log (\text{oxidized} / \text{reduced})$$

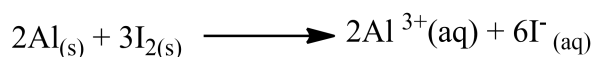


$$E_{\text{cell}} = 1.1 + (0.059 / 2) \log [0.1 / 0.1]$$

$$E_{\text{cell}} = 1.1 \text{ v}$$

Problem 3:

Calculate E_{cell} for the following cell reaction:



When $(\text{Al}^{3+}) = 4.0 \times 10^{-3}\text{M}$ and $(\text{I}^-) = 0.001 \text{ M}$, $E^\circ_{\text{ox}} = 1.66\text{v}$ and $E^\circ_{\text{red}} = 0.54\text{v}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{catode}} - E^\circ_{\text{anode}} = 0.54 - (-1.66) = 2.5\text{v}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.059 / n) \log (\text{product} / \text{reactant})$$

$$= 2.5 - (0.059 / 6) \log (4 \times 10^{-3})^2 (0.01)^6 / 1 \times 1$$

$$= 2.097\text{v}$$

Problem 4: For the following cell calculate emf

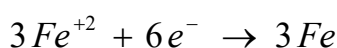
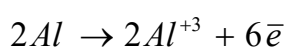
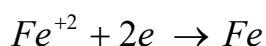


$$e^{\circ} \text{Al} = -1.7 \text{ volt}$$

$$e^{\circ}_{\text{fe}} = -0.409 \text{ V}$$

both e° as reduction. $C_{\text{Al}} = 0.01$

$$C_{\text{fe}} = 0.1$$



$$emf = e^{\circ}_{cathode} - e^{\circ}_{anode} + \frac{0.0591}{6} \log \frac{[\text{Fe}^{+2}]^3}{[\text{Al}^{+3}]^2}$$

$$emf = e^{\circ}_{cathode} - e^{\circ}_{anode} + \frac{0.0591}{6} \log [\text{Fe}^{+2}]^3 - \frac{0.0591}{6} \log [\text{Al}^{+3}]^2$$

$$= (-0.409 - (-1.7)) + \frac{0.0591}{6} \log [\text{Fe}^{+2}]^3 - \frac{0.0591}{6} \log [\text{Al}^{+3}]^2$$

$$= 1.29 + \frac{0.0591}{6} \log (0.1)^3 - \frac{0.0591}{6} \log (0.01)^2.$$

$$= 1.30085\text{v}$$

Example:5

For the following cell, if the standard EMF is 1.10 V calculate the value of K:



$$E^{\circ}_{\text{cell}} = (0.0592 / n) \log K$$

Note that $n = 2$. Substituting into the equation relating E°_{cell} and K gives:

$$1.10 \text{ V} = (0.0592 / 2) \log K$$

$$\log K = (1.10 \times 2) / 0.0592 = 37.2$$

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.

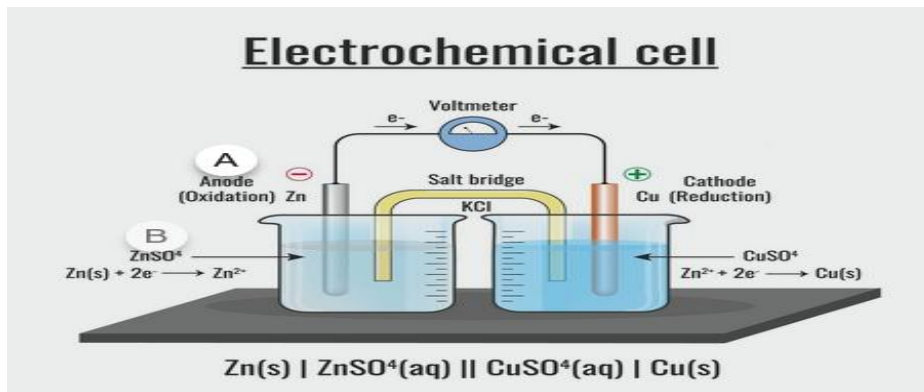
Reduction half cell:

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)



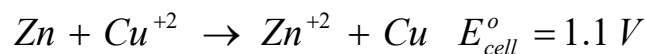
(2) At cathode: (Reduction)



$$E^\circ_{\text{cell}} = [E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}]$$

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.1 \text{ volt.}$$

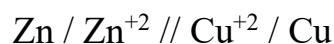
The over all reaction:



Cell notation : ترميز الخلية



Anode / anode ion // cathode ion / cathode



- Since Zn^{+2} ion increase and Cu^{+2} ions decrease as it precipitated at cathode so salt bridge of Na_2SO_4 , KCl , KNO_3 , and K_2SO_4 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.

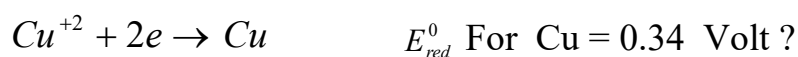
Function of salt bridge:

- (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

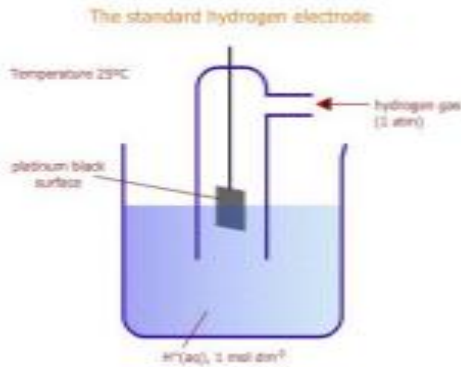
0.1μ



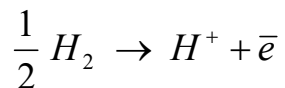
$$E = E^0 + \frac{0.0591}{n} \log \frac{\text{oxidized}}{\text{reduced}}$$
$$= 0.34 + \frac{0.0591}{2} \log 0.1$$

Reference Electrode

[1] Primary reference electrode (hydrogen electrode) :



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



$$e^o = Zero$$

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

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

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

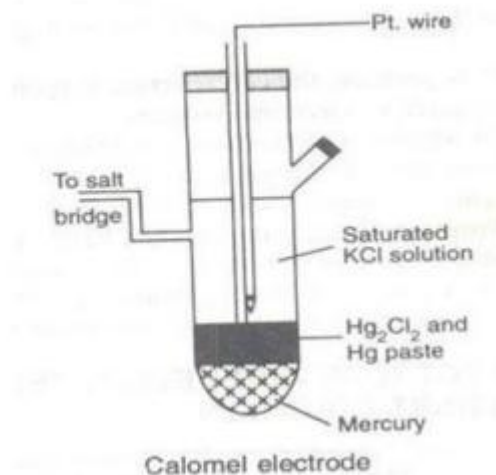
This electrode can be connected with any element to measure its E^o_{ox} or E^o_{red}.

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

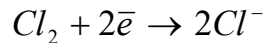
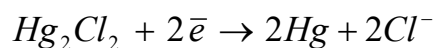
[2] Secondary reference electrode:

Calomel electrode:

Saturated Calomel Electrode:



- 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.



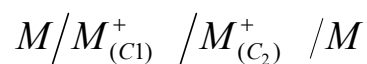
$$e = e^o + \frac{0.059}{2} \log \frac{1}{Cl^{-2}}$$

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

Concentration Cell

Two types:

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



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. .



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

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

Determination of PH & POH

$$\text{PH} = -\log [\text{H}^+]$$

$$\text{POH} = -\log [\text{OH}^-]$$

$$\text{PH} + \text{POH} = 14$$

(1) For strong acid:

Calculate the PH for 0.3M (H₂SO₄) and 0.3 N H₂SO₄.

$$0.3 \text{ M}$$

$$\text{PH} = -\log [\text{H}^+] \qquad \text{PH} = -\log (0.3 \times 2) = -\log (0.6)$$

$$0.3 \text{ N}$$

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

Calculate the pH for 0.1N or 0.1M NaOH

$$\text{POH} = -\log [\text{OH}^-]$$

$$-\log [0.1] = 1$$

$$\text{PH} + \text{POH} = 14$$

$$\text{PH} = 14 - 1 = 13$$

Calculate the PH for 0.05M Ca(OH)₂

$$\text{POH} = -\log (0.05 \times 2) = 1$$

$$\text{PH} = 14 - 1 = 13$$

To calculate the PH for weak acid and weak base:



$$C(1 - \alpha)$$

$$C\alpha$$

$$C\alpha$$

Calculate the PH and POH for 0.1 CH₃COOH

$$\mathbf{K_a = 10^{-5}}$$

$$[H^+] = C\alpha$$

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

$$\alpha = 10^{-2}$$

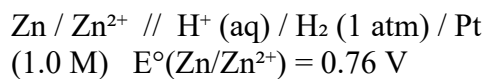
$$[H^+] = 0.1 \times 10^{-2} = 10^{-3} \quad (3)$$

$$PH = -\log [10^{-3}] = 3$$

$$POH = 14 - 3 = 11$$

Problem

For the following cell:



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:

$$E_{\text{cell}} = E^\circ_{\text{cell}} + (0.0591/n) * \log((\text{cathode ion concentration}) / (\text{anode ion concentration}))$$

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

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

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