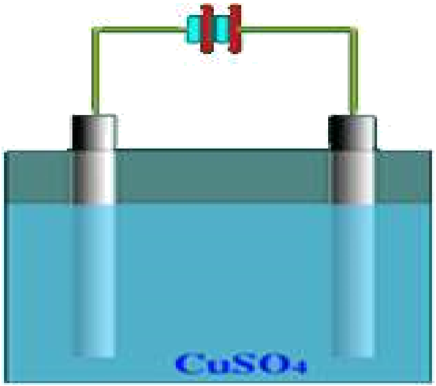
ELECTROCHEMISTRY 1
PART 1

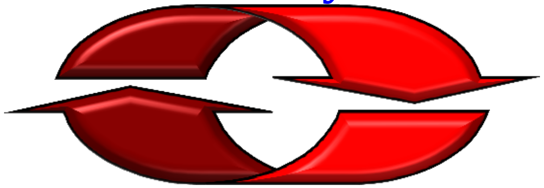
Electrochemical Cells

1. Galvanic cells
2. Electrolytic cells

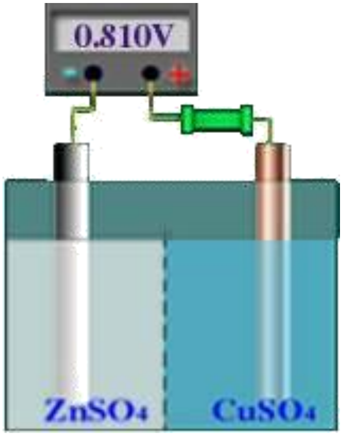


Electrolytic cell

Electric Energy



Chemical Energy



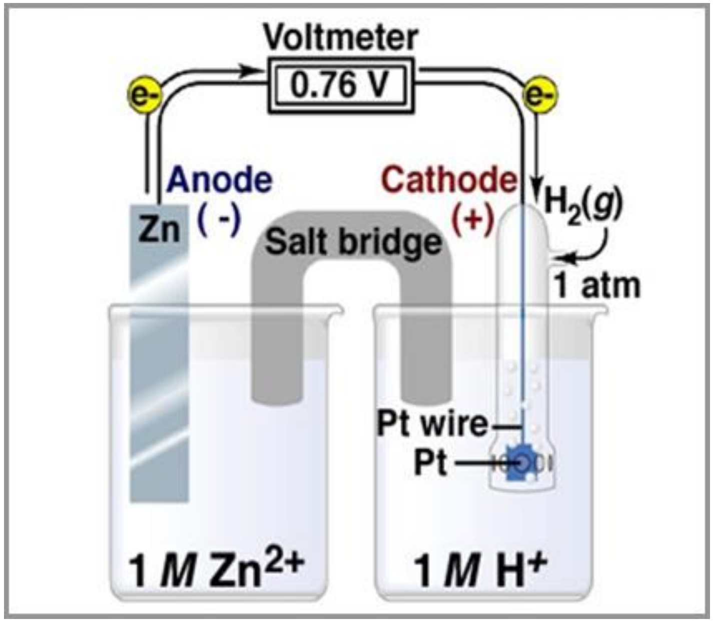
Galvanic cell

The ANODE…	**The CATHODE…**
Supplies electrons to external circuit (wire)	**Accepts electrons** from external circuit (wire)
Is **negative** pole of battery	Is **positive** pole of battery
Is site of **OXIDATION**	Is site of **REDUCTION**
Is written on **left- hand side** if convention is followed	Is written on **right-hand side** if convention is followed
Is half-cell with **lowest** electrode potential	Is half-cell with **highest** electrode potential

Origin of Electromotive Force or Cell Potential

Cell potential is the potential difference between anode and cathode and is called:

- **Cell potential or emf (electromotive force)**



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

- Suppose that we have a Daniel cell of potential 1.1 V in the standard conditions.

- The standard potential of the two half-cell is:

$$Cu^{2+}\ (aq) + 2e^{-} \rightarrow Cu \quad E^{o} = 0.337\ V$$

$$Zn^{2+}\ (aq) + 2e^{-} \rightarrow Zn \quad E^{o} = -0.7628\ V$$

- The experiment showed that zinc dissolves while copper deposited from solution
- The measured cell potential is called reduction potential:

- The reduction potential of the cell is the difference between the reduction potential of the cathode and the reduction potential of the anode

$$E_{cell} = E^{o}_{Right} - E^{o}_{Left}$$

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

$$E^{o}_{cell} = 0.337- (-0.7628) = 1.1 \text{ Volt}$$

- The question is wheatear the reduction potentials are affected by the concentration of the species?

- In the non-standard condition the cell potential is

$$E_{cell} = E_{rev,\ c} – E_{rev,\ a}$$

$$E_{rev.} = E^{o} + \frac{RT}{ZF}\ln\frac{a_{Ox}}{a_{Red.}}$$ (Nernest eqn).

- For a spontaneous reaction that leads to obtain electricity form a galvanic cell E = +ve

$$\mathrm{Cu}^{2+}\ (aq) + 2e^{-} \rightarrow \mathrm{Cu} \quad E^{o} = 0.337\ \mathrm{V}$$

$$\mathrm{Zn}^{2+}\ (aq) + 2e^{-} \rightarrow \mathrm{Zn} \quad E^{o} = -0.7628\ \mathrm{V}$$

$$\mathrm{Cu}^{2+}\ (aq) + \mathrm{Zn} \rightarrow \mathrm{Cu} + \mathrm{Zn}^{2+}\ (aq) \quad E_{cell} = 1.0998\ \mathrm{V}$$

- If E_{cell} has a negative value this means that the reaction is not spontaneous and it need a potential of 1.1 V from external source to force the chemical reaction to occur

$$\mathrm{Cu} + \mathrm{Zn}^{2+}\ (aq) \rightarrow \mathrm{Cu}^{2+}\ (aq) + \mathrm{Zn} \quad E_{cell} = -1.0998\ \mathrm{V}$$

Standard electrode potential

- When a piece of a metal is immersed in a solution of its ions, atoms will transfer to solution as positive ions leaving electrons on the metal under dissolution pressure.
- Ions in the solution tend to deposit on the metal surface under Osmotic pressure.

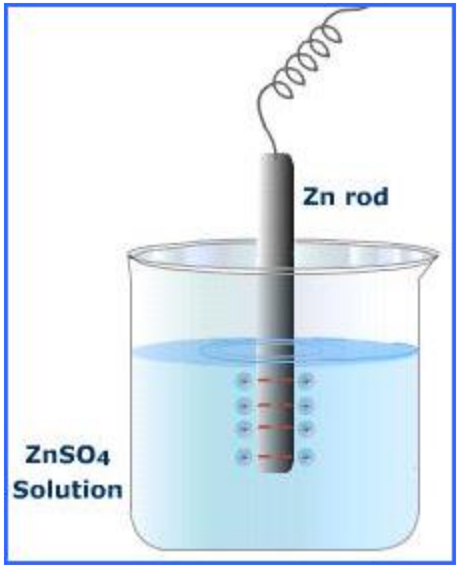
$$M \rightarrow M^{n+} + ne^{-} \quad \text{Ionization (oxidation) process}$$

$$M^{n+} + ne^{-} \rightarrow M \quad \text{Deposition (reduction) proces}$$

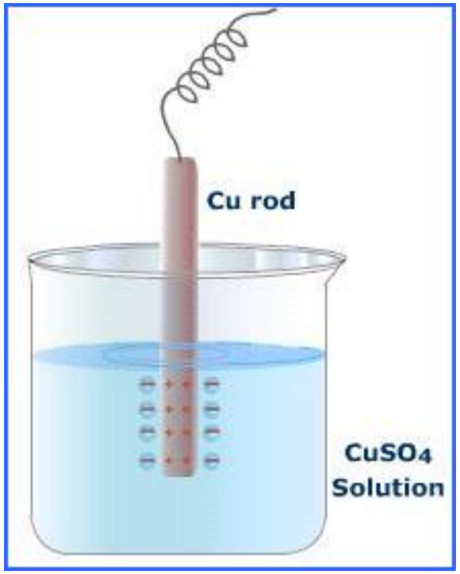
$$M^{n+} + ne^{-} = M \quad E^{o} \text{ Reversible Potentia}$$

- At beginning the electric dissolution pressure is much higher than the osmotic pressure.
- With increasing time the dissolution pressure decreases and the osmotic pressure increases till they equal each other and then the electrode is said to be at equilibrium.
- Electric dissolution and osmotic pressures depend on the nature of the metal.

- For zinc electric dissolution pressure > Osmotic pressure, zinc is charged negatively while the solution is charged positively.



- For copper electric dissolution pressure < Osmotic pressure, copper is charged positively while solution is charged negatively.



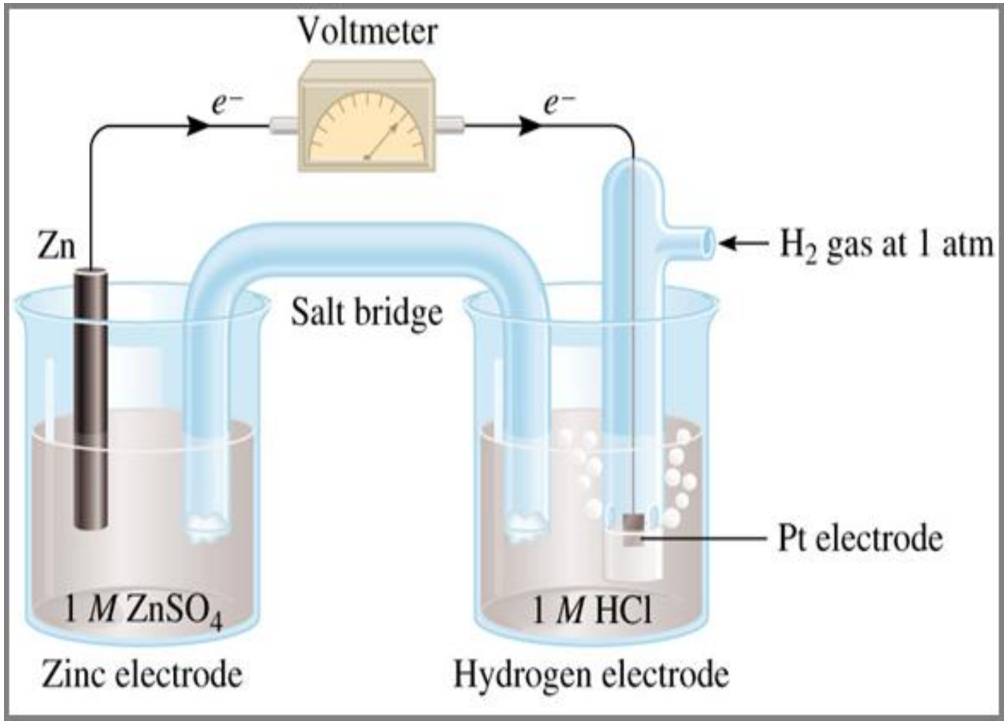
Standard reduction Potentials

Standard conditions are:

- Concentration is 1 M
- Temperature is 25°C
- Pressure of a gas is 1 atm.

Reference electrode is hydrogen electrode

- $[H^+]$ (1 M)
- H_2 (1 atm)



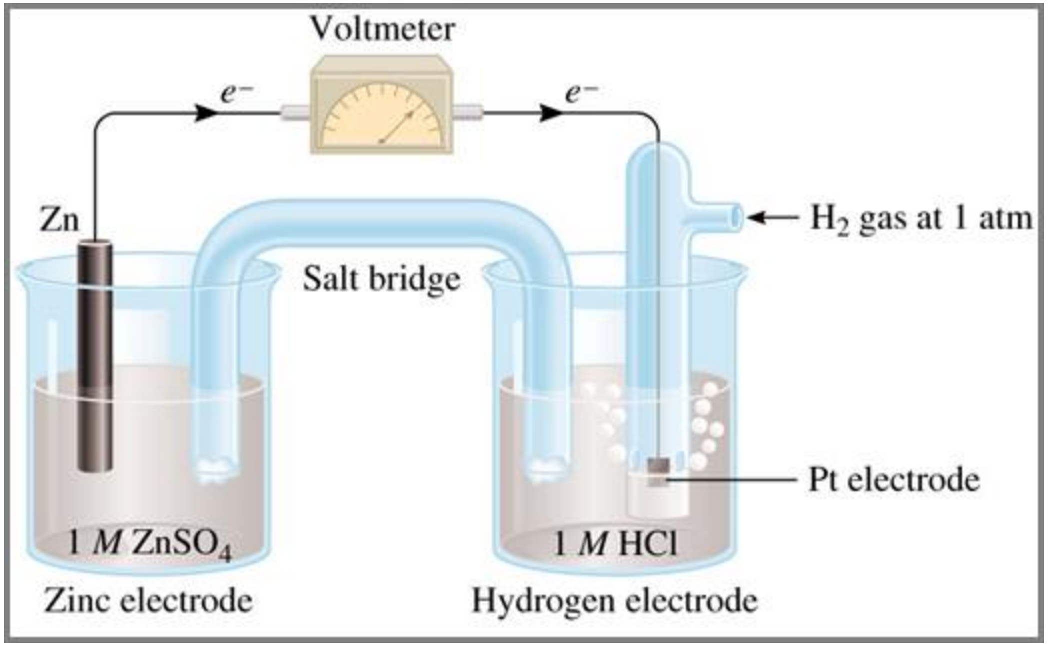
$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$$

Anode (oxidation): $Zn\ (s) \longrightarrow Zn^{2+}\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + 2H^+\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$$Zn\ (s) + 2H^+\ (1\ M) \longrightarrow Zn^{2+} + H_2\ (1\ atm)$$

$E^{0}_{cell} = 0.76\ V$



Standard emf (E^{0}_{cell})

$$\boxed{E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}}$$

Zn (*s*) | Zn^{2+} (1 *M*) || H^{+} (1 *M*) | H_2 (1 atm) | Pt (*s*)

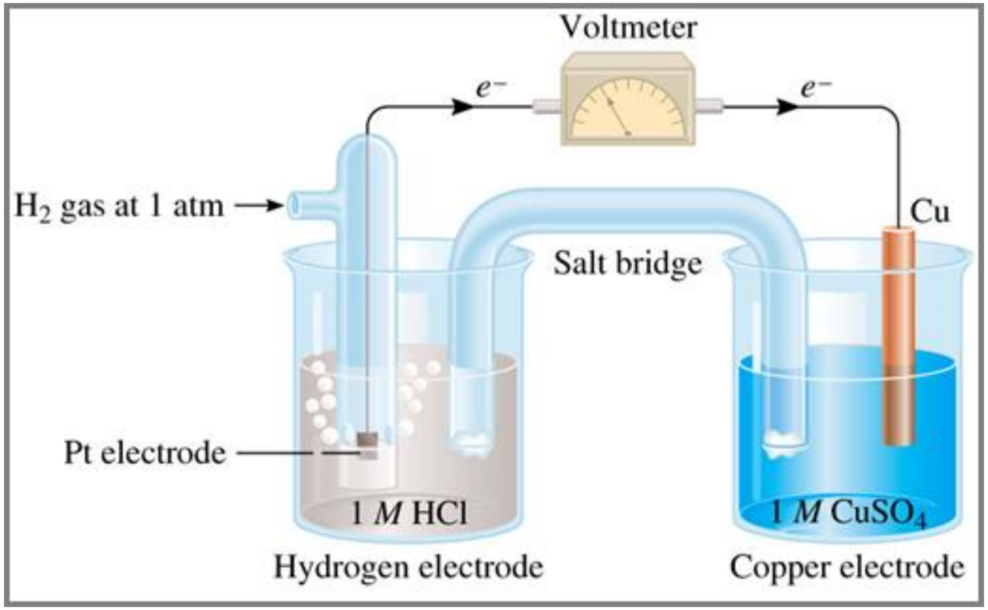
$$E^{0}_{cell} = E^{0}_{H^{+}/H_2} - E^{0}_{Zn^{2+}/Zn}$$

$$0.76\ V = 0 - E^{0}_{Zn^{2+}/Zn}$$

$$E^{0}_{Zn^{2+}/Zn} = -0.76\ V$$

$$Zn^{2+}\ (1\ M) + 2e^{-} \longrightarrow Zn \qquad E^{0} = -0.76\ V$$

$E^0_{cell} = 0.34\ V$



$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$

$0.34 = E^0_{Cu^{2+}/Cu} - 0$

$E^0_{Cu^{2+}/Cu} = 0.34\ V$

Pt (s) | H_2 (1 atm) | H^+ (1 M) || Cu^{2+} (1 M) | Cu (s)

Anode (oxidation): $H_2\ (1\ atm) \longrightarrow 2H^+\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s)$

$H_2\ (1\ atm) + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s) + 2H^+\ (1\ M)$

ELECTROCHEMISTRY 1
PART 2

Reference electrode

- Has a constant and known potential
- Non-polarizable electrodes

Types

- Primary reference electrodes
- Secondary reference Electrodes

Standard Hydrogen Electrode

Primary reference electrode

Electrode reaction

$2H^+ + 2e^- = H_2$

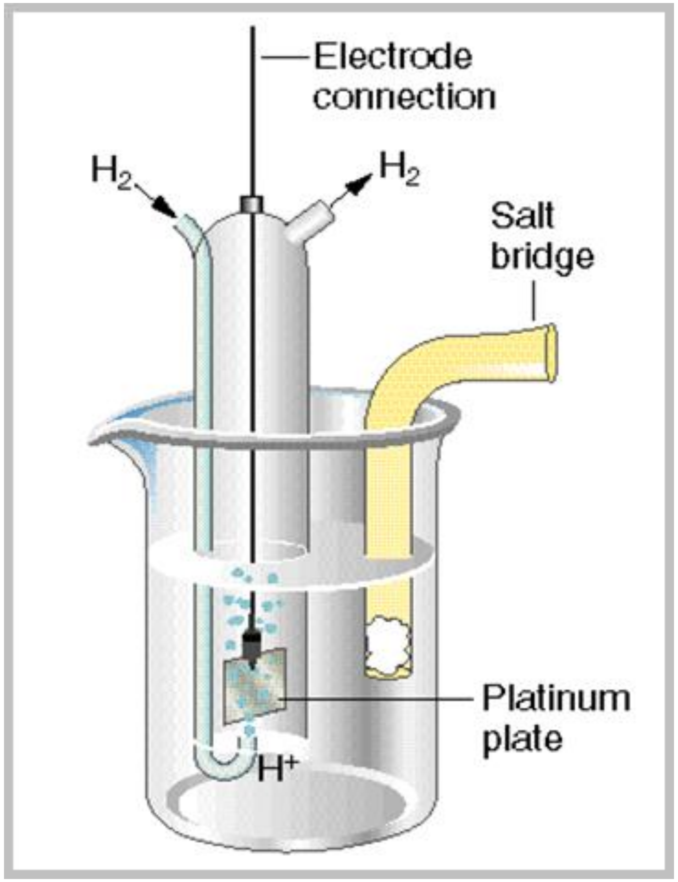
Half-cell:

Pt, H_2 | H^+ (1.0 M) | |

E° = zero

Disadvantages of the electrode

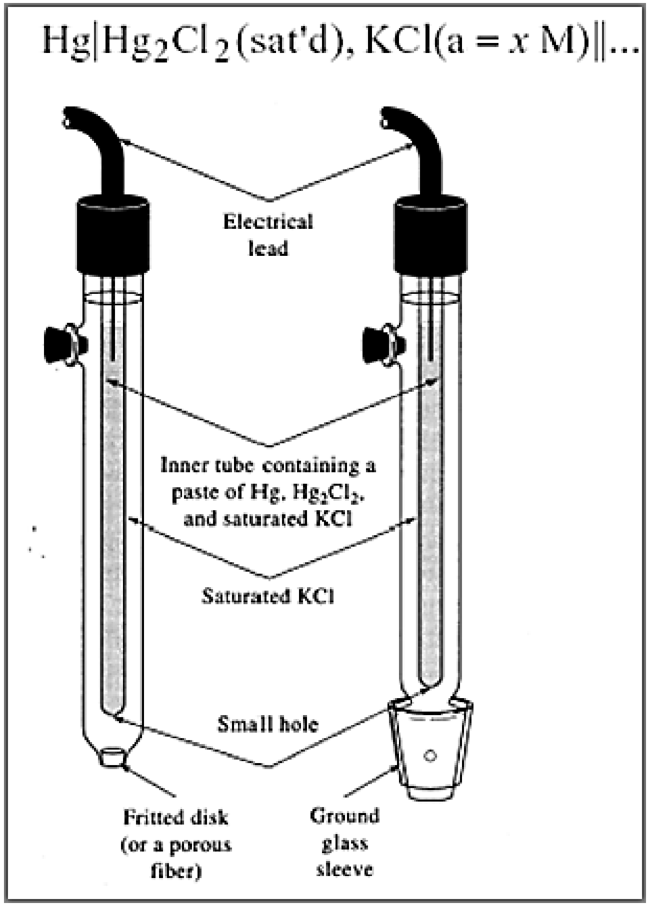
1. Difficult to be used regularly since we should keep the gas pressure constant at 1 atm during experiments.
2. It is needed to plate the platinum electrode periodically with black platinum



Seondary Reference Electrodes

Calomel electrode

KCl	E volt
Saturated	0.241
1M	0.280
0.1 M	0.334



$Hg|Hg_2Cl_2(sat'd), KCl(a = x\ M)\|...$

The electrode potential shifts to more negative value with increasing chloride ion concentration

$$E_{25} = E^{o}_{Hg/Hg_2^{+}} + \frac{0.059}{2}\log[Hg_2^{+2}]$$

$$Hg_2Cl_2 \Leftrightarrow Hg_2^{+2} + 2Cl^{-}$$

$$K_{sp} = [Hg_2^{+2}][Cl^{-}]^2 \Rightarrow [Hg_2^{+2}] = \frac{K_{sp}}{[Cl^{-}]^2}$$

$$E_{25} = \boxed{E^{o}_{Hg/Hg_2^{+}} + \frac{0.059}{2}\log K_{sp}} - \frac{0.059}{2}\log[Cl^{-}]^2$$

$$E_{25} = E^{o\prime}_{Hg/Hg_2^{+}} - 0.059\log[Cl^{-}]$$

Silver/Silver Chloride reference electrode

Electrode reaction

$Ag^+ + e = Ag^o$

Half-cell

Ag/AgCl, saturated KCl ||
or 1.0 N KCl ||
or 0.1 N KCl ||

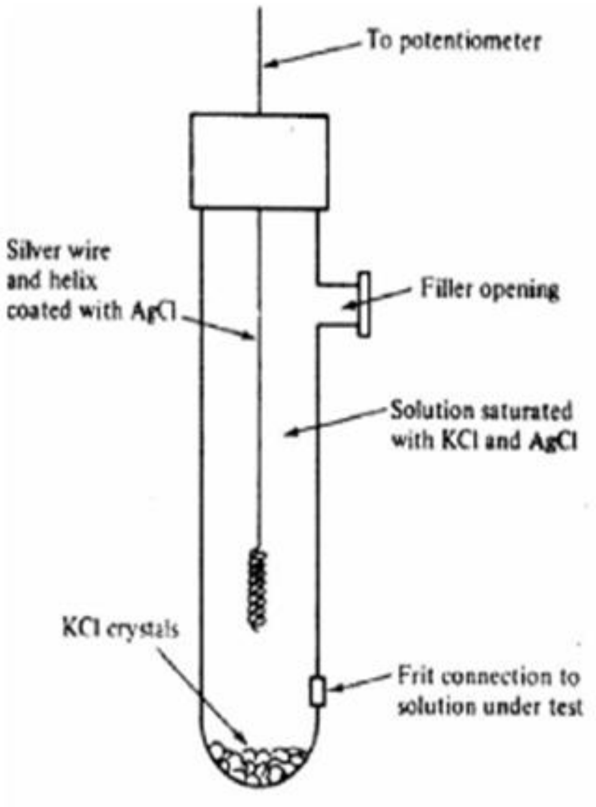
$$E_{Ag/Ag^+} = E^o - 0.059\log\frac{1}{[Ag^+]}$$

$$AgCl \Leftrightarrow Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-]$$

$$E_{25} = E^o + 0.059\log K_{sp} - 0.059\log[Cl^-]$$

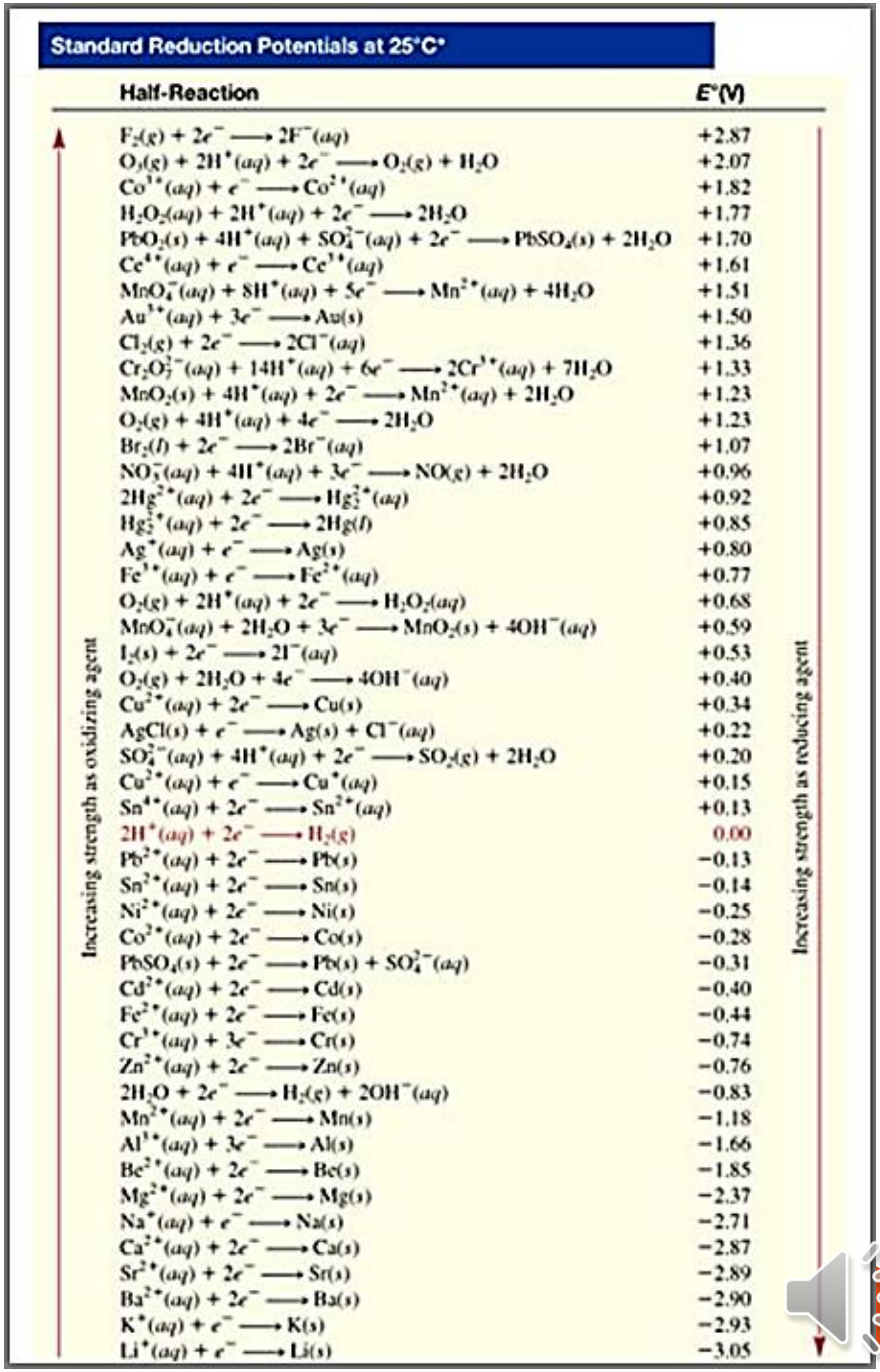
$$E_{25} = E^{o\backslash} - 0.059\log[Cl^-]$$



Saturated KCl Ag/AgCl electrode.

Electromotive series:

- Reduction reactions of the calf-cells are arranged according to their standard reduction potentials.
- The reactions on the **bottom** of the series has negative potentials.
- The reactions on the **top** of the series has positive potentials.
- For a cell consists of two half-cell reactions, the half-cell of more potential value will act as oxidant and will be reduced, i.e. will be cathode.
- The other half-cell reaction that of less potential value will act as reductant and will be oxidized, i.e. act as anode.



Standard Reduction Potentials at 25°C*

Half-Reaction	*E*°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

What is the standard potential of a cell consists of Cd and Cr electrodes immersed in solutions of their ions of concentrations 1 M.

$Cd^{2+}\,(aq) + 2e^{-} \longrightarrow Cd\,(s)$ $\quad E^{0} = -0.40\text{ V}$

Cd is the stronger oxidizer

$Cr^{3+}\,(aq) + 3e^{-} \longrightarrow Cr\,(s)$ $\quad E^{0} = -0.74\text{ V}$

Cd will oxidize Cr

Anode (oxidation): $Cr\,(s) \longrightarrow Cr^{3+}\,(1\,M) + \boxed{3e^{-}}$ $\quad$ x 2

Cathode (reduction): $\boxed{2e^{-}} + Cd^{2+}\,(1\,M) \longrightarrow Cd\,(s)$ $\quad$ x 3

$$2Cr\,(s) + 3Cd^{2+}\,(1\,M) \longrightarrow 3Cd\,(s) + 2Cr^{3+}\,(1\,M)$$

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$

$$E^{0}_{cell} = -0.40 - (-0.74)$$

$$E^{0}_{cell} = 0.34\text{ V}$$

ELECTROCHEMISTRY 1
PART 3

Ex: Can you construct a galvanic cell from the following reactions?

A) $Sn^{2+} + Cu \rightarrow Sn + Cu^{2+}$

B) $3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$

$E^oCu^{+2}/Cu = 0.337\ V$

$E^o\ Sn^{2+}/Sn =-0.136\ V$

$E^oAl^{3+}/Al = -1.662\ V$

Answer

A)

$Cu \rightarrow Cu\ ^{2+} + 2e^-$

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

$Sn^{2+}\ \ +Cu \rightarrow Sn + Cu^{2+}$

$E_{cell} = E^o_{cathode} - E^o_{anode}$

$E_{cell} = -0.136 - 0.337 = -0.463\ Volt$

This means that the reaction will not occur spontaneously in a galvanic cell and no current will be obtained. For this reaction to occur it is needed to apply a potential of 0.46 V from outside source in electrochemical cell.

B)

$$2Al \rightarrow 2Al^{3+} + 6e^-$$

$$3Cu^{2+} + 6e^- \rightarrow 3Cu$$

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$$

$$E_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E_{cell} = E^o_{Cu} - E^o_{Al}$$

$$E_{cell} = 0.337 - (-1.662) = 1.999 \text{ Volt}$$

The reaction is spontaneous and the cell is galvanic cell

Liquid Junction Potential جهد الاتصال

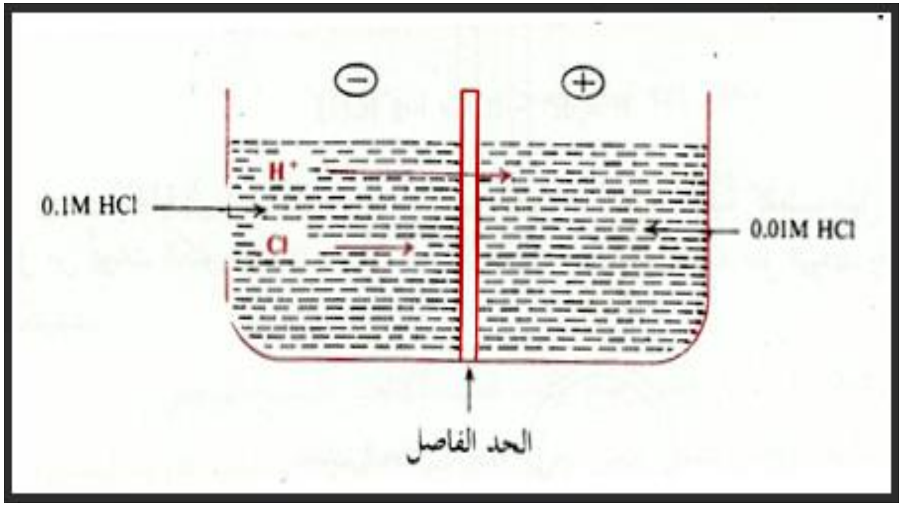
مؤجل

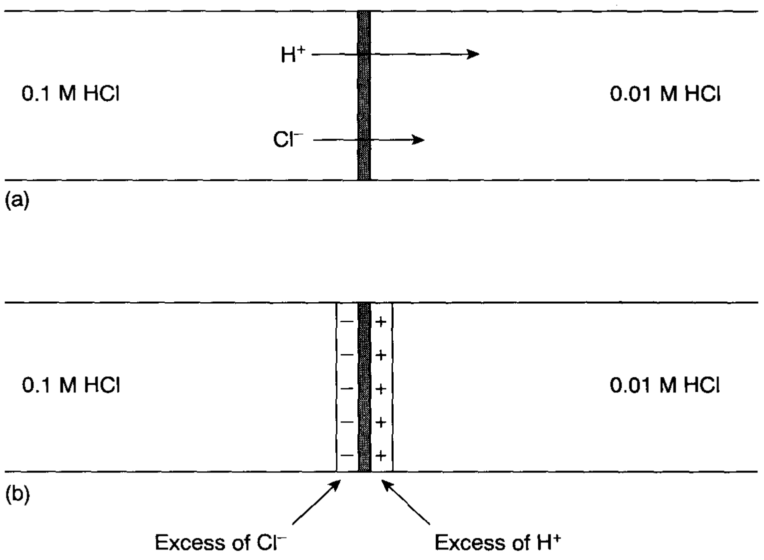
For correct calculations the cell potential is:

$$\boxed{E_{cell} = E_c - E_a + E_j}$$

- Where E_j is the liquid junction potential
- Junction potential may have positive or negative values.

- It's origin arises from the contact of the solutions of two different concentration or composition of the two electrodes, working electrode and reference electrode, in the porous membrane.
- Suppose that we have two solutions separated with a porous membrane, the solution of the reference electrode is of concentration of 0.01 M and the solution of the working electrode have a concentration of 0.1 M





- Hydrogen and chloride ions will move from the concentrated to the diluted solutions through the porous membrane

.

- Since the diffusion velocity of hydrogen ion is much greater than that of chloride ions then the diluted solution will charged positively while the concentrated solution will charged negatively and liquid junction potential will be formed and will have a value of -40 mV.

- Liquid junction potential could be minimized by using a salt bridge contains a salt of two ions have equal diffusion velocities as KCl

Evolution of hydrogen from molar acidic solutions

- Metals lie **after** hydrogen in the electromotive force series , I.e. have negative potential values, can replace hydrogen ions and evolve hydrogen gas.

$$\mathrm{Zn}\ (s)\ |\ \mathrm{Zn}^{2+}\ (1\ M)\ ||\ \mathrm{H}^{+}\ (1\ M)\ |\ \mathrm{H}_2\ (1\ \mathrm{atm})\ |\ \mathrm{Pt}\ (s)$$

$$E^{0}_{cell} = E^{0}_{H^+/H_2} - E^{0}_{Zn^{2+}/Zn}$$

$$0.76\ \mathrm{V} = 0\ -\ -0.76$$

$$\mathrm{Zn} + \mathrm{H}^{+}\ (1\ M) \longrightarrow \mathrm{Zn}^{+2} + \mathrm{H}_2 \qquad E^{0}_{cell} = 0.76\ \mathrm{V}$$

- The tendency to replace hydrogen ion decreases as the potential value increases, i.e. shifts to less negative value.

- Metals lie **before** hydrogen in the electromotive force series, has positive potential values, cannot replace hydrogen from standard acidic solutions.

Thermodynamic of Galvanic Cells

Change in the Gibbs free energy, ΔG, gives an indication weather the reaction is spontaneous, nonspontaneous or at equilibrium.

$\Delta G < 0$:Spontaneous reaction
$\Delta G > 0$:Non-spontaneous reaction
$\Delta G = 0$:equilibrium

$\Delta G = W_{max}$:
W_{max} Is the maximum work

Change in free energy, cell potential and rate constant are related via the following equations:

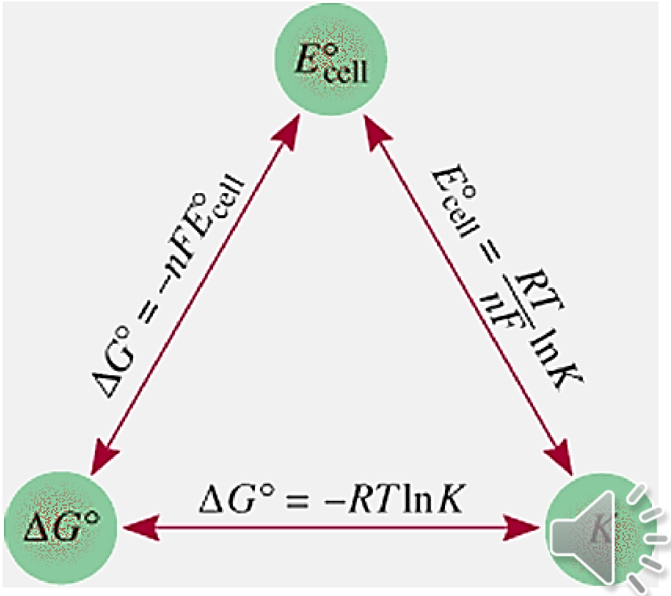
$\Delta G = -nFE_{\text{cell}}$ n = number of moles of electrons in reaction

$\Delta G^0 = -nFE^0_{\text{cell}}$ $F = 96{,}500 \dfrac{\text{J (Joul)}}{\text{V (Volt)} \cdot \text{mol}} = 96{,}500 \text{ C/mol}$

$$\Delta G^0 = -RT \ln K = -nFE^0_{\text{cell}}$$

$$E^0_{\text{cell}} = \frac{RT}{nF} \ln K = \frac{(8.314\ \cancel{\text{J}}/\cancel{\text{K}}\bullet\cancel{\text{mol}})(298\ \cancel{\text{K}})}{n\ (96{,}500\ \cancel{\text{J}}/\text{V}\bullet\cancel{\text{mol}})} \ln K$$

$$E^0_{\text{cell}} = \frac{0.0257\ \text{V}}{n} \ln K$$



What is the rate constant of the following reaction at room temperature?

$$Fe^{2+}(aq) + 2Ag(s) \rightleftharpoons Fe(s) + 2Ag^{+}(aq)$$

$$E^{0}_{cell} = \frac{0.0257\ V}{n} \ln K$$

Oxidation: $2Ag \rightarrow 2Ag^{+} + \boxed{2e^{-}}$

Reduction: $\boxed{2e^{-}} + Fe^{2+} \rightarrow Fe$

$n = 2$

$$E^{0} = E^{0}_{Fe^{2+}/Fe} - E^{0}_{Ag^{+}/Ag}$$

$$E^{0} = -0.44 - (0.80)$$

$$E^{0} = -1.24\ V$$

$$k = e^{\left[\frac{E^{o}_{cell} x n}{0.0257V}\right]} = e^{\left[\frac{-1.24 x 2}{0.0257V}\right]}$$

$$k = 1.23 x 10^{-42}$$

Case	E	ΔG	K
Spontaneous	+ve	-Ve	large
Non-spontaneous	-ve	+ve	small
Equilibrium	0	0	1

For the following reaction

$$A + B \leftrightarrow C + D$$

مؤجل

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\boxed{Q = \frac{a_C . a_D}{a_A . a_B}}$$

$$\Delta G = W$$

بما أن

$$\Delta G = W_{ele}$$

$$W_{ele} = -nFE$$

حيث W_{ele} هو الشغل الكهربى

$$\Delta G = -zFE$$

$$\Delta G^0 = -zFE^0$$

حيث E^o هو الجهد القياسى للقطب

$$-zFE = -zFE^0 + RT \ln(Q)$$

$$E = E^0 - \frac{RT}{zF} \ln(Q)$$ ***Nernst equation***

$$E = E^0 - \frac{8.314 \times 298T}{Z \times 96500} \ln(Q)$$ **At 298 K**

$$E = E^0 - \frac{0.02567}{z} \ln(Q)$$

At standard conditions i.e. when the activity of ions is unity.

$$\boxed{\begin{array}{l} Q = 1 \\ \ln Q = 0 \\ \therefore E = E^o \end{array}}$$

Effect of concentration on the electrode potential

At non standard conditions, when a≠1

$M^{+2} + 2e \leftrightarrow M$

$$Q = \frac{a_M}{a_{M^{+2}}} \neq 1$$

$$\ln Q \neq 0$$

$$\therefore E \neq E^o$$

$$E = E^0 - \frac{0.02567}{z} \ln (Q)$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{a_{M^{+2}}}$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{10} = E^o + \frac{0.02567}{z} x2.3$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{10^{-1}} = E^o - \frac{0.02567}{z} x2.3$$

- By increasing metal ion concentration, the equilibrium shifts to right side of the reaction and the potential will shift to less negative or more positive value, i.e. increases.

- By decreasing metal ion concentration, the equilibrium shifts to left side of the reaction and the potential will shift to more negative or less positive value, i.e. decreases.

Example:

Calculate the potential of the following half-cell:

Zn^{2+} (a=0.1) | Zn

From the electrochemical series:

Zn^{2+} (a=0.1) +2e → Zn **E^0 = -0.7628 V**

$$\boxed{\begin{aligned} E &= E^o - \frac{0.02567}{2}\ln\frac{1}{0.1} \\ E &= -0.7628 - \frac{0.02567}{2}\ln\frac{1}{0.1} \\ E &= -0.7923 \end{aligned}}$$

Is the following reaction occurs spontaneously at room temperature?

$[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

$Fe^{2+}\ (aq) + Cd\ (s) \rightleftharpoons Fe\ (s) + Cd^{2+}\ (aq)$

Oxidation: $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction: $2e^- + Fe^{2+} \longrightarrow Fe$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04\ V$$

$$E = E^0 - \frac{0.0257\ V}{n} \ln Q$$

$$E = -0.04 - \frac{0.0257}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

Reaction of metals with water

- Some metals with negative potential values can replace hydrogen ions and evolve hydrogen gas from water while others with negative potential values cannot depending on the value of the cell potential.
- Ex:Zn/Zn^{+2} (IM)//H^{+} (10^{-7} M)/H$_2$ (1 atm),Pt

$$Zn^{+2} + 2e \Leftrightarrow Zn \qquad E^{o} = -0.76V$$

$$2H^{+}(10^{-7}M) + 2e \Leftrightarrow H_2 \qquad E^{o} = 0V$$

$$Zn + 2H^{+}(10^{-7}M) \Leftrightarrow Zn^{+2} + H_2 \qquad E = ?V$$

$$E_{H^{+}/H_2} = E^{o} - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = 0 - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = -0.2$$

$$E_{cell} = E_c - E_a = -0.2 - (-0.76) = 0.55V$$

Zn can do

- Ex: Sn/Sn^{+2} (IM)//H^{+} (10^{-7} M)/H_2 (1 atm), Pt

$$Sn + 2e \Leftrightarrow Sn^{+2} \qquad E^{o} = -0.14V$$

$$2H^{+}(10^{-7}M) + 2e \Leftrightarrow H_2 \qquad E^{o} = 0V$$

$$Sn + 2H^{+}(10^{-7}M) \Leftrightarrow Sn^{+2} + H_2 \qquad E = ?V$$

$$E_{H^{+}/H_2} = E^{o} - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = 0 - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = -0.21$$

$$E_{cell} = E_c - E_a = -0.21 - (-0.14) = -0.07V$$

Sn cannot do

ELECTROCHEMISTRY 1
PART 4

Reversible and irreversible cells

a) Reversible cells

- Ex: Zn/Zn^{+2} (IM)//Cu^{+2} /Cu
- In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while copper will deposit in the copper half-cell.

$$\boxed{\begin{array}{l} Zn \Rightarrow Zn^{+2} + 2e \\ Cu^{+2} + 2e \Rightarrow Cu \\ \hline Zn + Cu^{+2} \Rightarrow Zn^{+2} + Cu \end{array}}$$

- If an equal amount of current is passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$\boxed{\begin{array}{l} Zn^{+2} + 2e \Rightarrow Zn \\ Cu \Rightarrow Cu^{+2} + 2e \\ \hline Zn^{+2} + Cu \Rightarrow Zn + Cu^{+2} \end{array}}$$

b) Irreversible cells

- Zn/H_2SO_4 (aq)/Cu
- In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while hydrogen gas will be evolved in the copper half-cell

$$\boxed{\begin{array}{l} Zn \Rightarrow Zn^{+2} + 2e \\ 2H^{+} + 2e \Rightarrow H_2 \\ \hline Zn + 2H^{+} \Rightarrow Zn^{+2} + H_2 \end{array}}$$

- If an equal amount of current passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$\boxed{\begin{array}{l} Zn^{+2} + 2e \Rightarrow Zn \\ Cu \Rightarrow 2Cu^{+2} + 2e \\ \hline Zn^{+2} + Cu \Rightarrow Zn + Cu^{+2} \end{array}}$$

Changes in Enthalby and Entropy

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

$$\because \Delta G = -zFE$$

$$\therefore \Delta H = -zFE + zFT\left[\frac{\partial E}{\partial T}\right]_P$$

$$\left[\partial\frac{\Delta G}{\Delta T}\right]_P = 0 \qquad \text{at constant } T$$

From Gibbs – Helmholtz equation

$$\left[\partial\frac{\Delta G}{\Delta T}\right]_P = -\Delta S$$

$$;\Delta H = \Delta G + T\Delta S$$

$$\therefore \Delta S = zF\left[\frac{\partial E}{\partial T}\right]_P$$

Calculate the standard potential of the following cell at 80°C

$$\text{Ag, AgCl}\,|\,\text{KCl}\,||\,\text{KBr}\,|\,\text{Br}_2\text{,Pt}$$

الحل:

$$Br_2 + \boxed{2e^-} \rightarrow 2Br^-$$

$$2Ag + 2Cl^- \rightarrow 2AgCl + \boxed{2e^-}$$

$$\overline{\quad Br_2 + 2Ag + 2Cl^- \rightarrow 2Br^- + 2AgCl \quad}$$

At 25°C, the standard potential of the cell is 0.8428 and we will calculate it at 80°C as follows:

Substance	ΔH^o_f kJ mol^{-1}	S^0 J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
Br^{-}	-121.55	82.4	-141.8
AgCl	-127.07	96.11	50.74
Br2	0	152.32	75.69
Ag	0	42.55	25.35
Cl^{-}	-167.16	56.5	-136.4

$$\Delta H^o = -162.92\,\mathrm{kJ}$$

$$\Delta S^o = 6.69\,\mathrm{J\,K^{-1}}$$

$$\Delta C_p^o = -35.611\,\mathrm{J\,K^{-1}}$$

$$\because T_1 = 298\,\mathrm{K}, \qquad T_2 = 353\,\mathrm{K}$$

$$\because \Delta \mathrm{H}_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)$$

$$\because \Delta \mathrm{S}_2 = \Delta S_1 + \Delta C_P (T_2 - T_1)$$

$$\therefore \Delta H^0(353) = -164.878\,\mathrm{kJ}$$

$$, \Delta S^0(353) = 0.658\,\mathrm{J\,K^{-1}}$$

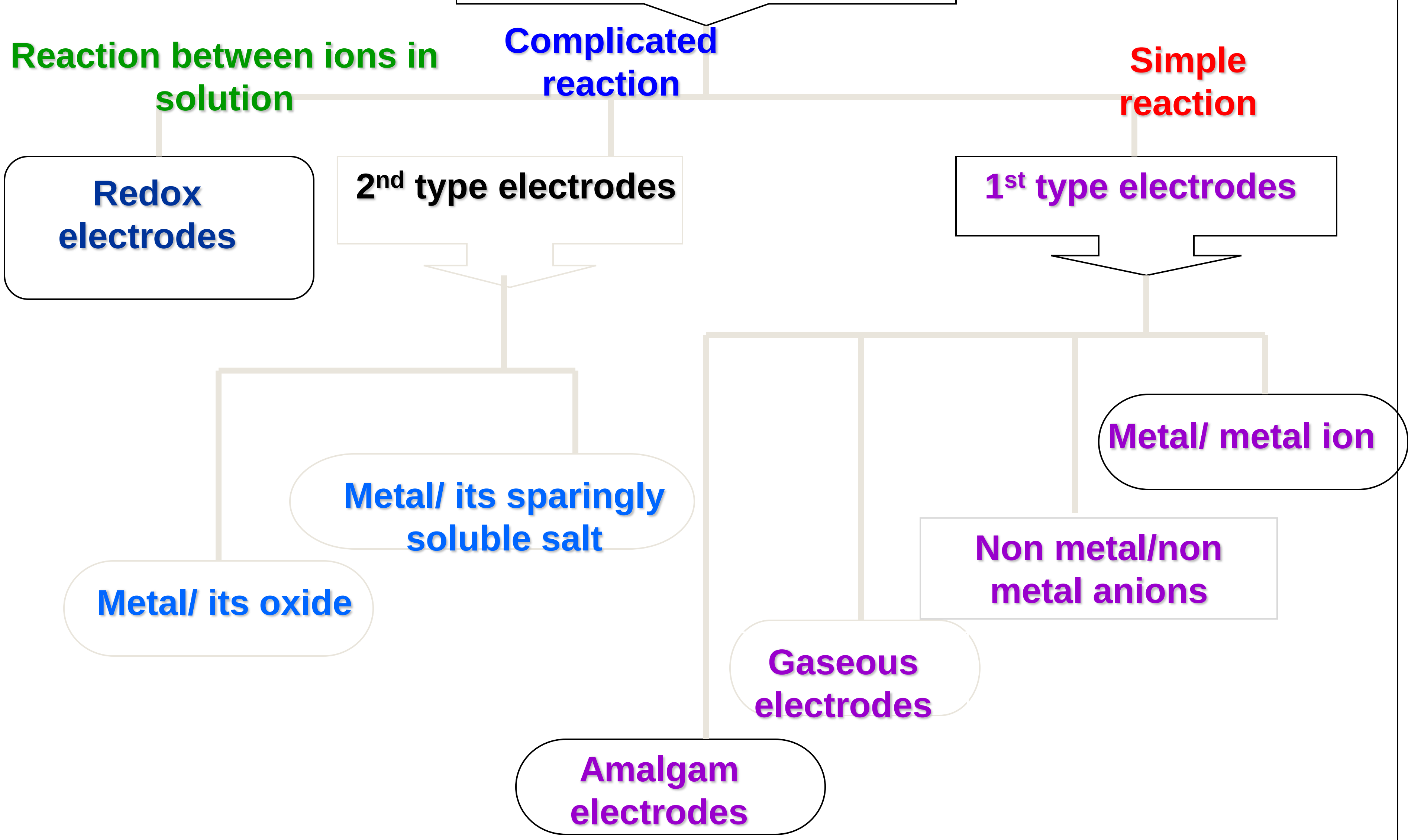
$$\because \Delta G^o = \Delta H^o - T\Delta S^0$$

$$\therefore \Delta G^o = -165.11\,\mathrm{kJ}$$

$$, \because E^o = -\frac{\Delta G^o}{2F}$$

$$\therefore E^o = 0.855 \qquad \mathrm{at\,353}$$

Electrodes



Reaction between ions in solution

Complicated reaction

Simple reaction

Redox electrodes

2nd type electrodes

1st type electrodes

Metal/ its sparingly soluble salt

Metal/ its oxide

Metal/ metal ion

Non metal/non metal anions

Gaseous electrodes

Amalgam electrodes

I- 1st typt electrodes

Electrode notation

2- non metal/ its anion

$$Me|Me^{-z}$$

$$Se|Se^{-2}$$

Electrode reaction

$$Me + ze^{-} \Leftrightarrow Me^{-z}$$

$$Se + 2e^{-} \Leftrightarrow Se^{-2}$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} \ln a_{Me^{-z}}$$

$$E = E^{\circ} - \frac{RT}{2F} \ln a_{Se^{-2}}$$

1- metal/ metal ion

$$M^{+z}|M$$

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

Electrode reaction

$$M^{+z} + ze^{-} \Leftrightarrow M$$

$$Cu^{+2} + 2e^{-} \Leftrightarrow Cu$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} \ln \frac{1}{a_{M^{+z}}}$$

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{+2}}}$$

3-gaseous electrode

$Pt, X_2 | X^{-z}$ ← **Electrode notation** → $X^{+z} | X_2, Pt$

$Pt, Cl_2 | Cl^-$

Electrode reaction

$$X_2 + 2ze^- \Leftrightarrow 2X^{-z}$$

$$Cl_2 + 2e^- \Leftrightarrow 2Cl^-$$

Nernst equation

$$E = E^\circ - \frac{RT}{2zF} \ln \frac{\left(a_{X^{-z}}\right)^2}{a_{X_2}}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{\left(a_{Cl^-}\right)^2}{a_{Cl_2}}$$

$H^+ | H_2, Pt$

Electrode reaction

$$2X^{+z} + 2ze^- \Leftrightarrow X_2$$

$$2H^+ + 2e^- \Leftrightarrow H_2$$

Nernst equation

$$E = E^\circ - \frac{RT}{2zF} \ln \frac{a_{X_2}}{\left(a_{X^{+z}}\right)^2}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{H_2}}{\left(a_{H^+}\right)^2}$$

Amalgam electrode

Electrode notation

$$M^{+z}|M,Hg$$

$$Cd^{+2}|Cd,Hg$$

Electrode reaction

$$M^{+z}+ze^{-}\Leftrightarrow M(Hg)$$

$$Cd^{+2}+2e^{-}\Leftrightarrow Cd(Hg)$$

Nernst equation

$$E=E^{\circ}-\frac{RT}{zF}\ln\frac{a_{M(Hg)}}{a_{M^{+z}}}$$

$$E=E^{\circ}-\frac{RT}{2F}\ln\frac{a_{Cd(Hg)}}{a_{Cd^{+2}}}$$

II. 2nd type electrodes

Metal/ its oxide electrode

- $OH^-|HgO,Hg$
- $OH^-|Sb_2O_3,Sb$

Metal/ its sparingly soluble salt electrode

As calomel electrode, Ag/AgCl, Hg/Hg_2SO_4. The metal is immersed in a solution of the anions of its sparingly soluble salt.

Electrode notation $SO_4^{-2}|Hg_2SO_4,Hg$

Electrode reaction $Hg_2SO_4\ (s)+2e^- \Leftrightarrow 2Hg(l)+SO_4^{-2}(aq)$

Nernst equation

$$E=E^\circ-\frac{RT}{2F}\ln a_{SO_4^{-2}}$$

This electrode is sensitive to the sulphate ion concentration therefore it is used to the determination of sulphate ion concentration

Metal / metal oxide electrode

1. stibium / stibium oxide (Antimony/Antimony oxide) electrode

Electrode notation

$$OH^{-}|Sb_2O_3,Sb$$

Electrode reaction

$$Sb_2O_3(s)+3H_2O+6e^{-}\Leftrightarrow 2Sb+6OH^{-}(aq)$$

Nernst equation

$$E=E^{\circ}-\frac{RT}{6F}\ln\left(a_{OH^{-}}\right)^{6}$$

This electrode is reversible to hydroxide ion concentration so its potential depends on pH and is called indicator electrode

2. Mercury / mercuric oxide electrode

Electrode notation

$$OH^- | HgO, Hg$$

Electrode reaction

$$HgO(s) + H_2O + 2e^- \Leftrightarrow Hg + 2OH^-(aq)$$

Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln\left(a_{OH^-}\right)^2$$

Generally, this kind of electrodes is used as reference electrodes in acidic and alkaline solutions.

$$a_{OH^-} = \frac{K_W}{a_{H^+}}$$

$$\ln a_{OH^-} = \ln K_W - \ln a_{H^+}$$

$$\ln a_{OH^-} = \ln K_W - 2.303 \log a_{H^+}$$

$$\ln a_{OH^-} = \ln K_W + 2.303\left(-\log a_{H^+}\right)$$

$$\ln a_{OH^-} = \ln K_W + 2.303\, pH$$

From Nernst equation

$$E = E^\circ - \frac{RT}{F} \ln a_{OH^-}$$

$$E = E^\circ - \frac{RT}{F} \ln K_W - \frac{2.303\,RT}{F} pH$$

This electrode is sensitive to the change in solution pH.

III. Redox electrodes

Electrode notation

$$M^{+X}, M^{(X-Z)+}|Pt$$

$$Cu^{+2}, Cu^{+}|Pt$$

Electrode reaction

$$M^{+X} + ze \Leftrightarrow M^{(X-Z)+}$$

$$Cu^{+2} + e \Leftrightarrow Cu^{+}$$

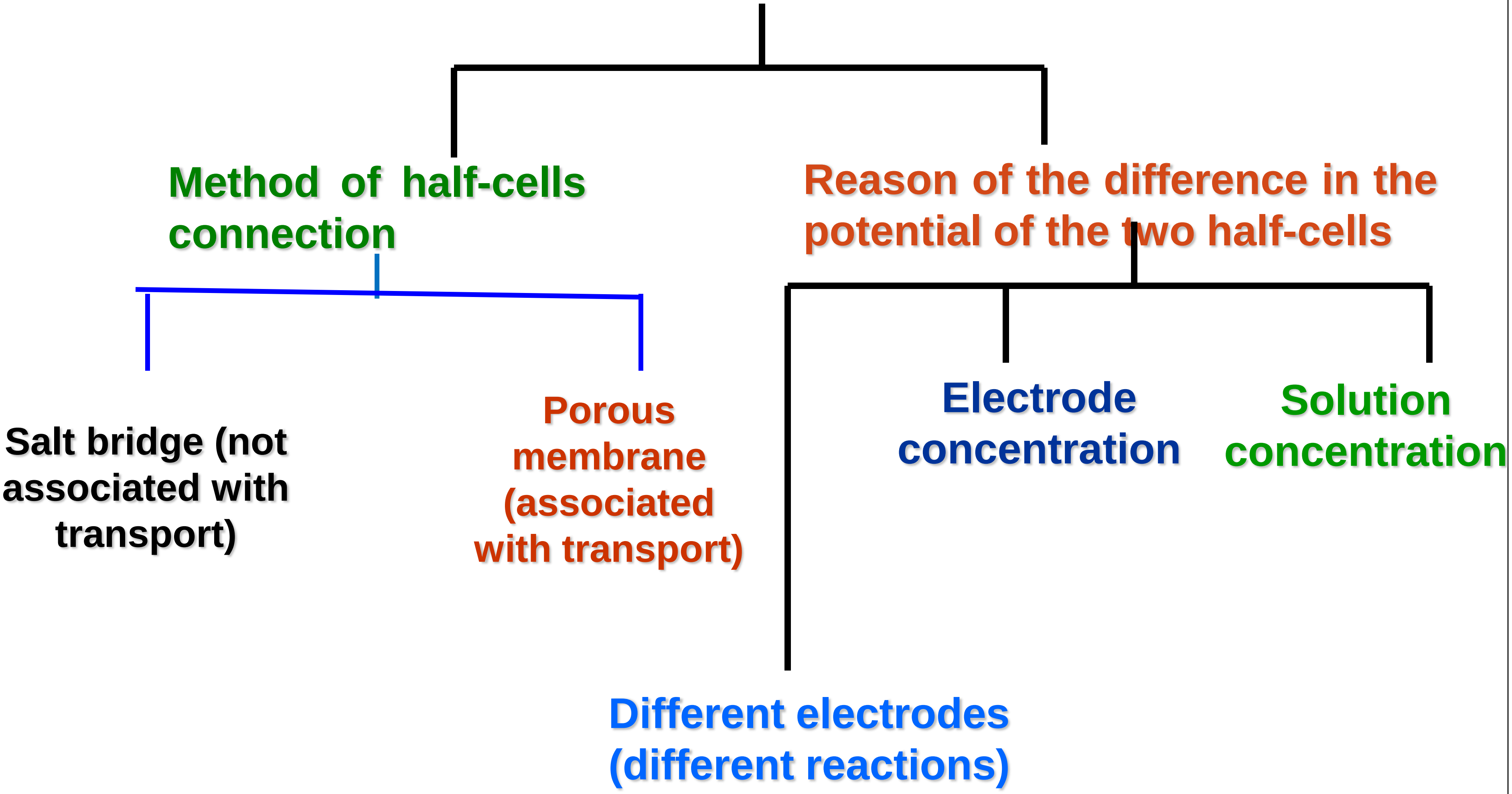
Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} ln \frac{a_{M^{(X-Z)+}}}{a_{M^{+X}}}$$

$$E = E^{\circ} - \frac{RT}{F} ln \frac{a_{Cu^{+}}}{a_{Cu^{+2}}}$$

ELECTROCHEMISTRY 1
PART 5

Classification of Cells



Method of half-cells connection

Salt bridge (not associated with transport)

Porous membrane (associated with transport)

Reason of the difference in the potential of the two half-cells

Electrode concentration

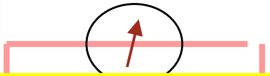
Solution concentration

Different electrodes (different reactions)

Classification of Cells

- **Concentration cells**
  - Associated with transport
    1. Associated with E_j
    2. Not associated with E_j
  - Not associated with transport
    - 1- amalgam electrode cells
    - 2. Gaseous electrode cells
    - 3. Electrolytic cells
- **Chemical cells**
  - Associated with transport
    1. Associated with E_j
    2. Not associated with E_j
  - Not associated with transport
- **Other cells**
  - Commercial cells
  - Redox cells

I. concentration cells: *a. not associated with transport*



$$E_{Cell}=E_c-E_a$$

$$E_{Cell}=[E_c^o-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M^{+z}}]-[E_a^o-\frac{RT}{zF}\ln\frac{M_{(a1)}}{M^{+z}}]$$

$a_1 > a_2$

$$E_{Cell}=[-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M^{+z}}]-[-\frac{RT}{zF}\ln\frac{M_{(a1)}}{M^{+z}}]$$

$$E_{Cell}=-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M_{(a1)}}$$

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *a. not associated with transport*

2. gaseous cells

it consists of two same electrodes of different gas pressures immersed in a solution containing a cation of the gas

$$Pt,H_{2(a_1)}|HCl|H_{2(a_2)},Pt$$

$$2H^+ + 2e \rightarrow H_{2(a2)}$$

$$H_{2(a_1)} \rightarrow 2H^+ + 2e$$

$$H_{2(a_1)} \rightarrow H_{2(a_2)}$$

$$E = -\frac{RT}{2F} ln\frac{(a_2)}{(a_1)}$$

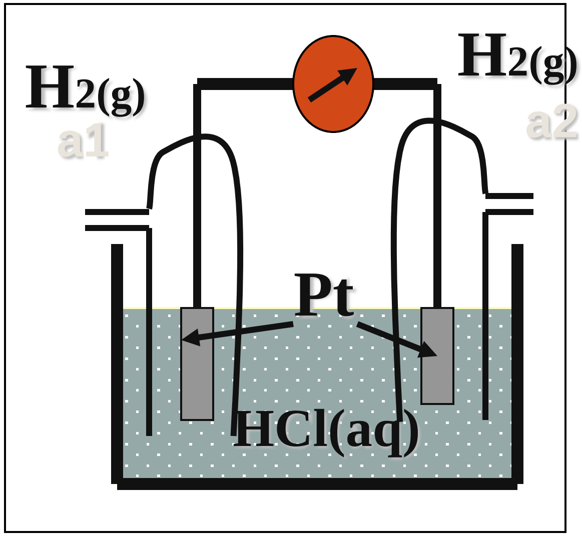
$$Pt,X_{2(a_1)}|X^{\pm z}|X_{2(a_2)},Pt$$

$$2X^{+z} + 2ze \rightarrow X_{2(a2)}$$

$$X_{2(a_1)} \rightarrow 2X^{+z} + 2ze$$

$$X_{2(a_1)} \rightarrow X_{2(a_2)}$$

$$E = -\frac{RT}{zF} ln\frac{(a_2)}{(a_1)}$$



$a_1 > a_2$

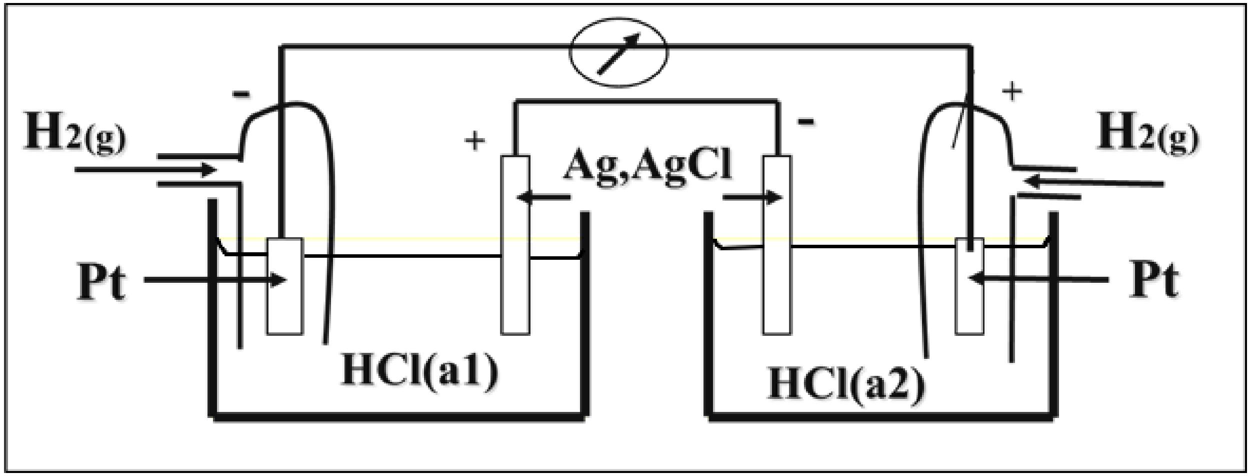
What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *a. not associated with transport*

3- Electrolytic concentration cells (not associated with transport)

- Each half-cell is a cell in itself consists of two different electrodes in the same solution that contains ions reversible to the two electrodes.
- Electrodes are arranged in opposite direction.
- Solutions concentration is different in the two half-cells
- There is no direct contact between the solutions in the two half cells either via porous membrane or salt bridge and the connection occurs via electrical wires



$$a_1 < a_2$$

Cell notation $Pt,H_2|HCl_{(a_1)}|AgCl,Ag$ 1st half-cell

$Pt,H_2|HCl_{(a_2)}|AgCl,Ag$ 2nd half-cell

$$Pt,H_2|HCl_{(a_1)}|AgCl,Ag \quad - \quad Ag,AgCl|HCl_{(a_2)}|H_2,Pt$$

Cell reaction

$$2H^+{}_{(a_2)} + 2Cl^-{}_{(a_2)} + 2Ag \rightarrow 2AgCl + H_{2(g)}$$

$$H_{2(g)} + 2AgCl \rightarrow 2H^+{}_{(a_1)} + 2Ag + 2Cl^-{}_{(a_1)}$$

$$\overline{\qquad 2HCl_{(a_2)} \rightarrow 2HCl_{(a1)} \qquad}$$

Nernst equation

$$E = -\frac{RT}{2F} ln\left(\frac{a_1}{a_2}\right)^2 \longrightarrow E = -\frac{RT}{F} ln\frac{a_1}{a_2}$$

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *b. associated with transport: 1. with E_j*

Two electrodes of the same material immersed in two half cells containing two solution of same solute but of different concentrations. The two half cells are contacted via porous membrane where some processes occurs in addition of redox processes..

Cell notation

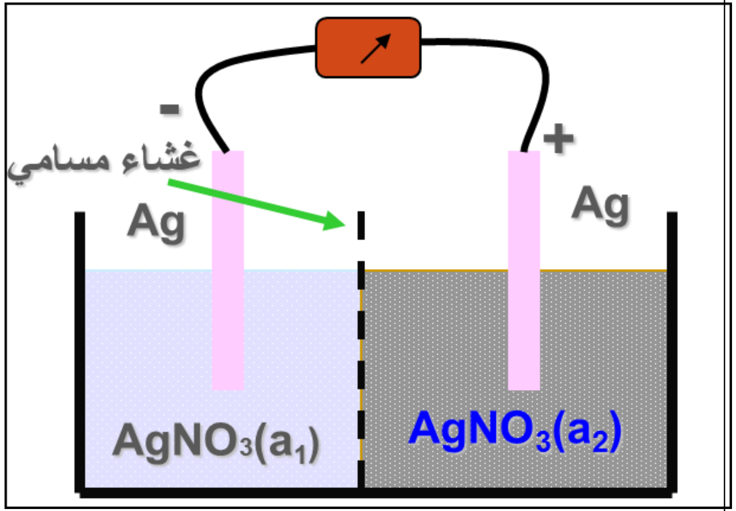
$$Ag|AgNO_3(a_1)\vdots AgNO_3(a_2)|Ag$$

Cell reaction

$$Ag^+(a_2)+e\rightarrow Ag$$

$$Ag\rightarrow Ag^+(a_1)+e$$

$$\overline{Ag^+(a_2)\rightarrow Ag^+(a_1)}$$



$a_1 < a_2$

Nernst equation

$$E=-\frac{RT}{F}\ln\frac{a_1}{a_2}$$

Where is E°?

What is the main demand to keep the cell working?

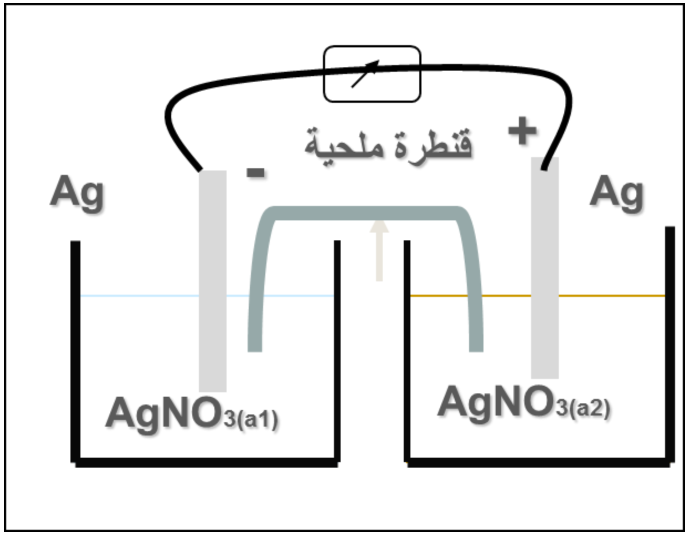
Answer: $a_1 \neq a_2$

I. concentration cells: *b. associated with transport: 2. without E_j*

Two electrodes of the same material immersed two half cells containing two solution of same solute but of different concentrations. The two half cells are contacted via salt bridge.

Cell notation

$$Ag|AgNO_3(a_1)\|AgNO_3(a_2)|Ag$$



Cell reaction

$$\begin{array}{l} Ag^+(a_2)+e \rightarrow Ag \\ Ag \rightarrow Ag^+(a_1)+e \\ \hline Ag^+(a_2) \rightarrow Ag^+(a_1) \end{array}$$

Nernst equation

$$E=-\frac{RT}{F}\ln\frac{a_1}{a_2}$$

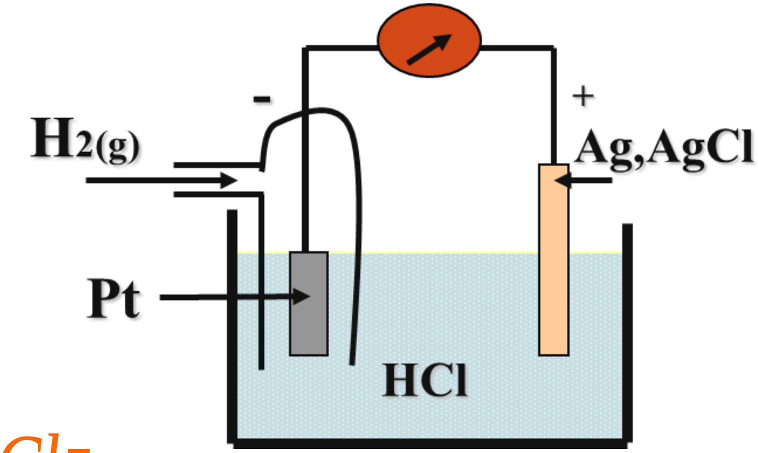
Where is E°?

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

II. Chemical cells: *a. not associated with transport*

- One electrolytic solutions contains cations and anions reversible to the two electrodes.
- Two Different electrodes.
- Different reactions occur at the two electrodes



Cell notation

$$Pt, H_2|HCl|AgCl, Ag$$

Cell reaction

$$2AgCl + 2e \rightarrow 2Ag + 2Cl^-$$

$$H_2 \rightarrow 2H^+ + 2e$$

$$2AgCl + H_2 \rightarrow 2Ag + 2Cl^- + 2H^+$$

remember that $E^\circ \neq 0$

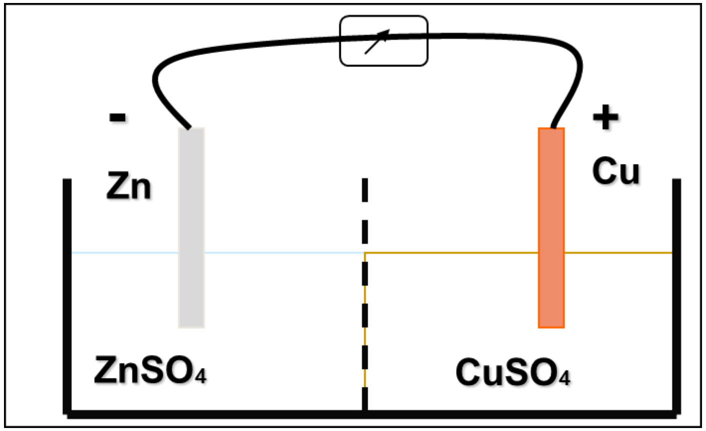
Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln \frac{(a_{H^+})^2 (a_{Cl^-})^2}{a_{H_2}}$$

II. Chemical cells: *b. associated with transport: 1. with E_j*

- Different two electrodes and two different solution connected via porous membrane..
- Different reactions occur in the vicinity of the two electrodes

Cell notation $Zn|ZnSO_4 \vdots CuSO_4|Cu$



Cell reaction

$$Cu^{+2} + 2e \rightarrow Cu$$

$$Zn \rightarrow Zn^{+2} + 2e$$

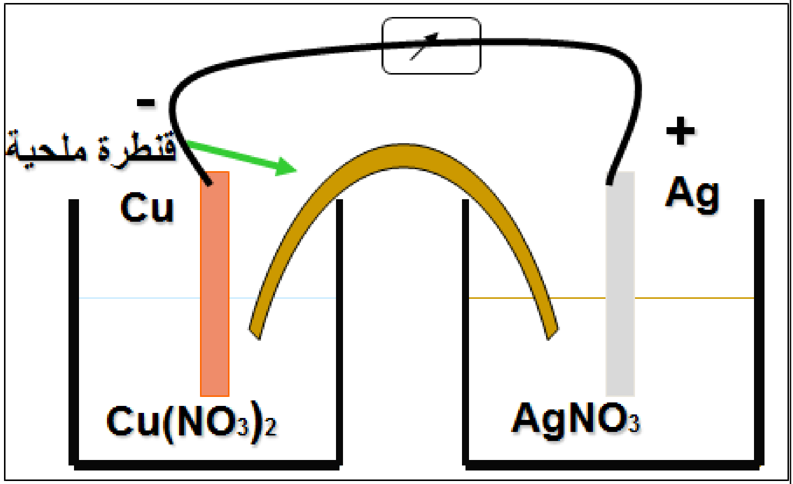
$$Cu^{+2} + Zn \rightarrow Zn^{+2} + Cu$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{2F} ln \frac{a_{Zn^{+2}}}{a_{Cu^{+2}}}$$

II. Chemical cells: *b. associated with transport: 2. without E_j*

- Different two electrodes and two different solution connected via salt bridge.
- Different reactions occur in the vicinity of the two electrodes



Cell notation $Cu|Cu(NO_3)_2\|AgNO_3|Ag$

Cell reaction

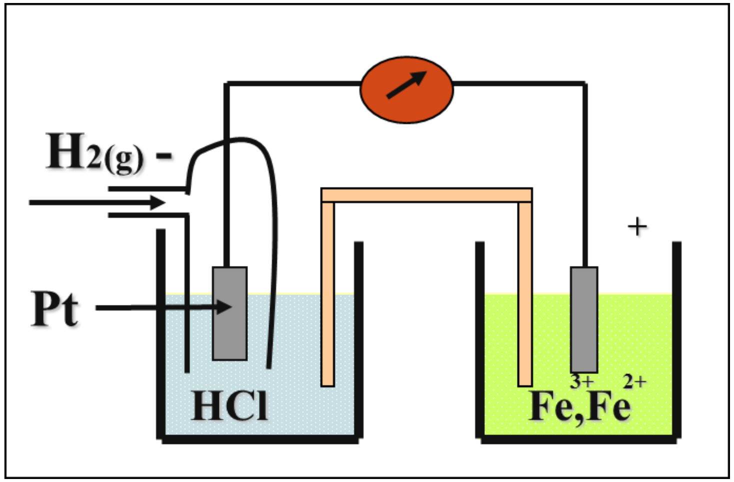
$$\begin{array}{c} 2Ag^+ + 2e \rightarrow 2Ag \\ Cu \rightarrow Cu^{+2} + 2e \\ \hline 2Ag^+ + Cu \rightarrow 2Ag + Cu^{+2} \end{array}$$

Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln \frac{a_{Cu^{+2}}}{(a_{Ag^+})^2}$$

III. a) Redox cells

- Different two electrodes (redox and inert) and two different solution connected via salt bridge.
- Different reactions occur in the vicinity of the two electrodes



Cell notation

$$Pt,H_2|H^+\|Fe^{+3},Fe^{+2}|Pt$$

Cell reaction

$$\begin{array}{l} 2Fe^{+3}+2e\rightarrow 2Fe^{+2} \\ H_2\rightarrow 2H^+ +2e \\ \hline 2Fe^{+3}+H_2\rightarrow 2Fe^{+2}+2H^+ \end{array}$$

Nernst equation

$$E=E^\circ-\frac{RT}{2F}\ln\frac{\left(a_{Fe^{+2}}\right)^2\left(a_{H^+}\right)^2}{\left(a_{Fe^{+3}}\right)^2\left(a_{H_2}\right)}$$

If we use NHE

$$E=E_c^\circ-\frac{RT}{F}\ln\frac{\left(a_{Fe^{+2}}\right)}{\left(a_{Fe^{+3}}\right)}$$

III. b) Commercial Cells

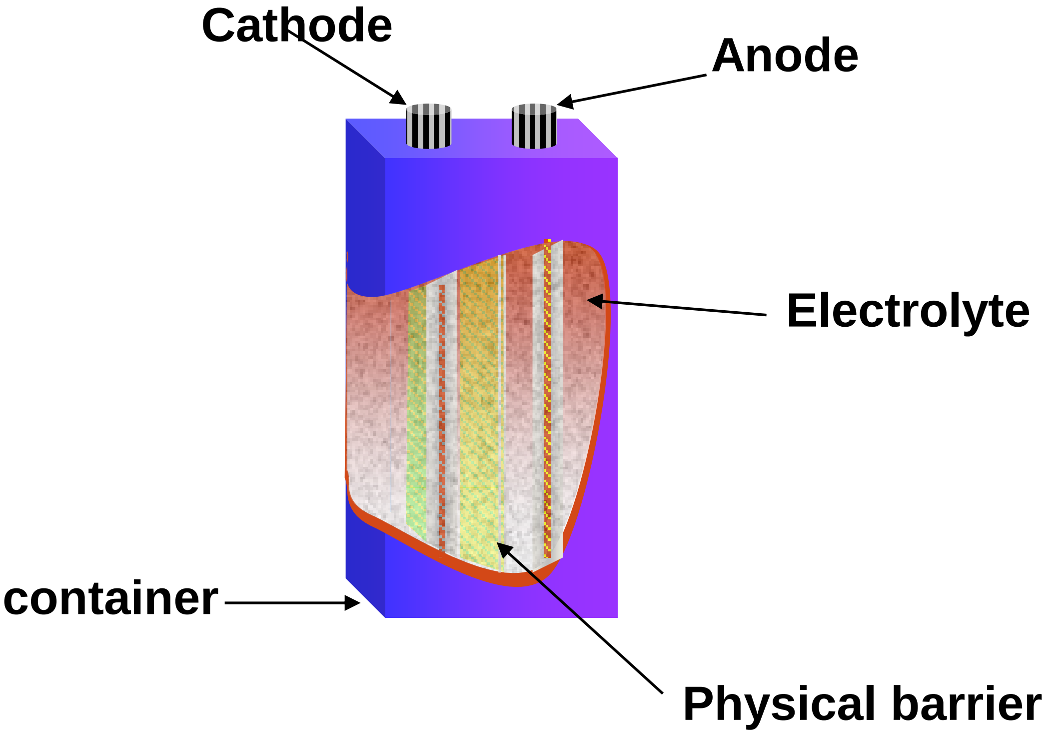
Primary cells

1. Non rechargeable batteries (disposable)
2. Conduct electricity till achieves equilibrium
3. Reactions could not be reversed during charging process
4. Example: Zn/Mg battery

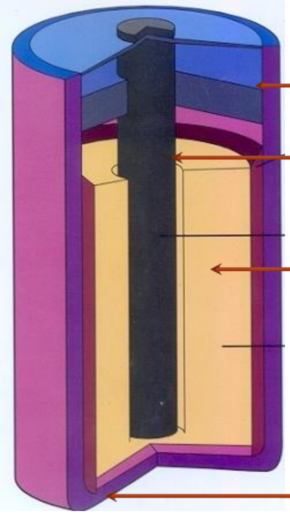
Secondary cells

1. Rechargeable batteries
2. Conduct electricity till discharge
3. Reactions could be reversed during charging process
4. Example: Pb/$PbSO_4$ battery

Primary constituents of the cell



Primary batteries : example: solid Zn/C



Zn anode

Carbon cathode

(carbon, electrolyte(NH_4Cl) and MnO_2)

insulator

Anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

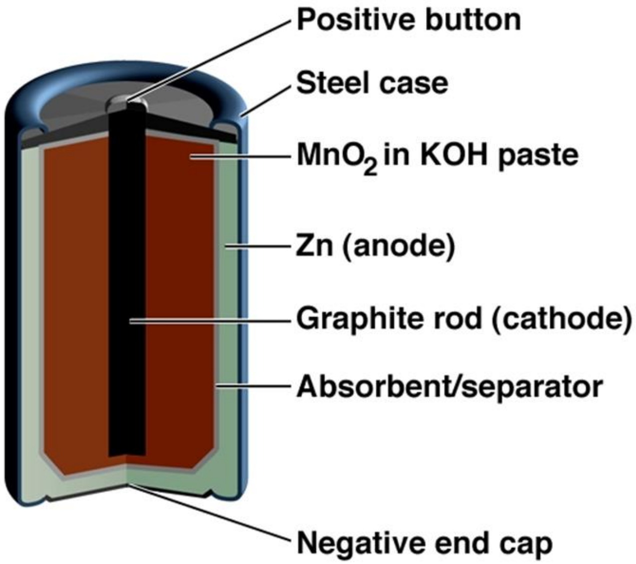
Cathode $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2OH^-(aq)$

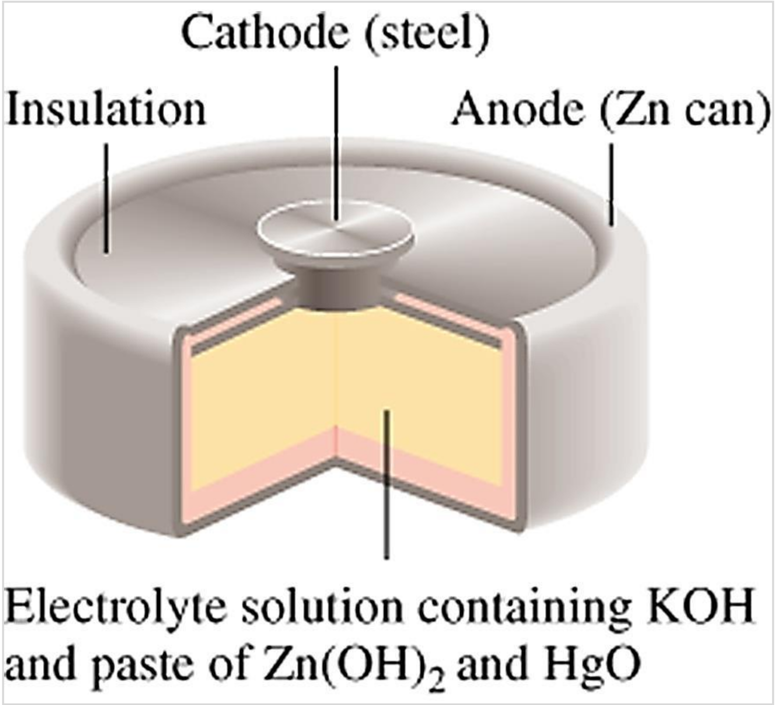
Electrolyte : NH_4Cl / $ZnCl_2$ / MnO_2 / C Powder

Solid alkaline batteries

- NH_4Cl is replaced with KOH or NaOH
- It has longer time than that of solid acidic batteries since Zn dissolves slowly in alkaline solutions
- The cathode is made of Graphite immersed in a paste composed of manganese dioxide, water and potassium hydroxide
- $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O + 2e^-$ (anode)
- $2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$ (cathode)
- EMF is 1.5 V
- It is non-rechargable



Mercury Battery



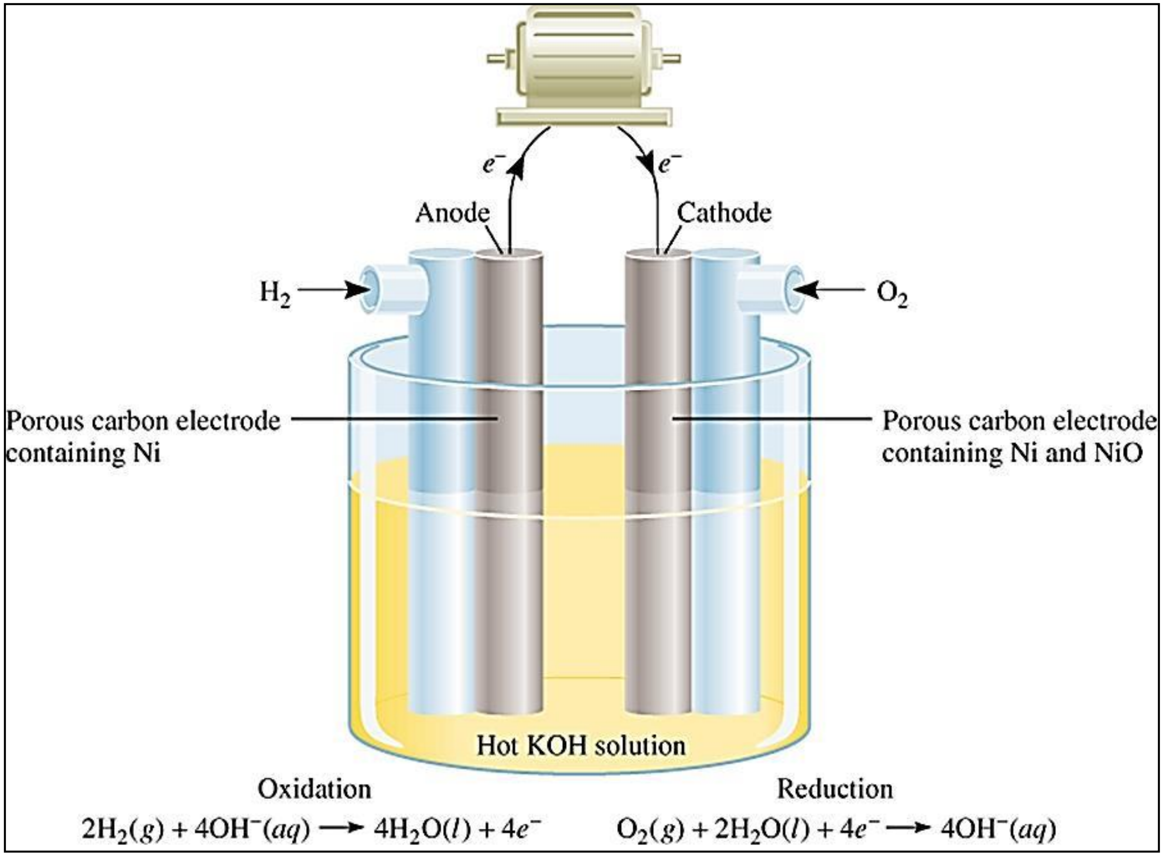
Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + \enclose{circle}{H_2O (l)} + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

fuel cell

A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning



Anode: $2H_2\ (g) + 4OH^-\ (aq) \longrightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq)$

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$$

Secondary batteries

Nickel / Cadmium Battery

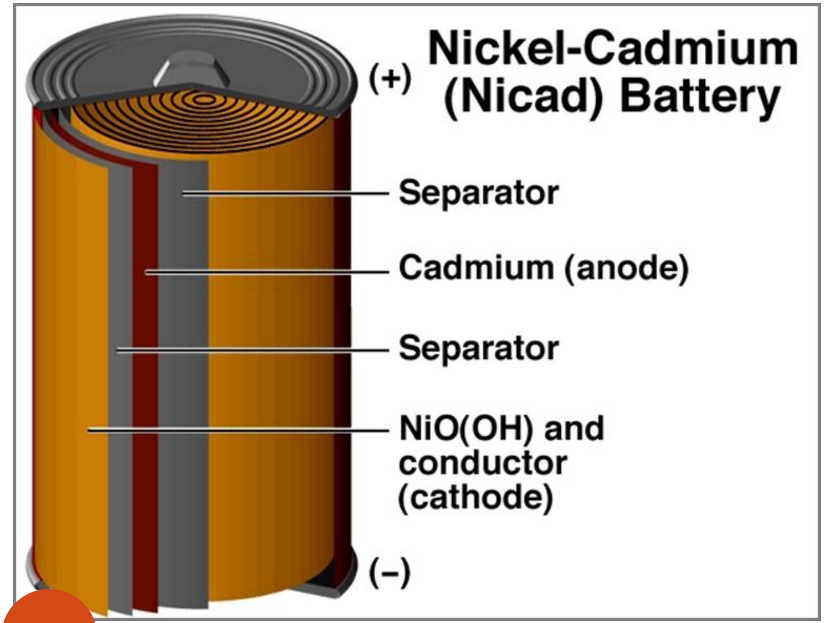
Electrolyte : KOH

Current collectors : Ni & Cd

Anode $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode $2NiO(OH)(s) \boxed{+ 2H_2O(l)} + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-$

$$2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$$



Lead / Acid Battery

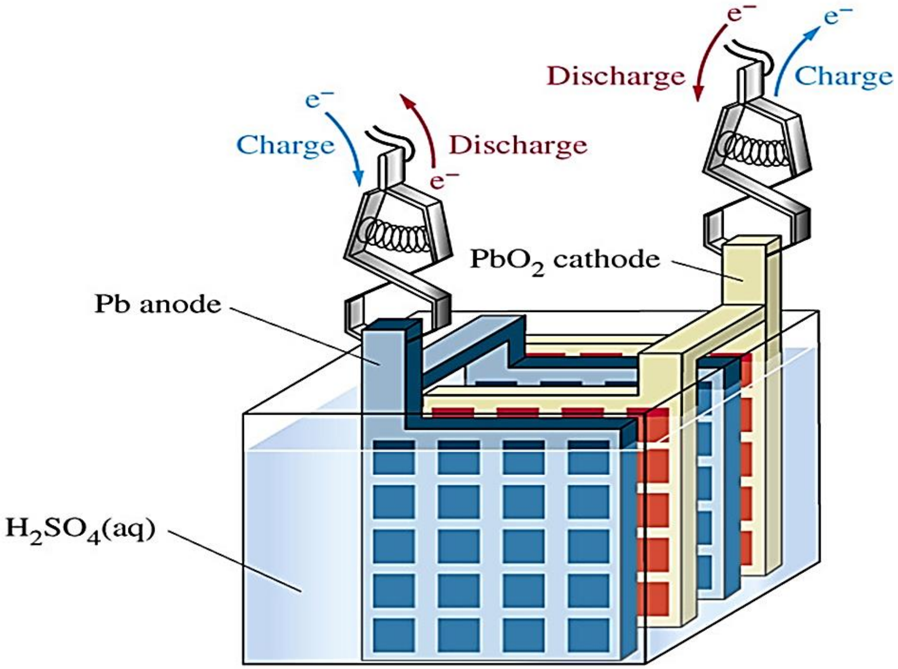
Electrolyte : H_2SO_4

Current collectors : Both Pb

Anode rxn $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode rxn $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow 2H_2O(l) + PbSO_4(s)$

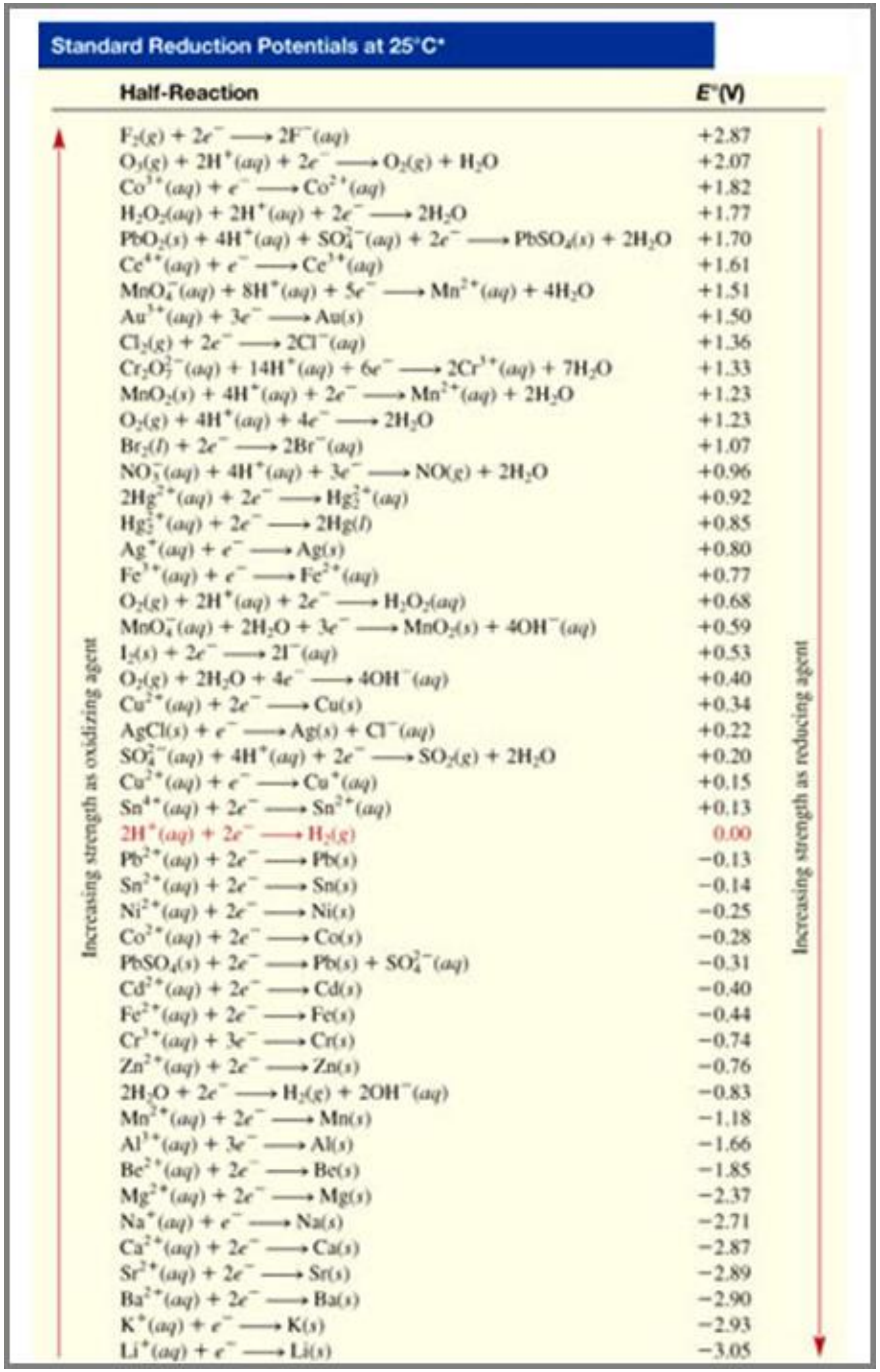
Cell rxn $PbO_2(s) + Pb(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$



Type of Battery	Advantages	Disadvantages
Lead acid	Rechargeable Long life 12 V	Heavy Contain acid Weather issues
Alkaline/Dry cell	Inexpensive No toxic metals used Lots of power (1.5 V down to 1.2 V)	Heavier
Lithium (solid state)	Lightweight Higher capacity (3.6-3.9 V) Rechargeable Longer lasting Less likely to leak/explode	Expensive
Fuel cells	No recharging No harmful pollutants	high initial cost Fuel not readily available
Nickel-Cadmium (Ni-Cd)	Fast/simple charge (rechargeable) High # charges 1.2 V continuously	Toxic metals Expensive
Mercury	More constant voltage (1.35 V) Longer life Lighter	More expensive

Why are some batteries rechargeable while others are not?

Attempting to recharge a non-rechargeable batteries does not regenerate the chemicals but usually forms hydrogen gas and case to burst explosively.



Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

ELECTROCHEMISTRY 1
PART 6

Measurement of the EMF of a cell

1. Direct method

- **The potential of an electrochemical cell is measured using voltammeter**
- **Disadvantages:**

  a) It is not accurate.

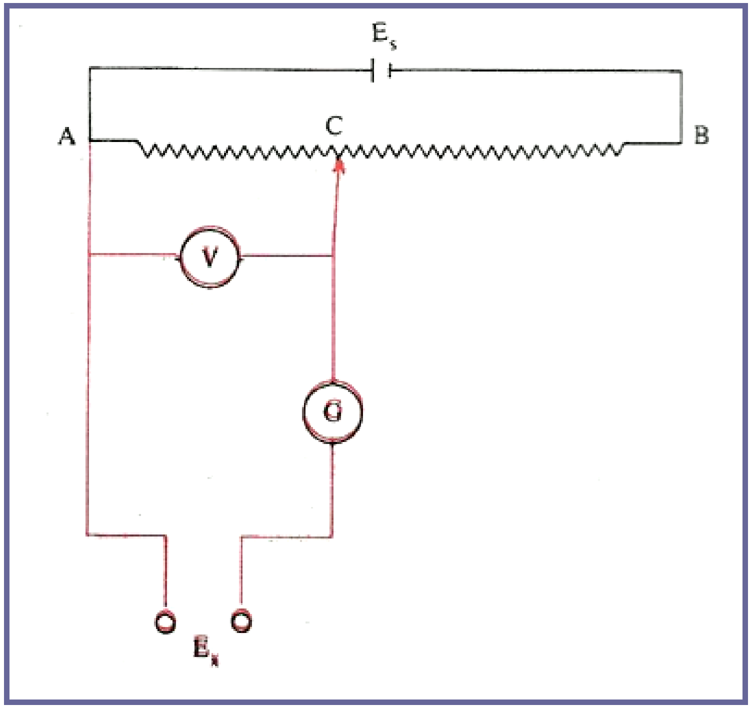
  b) A high current is drawn from the cell which causes the occurrence of chemical reactions in the vicinity of the electrodes leading to changes in the composition of the solution and/or the electrode. The voltage value obtained by the voltammeter is smaller in value than that obtained in measurements without current passage.

Potentiometric Method

- To determine the potential of a cell E_x it will be inserted in the following circuit
- The potential of the cell E_x will be equal to the potential of E_{AC} when the current passing in the galvanometer equals to zero

$$E_{AC} = i.R_{AC}$$

- The potential E_{AC} is given by the voltammeter



- AB: variable resistance
- G: Galvanometer
- V: Voltammeter

Applications of EMF measurements

1. Determination of solubility product of sparingly soluble salt

$$PbSO_4 \Leftrightarrow Pb^{+2} + SO_4^{-2}$$

cell

$$PbSO_4 + 2e \rightarrow Pb + SO_4^{-2}$$

cathode

$$Pb \rightarrow Pb^{+2} + 2e$$

anode

$$Pb / PbSO_4 // Pb^{+2} / Pb$$

$$E^\circ_{cell} = E^\circ_c - E^\circ_a$$

$$E^\circ_{cell} = -0.36 - \left(-0.126\right) = -0.234V$$

$$\ln K = \frac{ZFE^\circ}{RT} = -\frac{2 \times 96500 \times 0.234}{8.314 \times 298} = -18.23$$

$$K_{sp} = 1.21 \times 10^{-8}$$

2. Solubility product of complex ions

$$[Cu(NH_3)_4]^{+2} \Leftrightarrow Cu^{+2} + 4NH_3$$

$$1-\alpha \qquad\qquad \alpha \qquad\qquad 4\alpha$$

$$K_{dis} = \frac{[Cu^{+2}][NH_3]^4}{[Cu(NH_3)_4]^{+2}}$$

$$K_{dis} = \frac{\alpha.(4\alpha)^4}{(1-\alpha)}$$

$$\text{if } C \text{ is the solution concentration}$$

$$K_{dis} = \frac{\alpha C.(4\alpha C)^4}{(1-\alpha)C}$$

If we determine the concentration of Cu^{+2} the other values will be known

$$Cu/CuSO_4(0.1M)+NH_4OH(0.1M)//CuSO_4(0.1M)/Cu$$

The potential of the cell is given by the following equation

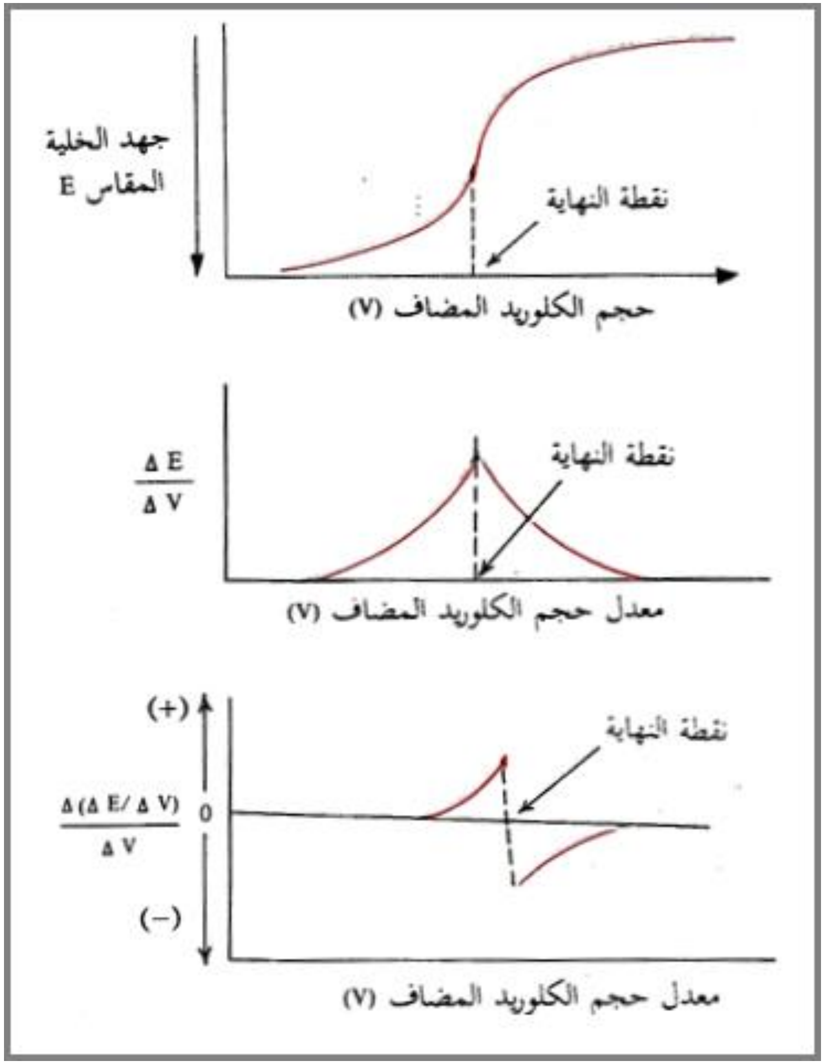
$$E=-\frac{2.303RT}{nF}\log\frac{[Cu^{+2}]}{0.1}$$

$$K_{dis}=\frac{\alpha C.(4\alpha C)^4}{(1-\alpha)C}$$

3.Potentiometric titration

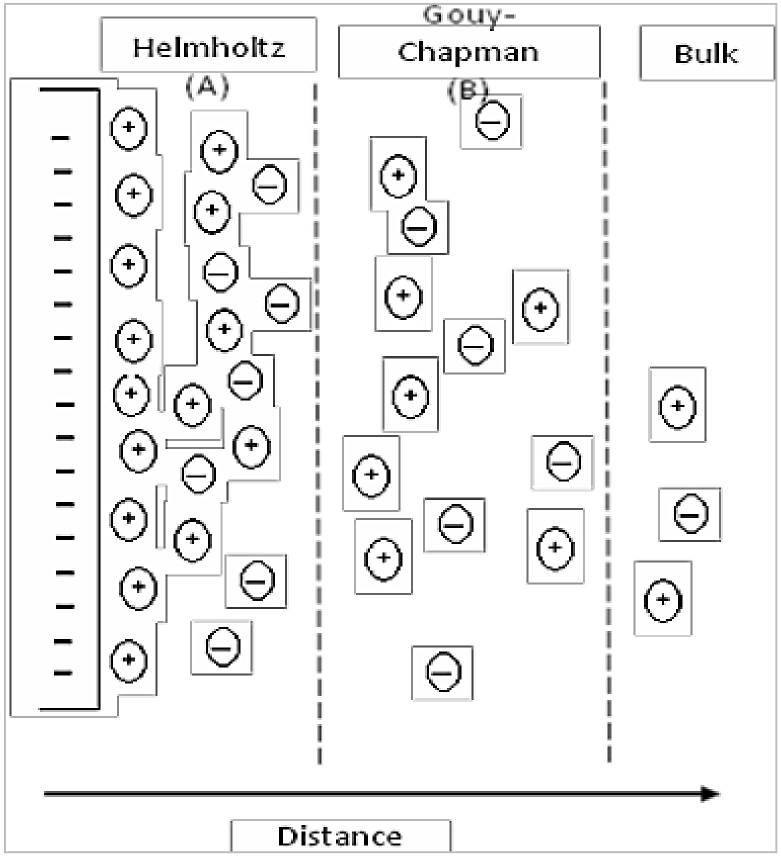
Potentiometric titration could be used to determine strong, weak and Polly-alkaline acids via titration with strong alkali using glass electrode which is sensitive to solution pH.

Determination of silver nitrate concentration is carried out using standard solution of NaCl and solid electrode which is sensitive to silver cation in solution. At end point sudden rise in cell potential is obtained

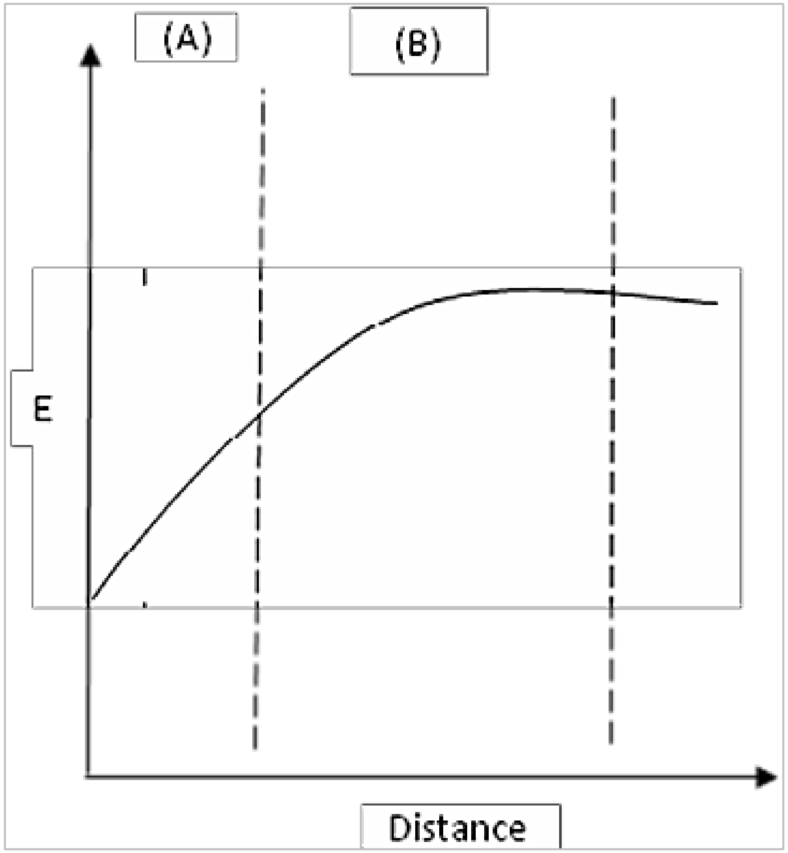


$$E_{cell} = (K + E^{o}_{Ag}) + 0.059 \log[Ag^{+}]$$

Ionic Double Layer and Potential Distribution

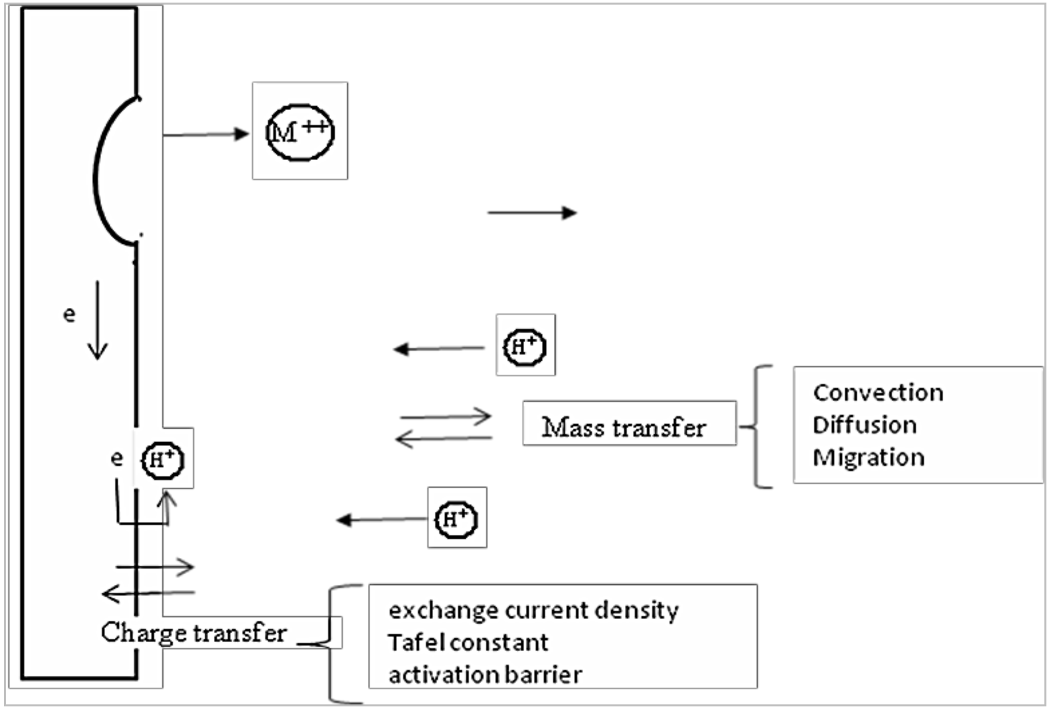


. *Double layer at electrode – solution interface*



Potential distribution across distance

Processes at an electrochemical interface are schematically represented below



Transport processes at electrochemical interface

Mass transport to metal surface involves forces such as convection, diffusion and migration, depending on presence or absence of electric field and flow conditions. Concentration polarization is controlled by diffusion gradients.

Polarization

- The deviation of voltage from the value at equilibrium upon the passage of current is called **polarization**.
- For an electrode, the deviation of electrode potential from its equilibrium state is called the **electrode polarization**.
- **overpotential**, denoted as *η* and expressed in volts.

$$\boxed{\begin{aligned}\eta_C &= E_C^o - E_C \\ \eta_a &= E_a - E_a^o\end{aligned}}$$

Various overpotentials

- **Concentration overpotential**
- **Activation overpotential** (electrochemical overpotential)
- **Ohmic overpotential**

Types of Polarization

Activation polarization

It is due to the decrease in the rate of the electrode reaction

Concentration polarization

It is due to the difference in the concentration of the electroactive species between baulk solution and electrode surface

Ohmic polarization

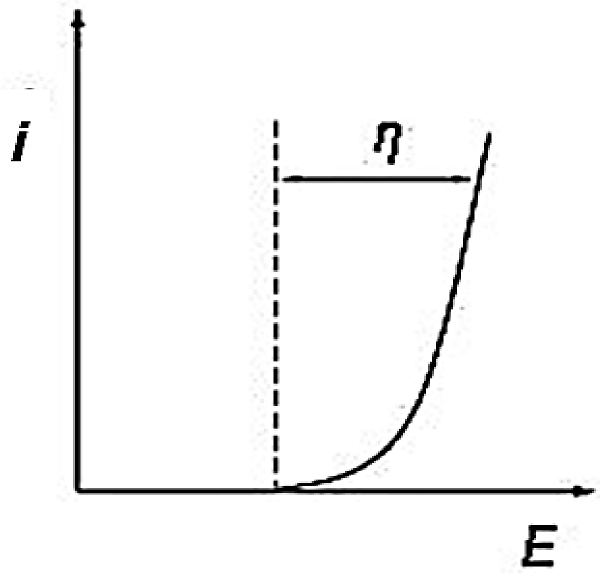
It arises from the inability to decrease the distance between the working and the reference electrodes to zero value

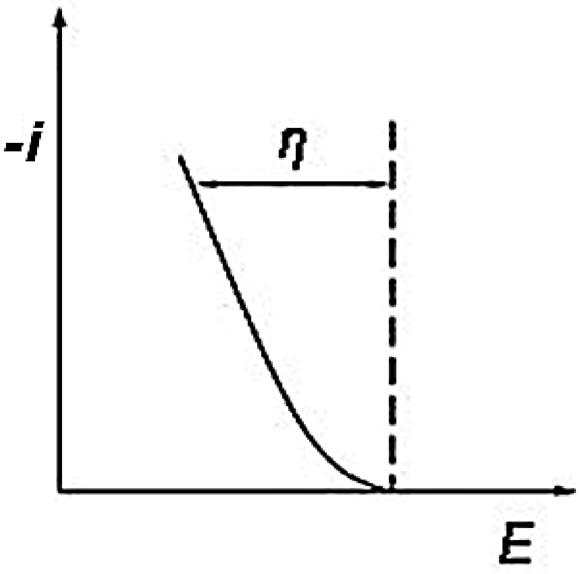
The contribution to polarization due to IR drops is referred to as Resistance polarization, so Total polarization:

$$\eta_T = \eta_{Act} + \eta_{Conc} + \eta_{resist}$$

Anodic and cathodic polarization

- Anodic polarization is the shift of the electrode potential to more positive (or less negative) value and the electrode acts as anode
- Cathodic polarization is the shift of the electrode potential to more negative (or less positive) value and the electrode acts as cathode





$$\boxed{\eta_a = E_a - E_a^o}$$

$$\boxed{\eta_C = E_C^o - E_C}$$

What happens in the cathodic polarization?

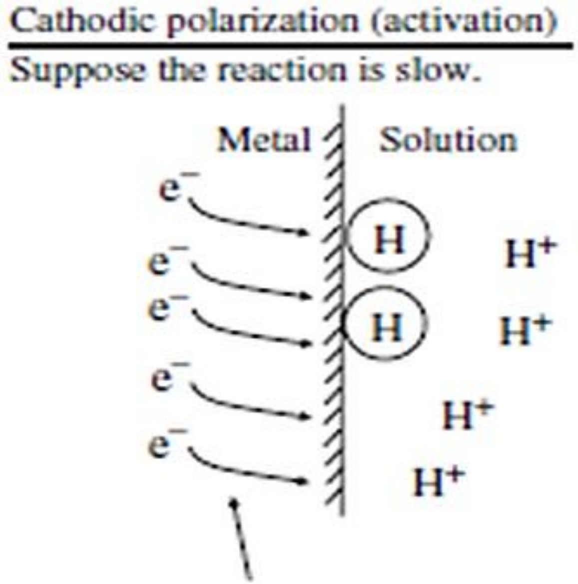
- Suppose the evolution of hydrogen gas at the electrode surface.
- Initially hydrogen atoms is formed at electrode surface as follows:

$$2H^+ + 2e \longrightarrow 2H_{ads}$$

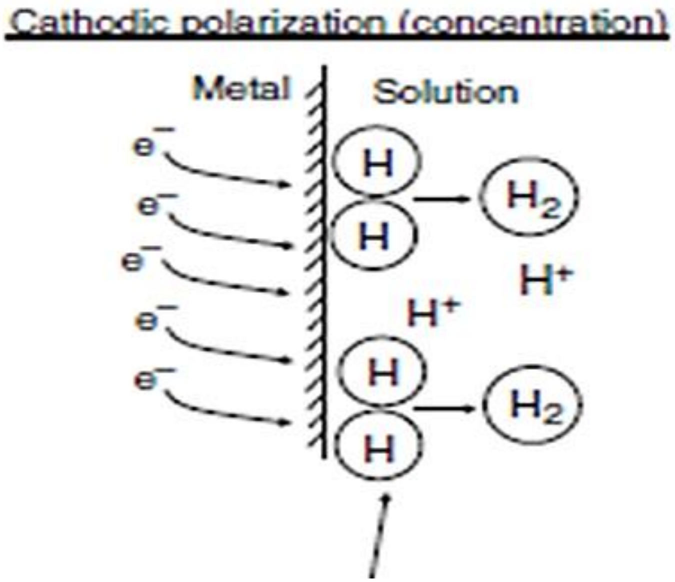
- The adsorbed hydrogen gas will combine to form hydrogen gas::

$$2H_{ads} \longrightarrow H_2$$

- If the electrons will arrive to the electrode faster than its reaction with hydrogen ions to form adsorbed atoms then the concentration of electrons in the metallic side of the interface will be increased where the electrode will be charged negatively and the electrode potential will be shifted to negative value due to activation polarization.



- If hydrogen ions diffuse slowly to the electrode surface then the gain of electrons will be slowly leading to electrons to be accumulated at the electrode surface and then the electrode will be charged negatively and the electrode potential is shifted to negative value but due to concentration polarization



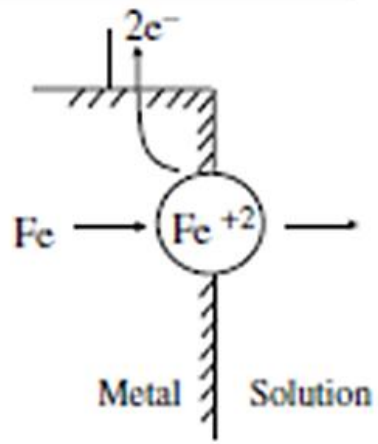
What happens in the anodic polarization?

- Suppose the reaction is slow

$$Fe \rightarrow Fe^{+2} + 2e$$

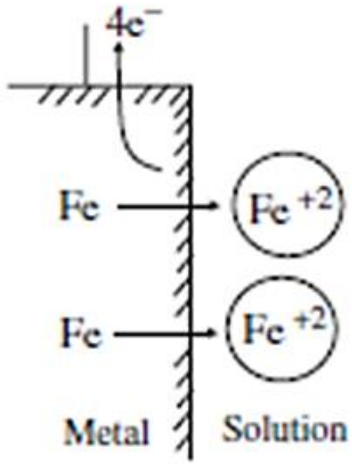
- Then the electrons exit from the surface faster than Fe atoms leave the matrix
- The concentration of electrons is decreased at the the metal side of the interface .
- The electrode potential is shifted to more positive value due to activation polarization.

Anodic polarization (activation)



- Suppose the products are slow to diffuse away from the interface.
- The surface will be charged positively and the electrode potential is shifted to more positive value due to concentration polarization.

Anodic polarization (concentration)



Concentration polarization

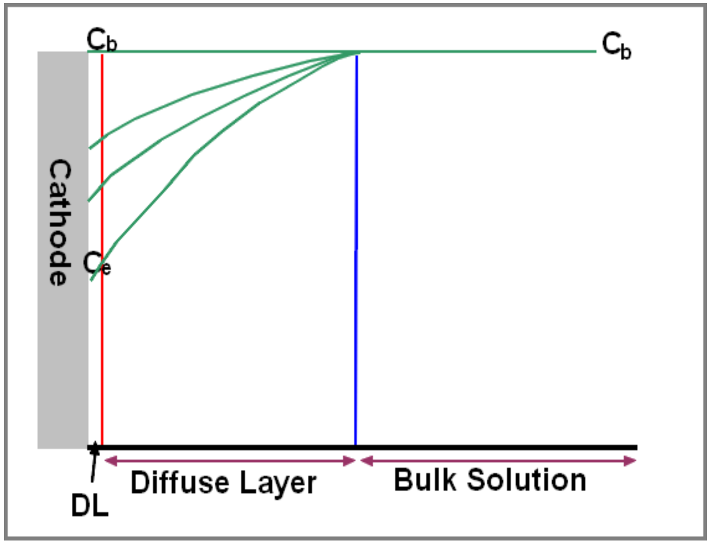
- If the concentration of hydrogen gas in the bulk solution is C_b and at he electrode surface is C_e
- When the circuit is opened, the electrode potential is

$$2H^{+} + 2e^{-} \Leftrightarrow H_2$$

$$E = E^{o} + \frac{RT}{zF}\ln\frac{Ox}{Red}$$

$$E = E^{o} + \frac{RT}{zF}\ln H^{+}$$

$$E_{rev} = E^{o} + \frac{RT}{zF}\ln C_b \rightarrow (1)$$



- Where E_{rev} is the reversible potential of the electrode
- When the circuit is closed and If the electrode reaction is fast and reversible and if the rate of diffusion of hydrogen ions (from bulk solution to the electrode surface) is slow, then the concentration of hydrogen ions at the elctrode surface will drop to Ce and the reaction is controlled with diffusion.

In this case, The electrode potential is the irreversible potential E_{irr}

$$2H^{+}+2e^{-}\Rightarrow H_2$$

$$E_{irr}=E^{o}+\frac{RT}{zF}\ln C_e \rightarrow (2)$$

- **To keep the rate of hydrogen gas evolution is constant and to keep the current is constant the potential is raised from E_{rev} to E_{irr} by amount is called overpotential (which is concentration overpotential)**

$$\eta=E_{irr}-E_{rev}$$

$$\eta=(E^{o}+\frac{RT}{zF}\ln C_e)-(E^{o}+\frac{RT}{zF}\ln C_b)$$

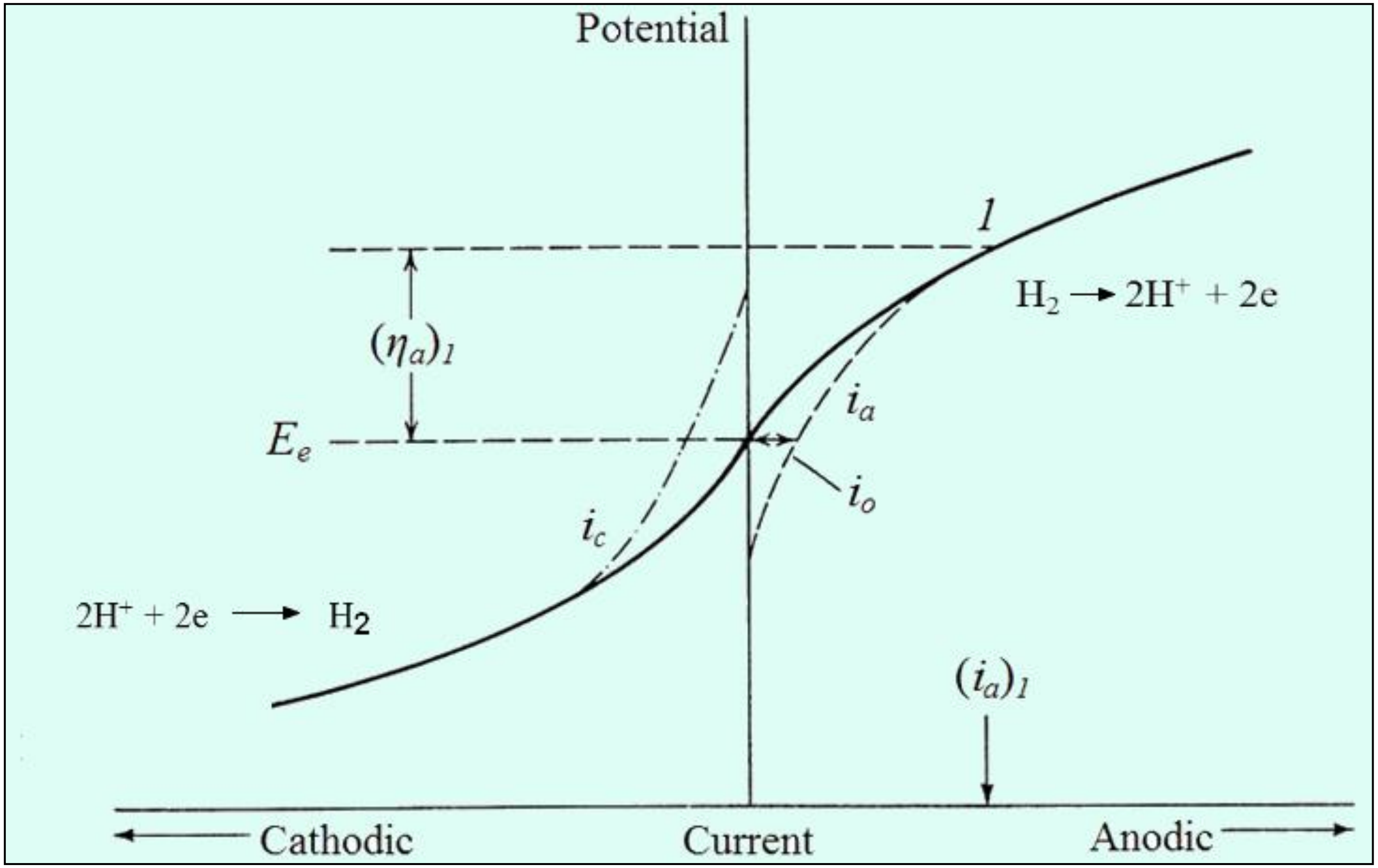
$$\eta=\frac{RT}{zF}\ln C_e-\frac{RT}{zF}\ln C_b$$

$$\eta=\frac{RT}{zF}\ln\frac{C_e}{C_b}$$

Activation polarization

Butler-Volmer equation

$$i_{net} = i_o \left\{ e^{\left(\alpha \frac{nF}{RT}\eta\right)} - e^{\left(-[1-\alpha]\frac{nF}{RT}\eta\right)} \right\}; \qquad \alpha : \text{is charge transfer coefficient}$$



Determination of polarization curves