

Electrode Potential

Potential difference between electrode and electrolyte.

$$E_{\text{cell}} = E^{\circ}_{\text{Right}} - E^{\circ}_{\text{Left}}$$

Also known as Daniel Cell:

Cathode: Copper
 Anode: Zinc
 Salt bridge: Agar-Agar
 Electrolyte: ZnSO_4 , CuSO_4
 Cell reaction:
 $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$
 Cell representation:
 $\text{Zn}(s) | \text{ZnSO}_4(aq) || \text{CuSO}_4(aq) | \text{Cu}(s)$

U Shaped inverted tube connecting two electrolyte solution

Salt Bridge

Anode
 + Vely charged
 Oxidation takes place

Cathode
 + Vely charged
 reduction takes place

Faraday Laws

Faraday 1st Law
 Amount of chemical reactions which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte $\rightarrow w = Zit$

Faraday 2nd Law
 Amount of substance deposited at electrodes during electrolysis is proportional to their chemical equivalents weights $\rightarrow \frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3}$

Nature of Electrode

Medium of Electrolyte

Corrosion

Electro chemical phenomenon in which metal oxide of metal forms coating on metal surface.

Prevention

- Painting, barrier protection, rust solution.

Example

- Rusting of iron.
- Furnishing of silver.

Standard Hydrogen Electrode (SHE)

Hydrogen gas at 1 atm

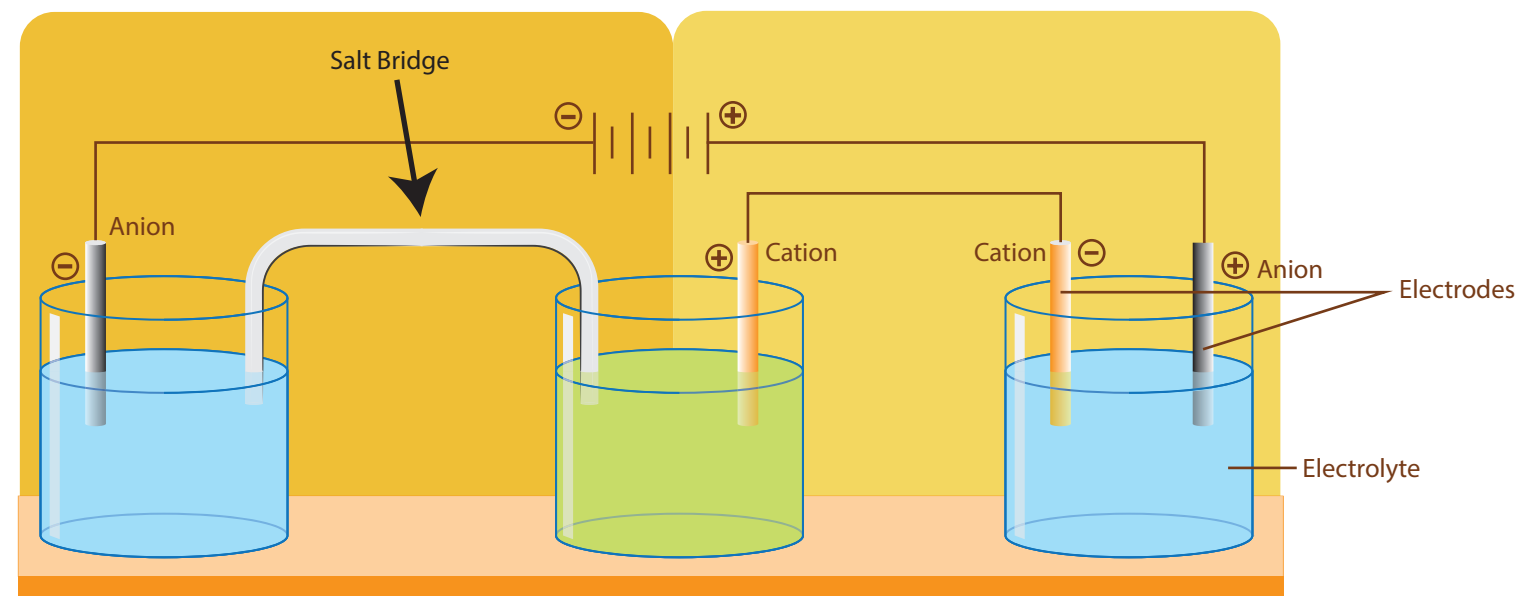
Platinum foil

Hydrogen ion

For SHE, $E^{\circ}_{\text{cell}} = 0$

Reduction Half-Reaction	$E^{\circ}(V)$
Stronger oxidizing agent	
$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$	2.87
$\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightarrow 2\text{H}_2\text{O}(l)$	1.78
$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$	1.51
$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$	1.36
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$	1.23
$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq)$	1.09
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	0.80
$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$	0.77
$\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70
$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq)$	0.54
$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$	0.40
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	0.34
$\text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}^{2+}(aq)$	0.15
$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$	0
$\text{Pb}_2^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$	0.13
$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$	0.26
$\text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s)$	0.40
$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$	0.45
$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$	0.76
$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	0.83
$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$	1.66
$\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$	2.37
weaker oxidizing agent	
$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$	-2.71
$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$	-3.04
	Stronger reducing agent

Galvanic/Voltic Cell



Electrolytic Cell

Device converting electrical energy into chemical energy.

Anode \rightarrow + vely charged: oxidation occurs

Cathode \rightarrow - vely charged: Reduction occurs

Cell representation

Oxidation half / Reduction half

Electrochemistry

Battery

(Primary)
 (reaction occurs only once cannot be reuse)

(Secondary)
 (Can be recharged by parring current f in opposite direction.)

Mercury

Anode: Zn-Hg
 Cathode: Paste HgO & C
 Electrolyte: Paste of KOH + ZnO

Lecclanche cell (dry cell)

Zn
 Graphite
 Powdered MnO_2 + C + Paste of NH_4Cl + ZnCl_2

Lead Storage battery Ni-cd cell

Pb
 Pb + PbO
 H_2SO_4 (38% by loss)

Nernst Equation

The arrangement of various electrodes in the increasing order of Standard reduction Potentials.

- For reaction: $\text{M}^{n+} + ne^- \rightarrow \text{M}(s)$

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{1}{(\text{M}^{n+})}$$
- For reaction: $aA + bB \rightarrow cC + dD$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
- A Equilibrium $E_{\text{cell}} = 0$

$$E^{\circ}_{\text{cell}} = \frac{2.303 RT}{nF} \log K_c$$
- $\Delta nG = nFE_{\text{cell}}$ or $\Delta nG = -nFE_{\text{cell}}$

Electrical Properties

- Conductance (G) = $\frac{1}{\text{Resistance}}$
 Unit: Ohm^{-1} or Siemens
- Specific conductivity (K) = $G \frac{l}{a}$ ($\frac{l}{a}$ = cell constant)
 Unit: $\text{Ohm}^{-1} \text{cm}^{-1}$ or S cm^{-1}
- Molar conductance (Λ_m) = $\frac{1000 \times K}{M}$
 Unit: $\text{Scm}^{-1}\text{mol}^{-1}$
- Equivalent conductance (Λ_{eq}) = $\frac{1000 \times K}{N}$
 Unit: $\text{Cm}^2 \text{ohm}^{-1} \text{g-eq}^{-1}$

Kohlrausch's law of Independent Migration of Ions

At infinite dilution the molar conductivity of electrolytic is given by sum of ionic conductivities of cation & anions.

$\Lambda_m^{\circ} = v_+ \lambda_+^{\circ} + v_- \lambda_-^{\circ}$

APPLICATION

- To determine Λ_m & Λ_{eq} of weak electrolyte at infinite dilution.
- To calculate degree of dissociation α : $\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}}$
- To calculate dissociation constant of weak electrolyte: $k_c = \frac{c \alpha^2}{1 - \alpha}$