Electrochemistry

Electrode Potential

Potential difference between electrode and electrolyte.

$E_{cell} = E^\circ_{right} - E^\circ_{left}$

Device converting chemical energy into electrical energy.

Also known as Daniel Cell:

Cathode: Copper
Anode: Zinc
Salt bridge: Agar-Agar
Electrolyte: $ZnSO_4$. $CuSO_4$
Cell reaction:

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Cell representation:

$Zn(s) | ZnSO_4(Sol) || CuSO_4(sol) | Cu(s)$

Salt Bridge: U shaped inverted tube connecting two electrolyte solution

Anode: Negatively charged Oxidation takes place

Cathode: Positively charged reduction takes place

Galvanic/Voltic Cell

Corrosion

Electrochemical phenomenon in which metal oxide or metal forms coating on metal surface.

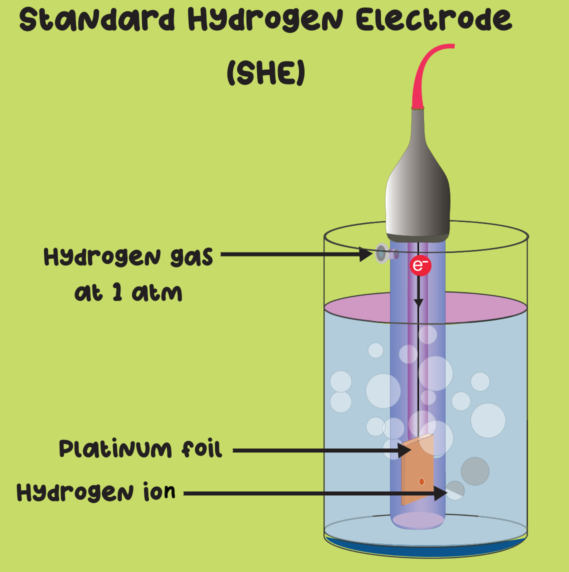
Prevention

- Painting, barrier protection, rust solutions.

Example

- Rusting of iron.
- tarnishing of silver.

Standard Hydrogen Electrode (SHE)



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

Electrochemical Series

The arrangement of various electrodes in the increasing order of standard reduction potentials.

	Reduction Half-Reaction		E°(V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2\ H_2O\ (l)$	1.78	
	$MnO_4^-\ (aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_2^{2-}\ (aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}\ (aq) + 7H_2O\ (l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(aq) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow 2Fe^{2+}\ (aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2\ (aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb_2+(aq) + 2e^-$	$\longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	-0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	-0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	-0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	1.66	
weaker oxidizing agent	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	-2.37	Stronger reducing agent
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71	
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04	

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 →

$\boxed{W = zit}$

Faraday 2nd Law

- Amount of substance deposited at electrodes during electrolysis is proportional to their chemical equivalent weights →

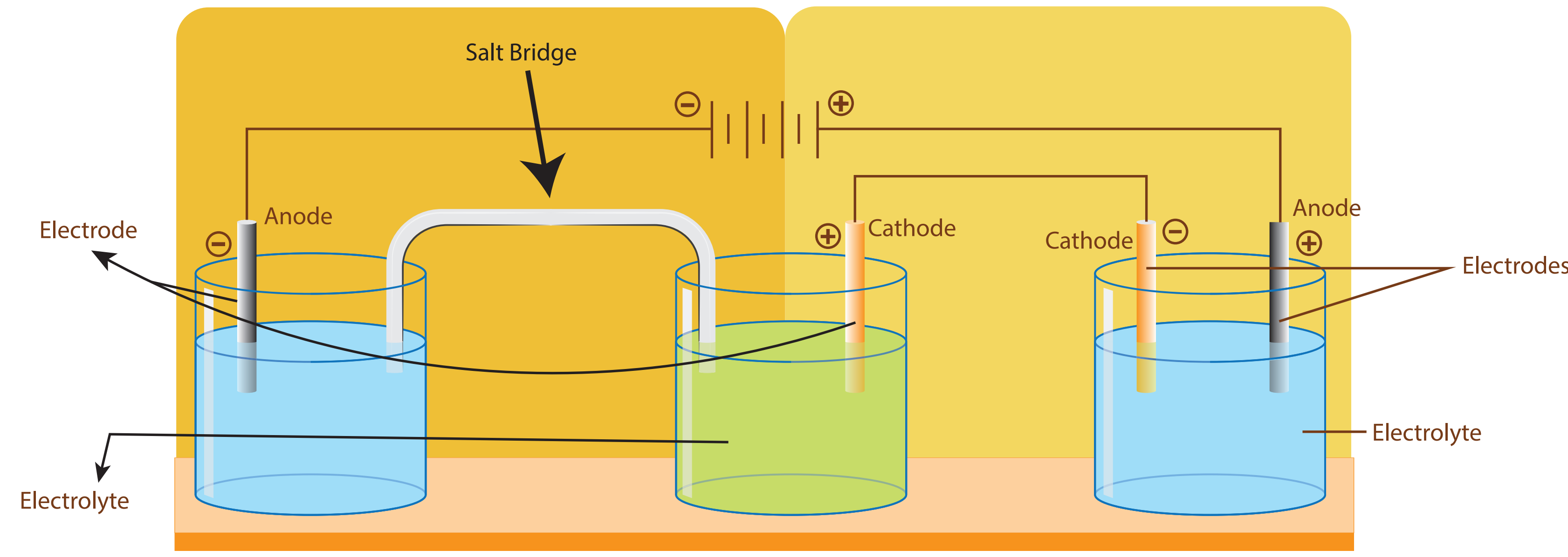
$\boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}}$

Quantitative aspects

Qualitative aspect depend on

- Nature of Electrode
- Medium of Electrolyte

Electrolytic Cell



Device converting electrical energy into chemical energy.

Anode → Positively charged: oxidation occurs
Cathode → Negetively charged: Reduction occurs

Cell representation

Oxidation half / Reduction half

Battery

Primary Battery

- reaction occurs only once.
- cannot be reuse.

Secondary Battery

Can be recharged by passing current in opposite direction.

Mercury

ANODE: Zn - Hg
CATHODE: paste of HgO & C
ELECTROLYTE: paste of KOH + ZnO

Leclanche cell (dry cell)

ANODE: Zn
CATHODE: Graphite
ELECTROLYTE: Powderd MnO_2 + C + Paste of $NH_4Cl + ZnCl_2$

Lead storage battery (Ni-Cd cell)

ANODE: Pb
CATHODE: Pb + PbO
ELECTROLYTE: H_2SO_4 (38% By mass)

Nernst Equation

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

$$E = E^\circ - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

- **For reaction:** $aA + bB \rightarrow cC + dD$

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

- **At Equilibrium** $E_{cell} = 0$

$$E^\circ_{cell} = \frac{2.303\ RT}{nF} \log K_c$$

- $\Delta G = -nFE_{cell}$ or $\Delta G = -nFE_{cell}$

Electrical Properties

- **Conductance** $[G] = \frac{1}{\text{Resistance}}$

Unit: Ohm^{-1} or Siemens

- **Specific conductivity** $(K) = G\frac{l}{a}\left(\frac{l}{a} = \text{cell constant}\right)$

Unit: $Ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$

- **Molar conductance** $(\Lambda_m) = \frac{1000 \times K}{M}$

Unit: $Scm^{-1}mol^{-1}$

- **Equivalent conductance** $(\Lambda_{eq}) = \frac{1000 \times K}{N}$

Unit: $cm^2\ ohm^{-1}\ g-eq^{-1}$

Kohlrausch's law of Independent Migration of Ions

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

$$\Lambda^0_m = \nu_+\lambda^0_+ + \nu_-\lambda^0_-$$

APPLICATION

1. To determine Λ_m & Λ_{eq} of weak electrolyt-es at infinite dilution.
2. To calculate degree of dissociation: (α) $\alpha = \frac{\Lambda^c_m}{\Lambda^0_m}$
3. To calculate dissociation constant of weak Electrolye $k_c = \frac{c\alpha^2}{1-\alpha}$