CHAPTER

3 Electrochemistry

Galvanic Cell

For a cell reaction in an electrochemical cell

$$Zn(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + ZnSO_4(aq)$$

Cell representation $\Rightarrow$ $\underset{\text{Anode}(-)}{Zn \mid Zn^{2+}(aq.)} \mid\mid \underset{\text{Cathode}(+)}{Cu^{2+}(aq.) \mid Cu}$

For half cell reaction

$M \rightarrow M^{n+}(aq.) + ne^-; E^o_{OX} = E^o_{M/M^{n+}}$

$M^{n+}(aq) + ne^- \rightarrow M;\ E^o_{red} = E^o_{M^{n+}/M}$

Emf of cell, $E^0_{cell} = E^0_{right} - E^0_{left} = \underset{R.P.}{E^0_{cathode}} - \underset{R.P}{E^0_{anode}}$

(R.P. = Reduction potential)

- Oxidation potential for half cell reaction:
  $M \rightarrow M^{+n} + ne^-$
  $$E_{OX} = E^0_{OX} - \frac{2.303RT}{nF}\log[M^{n+}]$$
- Reduction potential for half-cell reaction:
  $$M^{n+} + ne^- \rightarrow M,\ E_{red} = E^0_{red} + \frac{2.303RT}{nF}\log[M^{n+}]$$

Nernst's Equation

- $\Delta G = -nFE_{cell} = -W$
  $\Delta G = \Delta G^\circ + 2.303RT\log Q$
  $\Delta G^\circ = -nFE^o_{cell}$
  $$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log Q$$
  ΔG = Change in free energy
  W = Useful work done
  n = Number of electrons exchanged
  F = Faraday constant (96500 coulomb)
  Q = Reaction quotient
  At room temperature (25°C)
  $\Rightarrow$ Nernst's equation
  $$\Rightarrow E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log Q$$

Concentration Cell

- **For Electrode Concentration Cell**
  $Pt \mid H_2(P_1) \mid H^+(c\,M) \mid\mid H^+(c\,M) \mid H_2(P_2) \mid Pt$
  $$E_{cell} = \frac{0.0591}{2}\log\frac{P_1}{P_2};\ (P = \text{Pressure})$$
- **For Electrolyte Concentration Cell**
  $(\underset{\text{anode}(-)}{Cu \mid Cu^{2+}(C_1)} \mid\mid \underset{\text{Cathode}(+)}{Cu^{2+}(C_2) \mid Cu})$
  $$E_{cell} = \frac{0.0591}{2}\log\frac{C_2}{C_1}$$
  For concentration cells, $E^0_{cell} = 0$
- **At Equilibrium**
  $E_{cell} = 0$ (as $\Delta G = 0$)

Thermodynamics for the Cell

- **Temperature Coefficient (T.C.)**
  $$(T.C.) = \left(\frac{\partial E_{cell}}{\partial T}\right)_\rho$$
- **Change in Entropy**
  $$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$
- **Relation Between E_{Cell} & (T.C.)**
  $$E_{cell} = \left(\frac{-\Delta H}{nF}\right) + T\left(\frac{\partial E}{\partial T}\right)_p$$
  $\{\Delta H = \text{Heat of cell reaction}\}$
  $\left(\frac{\partial E}{\partial T}\right)_p > 0 \Rightarrow$ Cell reaction is endothermic and vice versa.

Quantitative Analysis

- **Faraday's 1st Law of Electrolysis**
  m = ZIt
  m = mass of substance deposited
  Z = electrochemical equivalent
  I = current
  t = time
  $$Z = \frac{\text{Atomic mass}}{n \times F}$$
- Faraday's 2nd Law of Electrolysis (Q = constant)

$$\frac{m_1}{m_2} = \frac{E_1}{E_2} \text{ (E = equivalent weight)}$$

Conductance

- **Ohm's Law**

  V = RI

  $$R = \rho\frac{\ell}{a}$$

  V = Potential difference

  R = Resistance

  I = Current

  ρ = Specific resistance (resistivity)

  ℓ = length of conductor

  a = cross-section area of conductor

- **Conductance**

  $$G = \frac{1}{R}$$

- **Specific Conductance (Conductivity)**

  $$\kappa = \frac{1}{\rho}$$

- **Cell Constant**

  $$G^* = \frac{\ell}{a}$$

  $$\kappa = G \times G^*$$

- **Molar Conductance**

  $$\Lambda_m = \frac{1000 \times \kappa}{C(\text{or } M)}$$

  {C = concentration of electrolyte in terms of molarity}

- **Equivalent Conductance**

  $$\Lambda_{eq} = \frac{1000 \times \kappa}{N}$$

  {N = Normality}

  $$\Lambda_{eq} = \frac{\Lambda_M}{(n-\text{factor})}$$

  $$\Lambda_0 = \lim_{C \to 0} \Lambda_C$$

  {Λ_0 = equivalent conductance at infinite dilution (or zero concentration)}

- **For Weak Electrolyte**

  $$\Lambda_C \propto \frac{1}{\sqrt{C}}$$

  For strong electrolyte, $\Lambda_C = \Lambda_0 - B(C)^{1/2}$ (B = constant)

- **At Infinite Dilution, for an Electrolyte A_xB_y**

  $$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

  $$\Lambda^0_{A_xB_y} = x\lambda^0_{A^{y+}} + y\lambda^0_{B^{x-}}$$

  {$\lambda^0_{A^{y+}}, \lambda^0_{B^{x-}}$ = equivalent conductance at infinite dilution of cation and anion}

- **Ionic Mobility**

  $$\mu = \frac{\text{Ionic Velocity}}{\text{Potential gradient}}$$

Degree of Dissociation

- **For a Weak Electrolyte**

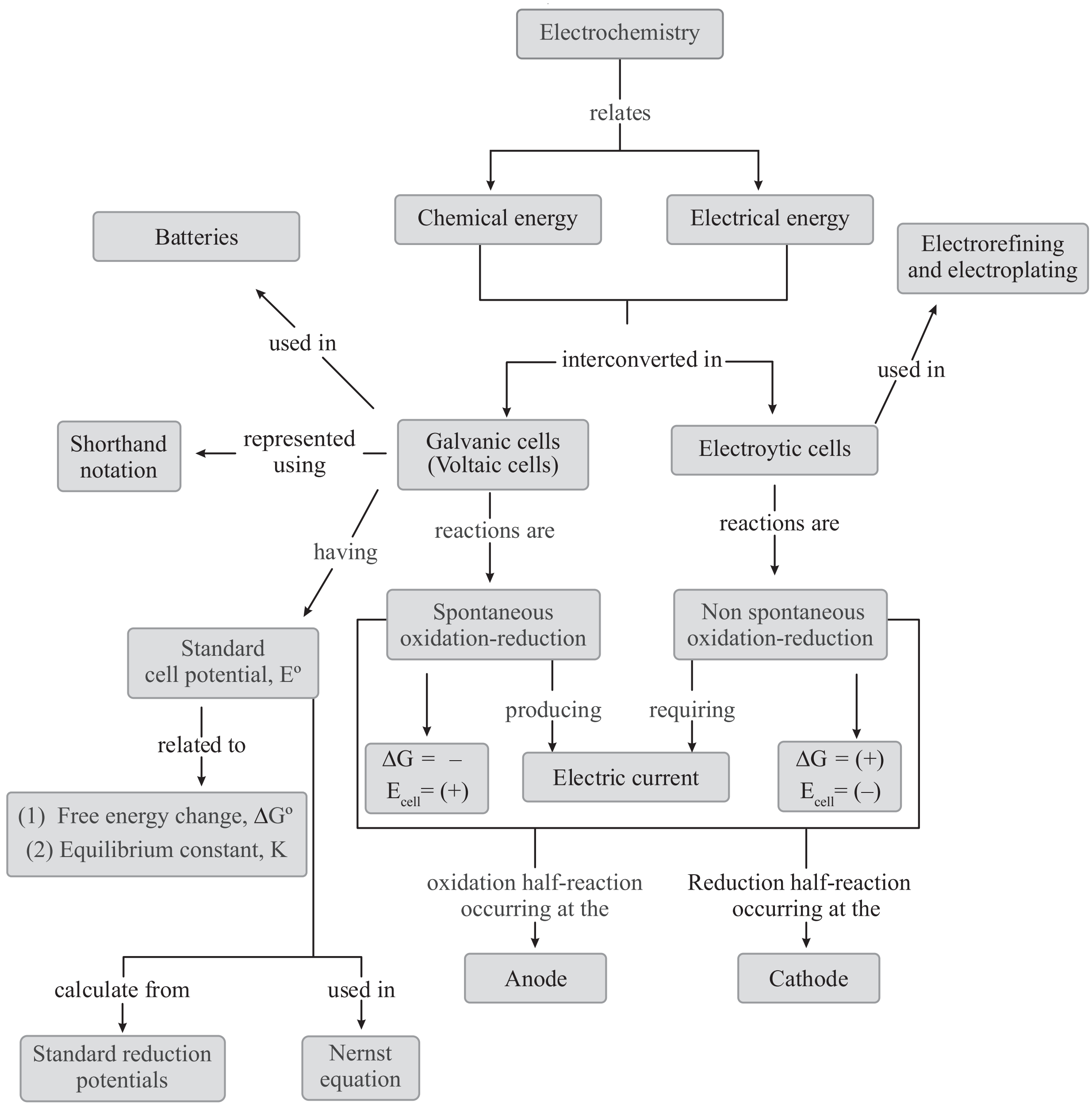
  $(CH_3COOH \rightleftharpoons CH_3COO^- + H^+)$

  $$\alpha = \frac{\Lambda_m}{\Lambda_0},\ K_a = \frac{C(\Lambda_m/\Lambda_0)^2}{1-(\Lambda_m/\Lambda_0)}$$

Solubility Product

For solubility of salt $(AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq))$

$$K_{sp} = \left(\frac{1000\kappa}{\Lambda_0}\right)^2$$


Electrochemistry
relates
Chemical energy
Electrical energy
interconverted in
Batteries
used in
Electrorefining and electroplating
used in
Shorthand notation
represented using
Galvanic cells (Voltaic cells)
Electroytic cells
having
reactions are
reactions are
Standard cell potential, E°
Spontaneous oxidation-reduction
Non spontaneous oxidation-reduction
related to
producing
requiring
ΔG = –
E_{cell} = (+)
Electric current
ΔG = (+)
E_{cell} = (–)
(1) Free energy change, ΔG°
(2) Equilibrium constant, K
oxidation half-reaction occurring at the
Reduction half-reaction occurring at the
Anode
Cathode
calculate from
used in
Standard reduction potentials
Nernst equation