Physical Chemistry
Electrochemistry

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Electrolysis and Electrolytic conductance

Electrolysis: The process of decomposition of chemical substances in presence of electricity.
Electrolytes: Electrovalent substances that form ions in solutions which conduct an electric current.
Example: all ionic substances.

Electricity and Electron: Historical reference

1. Egyptians from eel fish
2. 500 BC – Greek (Thelis) : Static current from Amber (a type of fossil)
3. 1600 – William Gilbert : de magnato – Electricus (latin)
4. Benzamin Franklin : Kite experiment – Lighning = Electricity
5. Michael Faraday : Faraday's laws of electrolysis

Faraday's Laws of Electrolysis

1st Law

The amount of substance deposited at the electrode during electrolysis is directly proportional to the current passing through the solution.

$$m \propto Q$$
$$m \propto it \qquad [Q = it]$$
$$m = Zit$$

m: deposited substance
Q: current (in Coulomb)
Z: Electrochemical equivalent
Z = 1 for i = 1 A and t = 1 s (Q = 1 C)

Electrochemical equivalent (Z): The amount of substance deposited at electrode for passing 1 C or 1 A current for 1 s time.

2nd Law

If the same quantity of electricity is passed through different electrolyte solutions for the same time, the amount of substances deposited at the electrodes is directly proportional to their equivalent weight/chemical equivalent.

$$\frac{\text{Amount of Ag deposited}}{\text{amount of Cu deposited}} = \frac{\text{Chemical equivalent of Ag}}{\text{Chemical equivalent of Cu}}$$

$$\frac{\text{Ag deposited}}{\text{Al deposited}} = \frac{\text{Chemical equivalent of Ag}}{\text{Chemical equivalent of Al}}$$

$$Ag^+ + e^- = 1F$$
$$Cu^+ + 2e^- = 2F$$
$$Al^+ + 3e^- = 3F$$

For 1 mol Ag → 1 F
For 1 mol Cu → 2 F
For 1 mol Al → 3 F

$$\text{Quantity of electricity} = n \times F$$

n: Valency of the ion
F: Faraday number (96500 C)
(Charge of 1 mole electron)

Electrolytic Conductance

The power of electrolytes to conduct electric current is termed conductivity or conductance.
Like metallic conductors, electrolytes obey Ohm's law.
The resistance of a conductor is directly proportional to its length l and inversely proportional to its cross-section A.

$$\text{Resistance, } R \propto \frac{l}{A}$$
$$R = \rho \times \frac{l}{A}$$

$$\text{Conductance, } C = \frac{1}{R} = \frac{A}{\rho l}$$

Specific Conductance

The conductacne of 1 cc electrolytic solution.

$$\kappa = \frac{1}{R} \cdot \frac{l}{A}$$

l = 1 cm
A = 1 cm^2

$$\text{Unit} = \frac{1}{ohm} \cdot \frac{cm}{cm^2} = ohm^{-1}cm^{-1} = S\ cm^{-1}$$

Equivalent Conductance

The conductance of 1 g-equivalent of electrolyte dissolved in V cc of water.

$$\Lambda = \kappa \times V$$

Λ = Equivalent conductance
V = Volume in cc

In general, if N gram-equivalent electrolyte is dissolved in 1000 cc of solution, the volume of hte solution containing 1 gram-equivalent will be $1000/N$. Thus,

$$\Lambda = \kappa \times \frac{1000}{N}$$

In the same way, if N gram-equivalent electrolyte is dissolved in V cc of solution, the volume of hte solution containing 1 gram-equivalent will be V/N. Thus,

$$\Lambda = \kappa \times \frac{V}{N}$$

$$\begin{aligned} \text{Unit: } \Lambda &= \kappa \times V \\ &= \frac{1}{R} \times \frac{l}{A} \times V \\ &= \frac{1}{ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{eqvt} \\ &= \text{ohm}^{-1} cm^2 \text{eqvt}^{-1} \end{aligned}$$

Molar Conductance

The conductance of 1 mole of electrolyte dissolved in V cc of solution.