Chapter 6

Solution of Electrolyte

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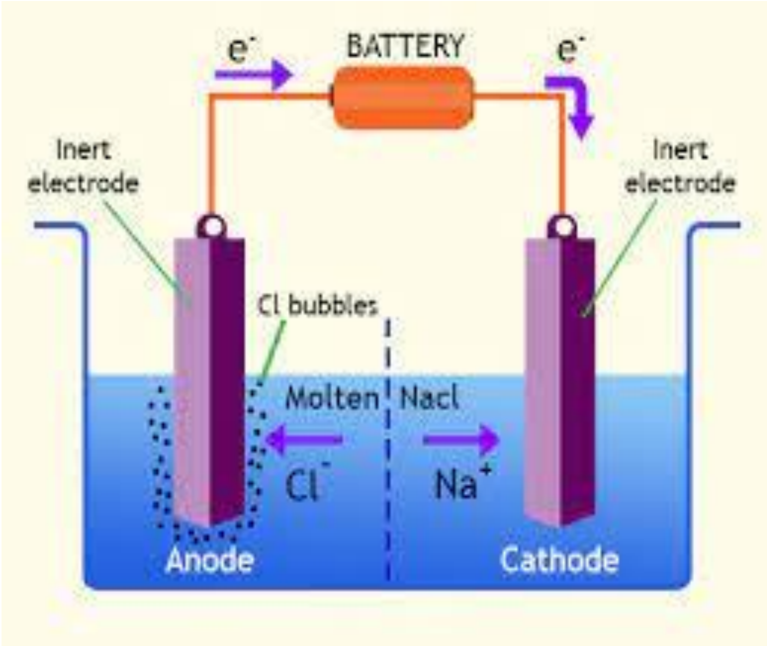
When a solute dissolved in solvent and dissociated into two ions or more, the solution called electrolyte solution.

A- strong electrolytes: are completely dissociated at moderated concentration (0.1 M).

B- weak electrolytes: are partially dissociated at moderated concentration (0.1 M).

Electrolyte properties
1- Electrolysis:

- In electrolytic cell a (DC) current flows and (redox) chemical reaction occurs.
- A- reduction (addition of **e**) occurs on cathode electrode
- $M^+ + \mathbf{e} \leftrightarrow M$
- B- oxidation (removal of **e**) occurs on anode electrode.
- $A^- \leftrightarrow A + \mathbf{e}$



Example of electrolysis

- $NaCl \leftrightarrow Na^+ + Cl^-$ **dissociation (ionization)**
- $Na^+ + \mathbf{e} \leftrightarrow Na$ **reduction reaction/cathode**
- $Na + H_2O \rightarrow NaOH + ½\ H_{2(g)}\uparrow$
- $Cl^- \leftrightarrow \mathbf{e} + ½\ Cl_{2(g)}\uparrow$ **oxidation reaction/anode**

- $NaCl \xrightarrow[H_2O]{electrolysis} NaOH + ½\ H_{2(g)}\uparrow + ½\ Cl_{2(g)}\uparrow$
- cathode anode

2- Transport

Transference number of ions t_+ and t_-

- In an electrolytic cell, the total current in solution carried by the cations and anions,
- The transferences number (t_+ , t_-) is the fraction of total current carried by ions, depend on velocity of ion.
- t_+ = ***current carried by cation/total current***
- **t-** = ***current carried by anion/total current***
- $t_+ + t_- = 1$
- $t_{\pm}$ depend on hydration, ion size and charge

- For example:
- t_{Na^+} = 0.385 in 0.1 M NaCl
- t_{Li^+} = 0.317 in 0.1 M LiCl
- Because Li^+ greatly hydrated than Na^+

3- faraday's law 1833

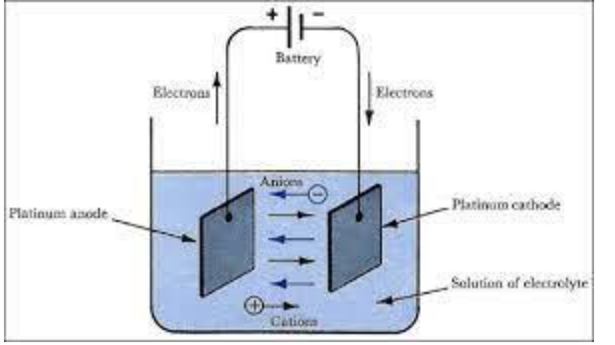
- The passage of 96,500 coulombs of electricity through an electrolytic cell produces a chemical change of 1 equivalent of any substance.

96500 coulombs≡ 1g H_2,8g O_2,35.5g Cl_2 ,108g Ag …

≡ ***1 equ., 1 equ., 1 equ., 1 equ.,…***

- N. of eq. = Q/F ⟹ $W/eq_w = It/F$
- $W = It\ eq_w/F$
- W :the weight of each substance lubricated at any electrode (cathode or anode)

4- Electrolyte conductance



- Conductance(**C**) is reciprocal of resistance (**R**)
- $C= 1/R$,
- $R= \rho l/A$,…. l: ***distance or length in cm,*** A: ***area in cm²***
- $C= A/\rho l$, ***ρ: specific resistance in Ω.cm***
- $C= \kappa A/l$,….. κ: $1/\rho$ ***specific conductance in*** $\Omega^{-1}.cm^{-1}$
- ***Ω : ohm***
- Ω^{-1} ***: mho or semence***
- So →
- $\kappa= C(l/A)$
- $\kappa= CK$,…. K: ***cell constant=(l/A)***

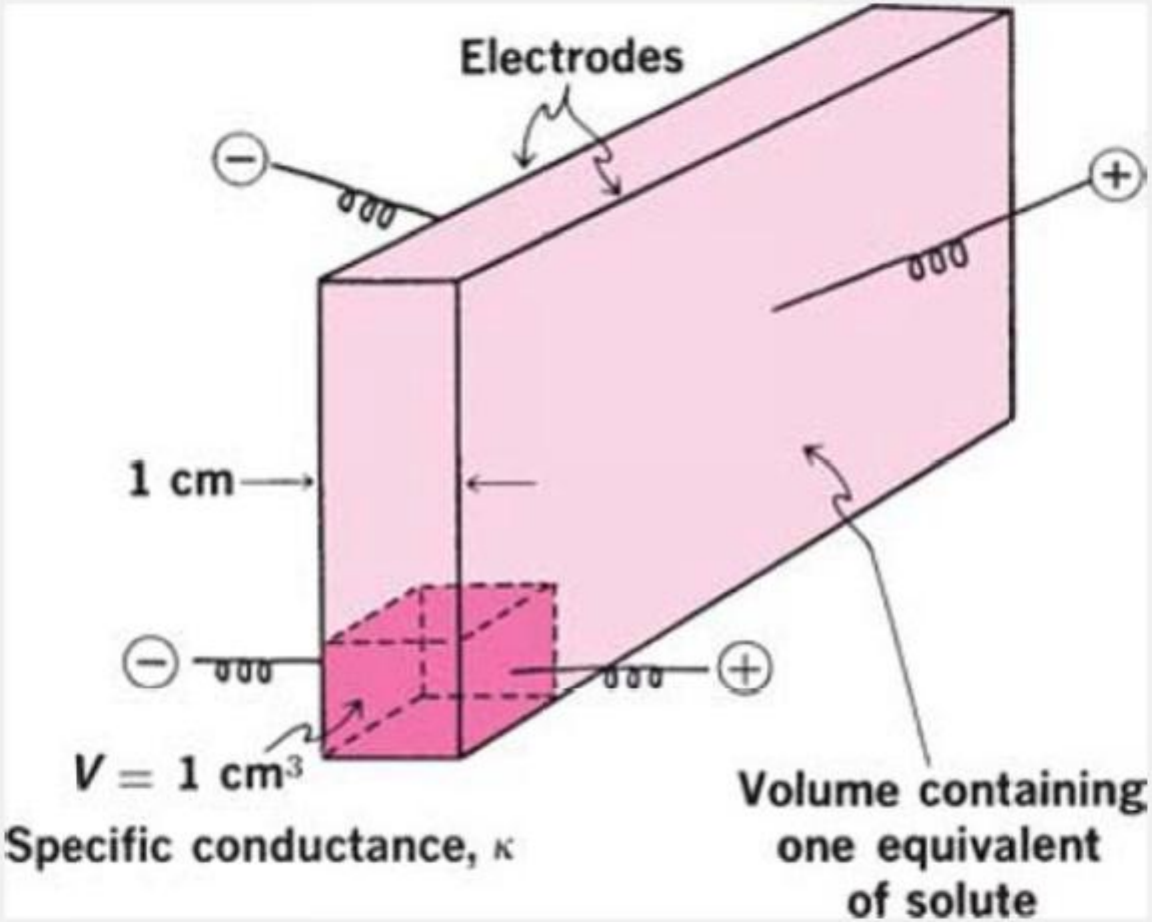


Fig. 6-2. Relationship between specific conductance and equivalent conductance.

5- Equivalent conductance (Λc)

Equivalent conductance define as the conductance of a solution has **1** eq. per cm^3 concentration when measured in a cell in which unity spaced electrode.

$\Lambda c = \kappa\ 1000\ cm^3 L^{-1} / N\ eq. L^{-1}$ ……… in unite of $\Omega^{-1} cm^2 eq^{-1}$

$\Lambda c = \kappa\ V$ …….. $V = 1000/N$ ***is the volume containing 1 eq***

So κ is the conductance per 1 cm^3 of the solution.

equation (6-19).

Example 6-1

Calculating *K*

A 0.1-demal solution of KCl was placed in a cell whose constant *K* was desired. The resistance *R* was found to be 34.69 ohms at 25°C. Thus,

$$K = \kappa R = 0.012856 \text{ mho/cm} \times 34.69 \text{ ohms} = 0.4460 \text{ cm}^{-1}$$

Example 6-2

Calculating Specific Conductance

When the cell described in Example 6-1 was filled with a 0.01 N Na_2SO_4 solution, it had a resistance of 397 ohms. What is the specific conductance? We write

$$\kappa = \frac{K}{R} = \frac{0.4460}{397} = 1.1234 \times 10^{-3} \text{ mho/cm}$$

Equivalent Conductance