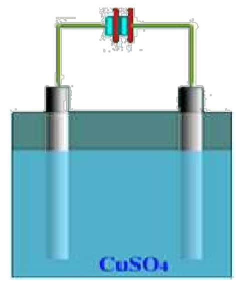
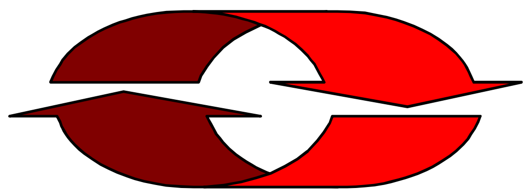
Electrochemistry



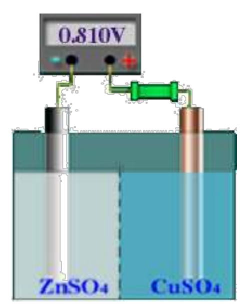
Electrolysis

Electric energy



Chemical energy

Galvanic cell



Definition of electrochemistry

- I: A science studying the relationship between chemical energy and electrical energy and the rules of conversion of two energies.

- II: Electrochemistry is the study of solutions of electrolytes and of phenomena occurring at electrodes immersed in these solutions.

Electrolytes

Substances whose solution in water conducts electric current. Conduction takes place by the movement of ions.

Examples are salts, acids and bases.

Substances whose aqueous solution does not conduct electricity are called **non electrolytes.**

Examples are solutions of cane sugar, glucose, urea etc.

Types of Electrolytes

Strong electrolyte are highly ionized in the solution.

Examples are HCl, H_2SO_4, NaOH, KOH etc

Weak electrolytes are only feebly ionized in the solution.

Examples are H_2CO_3, CH_3COOH, NH_4OH etc

Difference between electronic & electrolytic conductors

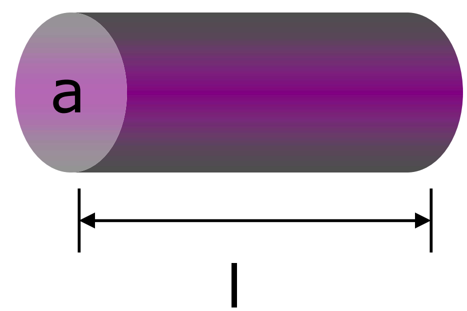
Electronic conductors	Electrolytic conductors
(1) Flow of electricity take place without the decomposition of substance.	(1)Flow of electricity takes place by the decomposition of the substance.
(2) Conduction is due to the flow of electron	(2) Flow of electricity is due to the movement of ions
(3) Conduction decreases with increase in temperature	(3) Conduction increases with increase in temperature

Resistance

Resistance refers to the opposition to the flow of current.

For a conductor of uniform cross section(a) and length(l); Resistance R,

$$R \propto l \quad \text{and} \quad R \propto \frac{l}{a} \qquad \therefore R = \rho\frac{l}{a}$$



Where ρ is called resistivity or specific resistance.

Conductance

The reciprocal of the resistance is called conductance. It is denoted by C.

$$C=1/R$$

Conductors allows electric current to pass through them. Examples are metals, aqueous solution of acids, bases and salts etc.

Unit of conductance is ohm^{-1} or mho or Siemen(S)

Insulators do not allow the electric current to pass through them.

Examples are pure water, urea, sugar etc.

Specific Conductivity

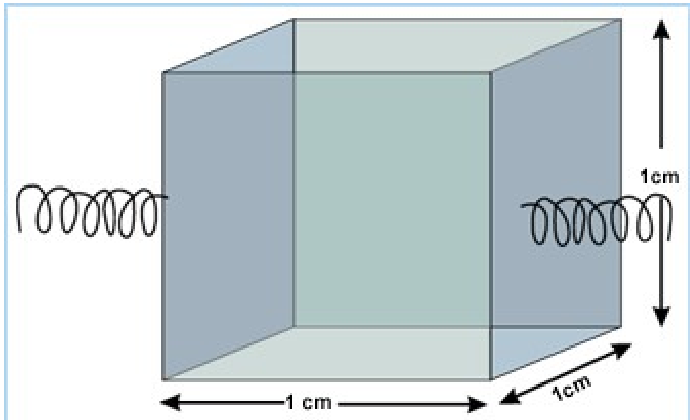
Specific conductance $\kappa = \frac{1}{\rho}$

Conductance of unit volume of cell is specific conductance.

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

$$\therefore K = \frac{\ell}{a.R}$$

$$K = \left(\frac{\ell}{a}\right) \text{ x Conductance}$$



Specific conductance

l/a is known as cell constant

Unit of specific conductance is $ohm^{-1}cm^{-1}$
SI Unit of specific conductance is **Sm^{-1}** where S is Siemen

Equivalent Conductance

It is the conductance of one gram equivalent of the electrolyte dissolved in V cc of the solution.

Equivalent conductance is represented by λ

Mathematically, $\lambda = k \times V$

$$\lambda = k \times \frac{1000}{\text{Normality}}$$

Where, k = Specific conductivity

V = Volume of solution in cc. containing one gram equivalent of the electrolyte.

Molar conductance

It is the conductance of a solution containing 1 mole of the electrolyte in V cc of solution. it is represented as μ.

$$\mu = k \times V$$

$$= k \times 1000/M$$

Where V = volume solution in cc

μ = Molar conductance

k = Specific conductance

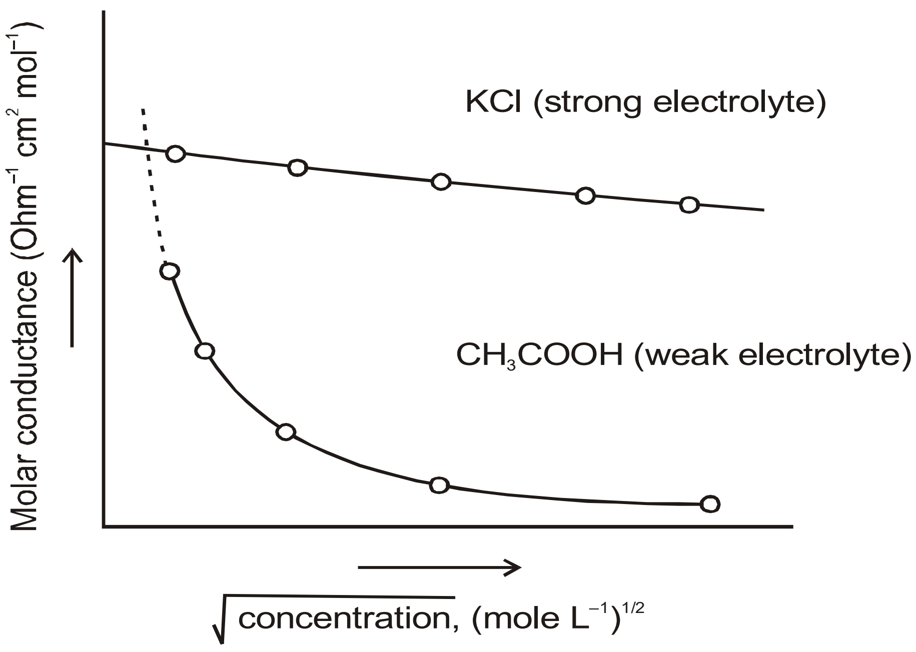
M=molarity of the solution.

Effect of Dilution on Conductivity

Specific conductivity decreases on dilution.

Equivalent and molar conductance both increase with dilution and reaches a maximum value.

The conductance of all electrolytes increases with temperature.



Relation between equivalent conductivity and molar conductivity

$\mu = \text{valency factor(or n - factor)} \times \lambda$

i.e.

Molar conductivity = n- factor x equivalent conductivity

Illustrative Example

The resistance of 0.01N NaCl solution at 25^0C is 200 ohm. Cell constant of conductivity cell is unity. Calculate the equivalent conductance and molar conductance of the solution.

Solution:

Conductance of the cell=1/resistance
=1/200
=0.005 S.

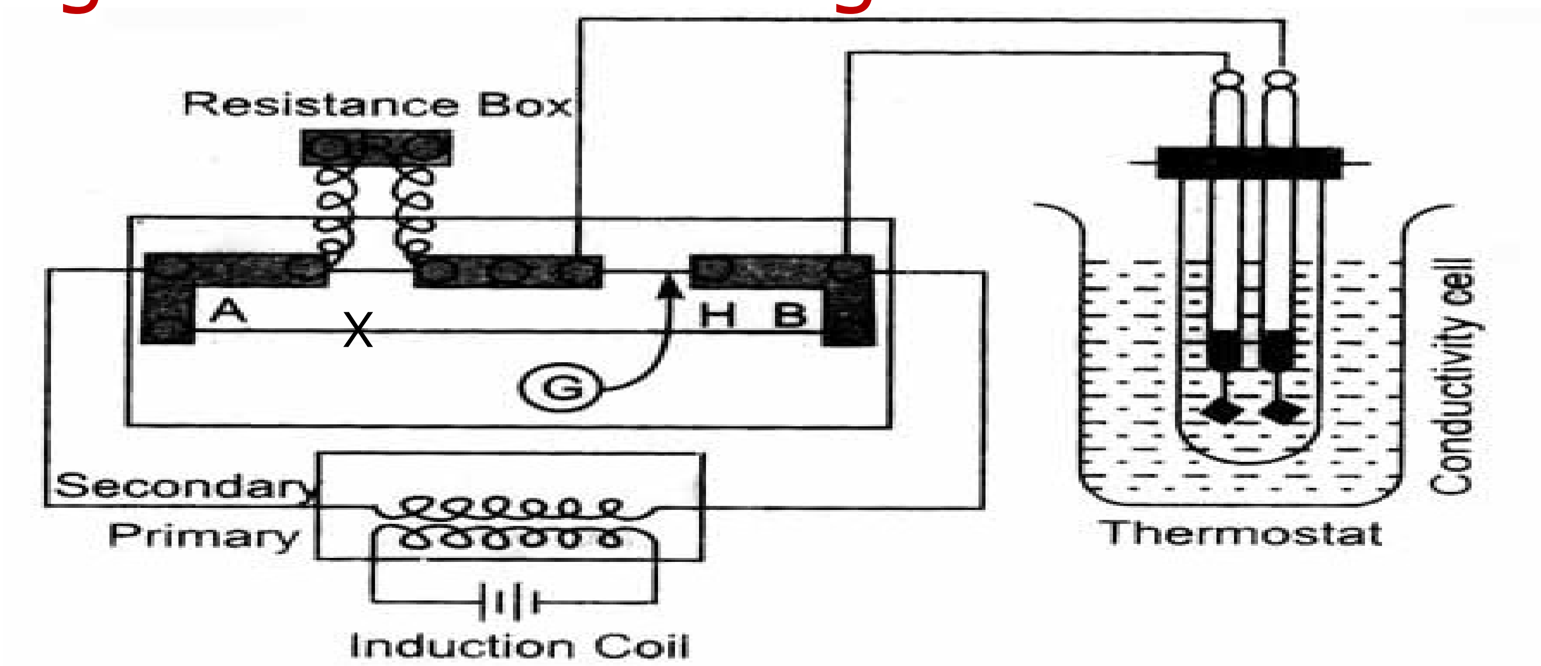
Specific conductance=conductance x cell constant
=0.005 x 1
=0.005 S cm^{-1}

Solution Cont.

Equivalent Conductance = Specific conductance x (1000/N)
= 0.005 x 1000/0.01
= 500 $ohm^{-1}cm^{2}eq^{-1}$

Molar Conductivity = Equivalent conductivity x n-factor
= 500 x 1
= 500 $ohm^{-1}mol^{-1}cm^{2}$

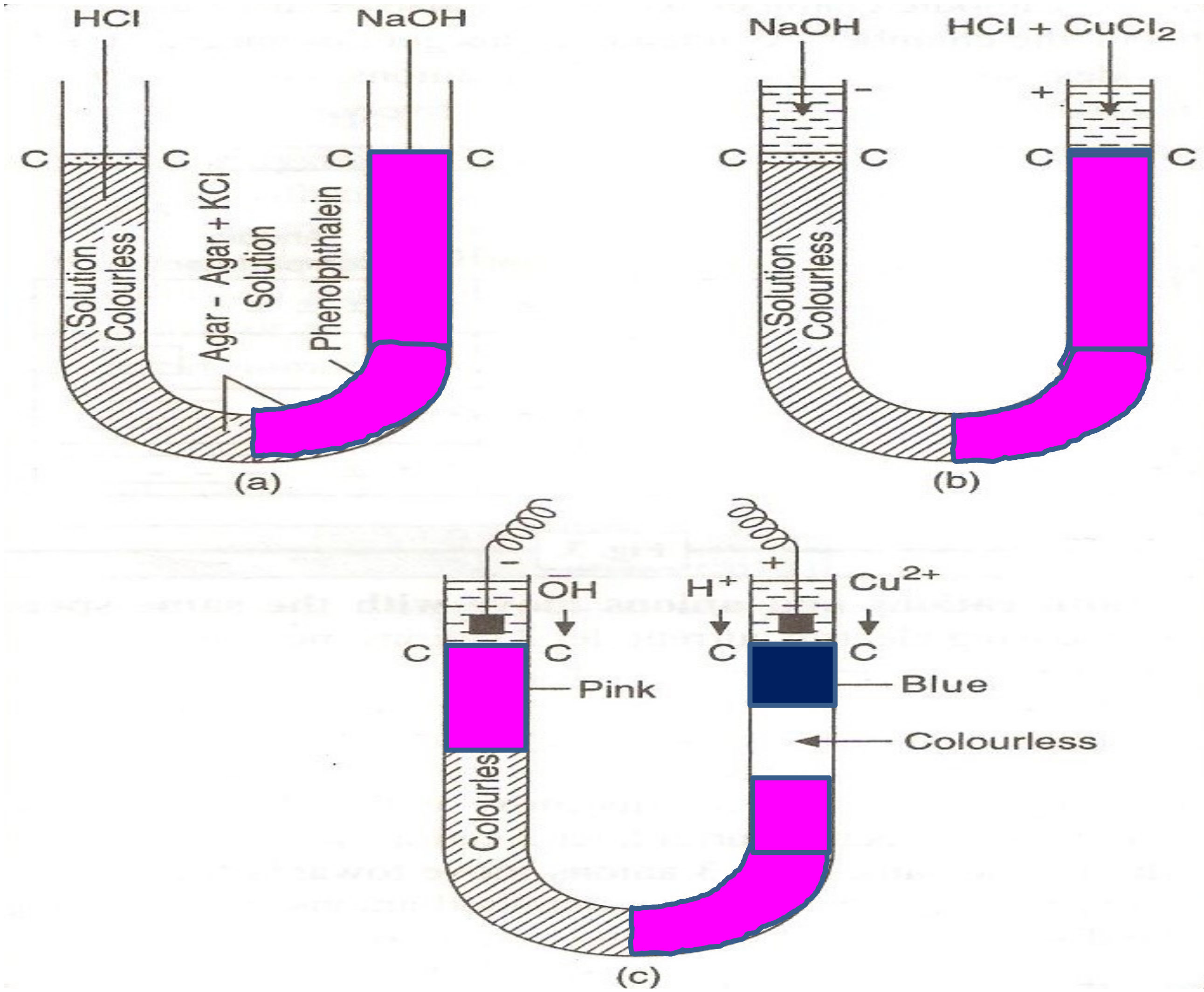
Determination of equivalent conductivity using wheatstone bridge.



Determination of specific conductivity

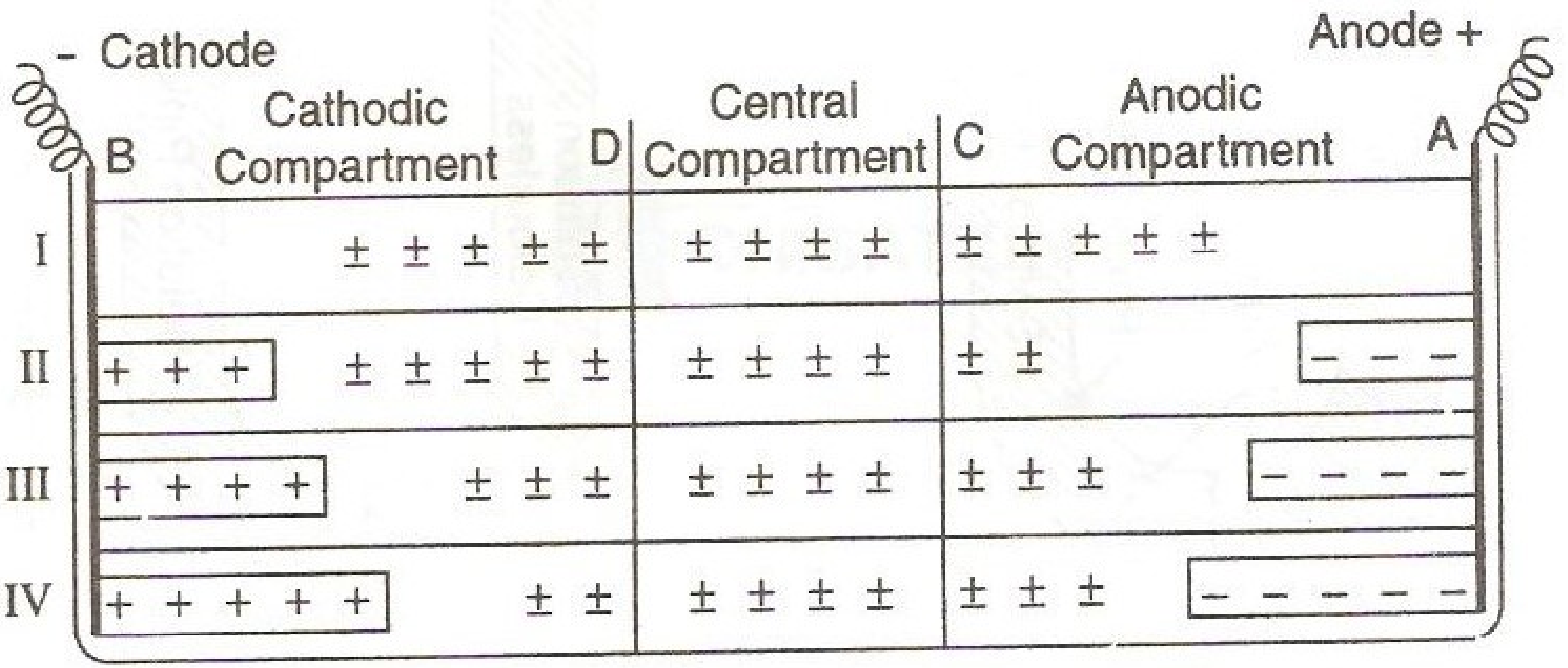
Observed conductivity of solution $= \frac{AX}{BX} \times \frac{1}{R}$

Ions move with different speeds to opposite electrodes

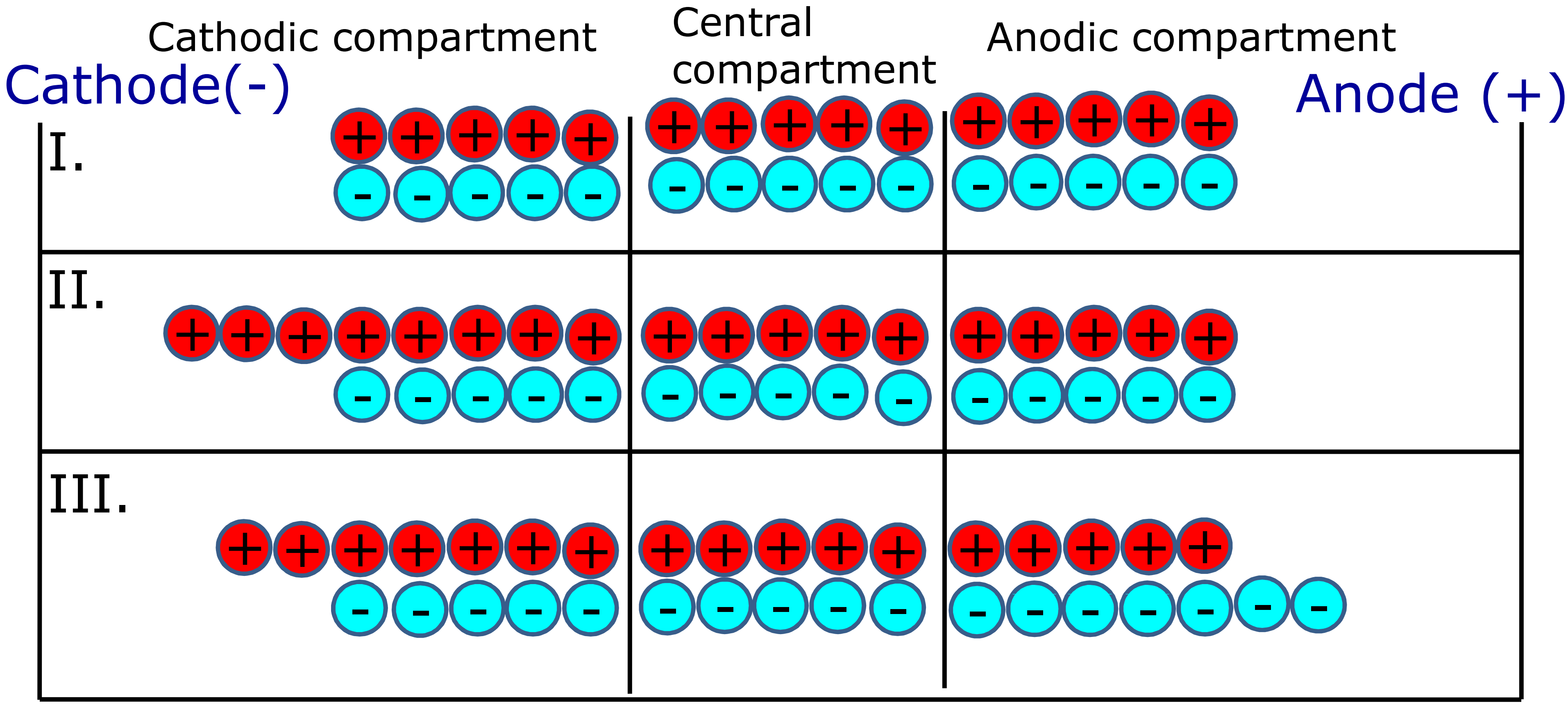


$H^{+} > OH^{-} > Cu^{2+}$

Theoretical device of Hittorf

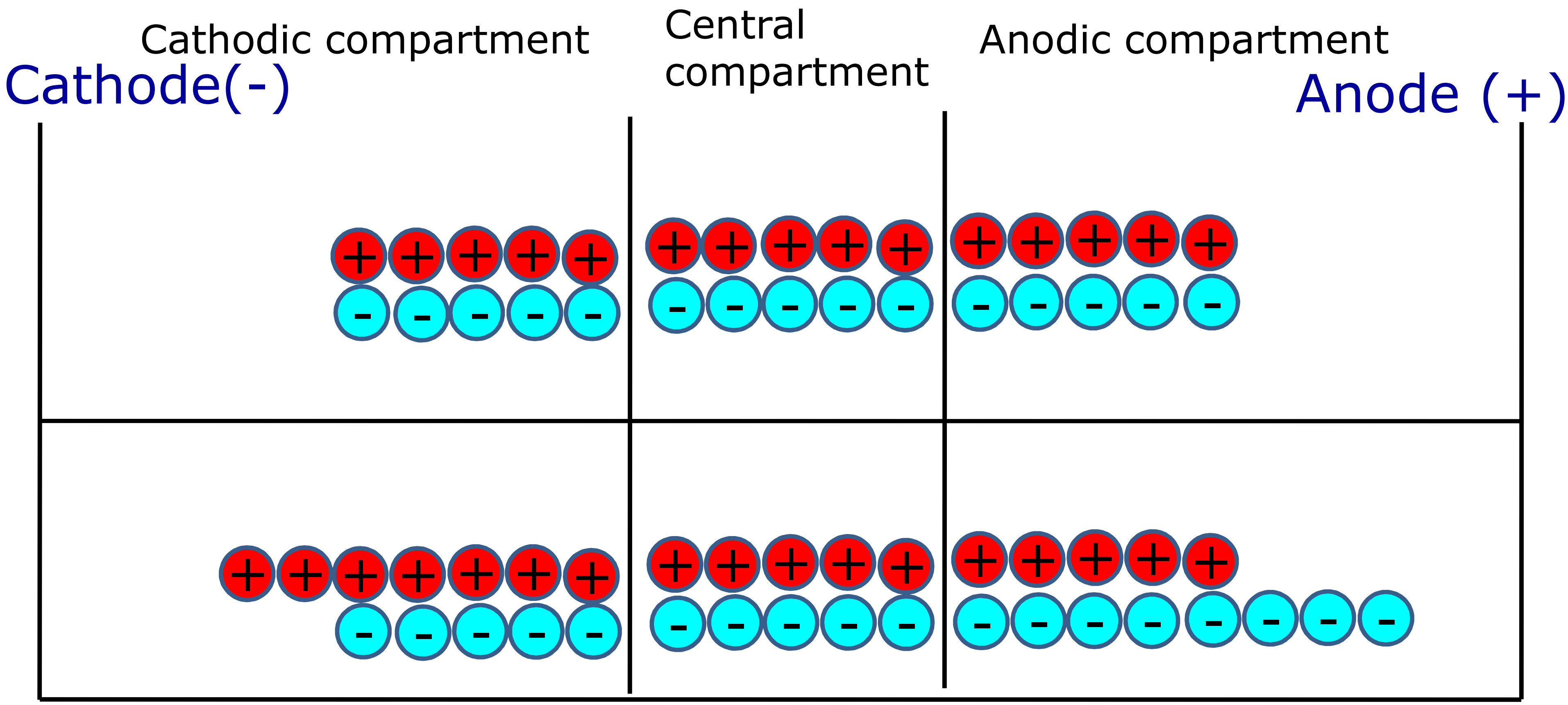


The ions are always discharged in equivalent amount, no matter what their relative speeds are and fall round electrode is proportional to the speed of ions moving away from this.



II. Only cations move: On passing electric current, let 3 cations move towards cathode.

III. Both cations and anions move with the same speed: Let two cations move towards cathode and at the same time, two anions move towards anode with the same speed.



IV. Both cations and anions move with different speeds:

Let 2 cations move towards cathode and in the same time three anions move towards anode.

$$\frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{2}{3} = \frac{\text{Fall in concentration round anode}}{\text{Fall in concentration round cathode}}$$

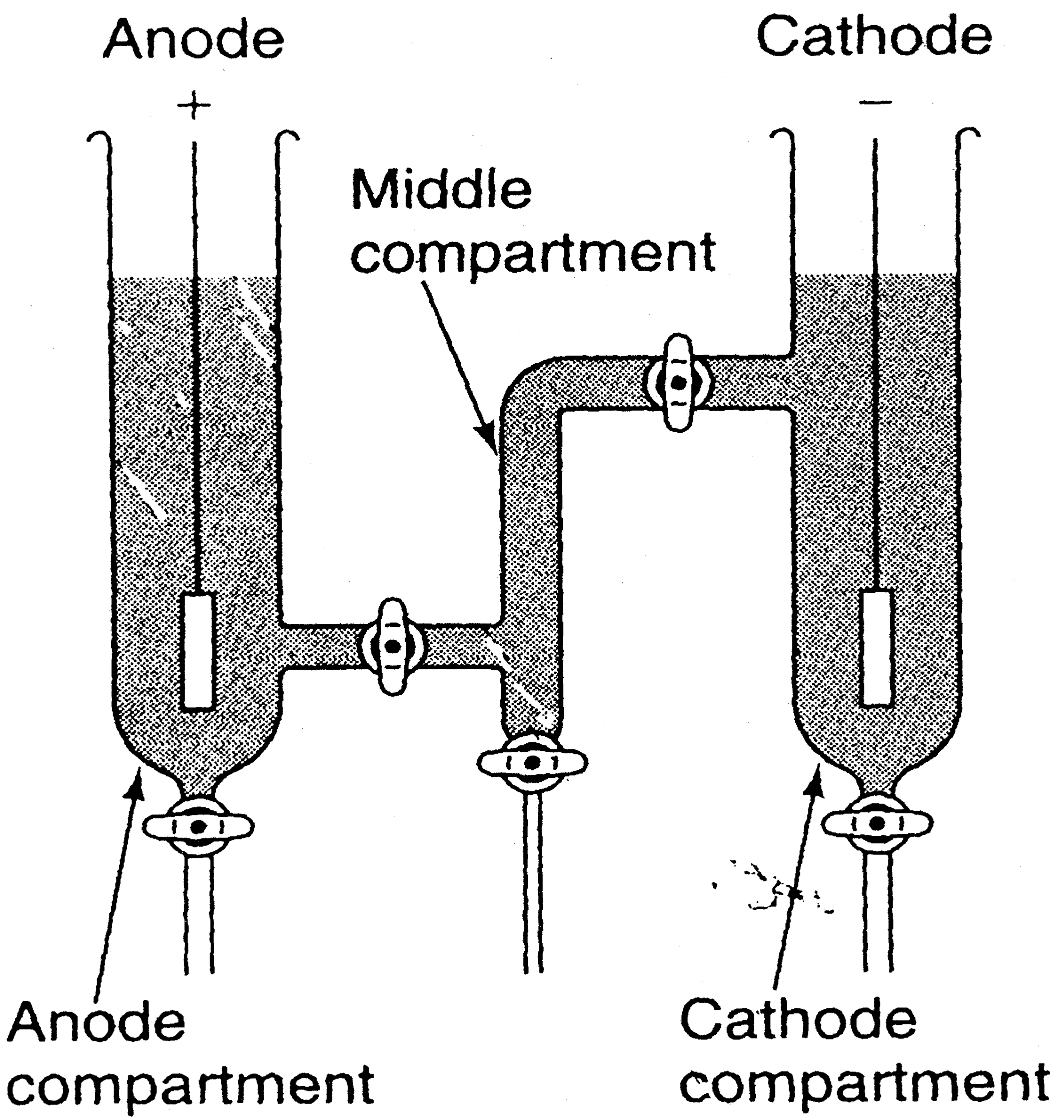
Transport or Hittorf Number

- The transport numbers of ions depend on the properties of ions and solvents, temperature, concentration, electric field strength and the like.
- The mobility u_B of an ion B is defined as its velocity in the direction of an electric field *E* of unit strength

$$u_B = v_B / E$$

$$t_+ = \frac{u_+}{u_+ + u_-} \qquad t_- = \frac{u_-}{u_+ + u_-} \qquad t_+ + t_- = \frac{u_+}{u_+ + u_-} + \frac{u_-}{u_+ + u_-} = 1$$

Measurement of transport numbers by Hittorf method



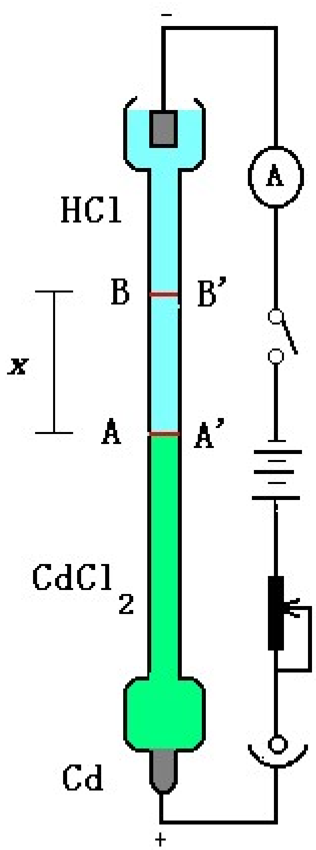
The method of Hittorf is based on concentration changes in the anodic region and cathodic region in an electrolytic cell, caused by the passage of current through the electrolyte.

$$t_+ = \frac{\text{Fall in concentration round anode}}{\text{Total fall in concentration}}$$

If we attach silver voltameter in series than total fall in concentration is equal to the amount of silver deposited in the volatameter.

$$t_+ = \frac{\text{Fall in concentration round anode}}{\text{Amount of silver deposited in silver voltameter}}$$

Measurement of transport number by the moving boundary method



Suppose the boundary moves a distant x from AA′ to BB′ for the passage of Q coulombs. All the ions, H^+, passed through the boundary AA′.

The amount of substances transported is then Q/F, of which t_+Q/F are carried by the positive ion. If the volume between the boundaries AA′ and BB′ is V, and the concentration of HCl is c, then

$$t_+Q/F = Vc$$

$$t_+ = \frac{FVc}{Q}$$

Kohlrausch's Law

"Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

Where λ_a and λ_c are known as ionic conductance of anion and cation at infinite dilution respectively.

Law of the independent migration of ions

Kohlrausch discovered relations between the values of Λ_m^∞ for different electrolytes. For example:

$$\Lambda_m^\infty(\text{KCl}) = 0.01499\ \text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$$

$$\Lambda_m^\infty(\text{LiCl}) = 0.01150\ \text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$$

$$\Lambda_m^\infty(\text{KNO}_3) = 0.01450\ \text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$$

$$\Lambda_m^\infty(\text{LiNO}_3) = 0.01101\ \text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$$

The difference in four pairs of salts having common ion is always approximately constant.

$$\Lambda_m^\infty(\mathrm{KCl}) - \Lambda_m^\infty(\mathrm{LiCl}) = \Lambda_m^\infty(\mathrm{KNO_3}) - \Lambda_m^\infty(\mathrm{LiNO_3}) = 0.00349\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

$$\Lambda_m^\infty(\mathrm{KCl}) - \Lambda_m^\infty(\mathrm{KNO_3}) = \Lambda_m^\infty(\mathrm{LiCl}) - \Lambda_m^\infty(\mathrm{LiNO_3}) = 0.00049\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

This behavior indicates that ions in an extremely dilute solution migrate independently. There is no interaction between different ions. Therefore

$$\Lambda_m^\infty = \nu_+ \Lambda_{m,+}^\infty + \nu_- \Lambda_{m,-}^\infty$$

For example

At 25℃,

Λ_m^∞ (NaAc) = 91.0×10^{-4} S·m^2·mol^{-1},

Λ_m^∞ (HCl)=426.2×10^{-4} S·m^2·mol^{-1},

Λ_m^∞ (NaCl)=126.5×10^{-4} S·m^2·mol^{-1},

What is the molar conductivity of HAc at 25℃?

Solution

$$\Lambda_m^\infty(\mathrm{NaAc}) = \Lambda_m^\infty(\mathrm{Na^+}) + \Lambda_m^\infty(\mathrm{Ac^-})$$

$$\Lambda_m^\infty(\mathrm{HCl}) = \Lambda_m^\infty(\mathrm{H^+}) + \Lambda_m^\infty(\mathrm{Cl^-})$$

$$\Lambda_m^\infty(\mathrm{NaCl}) = \Lambda_m^\infty(\mathrm{Na^+}) + \Lambda_m^\infty(\mathrm{Cl^-})$$

$$\Lambda_m^\infty(\mathrm{HAc}) = \Lambda_m^\infty(\mathrm{H^+}) + \Lambda_m^\infty(\mathrm{Ac^-})$$

$$= \Lambda_m^\infty(\mathrm{H^+}) + \Lambda_m^\infty(\mathrm{Cl^-}) + \Lambda_m^\infty(\mathrm{Na^+}) + \Lambda_m^\infty(\mathrm{Ac^-})$$

$$- \Lambda_m^\infty(\mathrm{Na^+}) - \Lambda_m^\infty(\mathrm{Cl^-})$$

$$= \Lambda_m^\infty(\mathrm{HCl}) + \Lambda_m^\infty(\mathrm{NaAc}) - \Lambda_m^\infty(\mathrm{NaCl})$$

$$= (426.3 + 91.0 - 126.5) \times 10^{-4} \quad \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

$$= 390.7 \times 10^{-4} \quad \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

Application of Kohlrausch' s law

(1). It is used for determination of **degree of dissociation** of a weak electrolyte.

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

Where,

λ^∞ represents equivalent conductivity at infinite dilution.

λ_v represents equivalent conductivity at dilution v.

(2). For obtaining the equivalent conductivities of weak electrolytes at infinite dilution.

Illustrative Example

A decinormal solution of NaCl has specific conductivity equal to 0.0092.If ionic conductance of Na^{+} and Cl^{-} ions are 43.0 and 65.0 ohm^{-1} respectively. Calculate the degree of dissociation of NaCl solution.

Solution:

Normality=0.10 N

Equivalent conductance of NaCl

$$\lambda_V = \text{Sp.conductivity} \times \frac{1000}{N}$$

$$= .0092 \times 10000$$

$$= 92 \ \text{ohm}^{-1}$$

$$\lambda_\infty = \lambda_{Na^+} + \lambda_{Cl^-} = 43 + 65 = 108$$

$$\therefore \alpha = \frac{\lambda_V}{\lambda_\infty} = \frac{92}{108} = 0.85$$

Illustrative Example

Equivalent conductance of NaCl, HCl and C_2H_5COONa at infinite dilution are 126.45, 426.16 and 91 $ohm^{-1}\ cm^2$ respectively.Calculate the equivalent conductance of C_2H_5COOH.

Solution:

$$\lambda_\infty\ C_2H_5COOH = \lambda_\infty\ C_2H_5COONa + \lambda_\infty\ HCl - \lambda_\infty\ NaCl$$

$= 91 + 426.16 - 126.45$

$= 390.71\ ohm^{-1}\ cm^2$

Illustrative Example

Calculate (a) the degree of dissociation and (b) the dissociation constant of 0.01M CH_3COOH solution; given the conductance of CH_3COOH is 1.65×10^{-4} S cm^{-1} and λ_m^o (CH_3COOH) = 390.6 S cm^2 mol^{-1}

Solution :

$$\lambda_m^c = \frac{K \times 1000}{\text{Molarity}}$$

$$\lambda_m^c = \frac{1.65 \times 10^{-4} \times 1000}{0.01} = 16.5 \text{ S cm}^2 \text{mol}^{-1}$$

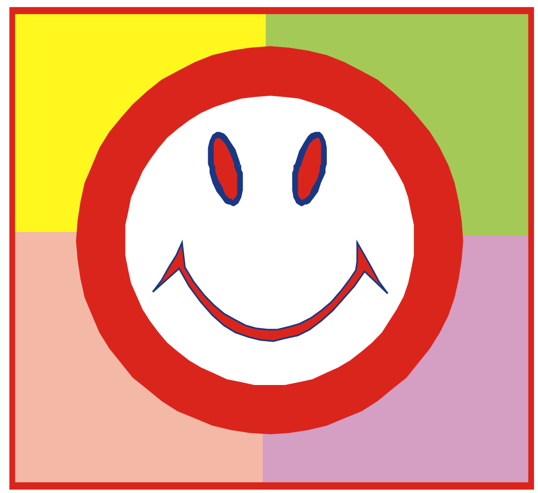
$$\alpha = \frac{\left(\lambda_m^c\right)}{\left(\lambda_m^o\right)}\lambda \qquad = \frac{16.5}{390} = 0.042$$

Solution

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

$$\frac{0.01 \times (0.042)^2}{1-0.042}$$

$$= 1.84 \times 10^{-5}$$



Thank you