# *Chemical Kinetics and Electrochemistry (Chem. 3062)*

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Introduction

- **Electrochemistry**: is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an **electron conductor** (a metal or a semiconductors) and **an ionic conductor** (the electolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution.
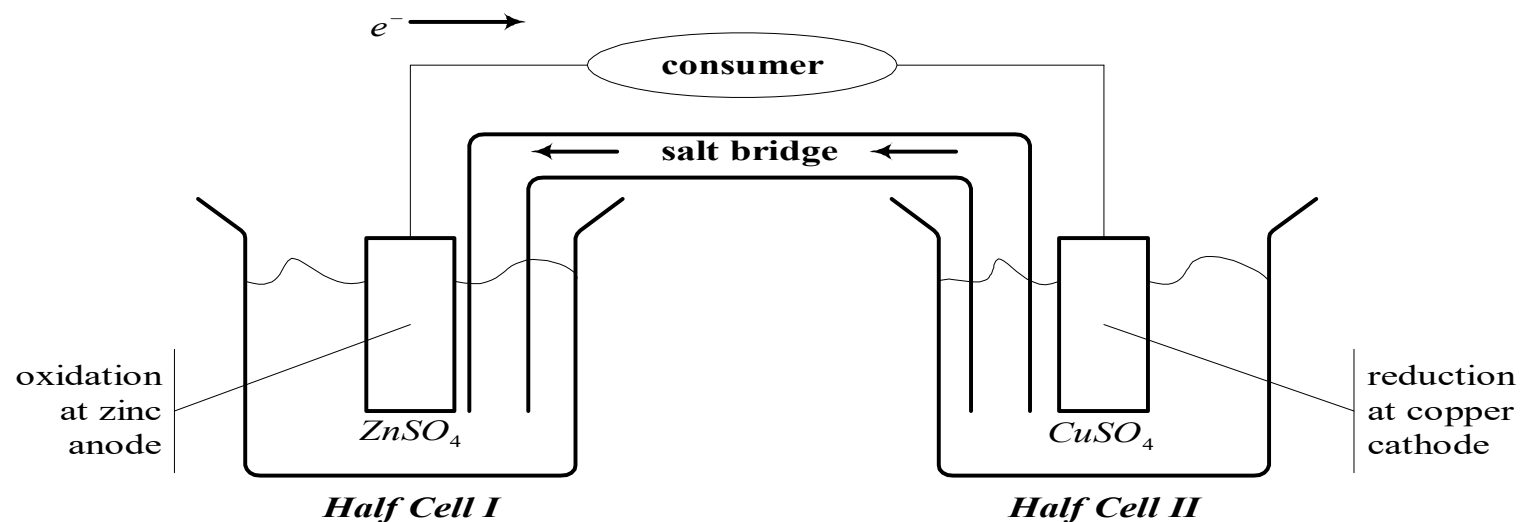
Fig 1. Electrochemical Cell

What is electrolytic conductivity?

✚ **An electric current** is a flow of electric charge. The flow of charge is carried by a conductor. Current is related to electric charge; $I = Q/t$. and unit of electric current is ampere, A. An amp is the flow of 1 C of charge per second.

There are two types of conductors:

1. **Electronic conductor:** The flow of charge in an electronic conductor is due to a flow of electrons.

◆ Therefore **no transfer** of material. Ex, Metals are electronic conductors.

2. Electrolytic conductor (electrolytes): The flow of charge in an electrolytic conductor is due to the movement of ions.

◆ There is thus a **transfer** of material. Ex, pure substances, such as molten salts, or solutions of salts, acids or bases in water.

Electrolytes

■ **Electrolyte** is a compound which produces an ionic solution when dissolved in an aqueous solution. Or

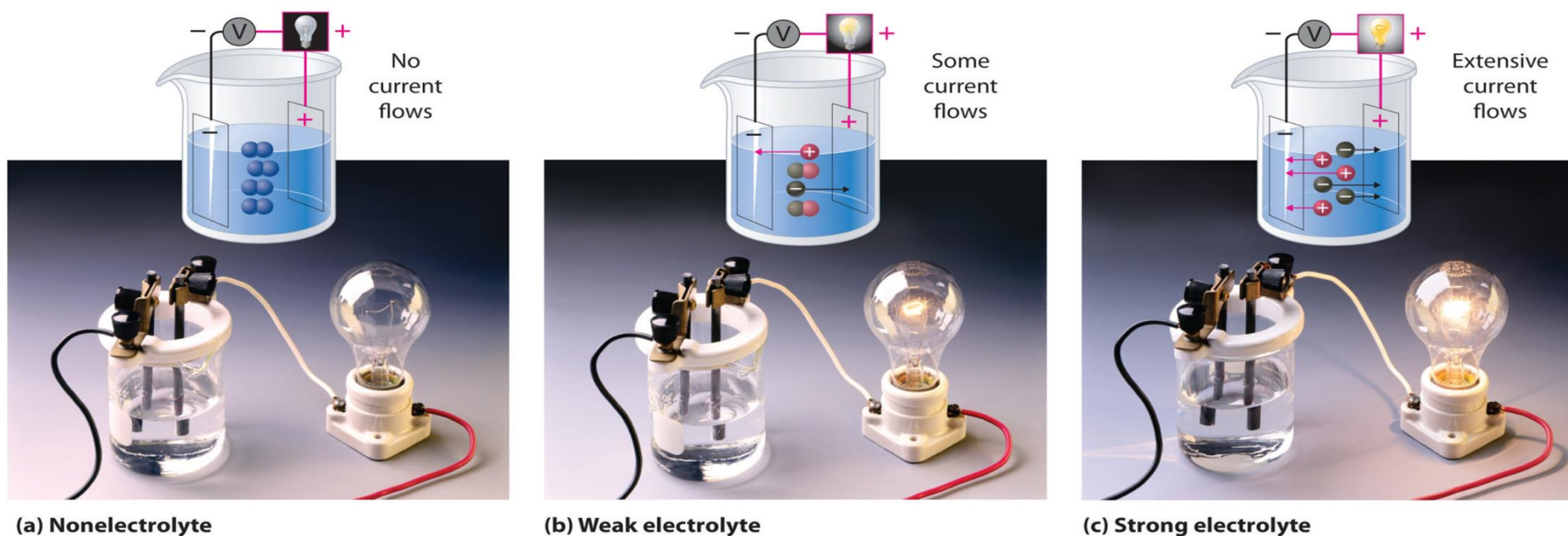■ The solution in which electricity is passed and causes ions to move towards their respective electrodes.

(a) Nonelectrolyte   (b) Weak electrolyte   (c) Strong electrolyte

Fig 2. Light bulb test (a, b and c).

Electronic vs ionic conductivity

■ **Electronic conductivity:** current is transported by electrons.

    i) conductors
    ii) semi conductors
    iii) insulators

■ **Ionic conductivity:** current is transported by ions.

    i) strong electrolytes
    ii) weak electrolytes
    iii) non electrolytes

Material	k (Scm^{-1})
Ag	1.59×10^5
Cu	1.68×10^5
Au	2.44×10^5
Pt	1.06×10^4
C (amorphous)	$5\text{-}8 \times 10^1$
C (graphite)	$2.5\text{-}5.0 \times 10^3$ / 3.0×10^1
Ge	4.6×10^{-2}
Si	10^{-1} - 10^{-5}
Water	10^{-9}
Glass	10^{-16} - 10^{-12}
PTFE (Teflon)	10^{-16} -10^{-12}

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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

Electric Units

- **Resistance (R)** is the opposition of flow of charge. The SI unit of resistance is the ohm (Ω).

- **Voltage (V)** is a potential energy (electric potential) that drives electric charge through a circuit. The SI unit of potential difference is the volt (V). i.e., $V = IR$

- **Conductance (G)** is the reciprocal of electrical resistance. The unit of electrical conductance is siemens (S) or mho (Ω^{-1}). i.e.,

$$G = 1/R$$

- **Resistivity (ρ)** is the length and cross-sectional area of a conductor are related to its resistance. The unit of resistivity is ohm meters (Ωm).

  i.e., $\rho = RA/L$

- **Conductivity (specific conductivity) (κ)** is the reciprocal of resistivity. The unit of specific conductivity is $\Omega^{-1}m^{-1}$ or Sm^{-1}

  i.e., $\kappa = 1/\rho = L/AR$

Example 1

1) A 0.40 amp current is produced when a 12 Volt battery is connected to a headlight. How much resistance is produced by the headlight?

Solution:

by using Ohm's law: R = V/I

$$= 12 \text{ V}/0.40\text{Amps}$$

R = 30 Ohms

Types of Electrolytes

■ Based on the extent of dissociation, electrolytes are classified into two types, but in general we categorized in to three:

1. **Strong electrolytes:** The electrolytes which completely dissociate into ions in aqueous solution. For example, HCl, HNO_3, NaOH, KOH, NaCl and KCl.

2. **Weak electrolytes:** The electrolytes which do not undergoes complete dissociation into its ions in aqueous solution. For example, CH_3COOH, H_2CO3 and NH_4OH.

3. **Non electrolytes**: Substances whose aqueous solution does not conduct electricity. For examples, solutions of cane sugar, glucose, urea etc.

(I) Strong Electrolytes

■ Completely **dissociates in solution** and produce ions.

$$Ex: NaCl \rightarrow Na^+(aq) + Cl^-(aq)$$

❖ **It can be:**

● Ionic compounds (metal and nonmetal)

  ✓ Ex: $BaCl_2$

● Strong acids (contains H^+ ion)

  ✓ Ex: HCl

● Strong bases (contains OH^- ion)
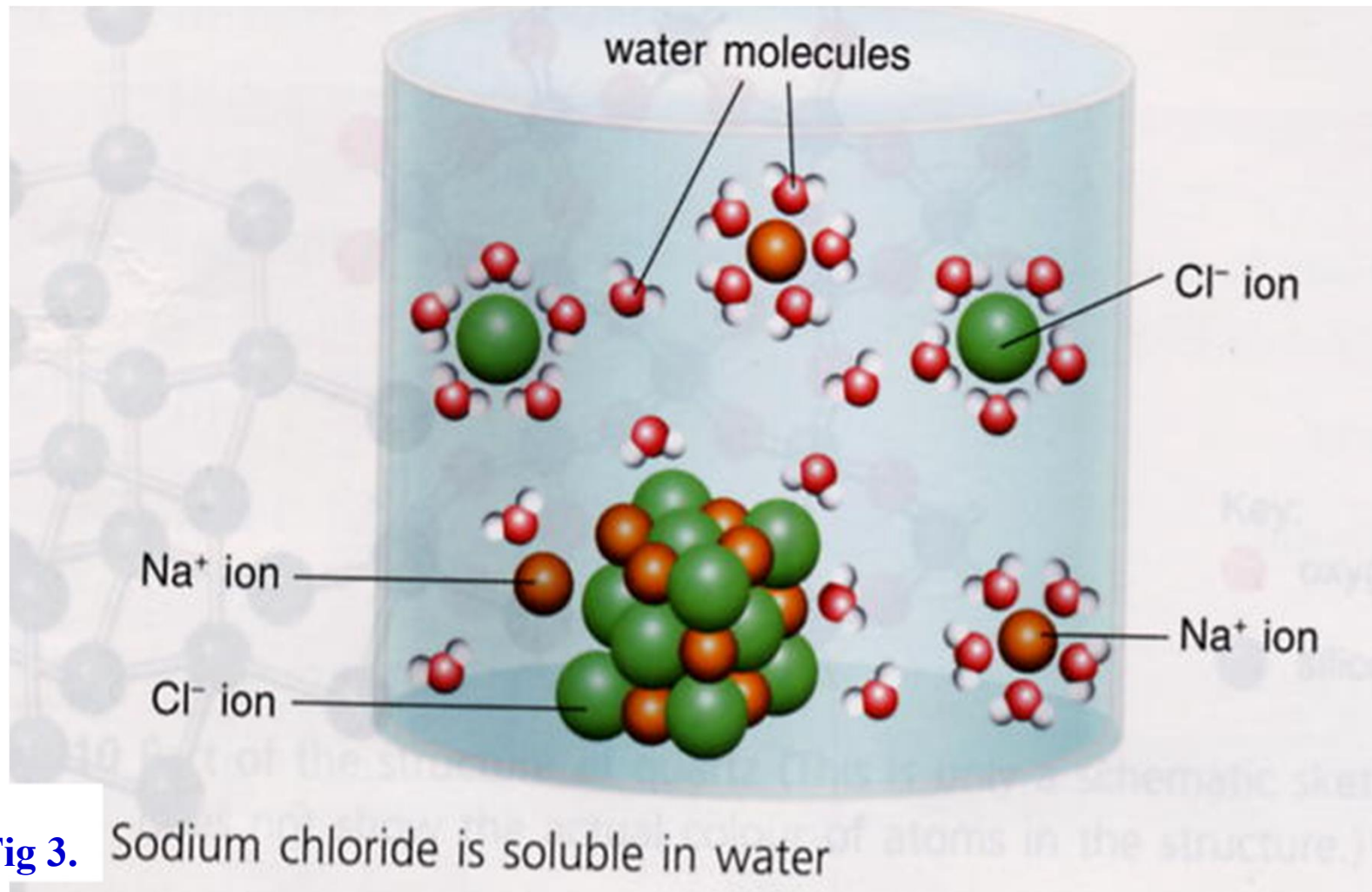
  ✓ Ex: NaOH

● Salts

  ✓ Ex: NaCl

NB: Solid Ionic compounds are non-conductors of electricity because ions are held by strong electrostatic forces and are not mobile.

How sodium chloride dissolves in water?

Fig 3. Sodium chloride is soluble in water

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- When the attractive forces b/n ions and water molecules are greater than that between **oppositely charged ions**, the ionic compound dissolves in water.

- However, some ionic compounds are insoluble in water. (i.e., Attractive forces between ions and water are smaller than that between oppositely charged ions.)

✓ Ex, Limestone (calcium carbonate), copper (II) oxide

Measuring electrolytic conductivity

➡ The electrolytic conductivity of a solution can be determined using a conductivity cell.

➡ This consists of a glass cell containing two electrodes of known area rigidly fixed at a set distance apart (1 cm).

➡ The electrodes are made of platinum black.

➡ The cell is dipped into the electrolyte solution, made up using conductivity water. This water has been passed through an ion exchange column.

NB: Normally distilled water is not suitable since it contains traces of ions H^+ and HCO_3^- from dissolved CO_2. These ions give the water a conductivity of the order $10^{-5}\ \Omega^{-1}cm^{-1}$. i.e., k.

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- The resistance of the cell is measured using a Wheatstone bridge circuit (see Fig 4). The sliding contact is adjusted until a minimum response is obtained on the oscilloscope. The resistance of the cell, R_{cell}, given by:
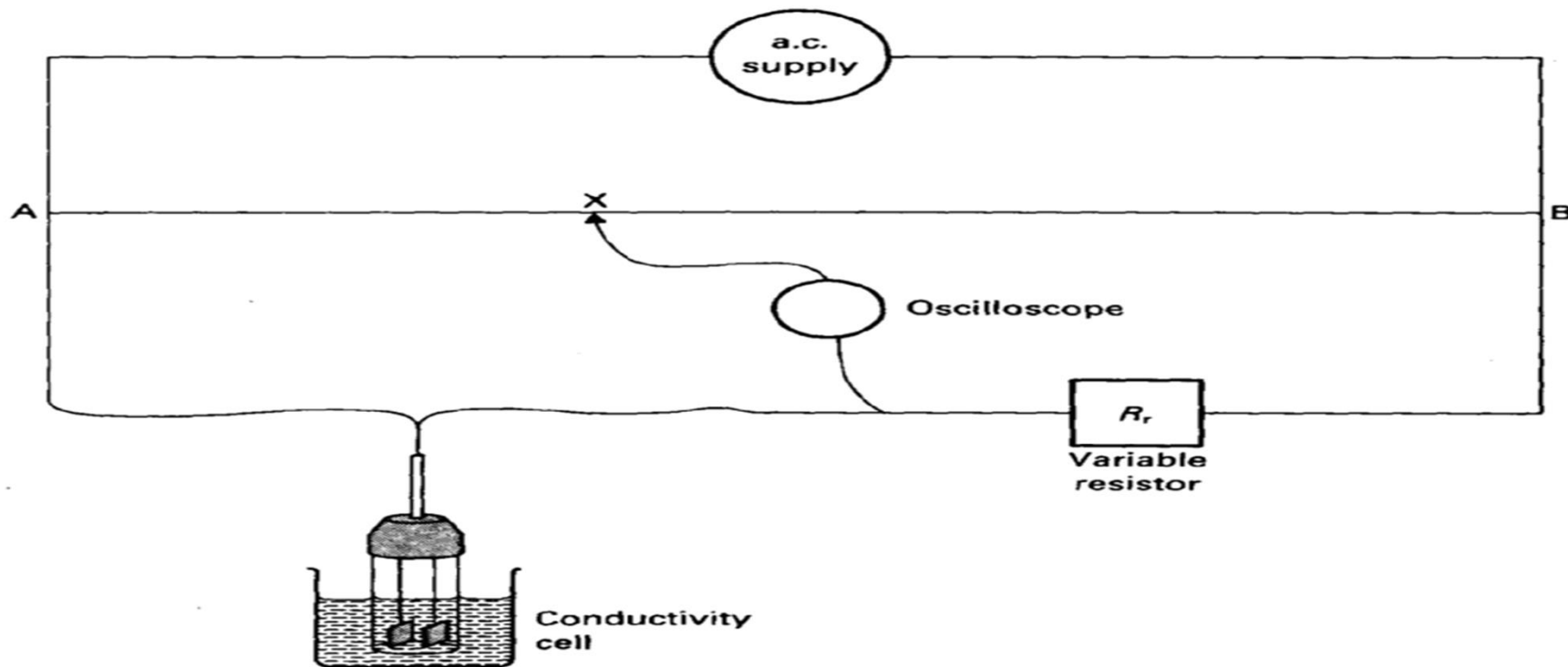
$$R_{cell} = \frac{BX \times R_r}{AX}$$


Fig 4. Wheatstone bridge circuit.

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- The electrolytic conductivity of the solution can then be calculated using equation, $\kappa = 1/\rho = L/AR = K_{cell}/R$

- A high-frequency source of alternating current (AC) necessary for conductivity measurement, however direct current (DC) cannot be used because electrolysis of the solution would occur.

- In above equation, **L/A** is a constant for the cell. It is thus known as the cell constant (K_{cell}).

- It can be found by using the cell to measure the resistance of a solution of known conductivity.

- A solution of potassium chloride (KCl) with concentration 0.1 M is often used for this purpose.
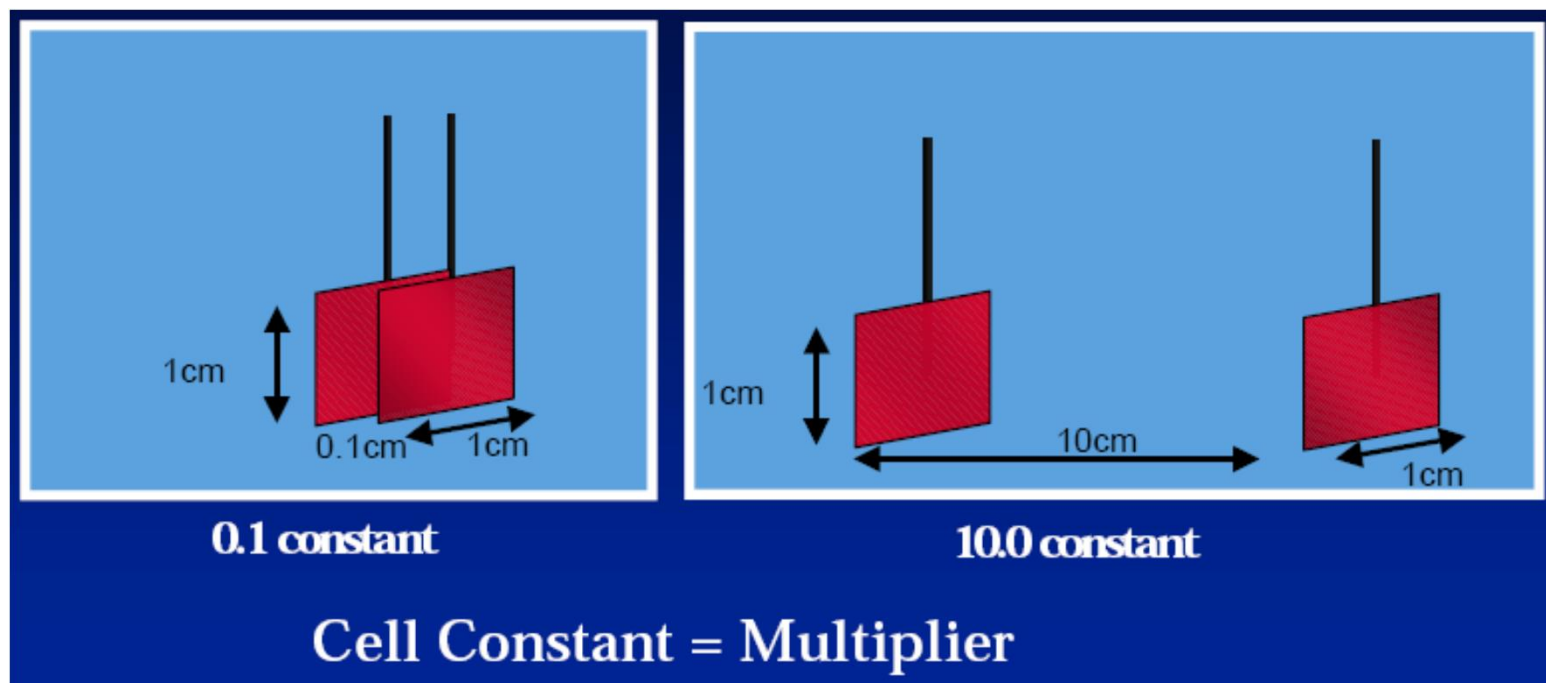
Cell Constant (K_{cell})

🞢 **Cell constant:**

✓ Measure of current response of a sensor conductive solution.

✓ Due to sensor's dimensions and geometry.

✓ Units: cm^{-1} (length divided by area).
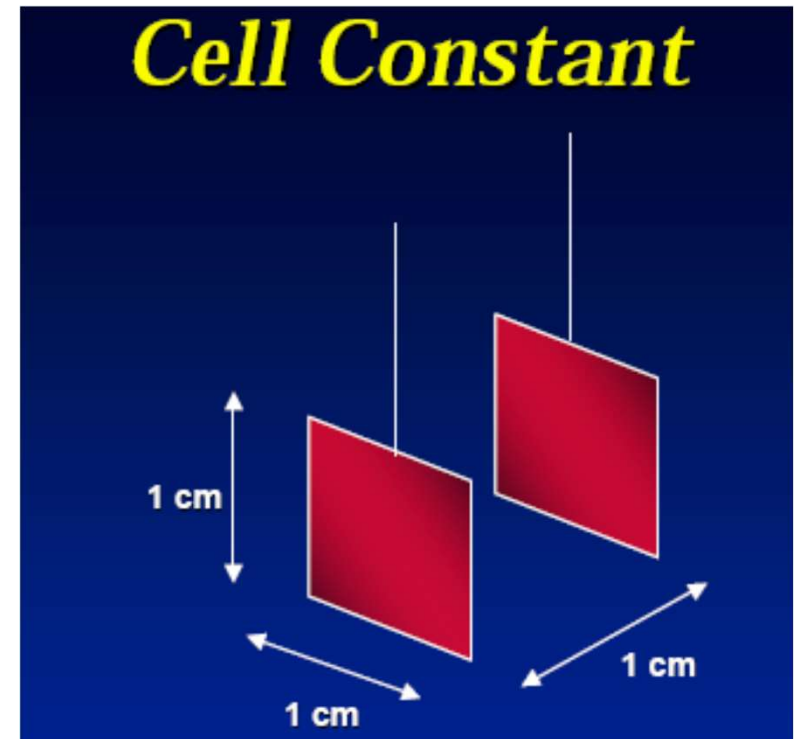
Conductivity Cell Constant $= \dfrac{Length}{Area} = \dfrac{1\ cm}{1\ cm^2} = 1\ cm^{-1}$

Other Cell Constants

Specific conductivity (k) = Measured conductivity (G) x electrode cell constant (L/A)

      L: length of the column of liquid between the electrode
      A: area of the electrodes

$$k = G \text{ x } (L/A)$$

Example 2

1) The resistance of a 0.1 M solution of KCl was found to be 35.2 Ω. Using the **same cell**, the resistance of a 0.1 M solution of $AgNO_3$ was found to be 42.4 Ω. Given that the electrolytic conductivity of KCl is 1.29 x 10^{-2} Scm^{-1}, calculate:

(A) the cell constant, K_{cell}?

(B) the electrolytic conductivity, k of the $AgNO_3$ solution?

Solution:

(A) $\kappa = 1/\rho = L/AR = K_{cell}/R$

➤ K_{cell} of KCl = kR

$\qquad\qquad$ = 1.29 x 10^{-2} S cm^{-1} x 35.2 Ω, since S = $Ω^{-1}$

$\qquad\qquad$ **= 0.454 cm^{-1}**

(B) κ of $AgNO_3$ = K_{cell}/R of $AgNO_3$

$\qquad\qquad$ = 0.454 cm^{-1}/42.4 Ω

$\qquad\qquad$ **= 0.011 $Ω^{-1}cm^{-1}$ or 0.011 S cm^{-1}**

Molar conductivity (Λ_m)

■ The conductivity of a solution is approximately proportional to the concentration:

$$\Lambda_m = \frac{\kappa}{C} \quad \text{i.e.,} \quad \Lambda_m = \frac{\kappa}{\frac{1}{V}} = V\kappa$$

V: degree of dilution

➡ Λ_m is the conductivity contributed by 1 mole of electrolyte between electrodes of 1 cm apart.

❖ Where κ is the electrolytic conductivity of the solution and C is the concentration of the solution expressed in mol dm^{-3}.

■ The units of Λ_m are Ω^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}.

Equivalent Conductance (λ)

🟢 It is the conductance of one gram equivalent of the electrolyte dissolved in volume of solution in cm^3.

🟢 Equivalent conductance is represented by λ

Mathematically, $\lambda = k \times V$

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

Where, **k** = Specific conductivity

V = Volume of solution in cm^3. containing one gram equivalent of the electrolyte.

NB: Molar conductivity = valency factor (n- factor) x equivalent conductivity

$$\Lambda_m = \text{valency factor (n- factor) x } \lambda$$

Example 3

1) The resistance of 0.01 N NaCl solution at 25 °C is 200 ohm. Cell constant of conductivity cell is unity (1 cm^{-1}). Calculate the equivalent conductance (λ) and molar conductance of the solution.

Given: **Required**

$R = 200 \; \Omega$ $\Lambda_m = ?$

$K_{cell} = 1 \; cm^{-1}$ $\lambda = ?$

Solution:

➡ Conductance of the cell, **G = 1/R**

$$= 1/200 \; \Omega$$

G = 0.005 Ω^{-1} or 0.005 S.

➡ Specific conductance, **κ = G x K$_{cell}$**

$$= 0.005 \; \Omega^{-1} \times 1 \; cm^{-1}$$

κ = 0.005 S cm^{-1}

Solution Cont'd

- Equivalent Conductance, λ = Specific conductance x (1000/N)

$$= 0.005 \text{ S cm}^{-1} \text{ x } 1000/0.01 \text{ eq cm}^{-3}$$

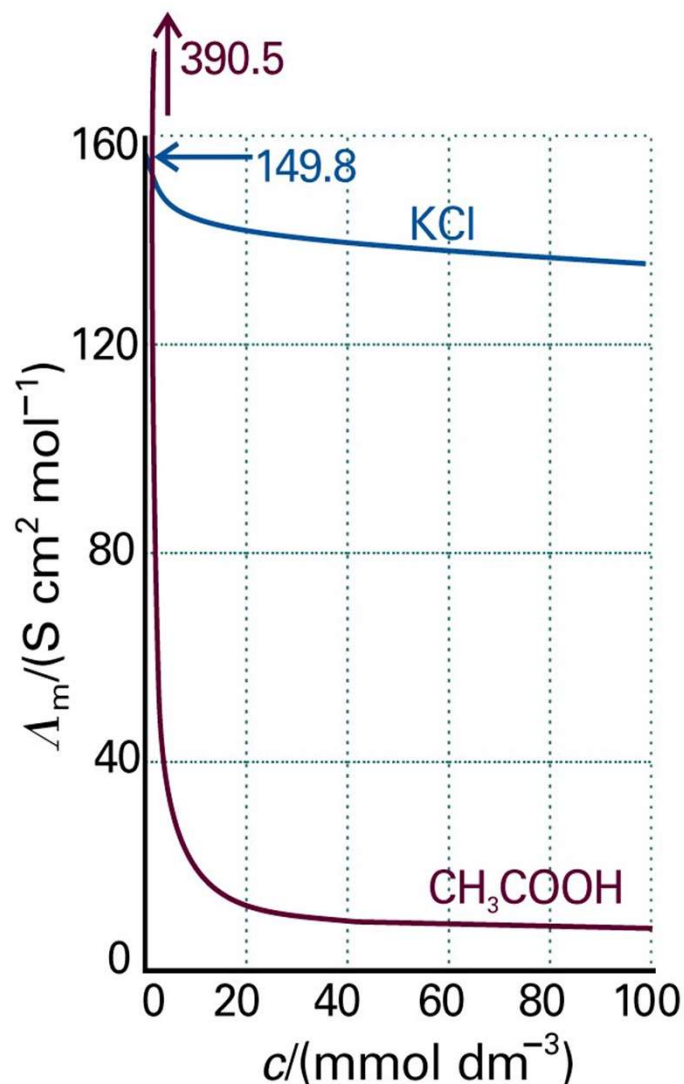$$\lambda = \underline{500 \ \Omega^{-1} \text{ eq}^{-1} \text{ cm}^2}$$

- Molar Conductivity, Λ_m = Equivalent conductivity x n-factor

$$= 500 \ \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1} \text{ x } 1$$

$$\Lambda_m = \underline{500 \ \Omega^{-1} \text{ mol}^{-1} \text{cm}^2}$$

Conductivity of Electrolyte Solution

🔵 The conductivity of a solution depends on the number of ions present.

❖ In real solutions, Λ_m depends on the concentration of the electrolyte. This could be due to:
   (1) Ion-ion interactions → $\gamma_\pm \neq 1$
   (2) Incomplete dissociation of electrolyte

➢ The concentration dependence of conductance indicates that there are 2 classes of electrolyte
   ✓ **Strong electrolyte**: molar conductivity depends slightly on the molar concentration
   ✓ **Weak electrolyte**: molar concentration falls sharply as the concentration increases

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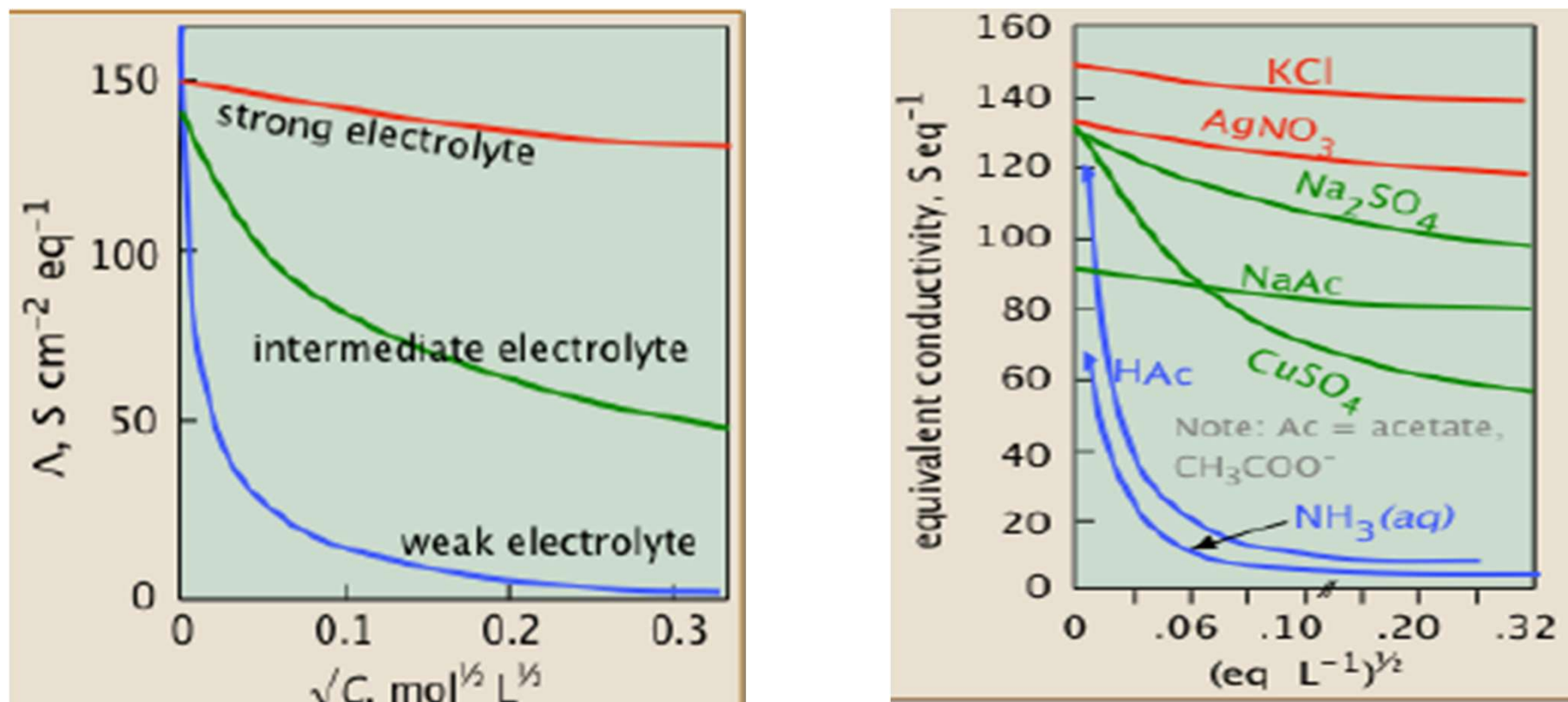
Figure 5: Variation of molar conductivity with concentration for potassium chloride solution and ethanoic acid (acetic acid).

➢ This led to the classification of electrolytes as strong, intermediate and weak.

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■ At low concentrations the molar conductivity of a strong electrolyte is found to be proportional to the square root of concentration. i.e.,

$$\Lambda \propto \sqrt{C}$$

■ The exact nature of the relationship is given by an empirical equation first formulated by Kohlrausch:

$$\Lambda^{\circ} = \Lambda^{\infty} - k\sqrt{C}$$

Where **k** = Kohlrausch's constant, which typically depends on the stoichiometry of the electrolyte

C = Concentration, arises from ion-ion interactions as estimated by the Debye-Hückel theory

Λ^{o} = Measured conductivity

Λ^{∞} = Limiting molar conductivity (molar conductivity at infinite dilution

NB: Kohlrausch's equation is valid for dilute solution not for strong (concentrated) solutions. Because for concentrated solution dissociation of ions is less and there is higher resistance.

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- You will notice that plots of **conductivities vs $\sqrt{C}$** start at $C = 0$.

- It is of course impossible to measure the conductance of an electrolyte at vanishingly small concentrations (not to mention zero).

- But for strong and intermediate electrolytes, one can extrapolate a series of observations to zero.

- To extrapolate the linear part of $\Lambda_m \sim \sqrt{C}$ at low concentration to $C = 0$, Λ^∞ can be obtained. i.e., $\Lambda^\circ = \Lambda^\infty$

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. i.e.,

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

$$\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_-$$

Where $\nu_\pm$ is the coefficient of the ions.

Kohlrausch's law of independent ionic mobilities

🌐 **Law of the independent migration of ions:** limiting molar conductivity can be expressed as a sum of ions contribution. i.e.,

$$\Lambda^0{}_m = \nu_+ \lambda_+ + \nu_- \lambda_-$$

◆ ions migrate independently in the zero concentration limit.

	$\lambda/(\text{mS m}^2\,\text{mol}^{-1})$		$\lambda/(\text{mS m}^2\,\text{mol}^{-1})$
H^+	34.96	OH^-	19.91
Na^+	5.01	Cl^-	7.63
K^+	7.35	Br^-	7.81
Zn^{2+}	10.56	SO_4^{2-}	16.00

For example, limiting molar conductivity of $BaCl_2$ in water will be: 12.73+2*7.63=27.98 mS m^2 mol^{-1}.

❖ **The table shows molar conductivity at infinite dilution for some electrolytes in water at 298 K.**

Salts	Λ_m^∞ /S mol^{-1} cm^2
HCl	426.16
LiCl	115.03
NaCl	126.45
KCl	149.85
LiNO$_3$	110.14
KNO$_3$	144.96
NaNO$_3$	121.56

Cont'd

Salts	KCl	NaCl	KNO$_3$	NaNO$_3$
Λ_m^{∞}/S mol^{-1} cm^2	149.85	126.45	144.96	121.56
$\Delta\Lambda_m^{\infty}$		23.4		23.4

➡ The difference in Λ_m^{∞} of the two electrolytes containing the same cation or anion is the same.

➡ The same differences in Λ_m^{∞} led Kohlrausch to postulate that molar conductivity at infinite dilution can be broken down into two contributions by the ions.

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

Λ_m at infinite dilution is made up of independent contributions from the cationic and anionic species.

Explanation to the same difference. i.e.,

$$\Lambda_m^\infty(\text{KCl}) - \Lambda_m^\infty(\text{NaCl}) = \lambda_{m,\text{K}^+}^\infty + \lambda_{m,\text{Cl}^-}^\infty - \lambda_{m,\text{Na}^+}^\infty - \lambda_{m,\text{Cl}^-}^\infty$$

$$= \lambda_{m,\text{K}^+}^\infty - \lambda_{m,\text{Na}^+}^\infty$$

$$\Lambda_m^\infty(\text{KNO}_3) - \Lambda_m^\infty(\text{NaNO}_3) = \lambda_{m,\text{K}^+}^\infty + \lambda_{m,\text{NO}_3^-}^\infty - \lambda_{m,\text{Na}^+}^\infty - \lambda_{m,\text{NO}_3^-}^\infty$$

$$= \lambda_{m,\text{K}^+}^\infty - \lambda_{m,\text{Na}^+}^\infty$$

How can you determine the limiting molar conductivity of weak electrolyte? Example 4

1) Calculate for ethanoic acid (acetic acid) given:

$$\Lambda^{\infty}(HCl) = 426 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

$$\Lambda^{\infty}(NaCl) = 126 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

$$\Lambda^{\infty}(CH_3COONa) = 91 \Omega^{-1} \ cm^2 \ mol^{-1}$$

Solution:

Applying Kohlrasch's law to the strong electrolytes:

$$\Lambda^{\infty}(HCl) = \Lambda^{\infty}(H^+) + \Lambda^{\infty}(Cl)$$

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

$$\Lambda^{\infty}(CH_3COONa) = \Lambda^{\infty}(CH_3COO^-) + \Lambda^{\infty}(Na^+)$$

And for the weak electrolyte:

$$\Lambda^{\infty}(CH_3COOH) = \Lambda^{\infty}(CH_3COO^-) + \Lambda^{\infty}(H^+)$$

$$= \left[\Lambda^{\infty}(CH_3COO^-) + \Lambda^{\infty}(Na^+)\right] - \left[\Lambda^{\infty}(Na^+) + \Lambda^{\infty}(Cl^-)\right] + \left[\Lambda^{\infty}(H^+) + \Lambda^{\infty}(Cl^-)\right.$$

$$= \left[(91) - (126) + (426)\right] \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

$$= 391 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

Verification

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

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

$$= \lambda_m^\infty(\text{H}^+) + \lambda_m^\infty(\text{Cl}^-) + \lambda_m^\infty(\text{Na}^+) + \lambda_m^\infty(\text{Ac}^-) - \lambda_m^\infty(\text{Na}^+) - \lambda_m^\infty(\text{Cl}^-)$$

$$\Lambda_m^\infty(\text{HAc}) = (426.16 + 91.00 - 126.45)\text{S} \cdot \text{m}^{-1} \cdot \text{mol}^{-1}$$

$$= 390.71 \text{S} \cdot \text{m}^{-1} \cdot \text{mol}^{-1}$$

$$\boxed{\Lambda_m^\infty = \lambda_{m,+}^\infty + \lambda_{m,-}^\infty}$$

(II) Weak electrolytes

- The molar conductivities of solutions of weak electrolytes are low compared to those of strong electrolyte solutions.

- Because molar conductivity depends on the proportion of ions present in solution.

- Even at low concentrations, the degree of dissociation (α) of weak electrolytes is low.

- However, when the concentration of the weak electrolyte becomes very low indeed, the degree of ionization does rise sharply (see Fig 5).

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➡ The graph is not linear since weak electrolytes do not obey the Kohlrausch equation. i.e.,

$$CH_3COOH\ (aq) + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$$
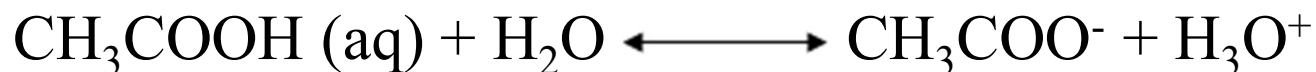
➡ The dissociation equilibrium constant written as:

$$K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

✚ Assume concentration of acetic acid is 'C' then,

$$CH_3COOH\ (aq) + H_2O \longrightarrow CH_3COO^- + H_3O^+$$

	CH₃COOH (aq) + H₂O	CH₃COO⁻	H₃O⁺
Before	C	0	0
During	-αC	+αC	+αC
After	C- αC	αC	αC

$$K = \frac{\alpha C . \alpha C}{C - \alpha C} = \frac{\alpha^2 C}{1 - \alpha}$$

Where α- degree of dissociation/ionization

Cont'd

- For 1:1 strong electrolyte such as KCl, Kohlrausch's law can be expressed mathematically as:

$$\Lambda^o = \Lambda^{o+} + \Lambda^{o-}$$

- ✓ Where Λ^{o+} is the ionic mobility of the cation and Λ^{o-} is the ionic mobility of the anion.

- For any strong electrolyte the limiting molar conductivity of ions is given by law of independent migration of ions. i.e.,

$$\Lambda^o = \Lambda^{o+} \nu_+ + \Lambda^{o-} \nu_-$$

  Where $\nu_\pm$ is the coefficient of the ions.

- ✓ E.g. $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$$\Lambda^o_{(Na2SO4)} = 2\Lambda^o_{(Na+)} + \Lambda^o_{(SO4^{2-})}$$

- The limiting conductivity for each ion is known.

Degree of dissociation (α)

- **Arrehenius** proposed that the molar conductivity of an electrolyte is related to its degree of dissociation by the following relationship:

$$\alpha = \frac{\Lambda}{\Lambda^{\infty}} \qquad (1)$$

- At almost zero concentration or infinite dilution, we have:

➡ C = 0, Λ^{∞} can be obtained. i.e., **$\Lambda^{\circ} = \Lambda^{\infty}$ and thus α = 1**

➡ Eq (**1**) together with Ostwald dilution law can be used to calculate the dissociation constant of a weak electrolyte from molar conductivities determined experimentally: $K_c = \dfrac{c\alpha^2}{1-\alpha}$ i.e.,

$$K_c = \frac{c\left(\Lambda/\Lambda^{\infty}\right)^2}{1 - \left(\Lambda/\Lambda^{\infty}\right)}$$

Ostwald dilution law

- The molar Conductivity (at higher concentrations) can be expressed as:

$$\Lambda_m = \alpha \Lambda^0{}_m$$

- At infinite dilution, the weak acid is fully dissociated ($\alpha = 100\%$).

- It can be proven by the Ostwald dilution law which allows estimating limiting molar conductance:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} + \frac{c\Lambda_m}{K_a(\Lambda^0{}_m)^2}$$

$$\Lambda_m = \alpha \Lambda^0{}_m$$

$$\frac{1}{\Lambda_m} = \frac{1}{\alpha \Lambda^0{}_m}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} \, x \, \frac{1}{\alpha}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} \, x \left(1 + \frac{\alpha c}{K_a}\right)$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0{}_m} + \frac{c}{K_a \Lambda^0{}_m} \, x \, \frac{\Lambda_m}{\Lambda^0{}_m}$$
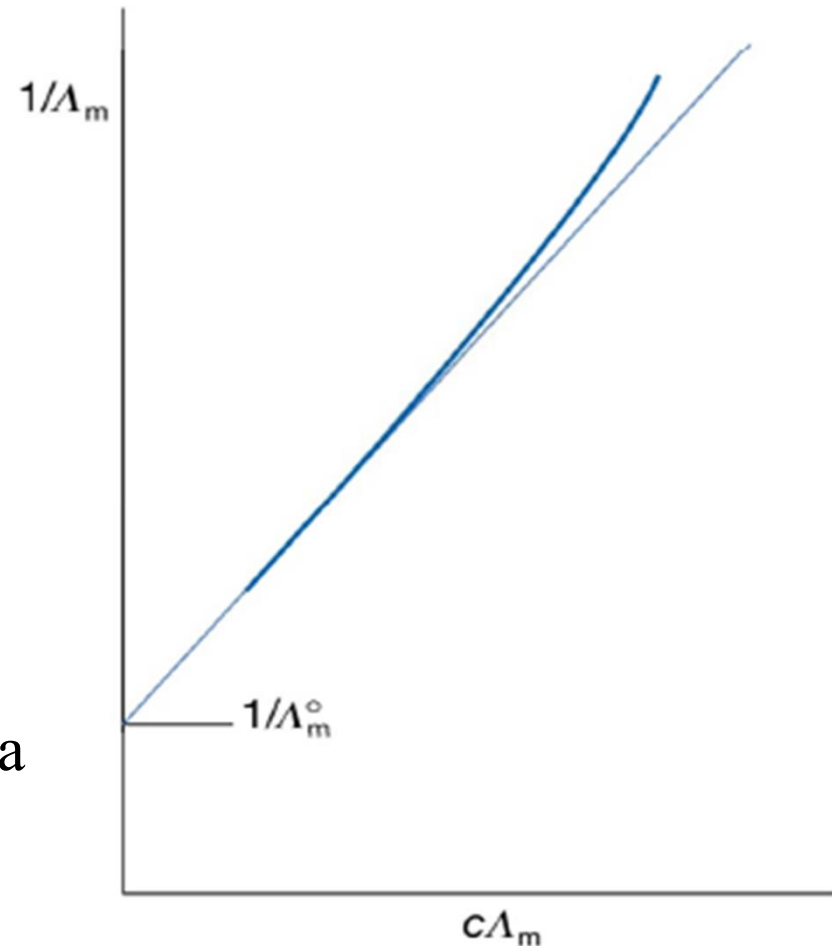
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- The limiting molar conductance:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0_m} + \frac{c\Lambda_m}{K_a(\Lambda^0_m)^2}$$

Hukum Pengenceran Ostwald

- Graph to determine the limiting value of the molar conductivity of a solution by extrapolation to zero concentration

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.

Example 5

1) A 0.10 N solution of NaCl has specific conductivity equal to 0.0092 ohm^{-1}cm^{-1}. If ionic conductance of Na^{+} and Cl^{-} ions are 43.0 and 65.0 ohm^{-1} mol^{-1} cm^{2} respectively. Calculate the degree of dissociation of NaCl solution.

Solution:

➢ Equivalent conductance of NaCl:

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

$$= 0.0092 \text{ ohm}^{-1}\text{cm}^{-1} \times 10000 \text{ mol}^{-1} \text{ cm}^{3}$$

$$= 92 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^{2}$$

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

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

Example 5

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

Solution:

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

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

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

b) Dissociation constant calculated by:

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

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

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

Transference Numbers (t)

How do transference number (t) and ionic mobility (u) relate?

When current passes through an electrolyte solution, it is carried in part by cations moving toward the cathode and in part by anions moving toward the anode.

The fractions of the total current carried by positive and negative ions are called the **transference numbers or transport number.**

i.e., $t_+ = \Lambda_+ \nu_+ / \Lambda$ and $t_- = \Lambda_- \nu_- / \Lambda$ where, since

$$\Lambda = \Lambda_+ \nu_+ + \Lambda_- \nu_-$$

At limiting molar conductivity condition:

$$\Lambda^o = \Lambda^o_+ \nu_+ + \Lambda^o_- \nu_-$$

Cont'd

■ The transference numbers must sum to 1. i.e.,

$$t_+ + t_- = 1$$

Example 6

(1) Compute the infinite dilution transference numbers in solution of KCl and $BaCl_2$.

Solution

➢ For KCl,

$$t_+^0 = \Lambda^0(K^+)/\Lambda^0(KCl) = 73.5/149.8 = 0.491$$

$$t_-^0 = 1 - t_+^0 = 0.509$$

➢ For BCl_2,

$$t_+^0 = \Lambda^0(Ba^{2+})/\Lambda(BaCl_2) = 127.7/280.3 = 0.456$$

$$t_-^0 = 1 - t_+^0 = 0.554$$

Ionic mobility (*u*) of ions

1) Ionic mobility (*u*):

■ Ionic mobility is a measure of the speed at which an ion travels through solution.

■ In general, ions with a small ionic radius travel more slowly than ions with a large ionic radius.

■ Because a small ion has a higher charge density and is thus more highly solvated.

■ Its hydration sphere and thus its effective size is larger than that of an ion with a greater ionic radius.

Cont'd

- Its larger effective size hinders its mobility in the solution.

- Ions with double or triple charges generally have higher ionic mobilities than singly charged ions.

- Exceptions are the oxonium and hydroxide ions, H_3O^+ and OH^- ions, which have the highest of all ionic mobilities.

- This is due to the rapid transfer of protons between the ions.

- Therefore, the mobilities of an ion is defined as the velocity per unit electric field strength. i.e.,

$$u_i \;=\; \frac{|v_i|}{|E|}$$

Where vi = veleocity of the ion

E = Electric field strength

The unit of ionic mobility is m^2/Vs

Cont'd

- Mobility is related to ionic conductivity, we start with Ohm's law:

$$i = d\Phi / R$$

Where dΦ- potential difference due to diffusion controlled process

- If the potential difference across a conductance cell of length, L, the field strength, E, is:

$$E = d\Phi / L$$

i.e., i = EL/R but from specific conductivity we can get R:

$$\kappa = 1/\rho = L/AR, \quad R = L/A\kappa$$

Therefore i = EL/R

$$R = EL/i = L/A\kappa$$

$$i = \kappa AE, \text{ but } i/A = J, \text{ where J} = \text{Current density}$$

Cont'd

- Now consider m^3 of solution containing C_i moles of ions carrying.

- Charge $z_i F$ coulombs mol^{-1} and moving with an average velocity of v_i.

- The contribution to the current density, J, across the end of the cubic meter is the product of these three factors:

$$\left(i / A\right)_i = C_i z_i F v_i$$

- By combining the preceding two equations, we have:

$i = \kappa AE$, but $\ i/A = J = \kappa E = C_i z_i F v_i$

$$v_i = \frac{\kappa_i E}{C_i z_i F} \quad \textbf{or} \quad u_i = -\frac{\kappa_i}{C_i \left|z_i\right| F}$$

❖ Finally, with the definition of molar conductivity we have:

$$u_i = -\frac{\Lambda_i}{\left|z_i\right| F}$$

Example 6

1) Compute the mobilities of sodium (Na^+) and barium (Ba^{2+}) ions at infinite dilution.

Solution: $u_i = -\dfrac{\Lambda_i}{|z_i|F}$

✓ The ionic mobility of the sodium ion ($z = 1$) is:

$$u^0(Na^+) = \Lambda^0(Na^+)/F = 5.2 \ x \ 10^{-8} \ m^2V^{-1}s^{-1}$$

✓ The ionic mobility of the barium ion ($z = 2$) is:

$$u^0(Ba^{2+}) = \Lambda^0(Ba^{2+})/2F = 6.6 \, x \, 10^{-8} m^2V^{-1}s^{-1}$$

Frictional coefficients (*f*)

■ It is the proportionality constant between viscosity drag force and effective force.

➡ **Viscous drag force (F):** is the force that hinders the moment of the ions in the solution.

➡ When an ion moves through solution, it is subject to a viscous drag force proportional to the negative of ion's velocity, v:

$$F_i = -f_i v_i$$

Where f_i is the proportionality constant is called a frictional coefficient.

Cont'd

➡️ **Effective force (F_i):** is the force that assists the moment of the ions in the solution.

Effective force = $z_i eE$

Where **e**- charge of electron (1.602×10^{-19} C = F/NA) and $\mathbf{z_i}$ - charge of the ion

➡️ In the solution these forces are opposite in direction.

➡️ Under steady-state conditions, the ion moves at constant velocity so that the viscous drag force exactly cancels the electrical driving force, and the net force is zero:

$$F_i = z_i eE - f_i v_i = 0$$

Cont'd

➡ **i.e.,** $\quad f_i v_i = z_i e E$

$$v_i = {z_i e E}\big/{f_i}$$

➡ Mobility of the ion, $u_i = \dfrac{|v_i|}{|E|}$, substitute for **v_i**:

$$u_i = \frac{|z_i e E|}{|E f_i|} = \frac{|z_i e|}{|f_i|}$$

$$u_i = \frac{|z_i| F}{f_i N_A}$$

or

$$\Lambda_i = \frac{z_i^{\,2} F^2}{f_i N_A}$$

Cont'd

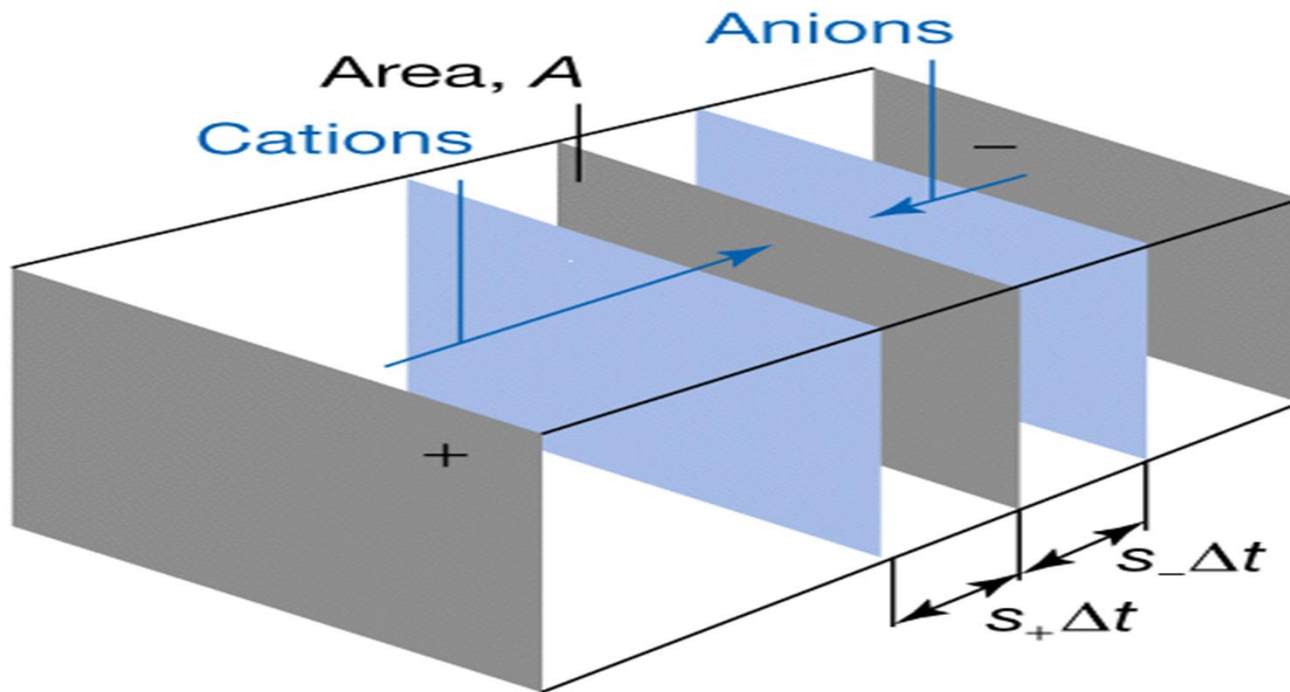➡ **Or** $\Lambda_i = \dfrac{z_i^2 Fe}{f_i}$

➡ Therefore, thus the motion of the ion through solution can be described equivalently in terms of molar ionic conductivities, ionic mobility's or frictional coefficients.

Mobility and conductivity

■ $\lambda = z\,u\,F$ (λ is an ion's molar conductivity)

• **For the solution (limiting molar conductivity):**

$$\Lambda^0_m = (z_+ u_+ v_+ + z_- u_- v_-)\,F$$

Stokes's Law Radii

➡ Still another way of thinking about the rate at which ions move through solution is by imagining the ion to be a hard sphere of effective hydrodynamic radius r_i and frictional coefficient given by Stokes' law:

$$f_i = 6\pi\eta r_i$$

➡ Where **η** - viscosity of the solvent and **r_i** – radius of the ion

$$u_i = \frac{|z_i|F}{f_i N_A}$$

$$but, f_i = 6\pi\eta r_i$$

$$u_i = \frac{|z_i|F}{6\pi\eta r_i N_A}$$

$$r_i = \frac{|z_i|F}{6\pi\eta u_i N_A}$$

Example 7

1) Compute the Stokes' law radii of Na^+ and Ba^{2+}. The viscosity of water at 25^0 C is 0.890 x 10^{-3} $kgm^{-1}s^{-1}$; inserting the mobility from example **6** above.

➡ Solution:

$$u_i = \frac{|z_i|F}{f_i N_A}$$

$$but, f_i = 6\pi\eta r_i$$

$$u_i = \frac{|z_i|F}{6\pi\eta r_i N_A}$$

$$r_i = \frac{|z_i|F}{6\pi\eta u_i N_A}$$

$$r(Na^+) = 1.84 x 10^{-10} \ m \qquad (184 \ pm)$$

$$r(Ba^{2+}) = 2.89 \ x \ 10^{-10} \ m \qquad (289 \ pm)$$

Conductimetric Titrations

- **Titration** is a process or a method of determining the concentration of an unknown solution (analyte or titrand) by reacting it completely with a standardized reagent that is a solution of known concentration (titrant). i.e., titrant taken in burette while titrand taken in conical flask.

- **Equivalence or endpoint** is the point at which all reagent of unknown solution react with known solution. i.e., titration is detected by some physical change (usually color change) produced by indicator

- In conductimetric titration, conductivity is measured as a function of volume of the titrant.

Cont'd

■ The titration of any acid with any base may be represented by the equation: $H^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$
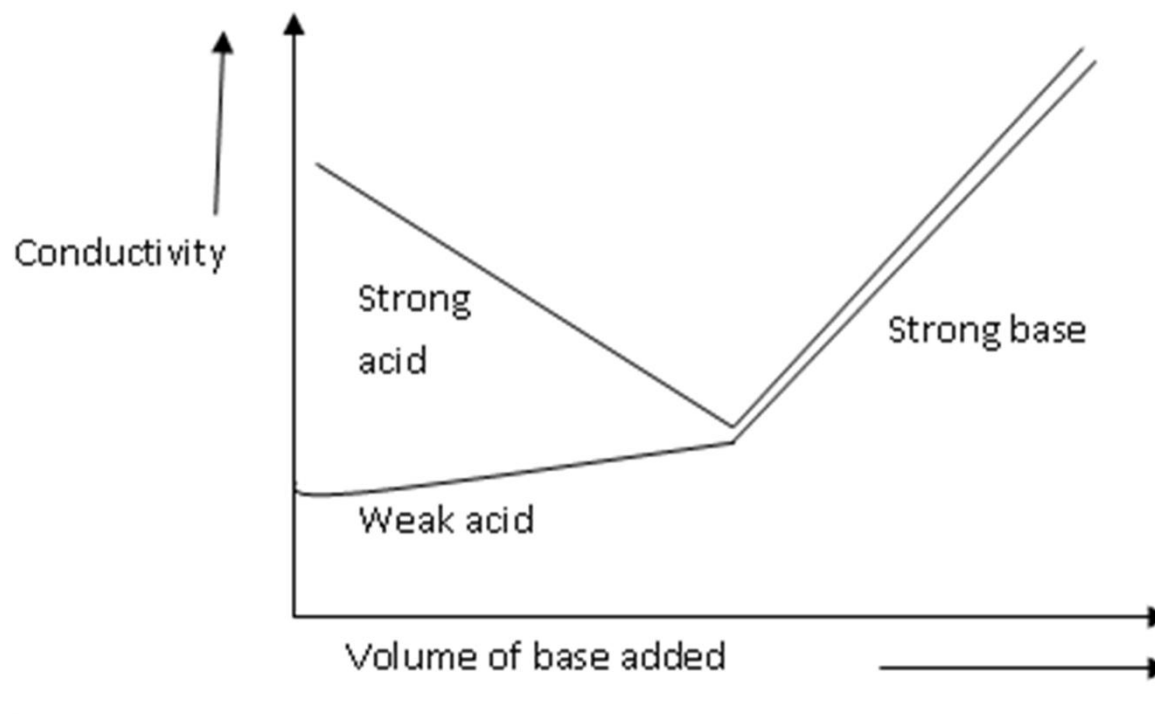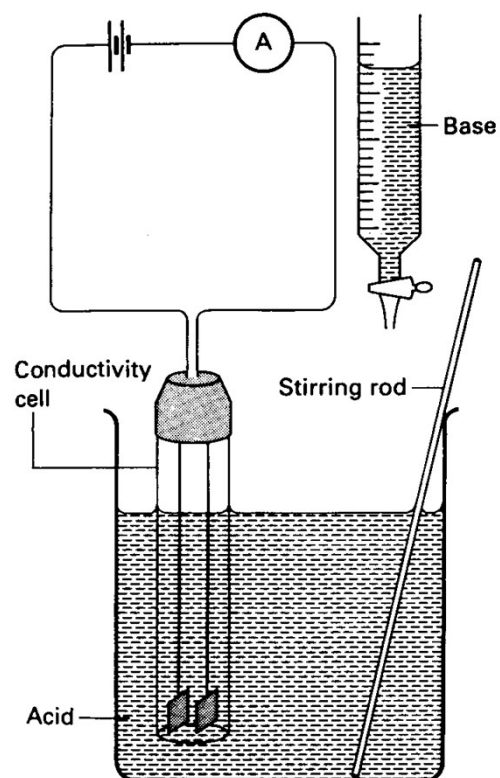

Figure 6: Conductimeteric titration curves for titration of acid with strong base

Diffusion

- Ionic and electric conductivity are measure of the rate of charge transport through solution under the influence of an electric potential gradient.

- Electrical conductivity is one of the classes of physical properties called transport properties.

- Other transport properties include:

➡ Thermal conductivity (transport of heat energy under the influence of a temperature gradient).

➡ Viscosity (transport of momentum under the influence of velocity gradient).

➡ Diffusion (transport of mass under the influence of a chemical potential or concentration gradient).

Fick's Law of Diffusion

- What is the difference between Fick's first law and Fick's second law?

- It is a law that used to describe diffusion phenomenon.

- Suppose that, in a time interval, Δt, a particle moves a distance, dx in the x-direction.

- Consider a section of the solution where there is a linear concentration gradient in the x-direction, and focus on a small section of cross sectional area, A and length, $2d$x.

- The flux, **J**, is the number of particles that pass through a unit area in a unit time.

Cont'd

$$J = \frac{dN}{A\Delta t} \propto -\frac{dC}{dx}$$

■ The concentration C in units of mol dm^{-3} is related to the number density, N, of the solute by: $N = CN_A$

■ The constant of proportionality is the diffusion coefficient, **D**:

$$J = -D\frac{dC}{dx}$$

■ This is Fick's first law of diffusion: $D = \frac{(\partial x)^2}{2\partial t}$

■ Diffusion coefficient and the ionic conductivity, the Nernst-Einstein equation: $D_i = \frac{\kappa T}{z_i^2 e^2}\Lambda_i$ or $D_i = -\frac{\kappa T}{|z_i|e}u_i = \frac{RT}{|z_i|F}u_i$

■ Whereas the Fick's second law is: $\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2}$

Cont'd

➡️ Suppose that we bring two solutions into contact at time $t = 0$.

➡️ In one solution the concentration of the diffusing species is C_0 and in the other solution, the concentration is zero; the initial interference is at $x = 0$.

➡️ We suppose that for $t > 0$, $C \rightarrow 0$ as $x \rightarrow \infty$ and $C \rightarrow C_0$ as $x \rightarrow \infty$.

➡️ With these initial and boundary conditions, the solution to equation above is: $\quad C(x,\, t) = \dfrac{1}{2} C_0 \left[1 - erf\left(\dfrac{x}{2\sqrt{Dt}} \right) \right]$

i.e., $\quad \dfrac{\partial C(x,t)}{\partial x} = \dfrac{C_0}{2\sqrt{\pi Dt}} \exp(-\dfrac{x^2}{4Dt})$

➡️ $erf(\Psi)$ is called the error function and defined by the integral:

$$erf(\Psi) = \dfrac{2}{\sqrt{\pi}} \int_0^{\Psi} e^{-u^2}\, du$$

Example 8

1) Assuming $D = 10^{-9}$ m²s⁻¹ and $C_0 = 0.1$ M, calculate the concentration gradient and flux at the position of original boundary 1, 10, and 100 s after the boundary is formed.

Solution:
$$\frac{\partial C(x,t)}{\partial x} = \frac{C_0}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt})$$

➡ At x = 0, the exponential term reduces to **1**. Substituting numbers, we obtain:
$$-\frac{\partial C(0, t)}{\partial x} = 8.92 \ x \ 10^5, \ 2.82 \ x \ 10^5, \ 8.92 \ x \ 10^5 \ mol \, m^{-4}$$

➡ At t = 1, 10, and 100 s. Substituting the concentration gradient into equation:
$$J = -D\frac{dC}{dx}$$

➡ we obtain the flux: **J = 892, 282, 89.2 μ mol m⁻²s⁻¹**

Example 9

1) Calculate the diffusion coefficients of Na^+ and Ba^{2+} at 25 ^{0}C in dilute solutions.

Solution:

uE = (DF)/(RT) = (zFED)/(RT) or $D_i = -\dfrac{\kappa T}{|z_i|e}u_i = \dfrac{RT}{|z_i|F}u_i$

➡ At 25 ^{0}C, the factor RT/F has the value 0.0257 V. Thus, using the mobilities computed example above, we have:

$$D^0(Na^+) = (0.0257\ V)(5.2x10^{-8}\ m^2V^{-1}s^{-1})$$

$$D^0(Na^+) = 1.34\ x10^{-9}\ m^2s^{-1}$$

$$D^0(Ba^{2+}) = (0.0257V)(6.6\ x10^{-8}\ m^2V^{-1}s^{-1})/2$$

$$D^0(Ba^{2+}) = 0.85\ x10^{-9}\ m^2s^{-1}$$