Electrochemistry

CHE 3053

Electrolytic Conductance

Ahmad Alakraa

Electrolyte's Conductance

- Electrolytes conduct electric currents by movement of their ions to the electrodes.
- The power of electrolytes to conduct electric currents is termed conductivity or conductance.
- Electrolytic conduction obey Ohm's law like metallic conductors, for which the current I flowing through a metallic conductor is given by the relation.

$$I = \frac{E}{R}$$

E: Potential difference at two ends (V)

R: Resistance in ohms (Ω)

- R of a conductor is directly proportional to its length, l, and inversely proportional to the area of its cross-section, A. That is,

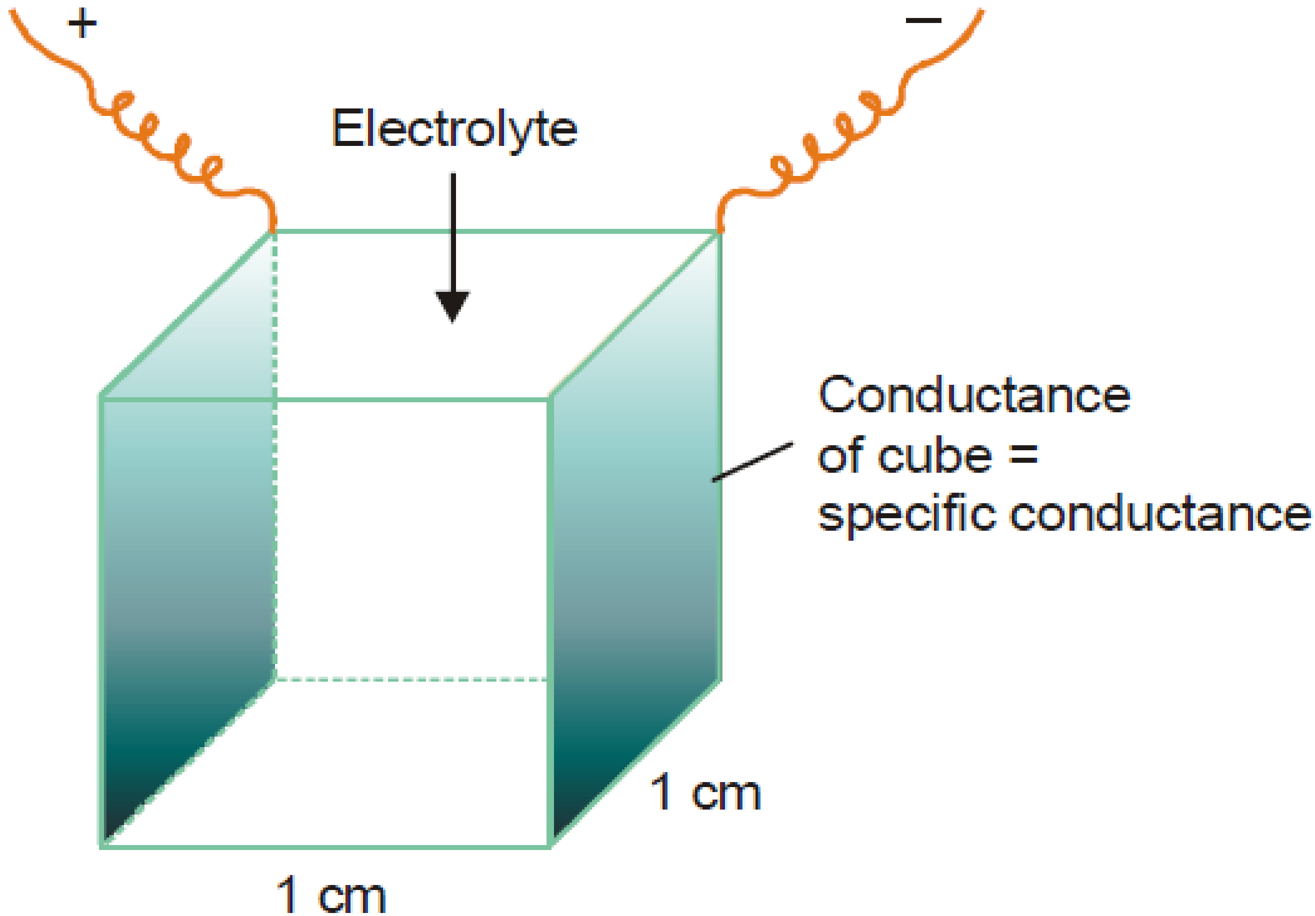
$$R \propto \frac{l}{A} \text{ (cell constant)} \quad \Rightarrow \quad R = \rho \times \frac{l}{A}$$

- where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. Its value depends upon the material of the conductor.

ρ (Ω cm) is the resistance (in Ω) to the passage of electricity of a cube 1 cm in a length and a 1 cm^2 in a cross sectional area.

Specific conductance (Conductivity): κ (kappa)

- "is the reciprocal of ρ"
- the conductance of 1 cm^3 of a solution of an electrolyte.



κ is measured as the conductance in a cell containing two identical Pt electrodes of area of 1 cm^2 each and placed 1 cm apart.

$$\kappa = \frac{1}{\rho} \Rightarrow R = \rho \times \frac{l}{A} \Rightarrow \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$\text{Unit of } \kappa = \Omega^{-1}\text{cm}^{-1} = \text{S cm}^{-1}$$

ohm^{-1} (or mho) = Ω^{-1} = Siemens, S

- κ increases with
  - ionic concentration, and
  - speeds of the ions concerned.

- In measuring κ of aqueous electrolytes, the volume (V_{cc}) of water in which a certain amount of the electrolyte is dissolved is always measured in cm^3 (cc).

Equivalent Conductance, Λ

- Lambda (Λ) is the conductivity of a cube (1 cm^3) of electrolytic solution that contains 1 equivalent of the electrolyte.
- It has a unit of $\Omega^{-1}cm^2\ eqvt^{-1}$.
- C: normality of solution in $eqvt\ L^{-1}$.
- For strong electrolytes, Λ increases with dilution.

$$\Lambda = \kappa \times V_{cc}$$

→ (V_{cc}) : volume in cm^3 containing 1 eqvt of electrolyte

C eqvt ⟶ 1000 cc

1 eqvt ⟶ V_{cc}

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

Equivalent conductance at infinite dilution, Λ_∞

$$\Lambda = \kappa \times V_{cc}$$

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

$$\Lambda = \frac{1}{R} \times \frac{l}{A} \times \frac{1000}{C}$$

$$\Lambda = \frac{1}{\Omega} \times \frac{cm}{cm^2} \times \frac{1000\ cm^3 L^{-1}}{eqvt\ L^{-1}}$$

Unit of $\Lambda = \Omega^{-1} cm^2 eqvt^{-1} = S\ cm^2\ eqvt^{-1}$

- At infinite dilution,
  - Complete ionization of electrolyte is assumed
  - $\Lambda = \Lambda_\infty$ (the infinite dilution equivalent conductance– maximum value)
  - $\Lambda_\infty = \lambda_\infty^+ + \lambda_\infty^-$

Equivalent mass

- The equivalent mass of an electrolyte is its molar mass divided by the charge of either the cation(s) or the anion(s) of this electrolyte.

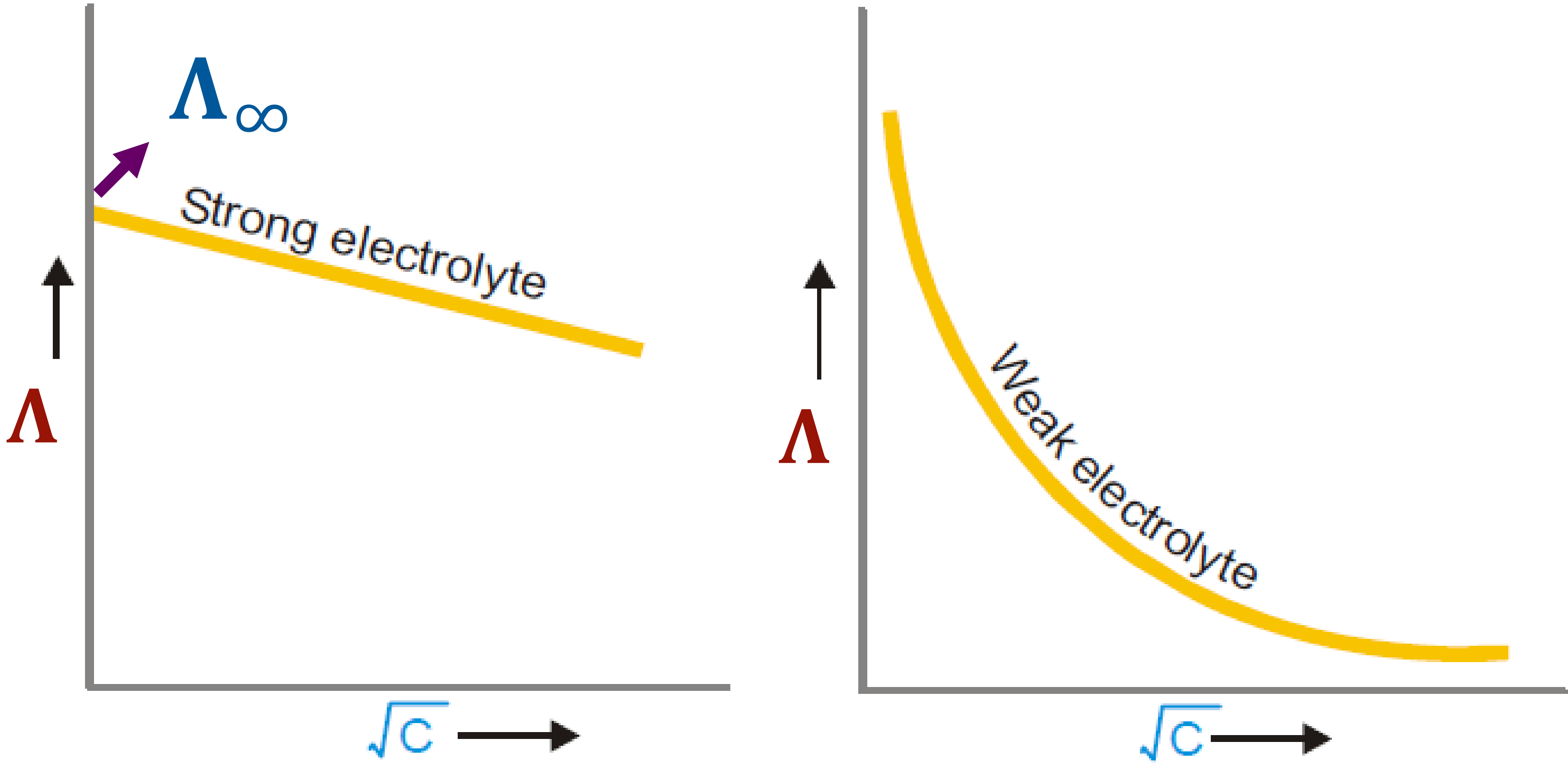
$$\Lambda_\infty(KCl) = \lambda_\infty^+(K^+) + \lambda_\infty^-(Cl^-)$$

$$\Lambda_\infty(Na_2SO_4) = \lambda_\infty^+(Na^+) + {}^1/_2\,\lambda_\infty^-(SO_4^{2-})$$

- Λ_∞ for weak electrolytes can not be reached regardless of the dilution.
- Degree of ionization (α) measures the ability of an electrolyte to dissociate.
- $\alpha = 1$ for strong electrolytes.
- $\alpha \ll 1$ for weak electrolytes.

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

Λ_∞ vs. dilution (V_{cc})



Dilution increases

Λ_∞ vs. (V_{cc})/Strong Electrolyte

- Strong electrolytes are completely ionized at all concentrations (or dilutions).
- The increase in Λ with dilution is not due to the increase in the number of current carrying species but due to the decrease in attraction between opposite charges ions (**Recombination**).
- At **high concentrations**, these attraction forces ($F \propto q_1q_2/r^2$) increase; affecting the speed of the ions in a phenomenon called "ionic interference".
- As the solution becomes more and more diluted ($\approx$ zero concentration), Λ increases up to a limiting value, Λ_∞.

Λ_∞ vs. (V_{cc})/Weak Electrolyte

- Weak electrolytes have low ionic concentrations and hence interionic forces are negligible.
- Ionic speeds are not affected with decrease in concentration (or increase in dilution).
- The increase in Λ with dilution is due to the increase in the number of current-carrier species (ions) or the degree of ionization (α).
- Λ_∞ in case of weak electrolytes is Λ when ionization is complete.

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

Example

- 0.5 eqvt/L solution of a salt placed between two Pt electrodes, 20 cm apart and of area of cross-section 4.0 cm^2 has a resistance of 25 ohms. Calculate the equivalent conductance of the solution?

Solution

$$\Lambda = \frac{1}{R} \times \frac{l}{A} \times \frac{1000}{C}$$

$$\Lambda = \frac{1}{25\ \Omega} \times \frac{20\ \text{cm}}{4.0\ \text{cm}^2} \times \frac{1000}{0.5\ \text{eqvt/L}}$$

$$\Lambda = 400\ \text{S cm}^2\ \text{eqvt}^{-1}$$

Example

- The resistance of a 0.1 g eqvt /L solution of a salt is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant, x = 1.15 cm^{-1}?

Solution

$$\Lambda = \frac{1}{R} \times \frac{l}{A} \times \frac{1000}{C}$$

$$\Lambda = \frac{x}{R} \times \frac{1000}{C}$$

$$\Lambda = \frac{1}{2.5 \times 10^3 \Omega} \times 1.15\ \mathrm{cm}^{-1} \times \frac{1000}{0.1\ \mathrm{g\ eqvt/L}}$$

$$\Lambda = 4.6\ \mathrm{S\ cm^2\ eqvt^{-1}}$$

Molar Conductance, μ

- Mu (μ) is the conductivity of a cube (1 cm^3) of electrolytic solution that contains 1 mole of the electrolyte.
- It has a unit of $\Omega^{-1} cm^2\ mol^{-1}$.
- M : molarity of solution in $mol\ L^{-1}$.

$$\mu = \kappa \times \frac{1000}{M} = \kappa \times V_{cc}$$

(V_{cc}): volume in cm^3 containing one mole of the electrolyte.

Dependence of $\kappa\downarrow$, $\Lambda\uparrow$ & $\mu\uparrow$ on $V_{cc}\uparrow$

- Upon dilution, the concentration of ions per 1 cm^3 decreases; hence $\kappa\downarrow$ falls.

- $\Lambda\uparrow$ and $\mu\uparrow$ increase as these are the products of κ and V_{cc} (volume of the solution in cm^3 containing one gram-equivalent or one mole of the electrolyte respectively).

- With dilution, κ decreases, but V_{cc} increases. The increase in V_{cc} is much more than the decrease in κ.

$$\Lambda = \kappa \times V_{cc}$$

NaCl solution at 18^{o}C

Volume, V in cc containing 1 mol	Specific conductance (κ), Ω^{-1} cm^{-1}	Molar conductance (μ) Ω^{-1} cm^{2} mol^{-1}
1,000	0.0744	74.4
5,000	0.01760	88.2
20,000	0.0479	95.9
500,000	0.000213	106.7
1,000,000	0.0001078	107.3
2,000,000	0.0000542	108.5
5,000,000	0.0000218	109.2
10,000,000	0.00001097	109.7

Increase in V_{cc} is much more than the decrease in κ

TABLE 24.2. EQUIVALENT CONDUCTANCE OF SOME COMMON ELECTROLYTES AT 18ºC

Volume, V in cc containing 1 g equivalent	Equivalent conductance Λ, $ohm^{-1}\ cm^{2}\ eqvt^{-1}$				
	NaOH	KCl	HCl	CH_3COOH	CH_3COONa
1,000	160	98.3	301	1.32	41.2
2,000	172	120.4	327	2.01	49.4
10,000	183	112.0	351	4.60	61.1
20,000	190	115.9	360	6.48	64.2
100,000	200	122.4	370	14.3	70.2
200,000	203	124.4	372	20.0	72.4
500,000	206	126.3	376	30.2	74.3
	210	127.3	377	41.0	75.2

TABLE 24.3. THE ELECTROCHEMICAL QUANTITIES, THEIR SYMBOLS AND UNITS

Quantity	Symbol	Unit
Resistance	R	ohm or Ω
Resistivity or Specific resistance	ρ (rho)	ohm cm
Conductance	$1/R$	ohm^{-1} or Siemens
Specific conductance	κ (kappa)	ohm^{-1} cm^{-1}
Dilution	V	cc
Equivalent conductance	Λ	ohm^{-1} cm^2 $eqvt^{-1}$
Molar conductance	μ	ohm^{-1} cm^2 mol^{-1}

Conductance/T relationship

- The conductance of a solution of an electrolyte generally increases with T (2-3 % increase for one degree rise in T).

- The conductance of a given electrolyte depends on:
  - The number of ions present in unit volume of solution (not affected by T)
  - The speed at which ions move towards the electrodes (highly affected by T).Why?

- With rise in temperature the viscosity of the solvent (water) decreases which makes the ions to move freely toward the electrodes.

Conductance/T relationship

- For weak electrolytes, the influence of T on conductance depends upon the value of ΔH accompanying the process of ionization.

- If ΔH is negative (exothermic), the degree of ionization decreases at higher T (Le Chatelier's principle) and conductance decreases.

$$AX \leftrightarrow A^{+} + X^{-} + \text{Heat}$$

- Conversely, If ΔH is positive (endothermic), the degree of ionization increases at higher T (Le Chatelier's principle) and conductance increases.

$$BY + \text{Heat} \leftrightarrow B^{+} + Y^{-}$$

Example

- The specific conductance of an N/50 solution of KCl at 25ºC is 0.002765 $\Omega^{-1}\text{cm}^{-1}$. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant?

Solution

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

$$\frac{l}{A} = x = \kappa \times R = 0.002765\ \Omega^{-1}\text{cm}^{-1} \times 400\ \Omega$$

$$x = 1.106\ \text{cm}^{-1}$$

Example

- The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 32 ohms. Calculate the equivalent conductance of the solution.

Solution

$$\kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{32\ \Omega} \times \frac{1.80\ \text{cm}}{5.4\ \text{cm}^2} = 0.0104\ \Omega^{-1}\text{cm}^{-1}$$

$$C = 0.1\ \text{g eqvt L}^{-1} \Rightarrow V_{cc} = 10{,}000\ \text{cm}^3\ \text{eqvt}^{-1}$$

$$\Lambda = \kappa \times V_{cc} = 0.0104\ \Omega^{-1}\text{cm}^{-1} \times 10{,}000\ \text{cm}^3\ \text{eqvt}^{-1}$$

$$\Lambda = 104\ \text{S cm}^2\ \text{eqvt}^{-1}$$

Example

A conductance cell on being filled with a 0.02 molar solution of KCl at 25°C showed a resistance of 165 ohms. The specific conductance of the KCl solution used is 2.77×10^{-3} mho cm^{-1}. The same cell containing 0.01 molar NaCl solution gave an electrical resistance of 384 ohms. Calculate the specific and equivalent conductance of NaCl solution.

Solution

Reference: KCl

$$\kappa(r) = \frac{1}{R(r)} \times \frac{l}{A} = \frac{1}{165\ \Omega} \times \frac{l}{A} = 2.77 \times 10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$$

$$\frac{l}{A} = 0.45705\ \text{cm}^{-1}$$

NaCl

$$\kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{384\ \Omega} \times 0.4455\ \text{cm}^{-1}$$
$$= 1.19 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$$

$$C = 0.01\ \text{mol}\ \text{L}^{-1} = 0.01\ \text{eqvt}\ \text{L}^{-1}$$

$$V_{cc} = 100{,}000\ \text{cm}^3\ \text{eqvt}^{-1}$$

$$\Lambda = \kappa \times V_{cc} = \kappa \times \frac{1000}{C}$$
$$= 1.19 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$$
$$\times 100{,}000\ \text{cm}^3\ \text{eqvt}^{-1} = 119\ \Omega^{-1}\text{cm}^2\ \text{eqvt}^{-1}$$