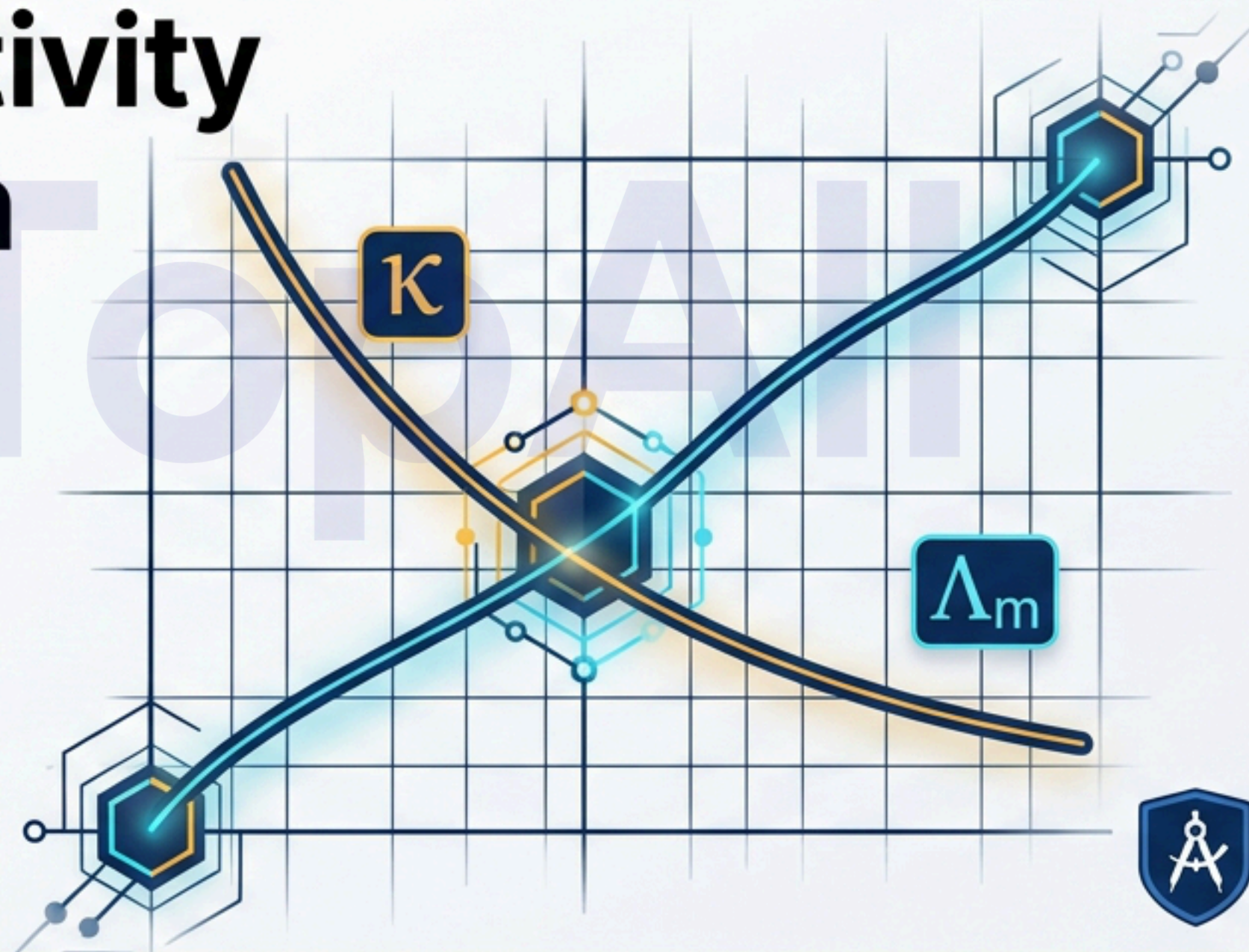


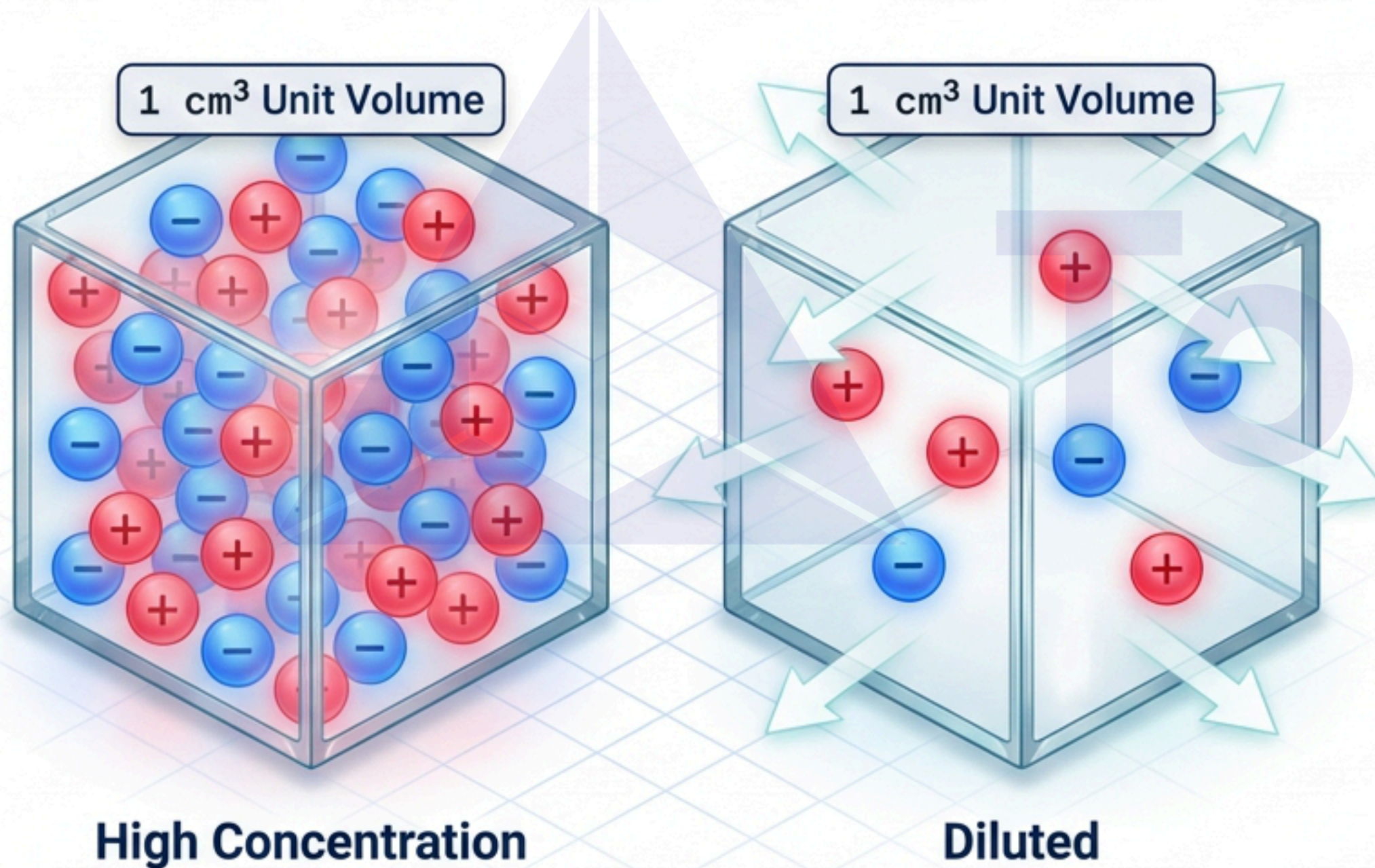
Variation of Conductivity and Molar Conductivity with Concentration

Unpacking the electrochemical paradox: Why dilution decreases conductance per unit volume, but increases conductance per mole.



THE BEHAVIOR OF CONDUCTIVITY

Why Conductivity (κ) Decreases on Dilution



The Principle

Conductivity always decreases with a decrease in concentration for both weak and strong electrolytes.

The Physical Reality

The conductivity (κ) of a solution is the conductance of exactly one unit volume of solution.

The Mechanism

On dilution, the number of current-carrying ions physically present inside that specific, fixed unit volume drops. Fewer ions = less conductance.

Dilution = Fewer ions per
unit volume = Lower κ

SHIFTING THE PARADIGM

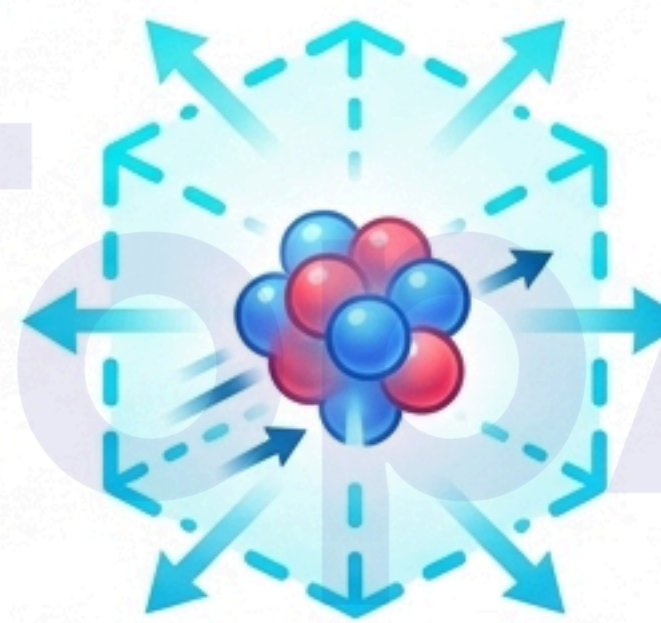
Molar Conductivity (Λ_m) as a More Meaningful Quantity

Conductivity (κ)



- **Constraint:** Fixed Volume (1 cm³)
- **Variable:** Amount of ions changes with dilution

Molar Conductivity (Λ_m)



- **Constraint:** Fixed Amount (Exactly 1 Mole of electrolyte)
- **Variable:** Volume changes with dilution

Because standard conductivity (κ) depends heavily on concentration, it's difficult to compare the inherent conducting power of different electrolytes. **Molar conductivity (Λ_m)** normalizes this by measuring the conducting power of all the ions produced by exactly one mole of the electrolyte, regardless of how much volume it occupies.



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$$E=mc^2$$



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Linking the Two Conductivities

Since **Molar Conductivity** (Λ_m) requires us to measure **exactly 1 mole**, the **volume (V)** of the solution we are measuring is intrinsically tied to its **concentration (c)**.

- If $\ell = 1$ and $\mathbf{A} = \mathbf{V}$ (the volume containing 1 mole of electrolyte), then: $\Lambda_m = \kappa V$
- Because **Volume (V)** is inversely proportional to **Concentration (c)**, we arrive at the master equation.

$$\Lambda_m = \frac{\kappa}{c}$$

Λ_m = Molar Conductivity (Units: $\text{S m}^2 \text{ mol}^{-1}$ or $\text{S cm}^2 \text{ mol}^{-1}$)

κ = Conductivity (Specific Conductance)

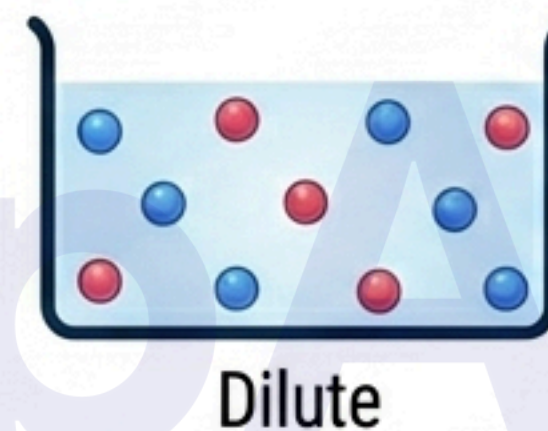
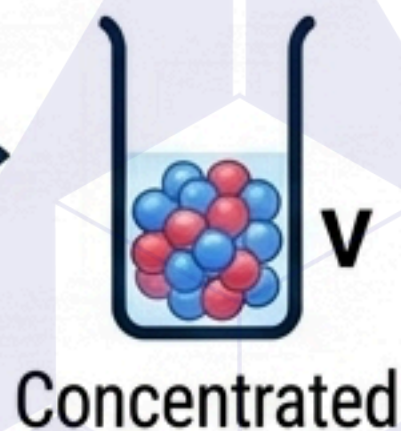
c = Concentration of the electrolyte

RESOLVING THE PARADOX

Why Λ_m Increases on Dilution

The Volume Expansion Sequence

Small volume
containing 1 mole.
High κ .



Massive volume
containing the
same 1 mole.
Very low κ .

The Opposing Forces

When we dilute a solution, κ decreases. However, the total volume V containing the 1 mole of electrolyte increases.

The Net Winner

The decrease in κ is more than compensated by the massive increase in total volume (V). Therefore, the product of the two ($\Lambda_m = \kappa V$) ultimately increases.

Λ_m reaches its maximum when concentration approaches zero.
This is called **Limiting Molar Conductivity (Λ_m°)**.

ELECTROLYTE BEHAVIOR

The Strong Electrolyte Trend

For **strong electrolytes** (which dissociate completely), **Molar Conductivity** (Λ_m) increases slowly with dilution. Because all ions are already dissociated, the slight increase is due to decreased inter-ionic attractions as the ions spread further apart.

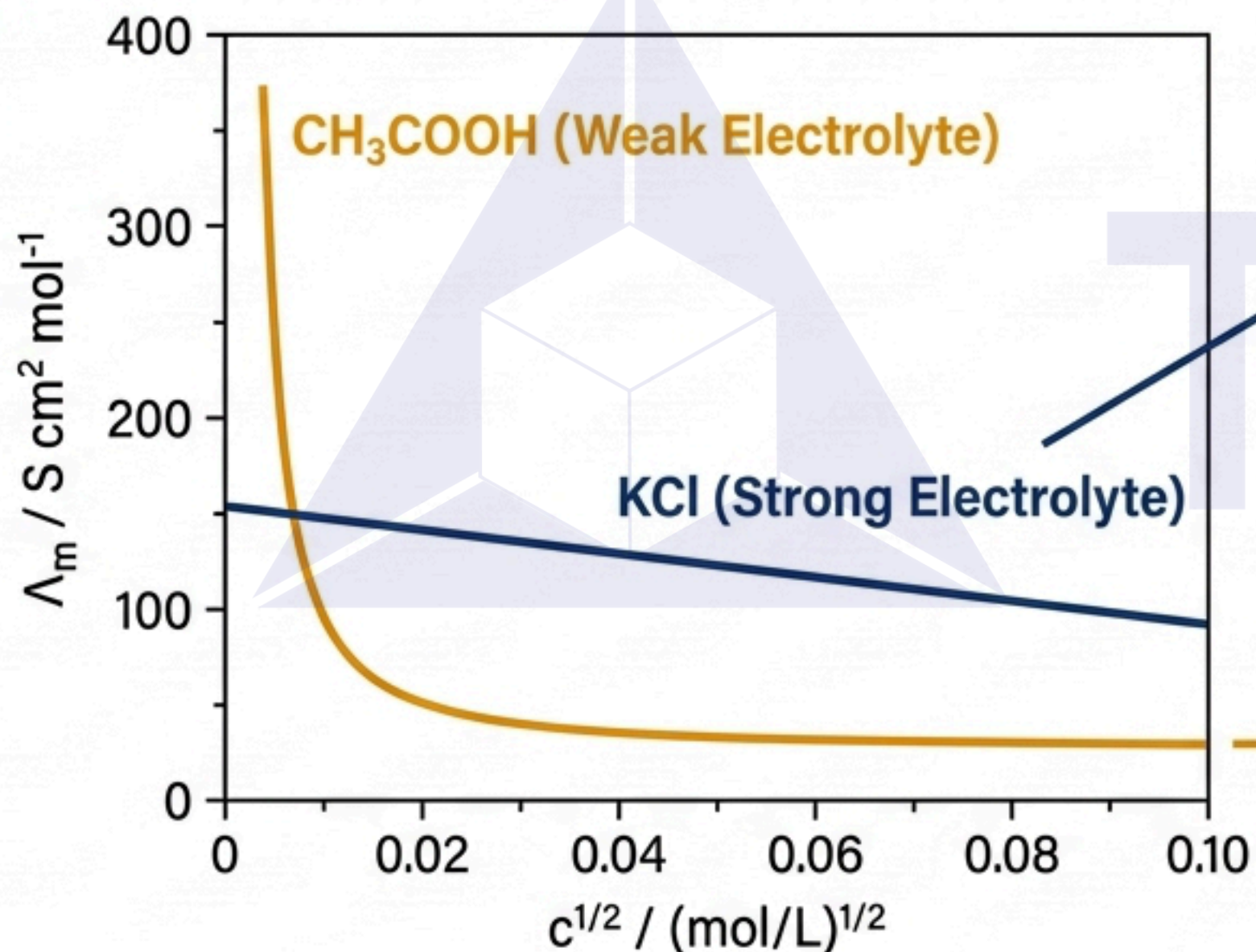
$$\Lambda_m = \Lambda_m^\circ - A c^{1/2}$$

- Λ_m° = Limiting Molar Conductivity (Intercept at $c \rightarrow 0$)
- A = Constant dependent on electrolyte type (e.g., 1-1 for NaCl)
- $c^{1/2}$ = Square root of concentration



This empirical equation takes the form of a straight line ($y = mx + c$). Plotting Λ_m against $c^{1/2}$ yields a linear graph where $-A$ represents the slope of the line.

Strong vs. Weak Electrolytes on Dilution



Strong Electrolyte

Increases slowly upon dilution. The straight line can be easily extrapolated back to the Y-axis to determine the Limiting Molar Conductivity (Λ_m°).

Weak Electrolyte

Increases steeply near low concentrations.

Reason: The degree of dissociation (α) drastically increases upon dilution, generating totally new ions. Λ_m° cannot be found by extrapolation and requires Kohlrausch's Law.

Master Diagnostic Matrix: κ vs Λ_m

Metric	Definition	Trend on Dilution	Primary Reason	Math Proof
Conductivity (κ)	Conductance of 1 unit volume	↓	Fewer ions physically present inside the fixed 1 cm ³ space.	$G = \kappa \left(\frac{A}{l} \right)$
Molar Conductivity (Λ_m)	Conductance of 1 mole total	↑	The total volume holding 1 mole expands much faster than κ drops.	$\Lambda_m = \frac{\kappa}{c}$



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