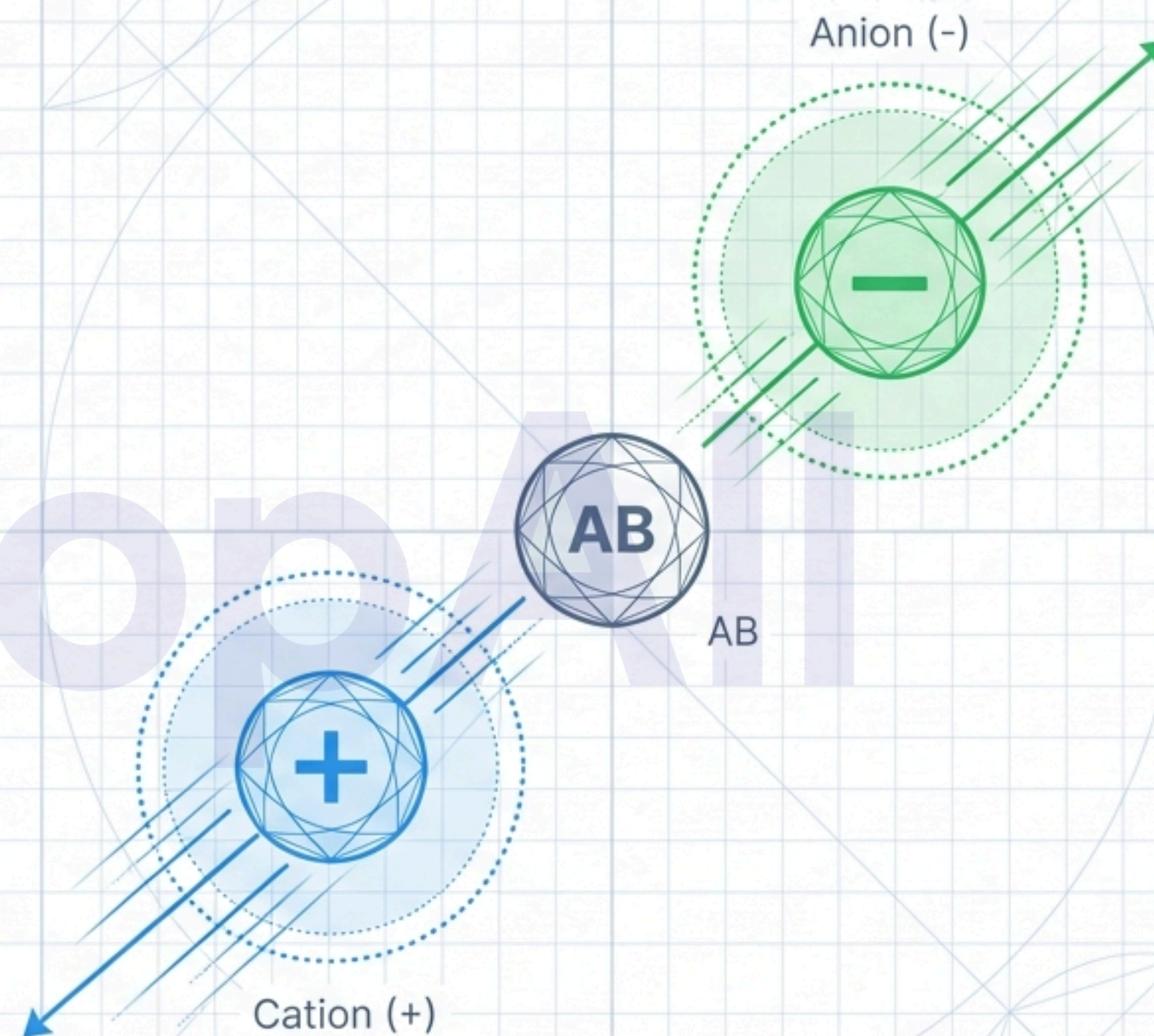


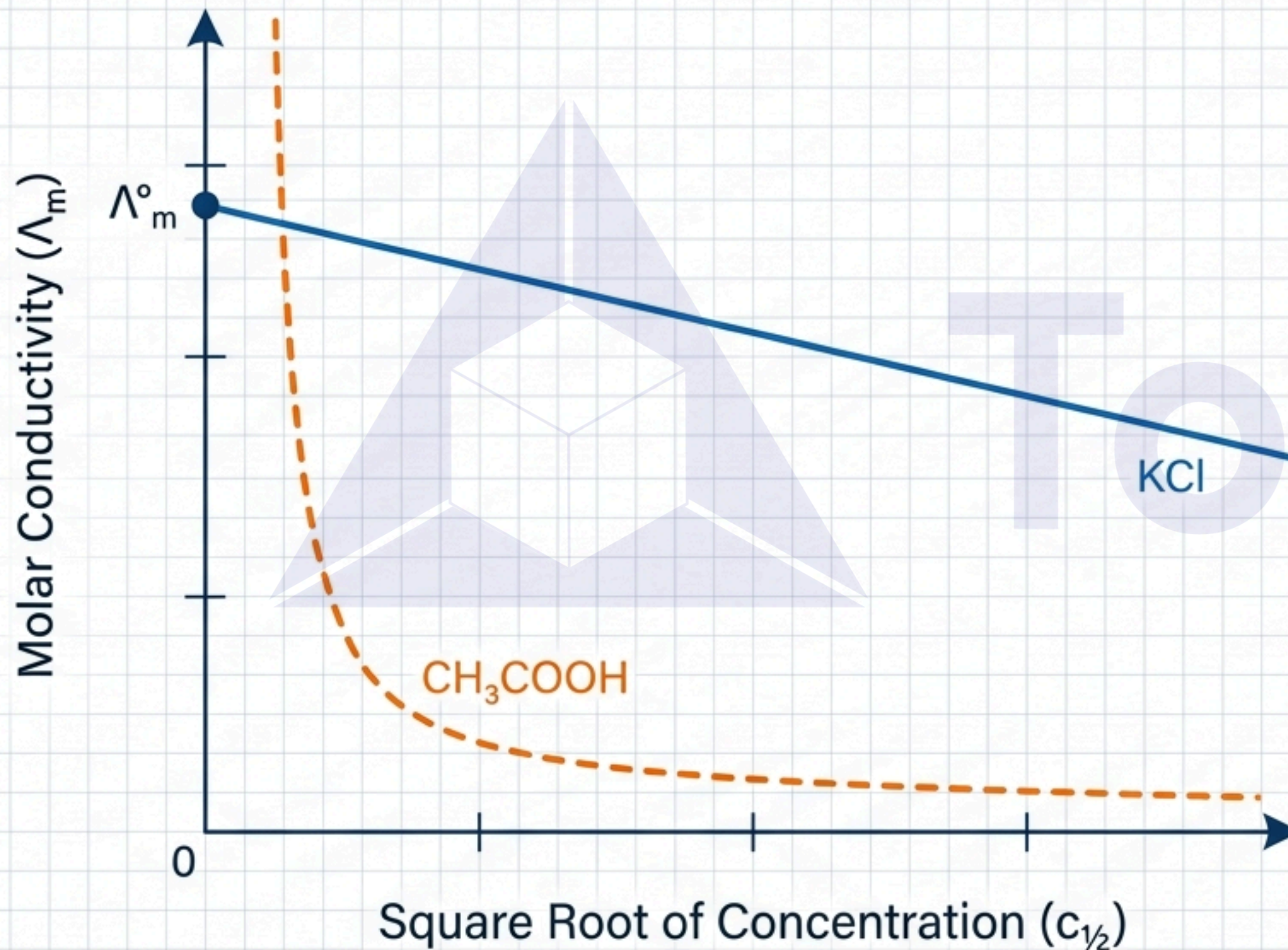
Kohlrausch Law — Conductivity Becomes Ionic

The independent migration of ions at infinite dilution.

Weightage: **HIGH**



Molar Conductivity on Dilution



STRONG ELECTROLYTES

Gradual Λ_m increase.
Ions are already 100% dissociated; dilution merely reduces interionic friction.

Λ_m° can be found via simple linear extrapolation.

WEAK ELECTROLYTES

Steep increase on dilution.
Adding solvent actively forces the degree of dissociation (α) to increase.

Curve is asymptotic. Direct extrapolation to zero is impossible.

The Additive Nature of Ions

At $c \rightarrow 0$, interionic attractions vanish. Ions migrate independently.

$$\Lambda_m^\circ(\text{KCl}) - \Lambda_m^\circ(\text{NaCl}) = 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{KBr}) - \Lambda_m^\circ(\text{NaBr}) = 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{KI}) - \Lambda_m^\circ(\text{NaI}) = 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

CORE INSIGHT

The difference remains identically 23.4 because the Cl^- , Br^- , and I^- contributions perfectly cancel out. This proves the value 23.4 is strictly the fundamental difference in conductivity between K^+ and Na^+ at infinite dilution.



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Law of Independent Migration of Ions

Limiting molar conductivity of the total electrolyte.

Stoichiometric coefficients (number of cations/anions per formula unit).

$$\Lambda_m^{\circ} = \nu_+ \lambda_+^{\circ} + \nu_- \lambda_-^{\circ}$$

JEE TRAP

Forgetting to multiply by the stoichiometric coefficients (ν). Example: MgCl_2 produces 2 moles of Cl^- , so $\nu_- = 2$.

Limiting molar conductivities of the individual ions.

Application: Strong Electrolytes

Determine limiting molar conductivity for Calcium Chloride (CaCl_2).

$$\Lambda_m^\circ(\text{CaCl}_2) = \lambda^\circ(\text{Ca}^{2+}) + 2\lambda^\circ(\text{Cl}^-)$$

$$[\lambda^\circ(\text{Ca}^{2+}) = 119.0] \quad [\lambda^\circ(\text{Cl}^-) = 76.3]$$

$$= 119.0 + 2(76.3)$$

FINAL RESULT

$$271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

The Weak Electrolyte Solution



Because CH_3COOH is a weak electrolyte, its graph is asymptotic. We cannot find its infinite dilution value by direct extrapolation.

At any given concentration c , the **degree of dissociation** (α) is simply the ratio of its measured conductivity to its theoretical maximum.

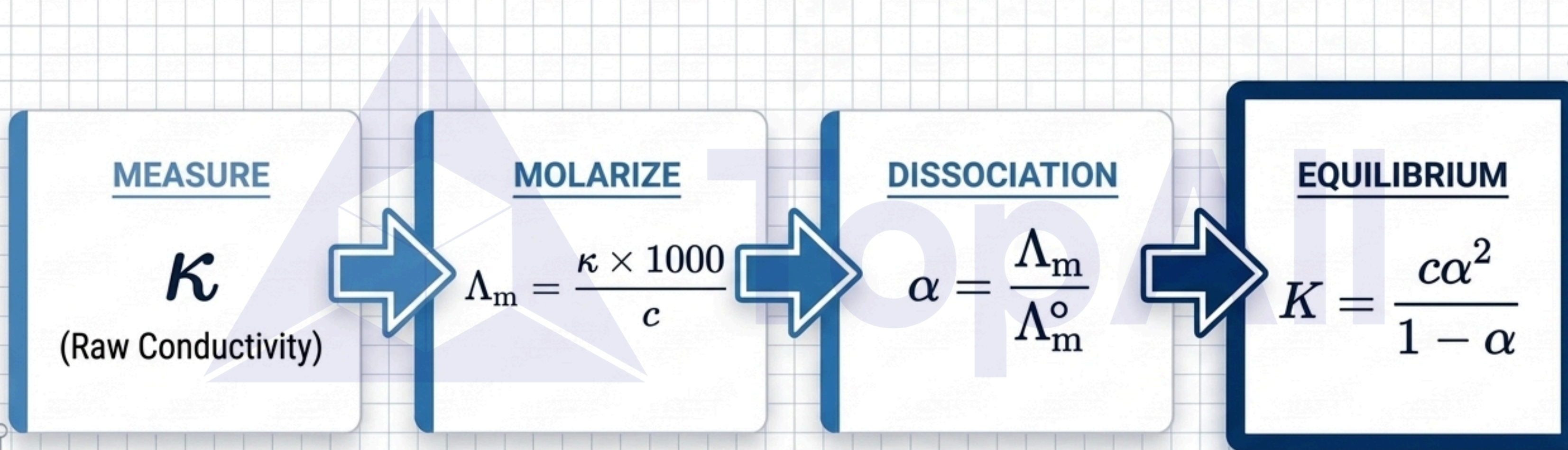
$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Measured directly at concentration c .

Calculated theoretically via Kohlrausch's Law.

The Conductivity-Equilibrium Pipeline

How experimental conductivity yields the dissociation constant.



This sequence is the most frequently tested electrochemistry pipeline in JEE Advanced.

Constructing Weak Electrolytes

Finding limiting molar conductivity for Acetic Acid (HAc) using only strong electrolytes.

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



KEY TAKEAWAYS

- Add strong electrolytes containing the required ions.
- Subtract the strong electrolyte containing the spectator ions.
- This bypassing technique perfectly solves the weak electrolyte extrapolation problem.



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