

PHYSICAL CHEMISTRY • ELECTROCHEMISTRY

Kohlrausch Law of Independent Migration of Ions

Unlocking the conductivity of electrolytes at infinite dilution.

Exam-Smart Summary Deck

EMPIRICAL FOUNDATION

The Pattern in the Data

Before formulating the law, Friedrich Kohlrausch analyzed the limiting molar conductivities (Λ°_m) of various strong electrolytes at 298 K. By comparing pairs of salts with common ions, he discovered a profound mathematical regularity.

Difference of Cations (Values in $\text{S cm}^2 \text{mol}^{-1}$)

$$\Lambda^\circ_m(\text{KCl}) - \Lambda^\circ_m(\text{NaCl}) \cong \mathbf{23.4}$$

$$\Lambda^\circ_m(\text{KBr}) - \Lambda^\circ_m(\text{NaBr}) \cong \mathbf{23.4}$$

$$\Lambda^\circ_m(\text{KI}) - \Lambda^\circ_m(\text{NaI}) \cong \mathbf{23.4}$$

Difference of Anions (Values in $\text{S cm}^2 \text{mol}^{-1}$)

$$\Lambda^\circ_m(\text{NaBr}) - \Lambda^\circ_m(\text{NaCl}) \cong \mathbf{1.8}$$

$$\Lambda^\circ_m(\text{KBr}) - \Lambda^\circ_m(\text{KCl}) \cong \mathbf{1.8}$$

The constant differences prove a critical reality: at infinite dilution, the identity of the counter-ion does not affect the mobility of an individual ion.

THE CORE PRINCIPLE

Independent Migration at Infinite Dilution



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

Infinite Dilution ($c \rightarrow 0$)



At near-zero concentration, ions are separated by massive volumes of solvent. Inter-ionic attractions and repulsions are completely eliminated.

Total Independence



Unfettered by neighboring charges, every ion migrates completely independently. It contributes a definite, constant value to the total conductivity, regardless of its co-ion.



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$$E=mc^2$$



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The Equation of the Law

Λ_m°

Limiting Molar Conductivity

The total conductivity of the electrolyte at zero concentration.

$\lambda_+^\circ / \lambda_-^\circ$

Ionic Conductivities

The individual limiting molar conductivities of the specific cation and anion.

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

$\frac{\nu_+}{\nu_-}$

Stoichiometric Coefficients

The number of cations and anions produced by the dissociation of one formula unit of the electrolyte.

The total conductivity is strictly additive—it is simply the weighted sum of its individual ionic parts.

Breaking Down Strong Electrolytes

1-1 Electrolyte (Sodium Chloride)

[NaCl]



[Na⁺]

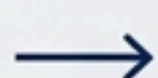


[Cl⁻]

$$\Lambda_m^\circ(\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$
$$50.1 + 76.3 = \mathbf{126.4 \text{ S cm}^2 \text{ mol}^{-1}}$$

2-1 Electrolyte (Calcium Chloride)

[CaCl₂]



[Ca²⁺]



[Cl⁻]



[Cl⁻]

$$\Lambda_m^\circ(\text{CaCl}_2) = \lambda_{\text{Ca}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ$$
$$119.0 + 2(76.3) = \mathbf{271.6 \text{ S cm}^2 \text{ mol}^{-1}}$$



Notice the multiplier! The stoichiometric coefficient ($\nu_- = 2$) must be applied because one formula unit of CaCl₂ yields two chloride ions.

Why Kohlrausch's Law Matters



Independence

Ions contribute to electrical conductance completely independently at infinite dilution ($c \rightarrow 0$) because inter-ionic forces vanish.



Additivity

Total conductivity is strictly additive. By knowing the individual λ_{+}° values of ions, we can calculate Λ_{m}° for any strong electrolyte using $\Lambda_{m}^{\circ} = \nu_{+}\lambda_{+}^{\circ} + \nu_{-}\lambda_{-}^{\circ}$.



The Ultimate Application

Solving for Weak Electrolytes

Weak electrolytes (like Acetic Acid) do not fully dissociate, so their **limiting** values **cannot** be found by plotting experimental data to zero. Kohlrausch's Law allows us to mathematically calculate these hidden values indirectly using data from strong electrolytes.



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