Colligative properties of solutions

Vapor pressure of the liquid

- $p^o(A)$...vapor pressure of the pure solvent
- $p(A)$...vapor pressure of the solution (solid substance B is dissolved)

$$p^o(A) > p(A)$$

t = const.

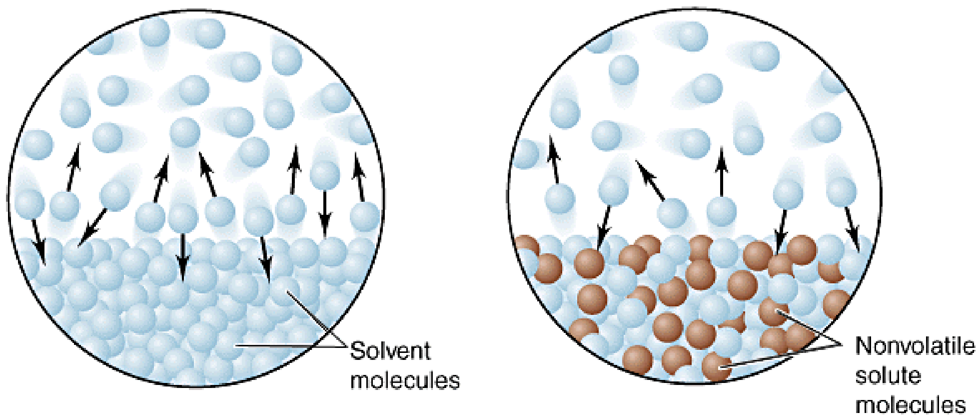
Raoult's law (end of 19th cent.):

$$p(A) = p^o(A) \cdot X(A)$$

t = const.

- $X(A)$... mole fraction of solvent A in the solution

In the solution is less likelihood of release solvent molecules in the vapor than in the pure solvent



Boiling point elevation and freezing point depression

- BOILING POINT.... the temperature at which the vapor pressure is equal to atmospheric pressure

- FREEZING POINT.... temperature at which the solid and liquid phases are in equilibrium, ie, have the same vapor pressure

Boiling point elevation and freezing point depression

Raoult: $X_A + X_B = 1 \longrightarrow p_A = p°_A (1 - X_B)$

$$p°_A - p_A = \Delta p = p°_A \cdot X_B$$

$$\Delta p \sim \Delta T$$

If Δp is proportional with X_B then is ΔT proportional with X_B ie

$$\Delta T \sim p°_A \cdot X_B$$

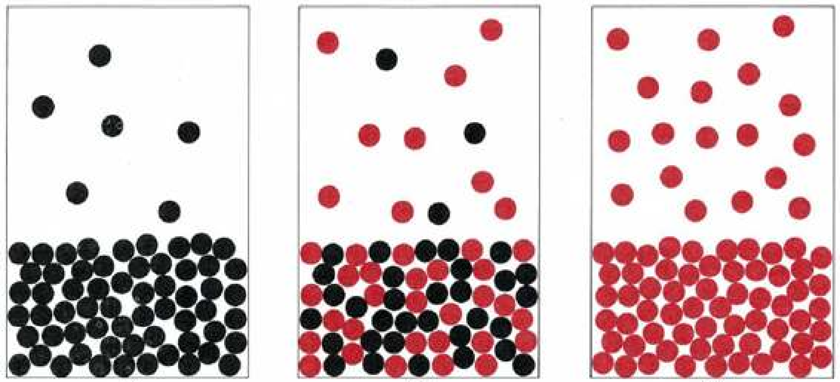
With various simplifications we get:

$\Delta T = K_b \cdot b_B$ respectively $\Delta T = E_b \cdot b_B$

ΔT…boiling point elevation and freezing point depression of solution
b_B…molality of dissolved substance B
K_b…cryoscopic constant of solvent
E_b…ebulioscopic constant of solvent

Ideal solutions

- Raoult's law is valid only for the ideal solution, that is a very diluted solution in which there is no attractive force between the dissolved particles
- Only at these conditions the vapor pressure of the solution depends only on the relative number of solvent molecules and solute particles, and not on their type.



(a) (b) (c)

Determination of molecular weight

- Experimental determination of ΔT of known mass of solvent (m_A) and solute (m_B), can determine the molar mass of the solute M_B:

$$M_B = \frac{K_B \cdot m_B}{\Delta T \cdot m_A}$$

Osmosis and osmotic pressure

- OSMOSIS... solvent molecules pass through the semi-permeable membrane from a solution of lower concentration in a solution of higher concentration.

- Passing of solvent continues until the hydrostatic pressure is equal to the force of diffusion. Then it establishes a dynamic equilibrium.

Osmosis and osmotic pressure

- The equilibrium hydrostatic pressure in amount is equal to the osmotic pressure of the solution Π
- Van't Hoff equation:

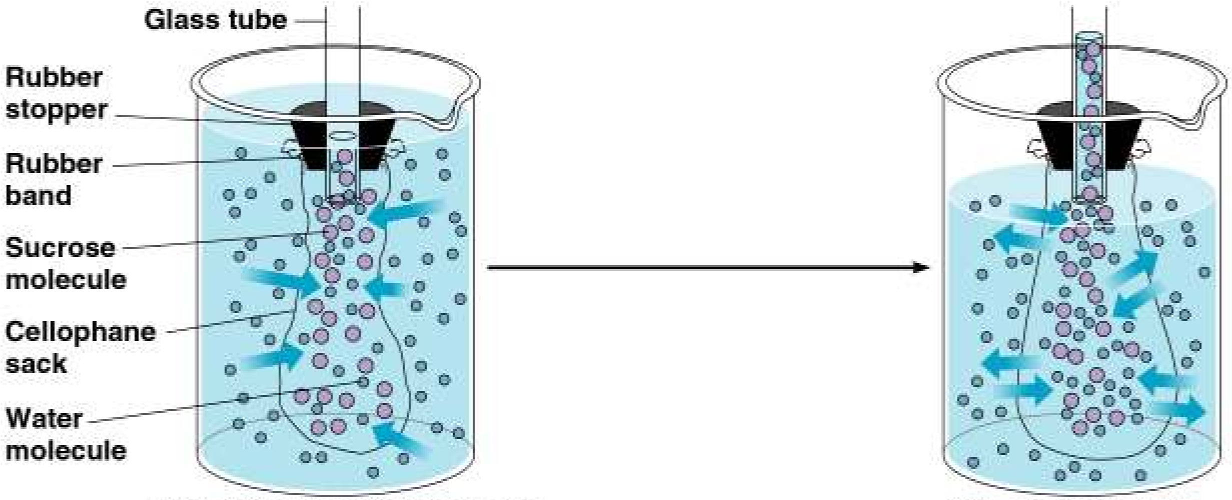
$$\Pi \cdot V = n \cdot R \cdot T$$

or

$$\Pi = c \cdot R \cdot T$$

applies for ideal solutions

- With experimental determination of Π the M of protein can be determined by.
- Osmosis is essential for cell function

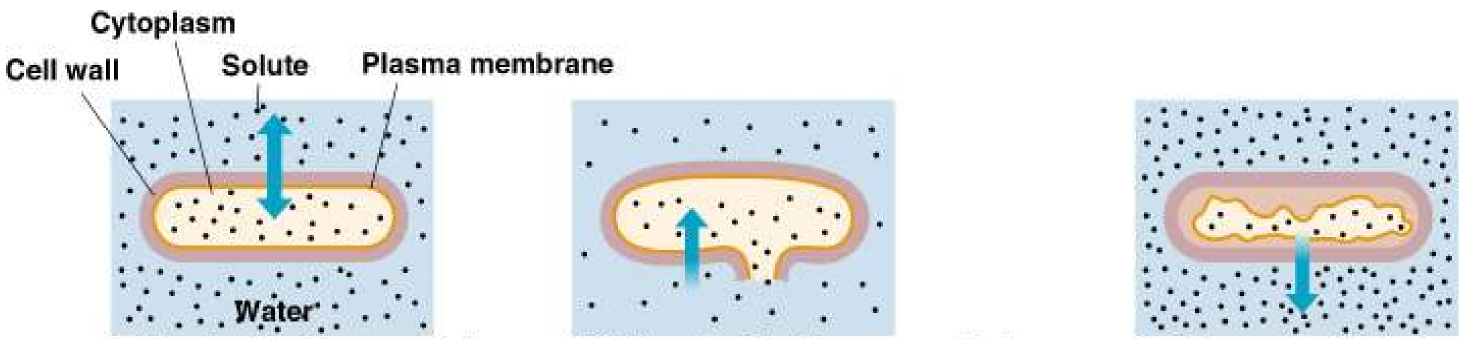


(a) At beginning of osmotic pressure experiment

(b) At equilibrium

Osmosis

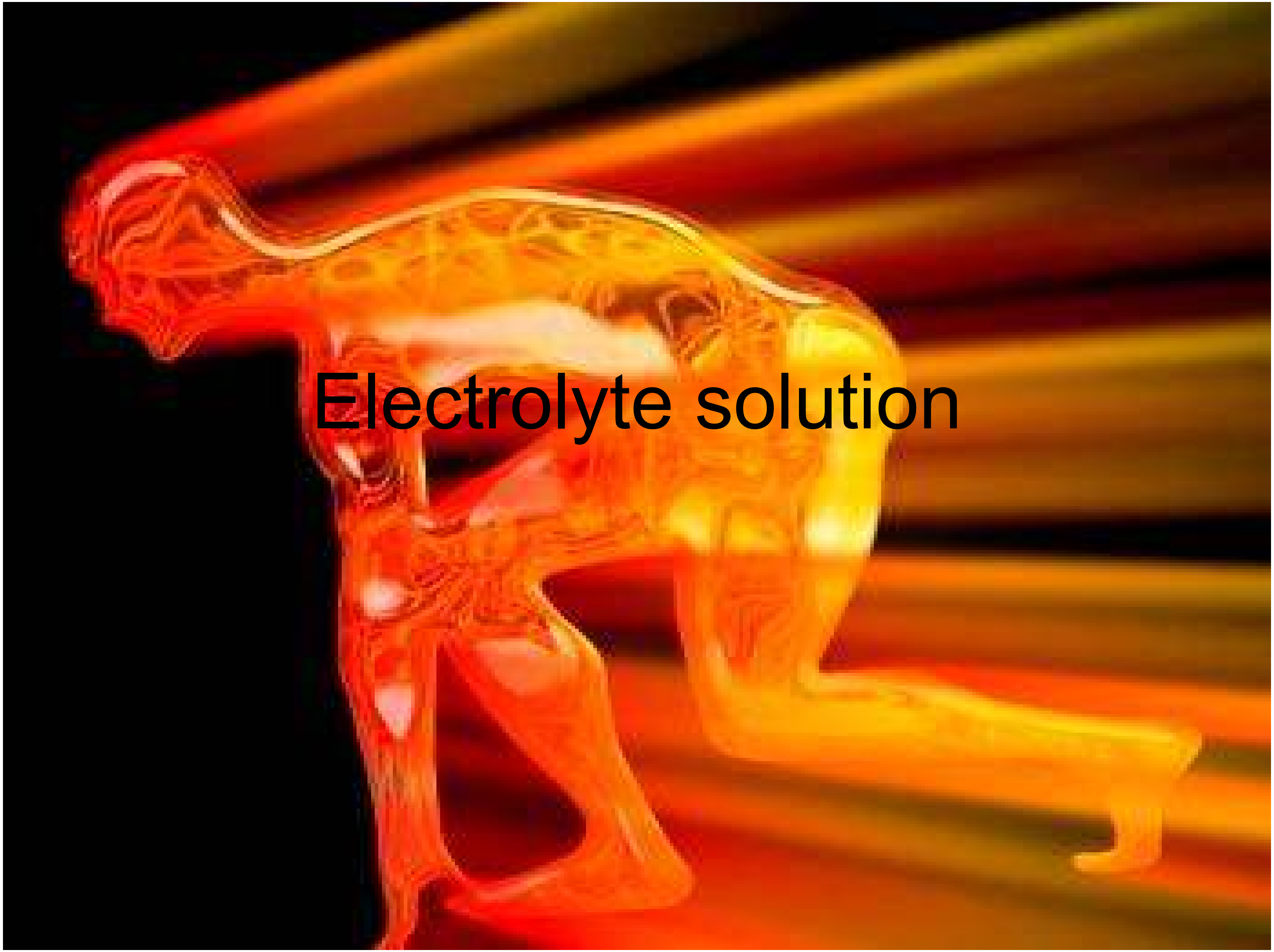
- The cell membrane is semipermeable
- The cell is a solution of various salts, sugars, etc..
- If the cells are in a solution of higher concentration, the water exits from the cell , it shrivels ..... plasmolysis
- If the cell is in a solution of lower concentration, the water enters in it and the cell ruptures.
- Isotonic solution .... solution of the same osmotic pressure as in the cell. 0.95% NaCl solution is isotonic with the blood cell solution.



(c) Isotonic (isosmotic) solution— no net movement of water

(d) Hypotonic (hypoosmotic) solution—water moves into the cell and may cause the cell to burst if the wall is weak or damaged (osmotic lysis)

(e) Hypertonic (hyperosmotic) solution— water moves out of the cell, causing its cytoplasm to shrink (plasmolysis)


Electrolyte solution

Electrolyte solution

- ELECTROLYTES.... substances which produce ions in water
- Strong electrolytes .... completely dissociated into ions (NaCl, HCl)
- Weak electrolytes ... partially dissociated into ions(CH_3COOH, $HgCl_2$)

Colligative properties of electrolytes

- For some electrolyte molality, b, there exists a greater number of particles, so it proportionately changes the partial pressure of solvent above the solution, freezing point, boiling point and osmotic pressure:

$$\Delta T = i \cdot K_b \cdot b_B$$

$$\pi \cdot V = i \cdot n \cdot R \cdot T$$

i... Van't Hoff factor, determined experimentally, and at low concentrations is equal to the number of dissociated ions

Molar conductivity of the electrolyte

- Ions in solution conduct electricity
- Electrical conductivity of the electrolyte, κ (S cm^{-1}) depends on: type of ions

  concentration of ions
- Molar conductivity of electrolyte, Λ (S cm^2 mol^{-1}) is defined:

$$\Lambda = \frac{\kappa}{c} \quad (\text{S cm}^2\ \text{mol}^{-1})$$

Molar conductivity of STRONG electrolytes

- Λ is independent of the concentration and electrolytes can be compared. Since Λ of strong electrolytes at low concentrations slightly dependent on the concentration, the term molar conductivity at infinite dilution Λ^{∞} is introduced

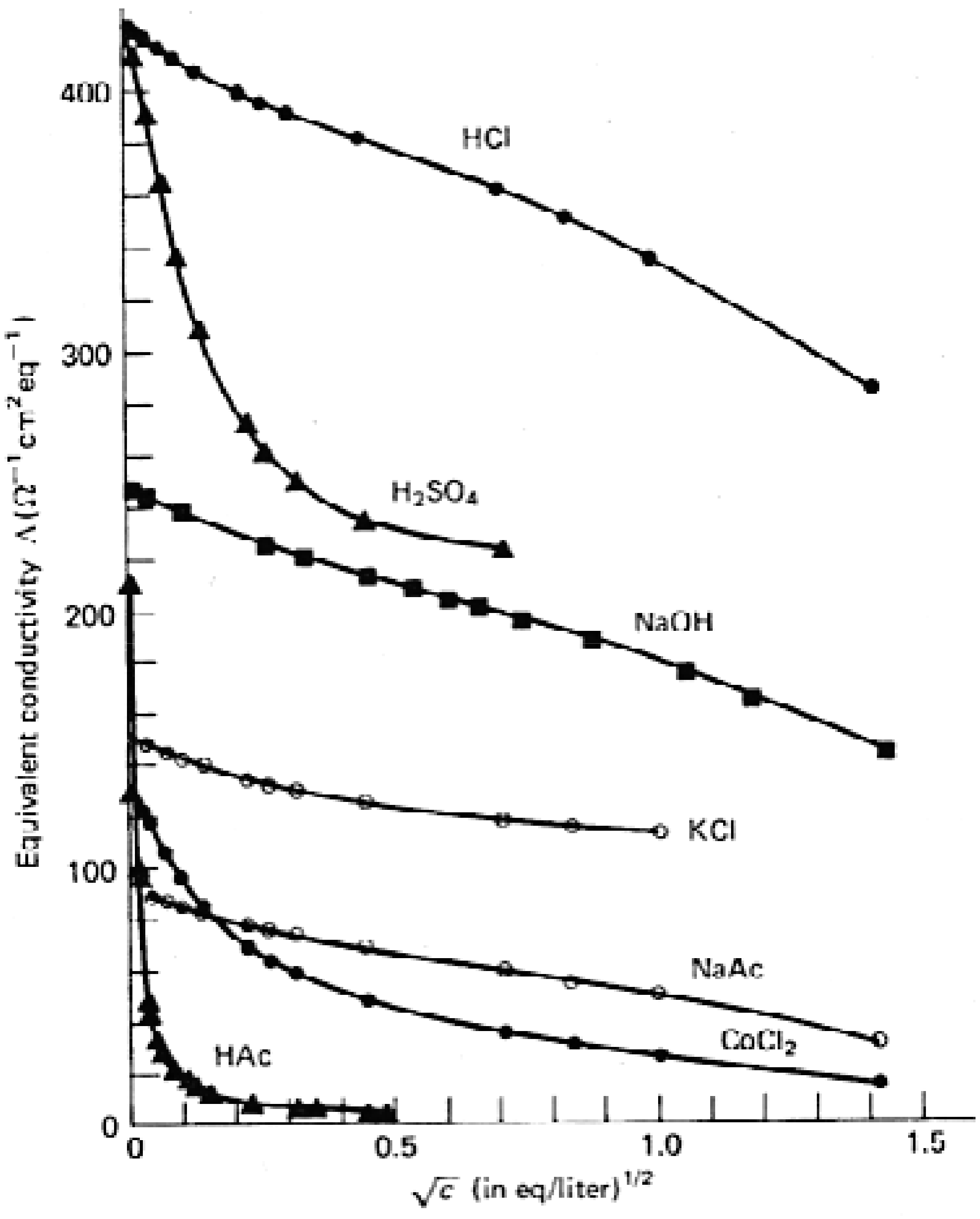
Molar conductivity of WEAK electrolytes

- Λ of weak electrolyte depends on the concentration, it is very low at high and medium concentrations, but at high dilution increases steeply up to the values that strong electrolytes have.
- This is because the proportion of dissociated molecules is less at higher and medium concentrations, and strong increases with dilution.
- German physicist Kohlrausch noticed that each type of ions characteristically contributes to the molar conductivity of electrolyte

Molarna provodnost (Λ) elektrolita
kao funkcija broja iona nastalih disocijacijom

	Λ/S cm² mol⁻¹
2 iona: $KCl(c) \rightarrow K^{+} + Cl^{-}$	127
3 iona: $BaCl_2(c) \rightarrow Ba^{2+} + 2Cl^{-}$	260
4 iona: $AlCl_3(c) \rightarrow Al^{3+} + 3Cl^{-}$	413
5 iona: $K_4[Fe(CN)_6](c) \rightarrow 4K^{+} + [Fe(CN)_6]^{4-}$	558

Sastav kompleksa	Λ/S cm² mol⁻¹
$Pt(NH_3)_4Cl_2$	260
$Pt(NH_3)_3Cl_2$	116
$Pt(NH_3)_2Cl_2$	0
$KPt(NH_3)Cl_3$	103
K_2PtCl_4	267



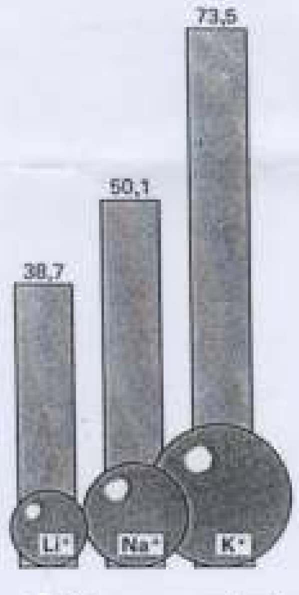
HCl
H_2SO_4
NaOH
KCl
NaAc
$CoCl_2$
HAc
Equivalent conductivity $\Lambda(\Omega^{-1}cm^2eq^{-1})$
400
300
200
100
0
0
0.5
1.0
1.5
$\sqrt{c}$ (in eq/liter)$^{1/2}$

- At infinite dilution molar conductivity of the electrolyte is the sum of the molar conductivity of ions
- $\Lambda^{\infty}(Na_2SO_4) = 2\ \Lambda^{\infty}(Na^+) + \Lambda^{\infty}(SO_4^{2-}) =$
$= (2 \cdot 50{,}1 + 160)\ S\ cm^2\ mol^{-1} = 260{,}2\ S\ cm^2\ mol^{-1}$

- Small Li^{+} is more hydrated from a larger K^{+}, and is less mobile. H^{+} is very small, but it has great conductivity.

ablica 8.1. Molarna provodnost pojedinih iona u vodi pri beskonačnom razrjeđenju 25 °C

ion	$\frac{\Lambda^{\infty}}{\text{S cm}^2\text{ mol}^{-1}}$	ion	$\frac{\Lambda^{\infty}}{\text{S cm}^2\text{ mol}^{-1}}$	ion	$\frac{\Lambda^{\infty}}{\text{S cm}^2\text{ mol}^{-1}}$	ion	$\frac{\Lambda^{\infty}}{\text{S cm}^2\text{ mol}^{-1}}$
H^{+}	350	Mg^{2+}	106	OH^{-}	199	NO_3^{-}	71,4
Li^{+}	38,7	Ca^{2+}	119	F^{-}	55,4	CH_3COO^{-}	40,9
Na^{+}	50,1	Ba^{2+}	127	Cl^{-}	76,4	SO_4^{2-}	160
K^{+}	73,5	Cu^{2+}	107	Br^{-}	78,1		
Ag^{+}	61,9	Al^{+3}	189	I^{-}	76,8		



8.7 Molarne provodnosti iona i ionski radijusi

8.8 Mehanizam vođenja vodikovim ionima u vodi