



Physical pharmacy

Solutions of non Electrolytes

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Solutions

Definition

- Solutions are homogeneous mixtures of two or more components.
- Solute molecules are dissolved and uniformly distributed in the solvent medium.
- It has the same composition and properties at all points of sampling (one phase).
- It consists of one or more solutes dissolved in one or more solvents.

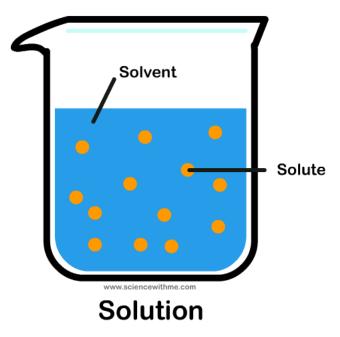


Solutions

Definition

- **Solution** is composed of:
 - **Solute:** is the substance that dissolves which may be solid, liquid, or gas (component in less amount).
 - **Solvent:** is the substance that does the dissolving which may be solid, liquid, or gas (component in greater amount).

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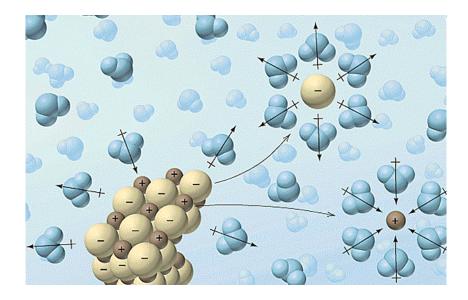
Solutions

Types of solute

• Non-electrolytes: do not yield ions when dissolved in water; therefore, do not increase electrical conductivity of solution (e.g. sugar, some polymers, some drugs).

• Electrolytes: form ions in solution; therefore, increase electrical

conductivity (e.g. salt).



Definition

- Solutions in which there is no change in the properties of the components when they are mixed.
- 1. Obey Raoults law over the entire range of conc.
- 2. No heat is evolved or absorbed ($\Delta H = 0$)
- 3. Volume of mixing ($\Delta V = 0$)

Definition

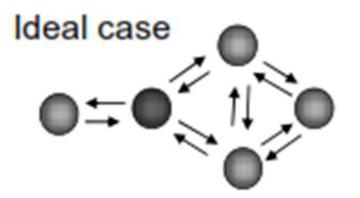
Ideal solution:

- E.g. 100 ml of ethanol + 100 ml of methanol = 200 ml solution.
- No heat is evolved or absorbed

Real solution:

- E.g. 100 ml of sulfuric acid + 100 ml of water = 180 ml solution.
- Heat is evolved (exothermic)

• in ideal solution There is complete uniformity of interaction between the components. Adhesive forces between solute-solvent molecules are the same as the cohesive forces between solute-solute and solvent-solvent molecules.



Raoult's Law

- In a closed container, each solution has a vapor above it that exert a pressure called *equilibrium vapor pressure*.
- The total vapor pressure of a solution (P_{total}) is the sum of the partial pressures of all the components (P_1 , P_2).
- $P_{total} = P_1 + P_2 + \cdots etc$.
- **Raoult's Law**: In an ideal solution, the partial vapor pressure of each component (e.g. P_1) is equal to the vapor pressure of the pure component (P°) multiplied by its mole fraction (X) in the mixture:

$$\bullet P_1 = X P^{\circ}_1$$

- If mole fraction of component 1 $(X_1) = 0.8$
- Then $P_1 = 0.8 P_1^{\circ}$

Raoult's Law

- For two constituents, toluene and benzene:
- $P_{total} = P_{toluene} + P_{benzene}$
- $P_{toluene} = X_{toluene} P_{toluene}^{\circ}$
- $P_{benzene} = Xbenzene P_{benzene}^{\circ}$

• The International System of Units (SI) recognizes pressure as a derived unit with the dimension of force per area and designates the pascal (Pa) as its standard unit. One pascal is one newton per square meter (N⋅m−2 or kg⋅m−1⋅s−2)

Raoult's Law: *Example*

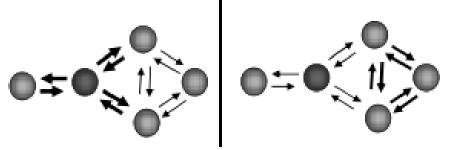
- •The vapor pressure of pure HFA 227 is 3.9×10^5 Pa and that HFA 134 is 5.7×10^5 Pa. What are the partial pressure and total pressure if a 50:50 weight mixture? M.wt for HFA 227 and HFA 134 are 170.03 and 102.03 respectively.
- n(HFA227) = 50 / 170.03 = 0.29
- n(HFA134) = 50 / 102.03 = 0.49
- Mole fraction (HFA227) = 0.29 / (0.29 + 0.49) = 0.37
- Mole fraction (HFA134) = 0.49 / (0.29 + 0.94) = 0.63
- $P(HFA227) = 3.9 \times 10^5 \times 0.37 = 1.4 \times 10^5 Pa$
- $P(HFA134) = 5.7 \times 10^5 \times 0.63 = 3.6 \times 10^5 Pa$
- $P_{total} = P_A + P_B = 1.4 \times 10^5 + 3.6 \times 10^5 = 5 \times 10^5 Pa$

Real Solutions

Definition

- In real solutions, the attractive forces are not uniform.
- The adhesive attraction of A for B might exceed the cohesive attraction between A and A or B and B.
- Oppositely, the cohesive forces between A and A or B and B might be greater than those between A and B.
- These real solutions not obey Raoult's law. There can be negative or positive deviations.

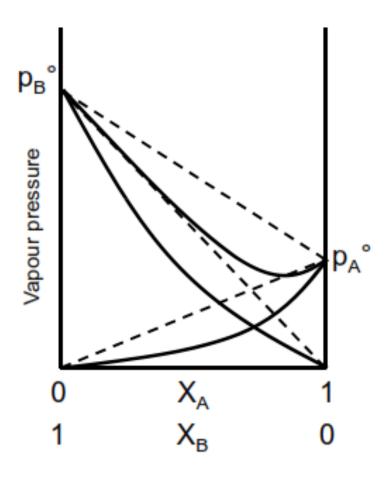
 Adhesive>Cohesive | Cohesive>Adhesive



Real Solutions

Negative Deviations

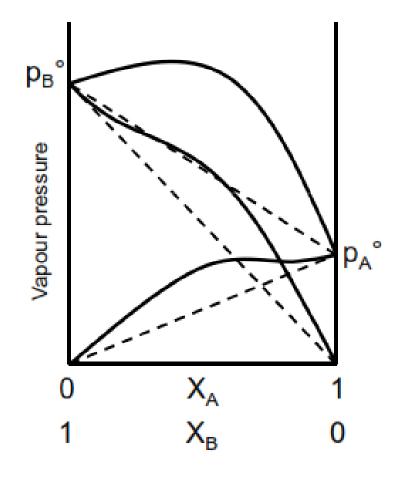
- Negative deviations occur when adhesive attractions (AB) are greater than cohesive attractions (AA and BB).
- As a result, partial pressures of components constituting real solutions are less than those in ideal solution.
- **E.g.** chloroform and acetone form hydrogen bonds
- CHCl₃ - O=C(CH₃)₂



Real Solutions

Positive Deviations

- Positive deviations occur when cohesive attractions (AA and BB) are greater than adhesive attractions (AB).
- As a result, partial pressures of components constituting real solutions are greater than those in ideal solution.
- E.g. CCl4 MeOH



Deviation	pressure	Δ H soln
Positive	Psoln > P ideal	Endothermic +ve
Ideal	Psoln = P ideal	zero
Negative	Psoln < P ideal	Exothermic -ve

- Example
- 2 mole of substance A mixed with 3 mole of substance B. The vapour pressure of A and B are 500 and 200 Pa respectively. The vapour pressure of the solution was found to be 294 Pa.
- Is this an ideal solution? Is there any deviation from Raoults law?if so, is it negative or positive deviation.?

Colligative Properties of Solutions

Lowering of Vapour Pressure Boiling Point Elevation Freeze Point Depression Osmotic Pressure Applications

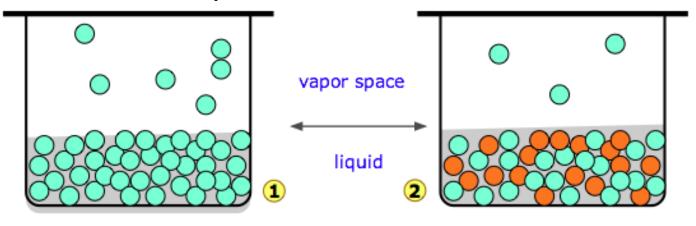
Colligative Properties of Solutions

- By definition a colligative property is a solution property (a property of mixtures) for which we consider the amount of solute dissolved in the solvent rather than the kind of solute
- This means that when considering the impact of solute on a colligative property,
- 1 mole of sugar≡ 1 mole Na+≡ 1 mole O2−≡ 1 mole urea do exactly the same thing

- change in the colligative properties of solution include:
- 1. Lowering of vapor pressure(antifreeze in radiator of the car)
- 2. Elevation of boiling point (cook faster by sea water)
- 3. Depression of freezing point(putting salt on roads to prevent ice forming)
- 4. Osmotic pressure
- Colligative properties of solution depend almost entirely on the number of particles (molecules or ions) present in the solution.

Lowering of Vapor Pressure

- When a non-volatile solute is dissolved in a volatile solvent, the vapor above the solution is provided by the solvent only.
- The solute particles at the surface block the solvent particles from escaping into the vapor state.
- Therefore, the tendency of the solvent molecules to exert vapor pressure is lowered in the presence of the solute.



the walls of any vessel in which they might be contained.

VAPOUR

(1) A substance which under ordinary conditions is a solid or a liquid but under specific conditions is in gaseous state is called vapour. *e.g.*, water vapours.

(2) A vapour is a gas produced by heating a solid or liquid that can return to its liquid or solid state under high pressure at ordinary temperatures.

(3) It is considered to be an unstable state and changes to liquid state at room temperature.

GAS

(1) When a substance exists in gaseous state under ordinary conditions i.e., at room temperature, then it is termed as a gas. e.g., oxygen, nitrogen, hydrogen, etc.

(2) Most of the gases need high pressure and low temperatures to return to their liquid or solid state.

(3) It is considered to be a stable state. It does not change into liquid easily.

Thus, we can conclude that, boiling point of any liquid is a measure of extent of force of attraction between the constituent particles. It means that greater is the boiling point of any liquid, greater will be attracted.

Lowering of Vapor Pressure

- Vapor pressure lowering of a solution depends on the number of solute molecules (mole fraction) present in the solution.
- The higher the solute fraction, the lower the vapor pressure above the solution.
- The degree of vapor pressure lowering can be determined by the following equation:

$$\bullet \Delta P / P_1^{\circ} = n_2 / (n_1 + n_2)$$

- $\Delta P/P1^{\circ}$: relative vapor pressure lowering.
- n1: no. of moles of the solvent, n2: no. of moles of the solute.

Lowering of Vapor Pressure Example

- •What is the relative vapor pressure lowering for a solution containing 171.2 g of sucrose (MW = 342.3) in 1000 g of water (MW = 18.02)?
- $\Delta P/P_1^{\circ} = n_2/(n_1 + n_2)$
- n = m/MW
- Moles of water = $n_1 = m_1/MWt_1 = 1000/18.02 = 55.5$
- Moles of sucrose = $n_2 = m_2/MWt_2 = 171.2/342.3 = 0.5$
- $\Delta P/P_1^{\circ} = n_2/(n_1 + n_2) = 0.5/(55.5 + 0.5) = 0.0089$
- The vapor pressure of this solution has been lowered 0.89% by sucrose

Boiling Point Elevation

- **Boiling Point:** is the temperature at which the vapor pressure of the liquid becomes equal to the atmospheric pressure.
- Presence of solute particles lower the vapor pressure of the solution (need to increase T to increase p to be equal to atmospheric pressure to get it to boil).
- The boiling point of a solution (T) is higher than that of the pure solvent alone (T°)
- The boiling point elevation (ΔT_h) is estimated by this equation:

$$\bullet \Delta T_b = K_b m$$

- ΔT_b : Boiling point elevation ($\Delta T_b = T T_0$)
- K_b : the ebullioscopic constant
- m: molality (mole per kg solvent).

Boiling Point Elevation Example

•An aqueous solution of a drug gave a boiling point elevation of 0.103 °C. Approximate Kb (ebullioscopic constant) for the solvent, water is 0.515 deg.kg/mol. What is the molality of the drug?

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•\Delta Tb = Kb m
•m = \Delta Tb / Kb
• = 0.103 / 0.515 = 0.2 mol kg<sup>-1</sup> = 0.0002 mol g<sup>-1</sup>
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Freeze Point Depression

- Solute particles will lower the freezing point of the solution
- The freezing point of pure water is 0°C .But freezing point of 1 M salt solution is -4°C i.e. water stays melted at temperature above -4°C, e.g at 0°C
- This is why salt is added to icy roads to melt the ice.
- The salt in this case is the solute that lowers the freezing point of the water.
- Solute interferes with ice crystal formation (ordered structure).
- Solute causing disorder (random state) preventing pure solvent to ice at 0°C and keep it melted.

Freeze Point Depression

- The freezing point of a solution is always lower than that of the pure solvent.
- The lowering of the freezing point of a solution is directly proportional to the molar concentration of the solute (i.e. number of particles in solution, (molecules or ions).

$$\bullet \Delta T_f = K_f m$$

- ΔT_f : Freezing point depression in °C ($\Delta T_f = T T_0$)
- K_f : Cryoscopic constant
- **m** : molality of the solution

Freeze Point Depression Example

- •What is the freezing point of a solution comprising 3.42 g of sucrose (MW = 342) and 500 g of water? Take K_f to be 1.86 (°C kg mol⁻¹)
- $\bullet \Delta T_f = K_f m$
- m = molality of sucrose

• =
$$\frac{\text{no. of mole}}{\text{Wt}_{\text{solvent}}} = \frac{\text{Wt/MW}}{\text{Wt}_{\text{solvent}}} = \frac{3.42/342}{0.5} = 0.02 \text{ mol kg}^{-1}$$

- $\Delta T_f = K_f m = 1.86 \times 0.02 = 0.037$ °C (i.e. ΔT_f , freezing point depression)
- Hence, the freezing point of this solution is -0.037 °C as (pure water $T_f = 0$ °C)

Freeze Point Depression

Biological Significance

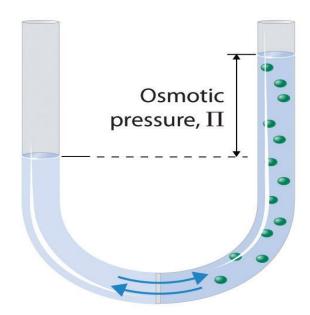
- The freezing point of blood serum and tears is − 0.52°C
- Any other solutions that freezes at 0.52°C will have the same osmotic pressure as these body fluids.
- Aqueous solutions such as injections and eye drops are formulated to be iso-osmotic (i.e. same osmotic pressure) with body fluids such as blood serum and lachrymal secretions.
- These solutions have a freezing point depression (FD) of 0.52°C

Osmotic Pressure

Definition

The compartment of pure solvent (on the left) is separated from the solution of solute and solvent (on the right) by a semi-permeable membrane

- Pure solvent attempts to flow from left to right to equalize the concentration difference.
- This movement of water across the semipermeable membrane is termed as *osmosis*.
- The pressure required for this movement is called the *osmotic pressure*.
- When there is no net movement of solvent molecules across the semi-permeable membrane, the two solutions are said to be isoosmotic.



Osmotic Pressure

Equation

• Osmotic pressure is determined by the total number of particles in the solution, regardless of their chemical nature.

$$\bullet \pi = MRT$$

- π : Osmotic pressure in atmospheres
- R: Gas constsant (0.082 L.atm/mol.deg)
- T: Absolute temperature
- *M*: Molarity of the solution
- The total number of particles will depend on the degree of dissociation of solutes in aqueous solution.
- An aqueous solution of sodium chloride of the same molarity will give twice as high osmotic pressure as the sucrose because sodium chloride dissociates into two ions per molecule; whereas sucrose doesn't.

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Osmotic Pressure Example

- •One gram of sucrose, molecular weight 342, is dissolved in 1000 L of water at 25 °C. What is the osmotic pressure in the solution?
- $n_{sucrose} = Wt/M.wt = 1/342 = 0.0029 \text{ mol}$
- Molarity = $n / V_{solution} = 0.0029/1 = 0.0029 m$
- $\bullet \pi = MRT$
- T = 273 + 25 = 298
- π = 0.0029 × 0.082 × 298 = 0.0708 atm

Osmotic Pressure

Biological Significance

Biological cell membrane acts as the semipermeable cell membrane and osmotic pressure is an important factor in regulating the intracellular fluid volume.





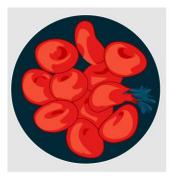
Hypertonic solutions cause movement of water out of the cell leading to cell shrinkage.





Isotonic solutions

cause no net flow of water into or out of the RBC and do not adversely affect the RBC membrane. They have the same osmotic pressure as blood serum (iso-osmotic)





Hypotonic solutions

cause movement of water into the cell leading to cell swelling and lysis.

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Osmotic Pressure

Osmole concentration

- Osmole (Osm) is the number of particles of solute that contribute to the osmotic pressure of a solution.
 - **E.g.1** Glucose does not dissociate and thus 1 mole of this solute gives 1 osmole of particles.
 - E.g.2 NaCl dissociates to form 2 ions and thus 1 mole of solute gives 2 osmole of osmotically active particles
- Solutions containing osmotically active particles is commonly expressed in terms of:
 - Osmolarity: osmoles (Osm) or milliosmoles (mOsm) per L of solvent
 - Osmolality: osmoles (Osm) or milliosmoles (mOsm) per kg of solvent
 - Aqueous solutions having 308 mOsm/L are said to be isoosmotic with body fluids.

Applications

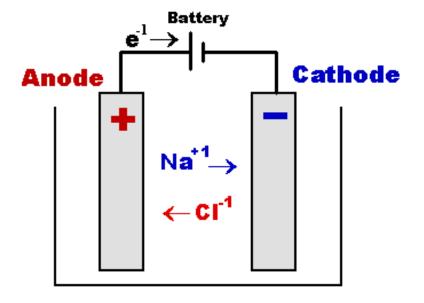
- Applications of colligative properties:
- 1. Preparation of isotonic solutions
- 2. Determination of the extent of ionization of electrolytes
- 3. Determination of the molecular weight of solutes.

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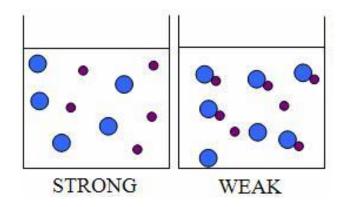
Solutions of Electrolytes

Definition

Electrolytes are substances that dissociate into ions in solution and acquire the capacity to conduct electricity through a process known as electrolysis (e.g. most drugs, buffers, and salts).



 Electrolytes can be classified as strong electrolytes and weak electrolytes.



- Strong electrolytes: The electrolytes which are almost completely dissociated into ions in solution like NaCl, KCl, HCl, NaOH, NH4NO3.
- Weak electrolytes: The electrolytes which do not ionize completely in solution.
- The extent of ionization of a weak electrolyte is expressed in terms of degree of dissociation or ionization (denoted by α). It is defined as the fraction of total number of molecules of the electrolyte which ionize in the solution. For strong electrolytes $\alpha = 1$ and for weak electrolytes $\alpha < 1$.

Colligative properties

Van't Hoff factor i

Van't Hoff observed that the osmotic pressure (π) of dilute solutions of nonelectrolytes, can be expressed by the equation: $\pi = MRT$

Electrolytes will dissociate and produce > 1 particle in solution

Van't Hoff Introduced a correction factor *i* to account for the dissociation of the electrolyte solutes:

 $\pi = iMRT$

Colligative properties

Van't Hoff factor i

Van't Hoff factor is calculated by the equation

$$i = 1 + \alpha (v-1)$$

 α : Degree of dissociation, v: Number of ions per solute molecule

For strong electrolytes: a = 1; Therefore i = v (e.g. i = 2 for NaCl and 3 for CaCl₂)

The Van't Hoff factor (i) expression of other colligative properties are:

Vapor pressure lowering $\Delta P = 0.018 i P^{\circ} m$ for aq.soln.

Boiling point elevation $\Delta T_b = iK_b m$ Freezing point depression $\Delta T_f = iK_f m$

Freeze Point Depression

Electrolytes: *Example*

What would be the freezing point of an aqueous solution of $Al_2(SO4)_3$ if the concentration was m = 0.667? the salt fully dissociates (α = 1) at this concentration, and kf = 1.86.

ANSWER:

Dissociation equation for Al₂(SO₄)₃

$$Al_2(SO_4)_3 + H_2O \rightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$$

Calculate the i factor

$$i = 1 + 1 (5-1) = 5$$

Calculate the freezing point using the freezing point depression equation :

$$\Delta T_f = i K_f m = 5 \times 1.86 \times 0.667 = 6.2 \text{ °C}$$

 $T_f = 0 - 6.2 = -6.2 \text{ °C}$

Electrolyte Conductance

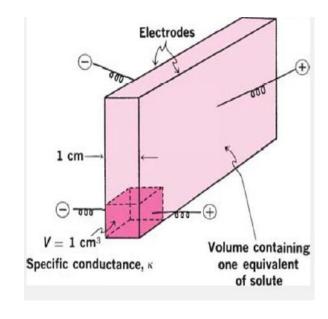
Specific and Equivalent Conductance

Conductance (C) is a measure of the ease with which current can pass through the conductor (the electrolyte solution). It is expressed in *mhos* (reciprocal of ohms)

$$C = 1/R$$
 R: resistance

Specific conductance (K) is the conductance of a solution restricted in a cube 1 cm³.

$$K = 1/p$$
 p: specific resistance



Equivalent Conductance

The conductance of certain volume of solution containing one equivalent of an electrolyte . It is denoted by Λ .

Let us consider the X cm3 of solution containing one equivalent of an electrolyte. Its conductance is equal to equivalent conductance, Λ .

i.e.,

the conductance of X cm3 ----- A

the conductance of 1 cm3 ----- κ specific conductance.

Therefore:

$$\Lambda$$
 = κ.V (ml) = Λ = $\kappa \cdot \frac{1000}{N}$

Electrolyte Conductance

Kohlrausch Theory

As the solution of a strong electrolyte is diluted, the specific conductance (K) decreases because the number of ions per 1 cm3 of solution is reduced.

Conversely, the equivalent conductance (Λ) of a solution of a strong electrolyte steadily increases on dilution because the ions are slowed down less by their neighbors in the more dilute solution and hence can move faster.



The equivalent conductance of a weak electrolyte also increases on dilution, but not as rapidly at first.

Electrolyte Conductance

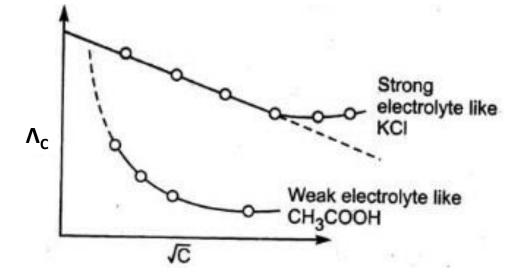
Kohlrausch Theory

Kohlrausch found that the equivalent conductance, $\Lambda_{\rm C}$ was a linear function of the square root of the concentration, C (Eq/L) for strong electrolytes.

$$\Lambda_{\rm C} = \Lambda_{\rm 0} - {\rm b} {\rm v} {\rm c}$$

 Λ_0 : equivalent conductance at infinite dilution.

b: slope of the line for strong electrolytes



The steeply rising curves for weak electrolytes result from an increase in their dissociation on dilution (increase in the number of ions capable of carrying the current).

Electrolytic Dissociation

Arrhenius Theory

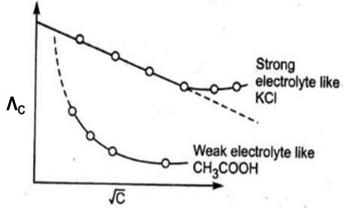
Arrhenius determined the degree of dissociation (α) directly from conductance measurements.

He considered that the equivalent conductance at infinite dilution (Λ_0) was a measure of complete ionization of the strong electrolytes; and the equivalent conductance at concentration \mathbf{c} (Λ_c) was a measure of partial ionization.

The fraction of molecules ionized (the degree of dissociation), was expressed by the equation:

$$\alpha = \Lambda_{\rm C}/\Lambda_{\rm 0}$$

 Λ_c/Λ_0 is known as the *conductance ratio*



Electrolytic Dissociation

Arrhenius Theory *Example 1*

• The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 mho. The equivalent conductance of a 5.9×10^{-3} M solution of acetic acid is 14.4 mho. What is the degree of dissociation of acetic acid at this concentration?

• $\alpha = \Lambda_{\rm C}/\Lambda_{\rm 0} = 14.4/390.7 = 0.037 = 3.7\%$

Methods of α measurement

Two methods can be used to determine the degree of dissociation:

First method: the degree of dissociation can be determined from conductance measurements.

Second method: The van't Hoff factor i can be

connected with the degree of dissociation α in the following way

$$\alpha = \frac{i - 1}{v - 1}$$

The cryoscopy method is used to determine i from the Expression

The cryoscopic method is used to determine i from

$$\Delta T_f = iK_f m$$

or

$$i = \frac{\Delta T_f}{K_f m}$$

Example: Calculate the degree of ionization of 0.1 m acetic acid providing that its freezing point is -0.188°C.

Answer: Acetic acid dissociates into two ions, so v = 2.

To calculate i:

$$i = \frac{\Delta T_f}{k_f m}$$

= 0.188/ (1.86*0.1)= 1.011

It is possible now to calculate the degree of ionization:

$$\alpha = \frac{i-1}{v-1}$$
= (1.011-1)/(2-1) = 0.011 or 1.1%

Example: Calculate the "degree of dissociation" of 0.01 m solution of ammonium chloride providing that its freezing point depression is 0.0367°C.

Answer: Ammonium chloride dissociates into two ions, so v = 2.

To calculate i:

$$i = \frac{\Delta T_f}{k_f m}$$
= 0.0367/ (1.86*0.01)= 1.97

It is possible now to calculate the degree of ionization:

$$\alpha = \frac{i-1}{v-1}$$
= (1.97-1)/(2-1) = 0.97 or 97%

Activity and Activity Coefficients Activity

For solution of weak electrolytes, regardless of concentration, the number of ions is small and the interionic attractive forces are insignificant. Hence, Arrhenius theory and degree of dissociation are valid.

The large number of oppositely charged ions in solutions of strong electrolytes influence one another through interionic attractive forces.

As for strong electrolytes, ions can associate at high concentrations into groups known as ion pairs. Thus, the values of the freezing point depression and the other colligative properties are less than expected for solutions of unhindered ions

Activity and Activity Coefficients Activity

The activity (a), in general, is less than the actual or stoichiometric concentration of the solute (m), not because the strong electrolytes are partly ionized, but rather because some of the ions are effectively "taken out of play" by the electrostatic forces of interaction

Activity and Activity Coefficients

Activity Coefficients

At infinite dilution the ions are so widely separated that they do not interact with each other so activity equals concentration:

$$a = m$$
 or $a/m = 1$

As concentration increases, ions interaction increases making the ratio less than 1. This ratio is known as *practical activity* coefficient (γ_m) on the molal scale:

$$a/m = \gamma_m$$

On the molarity scale, another practical activity coefficient, (γ_c) , is defined as: $a/c = \gamma_c$

and on the mole fraction scale, a rational activity coefficient (γ_x) is defined as: $\alpha/x = \gamma_x$

Activity and Activity Coefficients Mean Ionic Activity

A cation and an anion may each have a different ionic activity, therefore a₊ is used for activity of cation and a– for activity of anion.

Since both ions are present in solution, the activity of the electrolyte is defined by its *mean ionic activity* a₊:

$$a_{+} = (a_{+}^{m} a_{-}^{n})^{1/(m+n)}$$

m, n: stoichiometric number of ions in the solution

E.g.

For NaCl
$$a_{\pm} = (a_{(Na^{1+})}^{1} \ a_{(Cl^{1-})}^{1})^{1/(1+1)}$$

for FeCl₃ $a_{\pm} = (a_{(Fe^{3+})}^{1} \ a_{(Cl^{1-})}^{3})^{1/(1+3)}$

Ionic Strength

lonic strength is a measure of the interionic attraction in solutions of strong electrolytes.

It defined on the molar scale, as:

$$\mu = \frac{1}{2}(C_1Z_1^2 + C_2Z_2^2 + C_3Z_3^2 + ...)$$

$$\mu = \frac{1}{2}\sum_i C_iZ_i^2$$

c= concentration

Z= valency

Ionic Strength

Example

What is the ionic strength of a) 0.01 M KCl, b) 0.01 M BaSO₄, c) 0.01 Na₂SO₄ and d) a solution with all 3 mixed together?

a)
$$\mu = \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] = 0.01$$

b)
$$\mu = \frac{1}{2}[(0.01 \times 2^2) + (0.01 \times 2^2)] = 0.04$$

c)
$$\mu = \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)] = 0.03$$

d)
$$\mu = 0.01 + 0.04 + 0.03 = 0.08$$