لجان الدفعات

PHYSICAL PHARMACY

MORPHINE ACADEMY

Solutions of nonelectrolytes

Solutions

- Solution is a mixture of two or more components that form a homogenous molecular dispersion (one phase).
- It consists of one or more solutes dissolved in one or more solvents.
- Solute molecules or ions are "dissolved" and uniformly distributed in the solvent medium.

Solutions

- A true solution is a single phase system.
- NaCl and water, ethanol and water
  - Form a solution (one phase) ⟹ **a solution**
- Talc and water
  - Form a suspension (two phase) ⟹ **not solution**
- Oil and water
  - Form an emulsion (two phase) ⟹ **not solution**

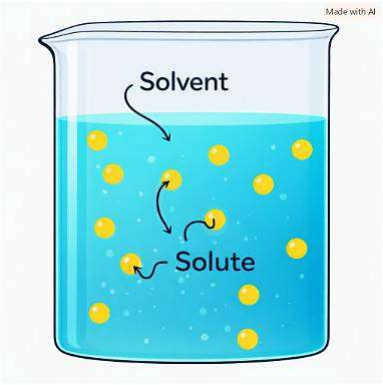
Solutions are composed of:

- **Solute:** is the substance that dissolves which may be solid, liquid, or gas.
- **Solvent:** is the substance that does the dissolving which may be solid, liquid, or gas.

Solutions

Which the solvent and which is the solute?

- **Solvent**: component in greater extent.
- **Solute**: component in minor extent.
- **Note:** When a solid is dissolved in liquid, it is the solute irrespective of relative amount.

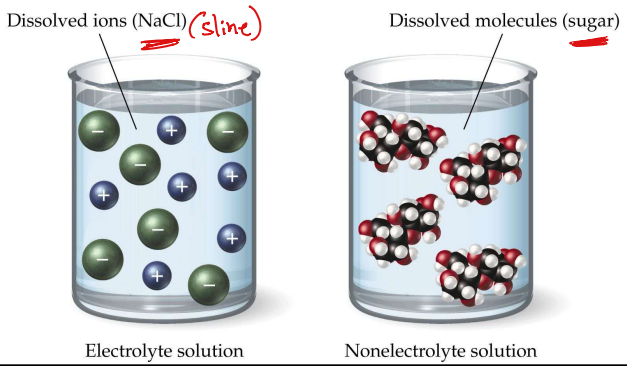


Types of Solutions

Solute	Solvent	Solution	Example
Gas	Gas	Gas	Air (O_2 in N_2)
Gas	Liquid	Liquid	Carbonated beverages (CO_2 in H_2O) Swimming pool (Cl_2 in H_2O)
Liquid	Liquid	Liquid	Wine (ethanol in H_2O) Vinegar (acetic acid in H_2O)
Liquid	Solid	Solid	Dental amalgam for fillings (liquid mercury in solid silver)
Solid	Liquid	Liquid	Saline (NaCl in H_2O) Sugar in water
Solid	Solid	Solid	14-karat gold (Ag in Au) Steel (carbon in iron)

Solutions

- **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. NaCl).



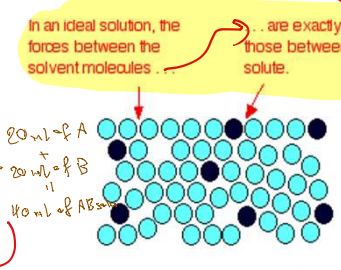
Solutions

Concentration expressions

- **Molarity(M):** no. of moles of solute in 1 litre of solution.
- **Molality (m):** no. of moles of solute in 1 kg of solvent.
- **Normality(N):** no. of equivalents in 1 liter of solution.
- **Mole fraction (X):** ratio of number of moles of one component to total moles of all constituents (solute and solvent).
- **Percent by weight (w/w):** no. of grams of solute in 100 g of solution.
- **Percent by volume (v/v):** no. of milliliters of solute in 100 ml of solution.
- **Percent weight in volume (w/v):** no. of grams of solute in 100 ml of solution.

Ideal solutions

- Solutions in which there is no change in the properties of the components when they are mixed.
- For a mix of molecules of A and B, the interactions between unlike neighbors (U_{AB}) and like neighbors U_{AA} and U_{BB} must be of the same average strength, i.e., $2U_{AB} = U_{AA} + U_{BB}$
- No heat is evolved or absorbed, the final volume is the sum of the volume of the individual components.



Ideal solutions

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).

إذا حكيتلك A عبارة عن 100 ml و B عبارة عن 100 ml والمحلول تبعهم اللي هو AB طلع 210 ml،هاد الفائض بخلي المحلول real ويدل عل، انه هدول المادتين لما ضفتهم على بعض خربوا الروابط اللي بيناتهم ،طيب كيف بيقدروا يخربوها؟ عن طريق أنهم يمتصوا حرارة فالتفاعل راح يصير endothermic rxn ،فبتكون حركة الجزيئات حرة اكثر بالحركة والمسافة بينها فضفاضة مش زي الexothermic بتكون اكثر compact

Ideal solutions

Raoult's Law

- Cohesive interactions in liquid prevent all molecules from escaping as a vapor. Disrupting the cohesion (by increasing T) will increase the tendency of molecules to escape from the liquid as a vapor.
- When the vapor pressure equals the external pressure, the system is said to be in equilibrium, and the vapor pressure is known as the *equilibrium vapor pressure (P)*
- A substance with a high vapor pressure at normal temperatures is often referred to as volatile.

Ideal solutions

Raoult's Law:

- The partial vapor pressure of each component in an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

$$P_A = P_A^{\circ} * \chi_A$$

χ_A = moles A / (moles A + moles B)

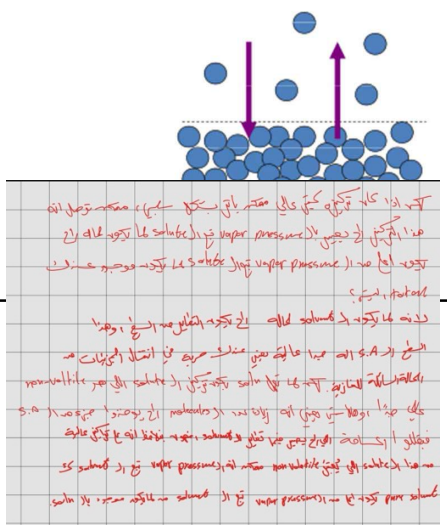
P_A: partial vapor pressure of A

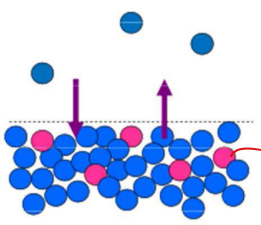
$$\therefore P_{total} = P_A + P_B + \cdots$$

Ideal solutions

Raoult's Law

- For a non-volatile solute, the total vapor pressure (P_{total}) is equal to the vapor pressure of the solvent ($P_{solvent}$) only: $P_{total} = P_{solvent}$
- $P1 = X\, P^{\circ}_1$ X: mole fraction of solvent



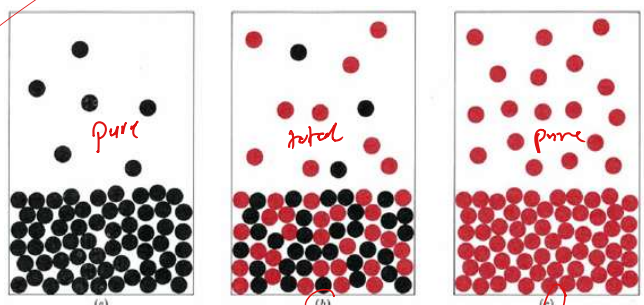


6

Ideal solutions

Raoult's Law

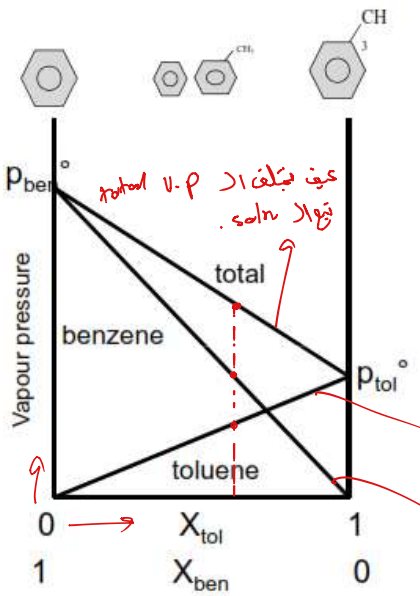
- If components constituting a solution are volatile, each will produce a partial pressure above the solution, which can be calculated from **Ideal Solutions Raoult's Law**
- The total pressure is the sum of the partial pressures of all the constituents.



Ideal solutions

Raoult's Law

- For two constituents, toluene and benzene:
- $P_{tol} = P_{tol}^{\circ} X_{tol}$
- $P_{ben} = P_{ben}^{\circ} X_{ben}$
- $P_{total} = P_{tol} + P_{ben}$
- P_{tol}, P_{ben}: partial vapor pressures
- P_{tol}°, P_{ben}°: vapor pressures of pure components.
- X_{tol}, X_{ben}: mole fractions

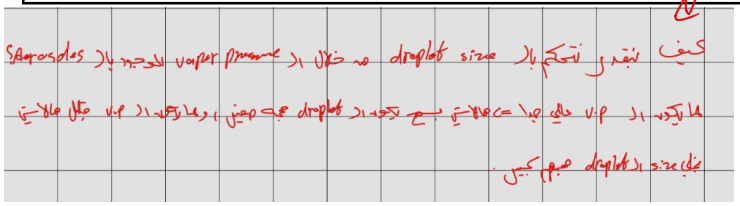


7

Ideal solutions

Aerosols and Raoult's law

- Raoult's law is important because it allows the calculation of vapour pressure from a knowledge of the composition of the solution.
- The requirement of the Montreal Protocol in 1989 for the replacement of chlorofluorocarbon (CFC) propellants in pressurised metered-dose inhalers with hydrofluoroalkanes (HFAs), because of the ozone-depleting properties of CFCs, led to a substantial review of the formulation of these devices as a consequence of major differences in physical and chemical properties of these propellants.
- The two most widely used HFAs are HFA 227 and HFA 134a.
- The vapour pressure of metered dose inhalers determines the aerosol droplet size and consequently has an important influence on the efficiency of deposition in the lungs



Ideal solutions

Example:

- Calculate the vapour pressure (in Pa) at 20°C above an aerosol mixture consisting of 30% w/w of HFA 134a (tetrafluoroethane, molecular weight 102) with a vapour pressure of 68.4 psig and 70% w/w of HFA 227 (heptafluoropropane, molecular weight 170) with a vapour pressure of 56.0 psig. Assume ideal behaviour.

Answer

No. of moles of HFA 134a in 100 g mixture = 30/102 = 0.2941 moles

No. of moles of HFA 227 in 100 g mixture = 70/170 = 0.4118 moles

$x_{134} = 0.2941/0.7059 = 0.4166$

$x_{227} = 0.4118/0.7059 = 0.5834$

$P = p^o_{134}x_{134} + p^o_{227}x_{227}$

$P = (68.4 \times 0.4166) + (56.0 \times 0.5834)$

$P = 61.17 \text{ psig} = 5.23 \times 10^5 \text{ Pa}$

Real solutions

- In real solutions, the attractive forces are not uniform.
- The adhesive attraction of A for B might be less or exceed the cohesive attraction between A and A or B and B.
- This can happen even if the liquids are completely miscible.
- The more dissimilar the nature of A and B, the more strongly the solution is expected to deviate from ideality.
- These real solutions may not obey Raoult's law. There can be negative or positive deviations.

Real solutions

Partial pressures of components less than in ideal solution.

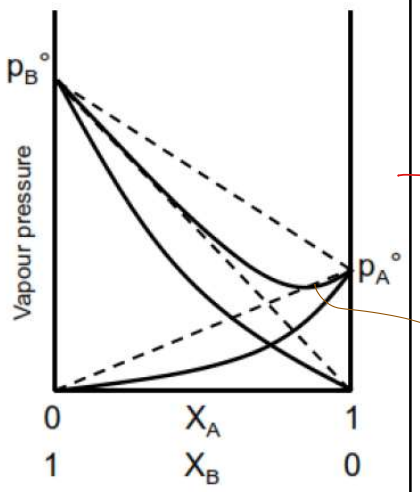
Adhesive attractions (AB) greater than cohesive attractions (AA and BB).

A holds B back and B holds A back.

Total vapor pressure may show a minimum.

E.g. chloroform and acetone form hydrogen bonds

$CHCl_3$ - - - $O=C(CH_3)_2$



Real solutions

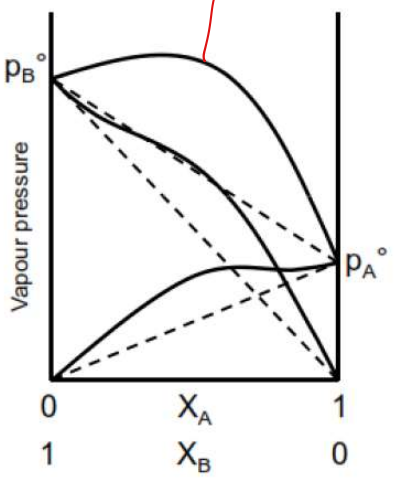
Partial pressures greater than in ideal solution.

Cohesive attractions (AA and BB) greater than adhesive attractions (AB).

A disrupts B cohesion so easier for B to escape and vice-versa

Total vapor pressure may show a maximum

E.g. CCl4 - MeOH



Colligative Properties of Solutions

- Colligative properties are properties of solutions that depend upon the ratio of the number of solute particles to the number of solvent molecules in a solution, and not on the type of chemical species present.

- Colligative properties of solution include:
  1. Lowering of vapor pressure
  2. Elevation of boiling point
  3. Depression of freezing point
  4. Osmotic pressure

Colligative Properties of Solutions

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 (atoms, molecules or ions) at the surface reduce the escaping tendency of the solvent
- Therefore, the tendency of the solvent molecules to exert vapor pressure is lowered in the presence of the solute.

Colligative Properties of Solutions

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.
- Vapor pressure lowering is the key to all four of the colligative properties.

Colligative Properties of Solutions

Lowering of vapor pressure

- The change of vapour pressure following the addition of a nonvolatile solute to a solvent may be determined by application of Raoult's law.

$$p = p_1 = p^o_1 x_1 = p^o_1 (1 - x_2)$$

$$(p^o_1 - p_1)/ p^o_1 = x_2 = n_2/(n_1+n_2)$$

- p_1: the vapor pressure of the solvent (with solute), p^o_1 : vapor pressure of the pure solvent x_1: mole fraction of solvent, x_2 = mole fraction of solute,

Colligative Properties of Solutions

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

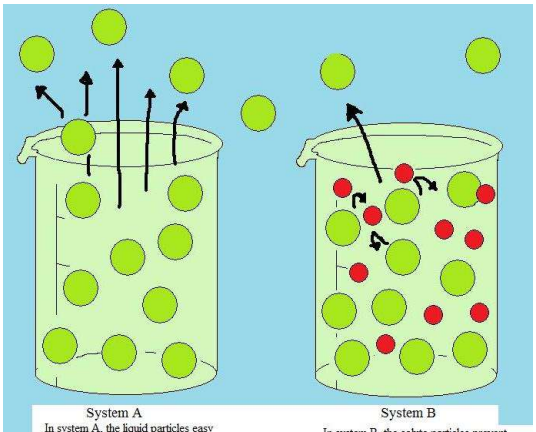
Colligative Properties of Solutions

Boiling Point Elevation

- **Normal Boiling Point:** is the temperature at which the vapor pressure (P) of the liquid becomes equal to the atmospheric pressure.
- Presence of solute particles lower the vapor pressure of the solution (we need to increase temperature to increase p to make it boil).
- The boiling point of a solution (T) is higher than that of the pure solvent alone (T°)

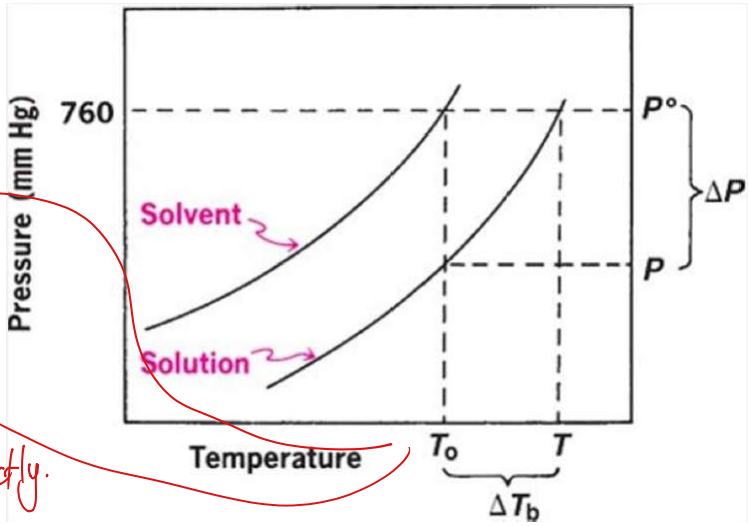
Colligative Properties of Solutions

Boiling Point Elevation



System A
In system A, the liquid particles easy shift into the gas phase at the normal boiling pressure. There are no obstacles for the liquid particles as there is in System B.

System B
In system B, the solute particles prevent the liquid particles from escaping the system to turn into gas. This requires the liquids to possess more energy to become a gas.



Boiling point elevation of solvent due to the addition of a solute

Colligative Properties of Solutions

Boiling Point Elevation

- The boiling point elevation, ΔT_b is estimated by this equation.

$$\Delta T_b = K_b\, m$$

$$T - T_0 = \Delta T_b$$

- $\mathbf{K_b}$: molal elevation constant (ebullioscopic constant)
- **m**: molality

Colligative Properties of Solutions

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.

a. What is the molality of the drug?

b. If the M.wt of the drug is 185, what is the concentration in % w/w?

$\Delta T_b = K_b\, m$

$m = \Delta T_b / K_b$

$= 0.103 / 0.515 = 0.2 \text{ mol kg}^{-1} = 0.0002 \text{ mol g}^{-1}$

% w/w = m × M.wt

$= 0.0002 \times 185$

$= 0.037 \text{ g / g} = 3.7 \text{ g / 100 g} = 3.7 \text{ \% w/w}$

Colligative Properties of Solutions

Depression of the Freezing Point

- Solute particles will lower the freezing point of the solution
- The freezing point of pure water is 0°C, but freezing point of aqueous solutions is lower
- Applications:
  - Anti-freeze solution (ethylene glycol)
  - Addition of salt to icy roads to melt the ice
- Solute interferes with ice crystal formation (ordered structure).
- Solute causing disorder (random state) preventing pure solvent to ice at 0°C and staying melted.

FP soln < FP pure

Colligative Properties of Solutions

Depression of the Freezing Point

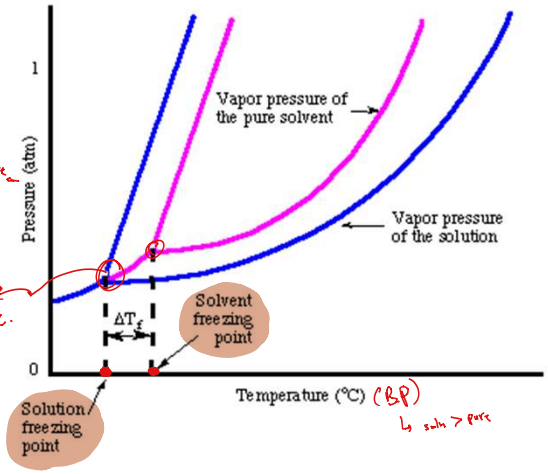
- The lowering of the freezing point of a solution is directly proportional to the molar concentraton of the solute (i.e. number of particles in solution, (molecules or ions).

$$\Delta T_f = K_f m$$

- ΔT_f: Freezing point depression
- K_f: Cryoscopic constant
- m: molality of solution

Colligative Properties of Solutions

Depression of the Freezing Point



Because the solute lowers the vapor pressure of the liquid solution, shifting the solid–liquid equilibrium to a lower temperature.

Colligative Properties of Solutions

Depression of the Freezing Point: Example

What is the freezing point of a solution comprising 3.42 g of sucrose (MW = 342) and 500 g of water? Take kf to be 1.86 (°C kg mol-1)

$\Delta T_f = K_f\, m$

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)

This solution will stay melted at temp of 0 °C

Colligative Properties of Solutions

Osmotic pressure

- Whenever a solution is separated from a solvent by a membrane that is permeable only to solvent molecules (referred to as a *semipermeable membrane*), there is a passage of solvent across the membrane into the solution.
- This is the phenomenon of *osmosis*.
- If the solution is totally confined by a semipermeable membrane and immersed in the solvent, then a pressure differential develops across the membrane, which is referred to as the *osmotic pressure*.

↳ is the pressure required to stop osmosis.

Colligative Properties of Solutions

Osmotic pressure

- Osmotic pressure is determined by the total number of particles in the solution, regardless of chemical nature
- Van't Hoff recognized a proportionality between osmotic pressure concentration and temperature and suggested a relationship that corresponds to an ideal gas:

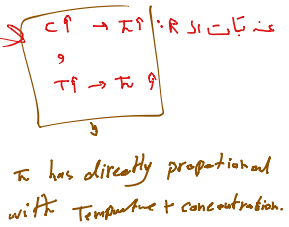
$\pi v = n R T$ ⇒ **Van't Hoff equation:** $\pi = c R T$

π: Osmotic pressure in atmospheres

c: molarity of solution

R: Gas constsant (0.082 L.atm/mol.deg)

T: Absolute temperature



Colligative Properties of Solutions

Osmotic pressure

- Morse and others have shown that when the concetration is expressed in molality rather than in molarity, the results compare more nearly with the experimental findings:

Morse equation: $\pi = m R T$

π: Osmotic pressure in atmospheres

m: molality of solution

R: Gas constsant (0.082 L.atm/mol.deg)

T: Absolute temperature

Colligative Properties of Solutions

Osmotic pressure: Example

One gram of sucrose, molecular weight 342, is dissolved in 1000 gm of solution at 25° C. What is the osmotic pressure in the solution?

Answer

Number of moles of sucrose = Wt/M.wt = 1/342 = 0.0029

Molality = number of moles/kg = 0.0029/1kg = 2.9×10^{-3} m

$\pi = mRT$

T = 273+25 = 298 K

$\pi = 2.9 \times 10^{-3} \times 0.082 \times 298 = 7.08 \times 10^{-2}$ atm

Molecular weight determination

- The colligative properties can be used to calculate molecular weights of non-electrolytes present as solutes.

Determination of molecular weight by boiling point elevation

$\Delta T_b = K_b\, m$

$$m = \frac{w_2/M_2}{w_1} \times 1000 = \frac{1000 w_2}{w_1 M_2}$$

$$\Delta T_b = K_b \frac{1000 w_2}{w_1 M_2}$$

$$M_2 = K_b \frac{1000 w_2}{w_1 \Delta T_b}$$

W_2 = weight of solute, W_1 = weight of solvent, M_2 = molecular weight of solute

Molecular weight determination

EXAMPLE - Determination of the Molecular Weight of Sucrose by Boiling Point Elevation

A solution containing 10.0 g of sucrose dissolved in 100 g of water has a boiling point of 100.149°C. What is the molecular weight of sucrose?

We write

M = (0.51 × 1000 × 10.0) / (100 × 0.149)

= 342 g/mole

$\Delta T_b = K_b \cdot m$

100.149 − 100 = 0.51

0.1 kg = 0.51 m

$m = \frac{0.149}{0.51}$

$m = 0.292$

$T_{a,n}$

1 kg

0.1 kg

$n = 0.1 \times 0.292$

$n = 0.0292$ moles

$\frac{n \cdot m}{M.M} = \frac{10}{0.0292}$

$M.M = 342$ g/mole

#

Molecular weight determination

- **Determination of molecular weight by freezing point depression**

$$M_2 = K_f \frac{1000 w_2}{\Delta T_f w_1}$$

EXAMPLE - Calculating Molecular Weight Using Freezing Point Depression

The freezing point depression of a solution of 2.000 g of 1,3-dinitrobenzene in 100.0 g of benzene was determined by the equilibrium method and was found to be 0.6095°C. Calculate the molecular weight of 1,3-dinitrobenzene.

We write

M = (5.12 × 1000 × 2.000) / (0.6095 × 100.0) = 168.0 g/mole