AL-Mustaqbal university
Pharmacy college

Physical pharmacy I

lec7

Dr.Ghada Ali
ghada.ali@uomus.edu.iq

Solutions of Non-electrolytes

Overview

Solutions

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Ideal and Real Solutions

Ideal Solutions

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Colligative Properties of Solutions

Lowering of Vapour Pressure

Boiling Point Elevation

Freeze Point Depression

Osmotic Pressure

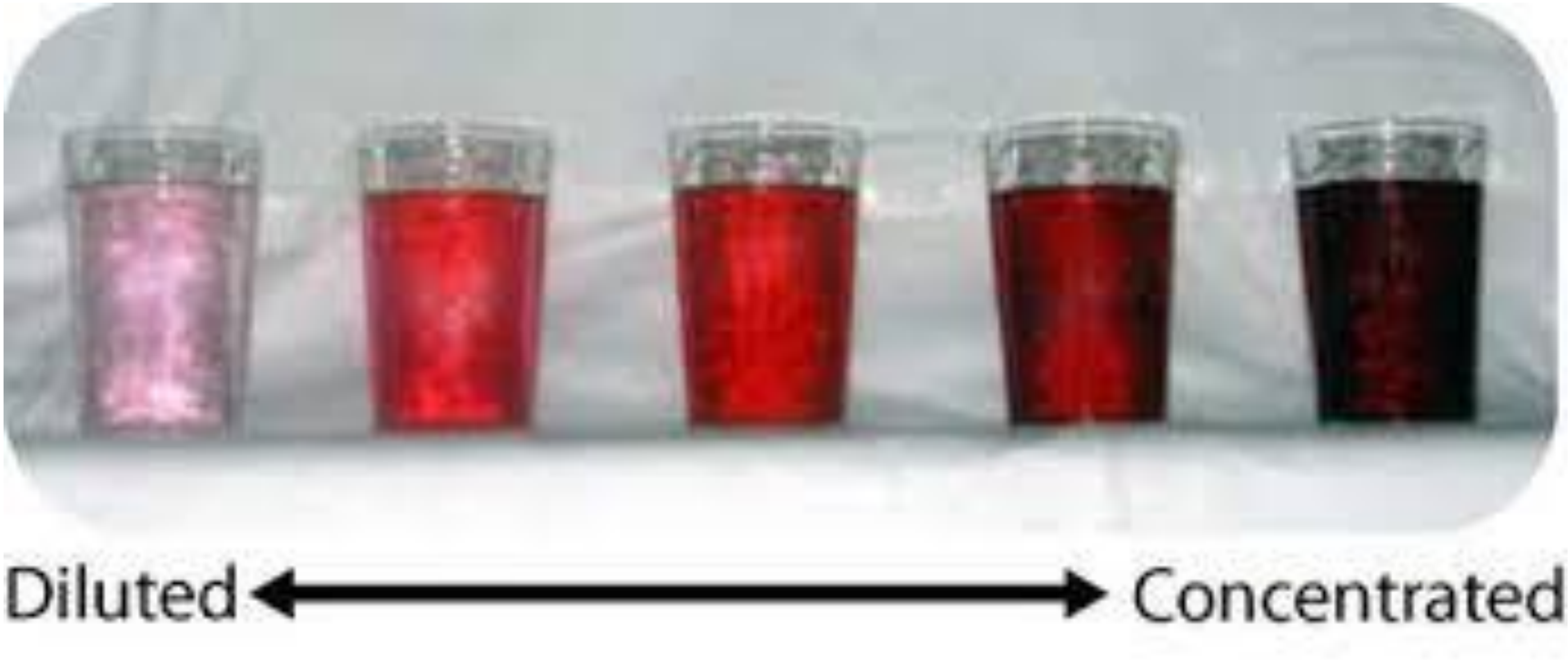
Applications

Learning objectives

- Calculate molarity, normality, molality, mole fraction, and percentage expressions.
- Calculate equivalent weights.
- Define ideal and real solutions using Raoult's ,Use Raoult's law to calculate partial and total vapor pressure.
- Identify and describe the four colligative properties of nonelectrolytes in solution.
- Calculate vapor pressure lowering, boiling point elevation, freezing point lowering, and pressure for solutions of nonelectrolytes.
- Use colligative properties to determine molecular weight.

Solutions

✓ Definition
✓ Types of solute
✓ Concentration expression

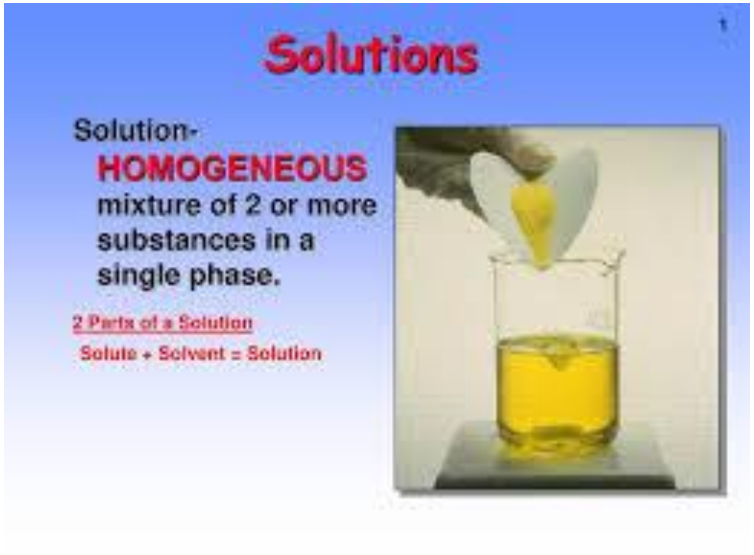


Definition

Solutions are homogeneous mixtures of two or more components. It has the same composition and properties at all points of sampling. 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.

A true solution is **a single phase system**.

☐ Sugar and water form a solution (one phase, up to a point!).
☐ Sand and water form a suspension (two phase).
☐ Oil and water form an emulsion (two phase).



Solutions

Solution-
HOMOGENEOUS
mixture of 2 or more substances in a single phase.

2 Parts of a Solution
Solute + Solvent = Solution

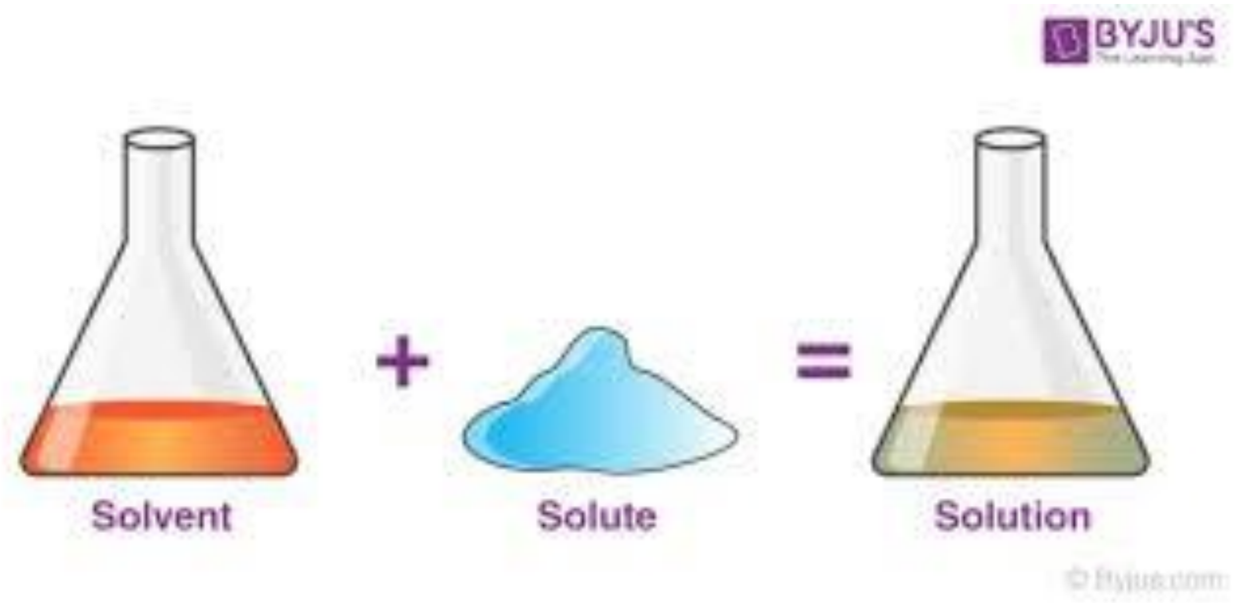
Solution are composed of:

Solute: are the substance that dissolves which may be solid, liquid, or gas.

Solvent: are the substance that does the dissolving which may be solid, liquid, or gas.

Solvent: component in greater extent.

Solute: component in minor extent.



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).

Concentration expressions

- **Molarity** (M): no. of moles of solute in 1 liter 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.

CONCENTRATION EXPRESSIONS

Expression	Symbol	Definition
Molarity	M,c	Moles (gram molecular weights) of solute in 1 liter of solution
Normality	N	Gram equivalent weights of solute in 1 liter of solution
Molality	*m*	Moles of solute in 1000 g of solvent
Mole fraction	*X*,N	Ratio of the moles of one constituent (e.g., the solute) of a solution to the total moles of all constituents (solute and solvent)
Mole percent		Moles of one constituent in 100 moles of the solution; mole percent is obtained by multiplying mole fraction by 100
Percent by weight	% w/w	Grams of solute in 100 g of solution
Percent by volume	% v/v	Milliliters of solute in 100 mL of solution
Percent weight-in-volume	% w/v	Grams of solute in 100 mL of solution
Milligram percent	—	Milligrams of solute in 100 mL of solution

Ideal Solutions
Real Solutions

Ideal solutions

Definition

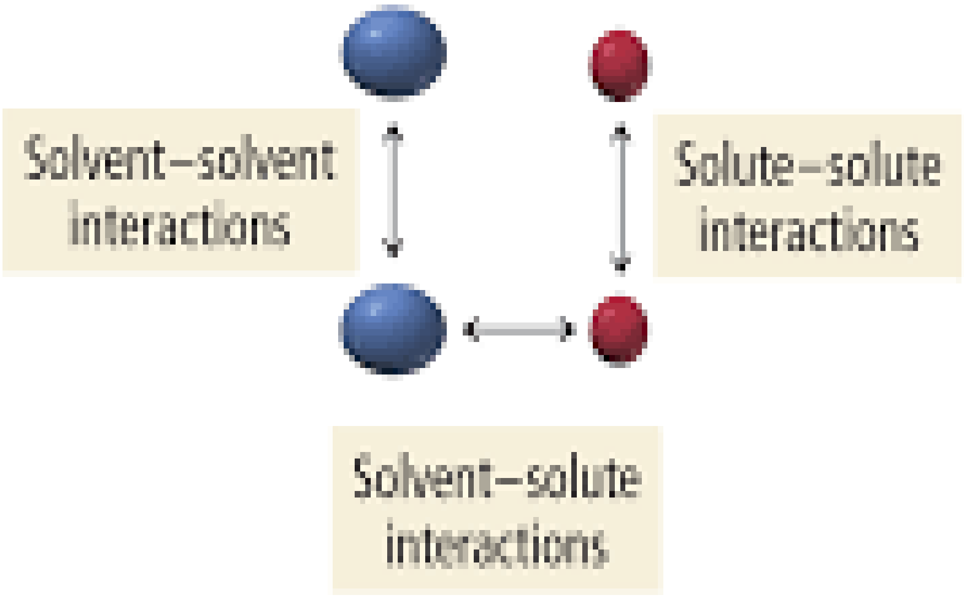
Solutions in which there is

- ✓ No change in the properties of the components when they are mixed.
- ✓ There is complete uniformity of interaction between the components.
- ✓ Forces between molecules solute-solute same as between solvent-solvent and between solute- solvent.
- ✓ No heat is evolved or absorbed.
- ✓ The final volume is the **sum** of the volume of the individual components.

  e.g. 100 ml of ethanol + 100 ml of methanol = 200 ml solution.

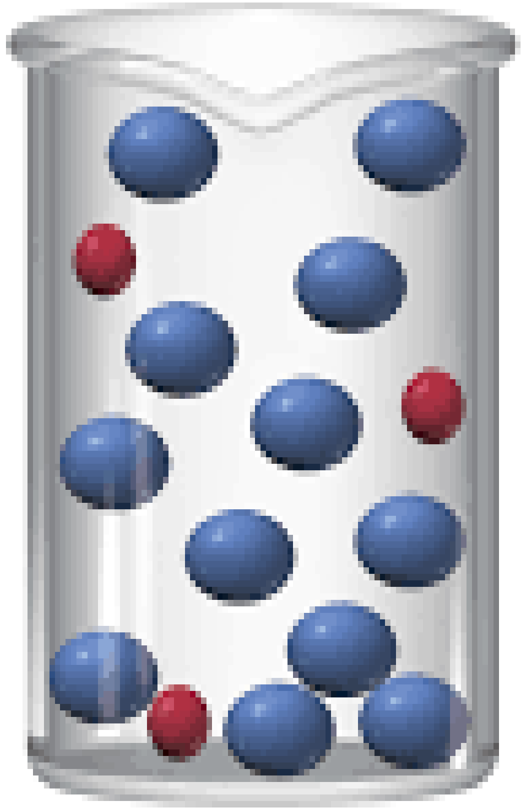
  No heat is evolved or absorbed

Solution Interactions


Solvent–solvent interactions

Solute–solute interactions

Solvent–solute interactions


Solution

Ideal Solutions and Raoult's Law

The vapor pressure of a solution is a particularly important property because it serves as a quantitative expression of escaping tendency. In 1887, Raoult recognized that, in an ideal solution, the partial vapor pressure of each volatile constituent is equal to the vapor pressure of the pure constituent multiplied by its mole fraction in the solution. Thus, for two constituents A and B

$$p_A = p_A{}^\circ X_A$$

$$p_B = p_B{}^\circ X_B$$

where P_A and P_B are the partial vapor pressures of the constituents over the solution when the mole fraction concentrations are X_A and X_B, respectively.

Example

What is the partial vapor pressure of benzene and of ethylene chloride in a solution at a mole fraction of benzene of 0.6? The vapor pressure of pure benzene at 50 °C is 268 mmHg , and the corresponding p_A° for ethylene chloride is 236 mmHg . We have

$$p_B = 268 \times 0.6 = 160.8 \text{ mmHg}$$

$$p_A = 236 \times 0.4 = 94.4 \text{ mmHg}$$

the total vapor pressure P is calculated as follows:

$$P = p_A + p_B = 160.8 + 94.4 = 255.2 \text{mmHg}$$

Real Solutions

Definition

In real solutions, the attractive forces are <u>not uniform</u>. 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. This can happen even if the liquids are completely miscible. These real solutions may not obey Raoult’s law.

e.g. 100 ml of sulfuric acid + 100 ml of water = 180 ml solution.

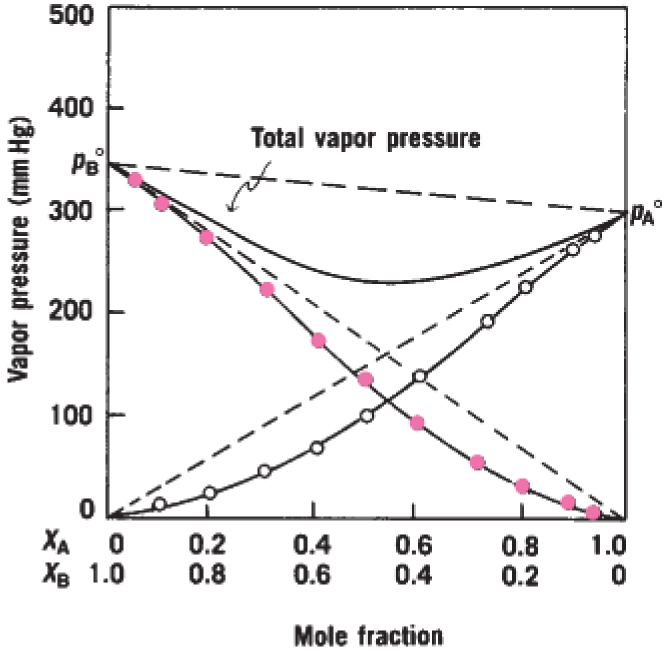
Heat is evolved (exothermic).

<u>Note</u>

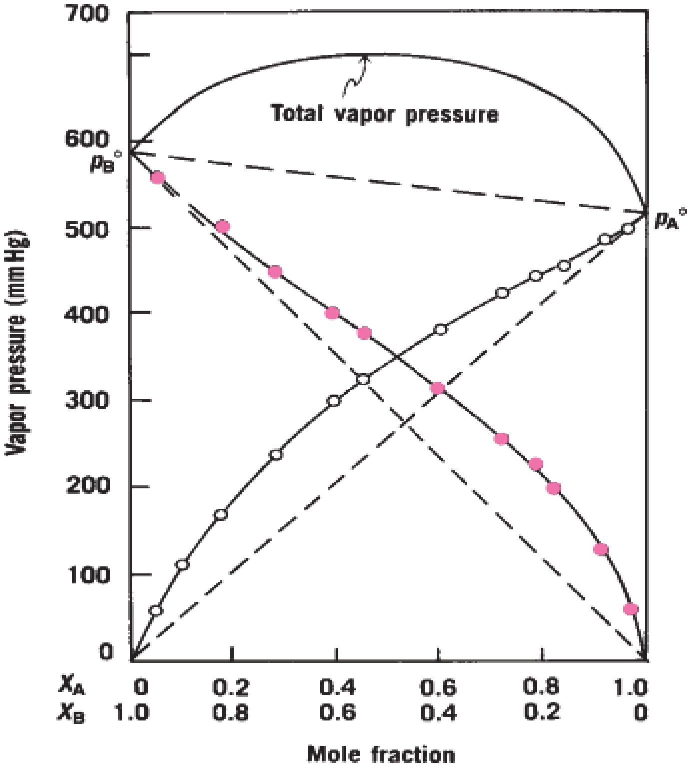
- Attractive forces between molecules of the <u>same</u> type are called **cohesive forces.**
- Attractive forces between molecules of <u>different</u> types are called **adhesive forces.**

Two types of deviation from Raoult's law are recognized, **negative deviation** and **positive deviation**

When the "adhesive" attractions between molecules of different species **exceed** the "cohesive" attractions between like molecules, the vapor pressure of the solution is **less** than that expected from Raoult's ideal solution law, and ***negative deviation*** **occurs**. If the deviation is sufficiently great, the total vapor pressure curve shows a minimum, as observed in **Figure below**, where A is chloroform and B is acetone.



When the interaction between A and B molecules is less than that between molecules of the pure constituents the presence of B molecules reduces the interaction of the A molecules, and A molecules correspondingly reduce the B B interaction. Accordingly, the dissimilarity of polarities or internal pressures of the constituents results in **a greater** escaping tendency of both the A and the B molecules. The partial vapor pressure of the constituents is **greater** than that expected from Raoult’s law, and the system is said to exhibit ***positive deviation***.



Colligative Properties of Solutions

- ☐ Lowering of Vapor Pressure
- ☐ Boiling Point Elevation
- ☐ Freeze Point Depression
- ☐ Osmotic Pressure
- ☐ Applications

Colligative Properties of Solutions

Colligative properties of solution include:

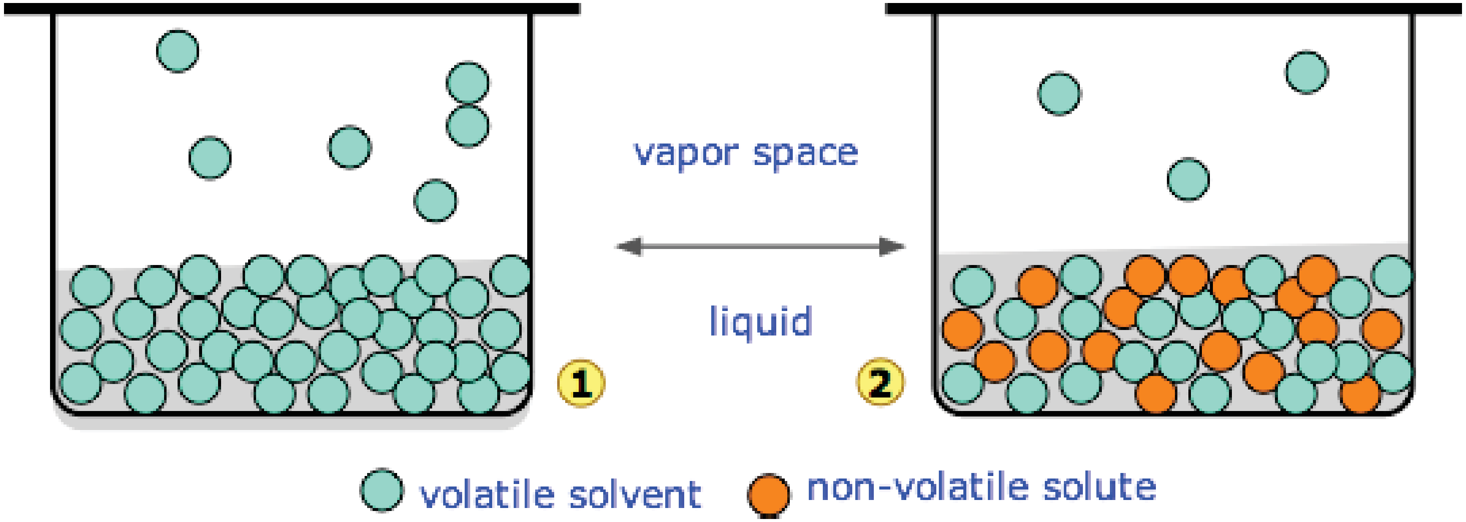
1. Lowering of vapor pressure
2. Elevation of boiling point
3. Depression of freezing point
4. Osmotic pressure

- Colligative properties of solution depend almost entirely on the number of particles (molecules or ions) present in the solution.

- Colligative properties almost do not depend on the actual properties of the molecules or ions with the same number of particles

➢ 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 <u>the solvent molecules to exert vapor pressure is lowered in the presence of the solute</u>. 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.



Example1

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)?

$$\Delta P / P_1° = n_2/(n_1 + n_2)$$

n_1: mole fraction of the solvent

n_2: mole fraction of the solute

ΔP: lowering of the vapor pressure

$\Delta P/P_1°$: relative vapor pressure lowering

P_1: vapor pressured of the solvent (with solute in it)

$P_1°$: vapor pressure of pure solvent

$$n = m/MW$$

Moles of water = $n_1 = m_1/MWt_1$ = 1000/18.02 = 55.5

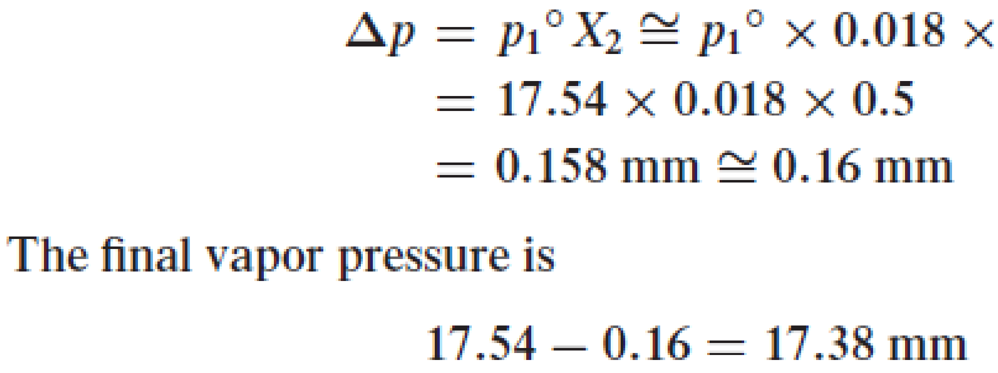
Moles of sucrose = $n_2 = m_2/MWt_2$ = 171.2/342.3 = 0.5

$\Delta P / P_1° = n_2 / (n_1 + n_2)$ = 0.5/(55.5 + 0.5) = 0.0089

The vapor pressure of this solution has been lowered 0.89% by sucrose

Example 2

Calculate the vapor pressure when 0.5 mole of sucrose is added to 1000 g of water at 20 °C. The vapor pressure of water at 20 °C is 17.54 mm Hg. The vapor pressure lowering of the solution is



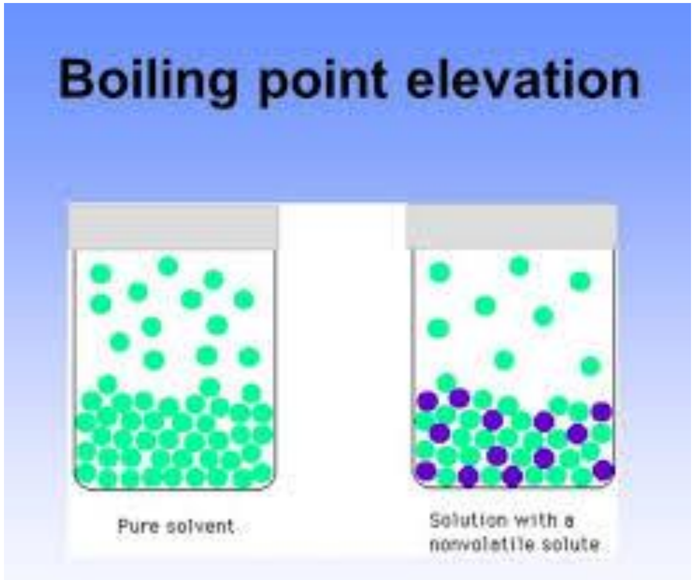
$$\begin{aligned}\Delta p &= p_1{}^\circ X_2 \cong p_1{}^\circ \times 0.018 \times m \\ &= 17.54 \times 0.018 \times 0.5 \\ &= 0.158\ \text{mm} \cong 0.16\ \text{mm}\end{aligned}$$

The final vapor pressure is

$$17.54 - 0.16 = 17.38\ \text{mm}$$

➢ Boiling Point Elevation

The normal boiling point is the temperature at which the vapor pressure of the liquid becomes equal to an external pressure of 760 mm Hg. A solution will boil at a higher temperature than will the pure solvent. This is the colligative property called boiling point elevation. the more of the solute that is dissolved, the greater is the effect. The boiling point of a solution of a nonvolatile solute is higher than that of the pure solvent owing to the fact that the solute lowers the vapor pressure of the solvent.



Example

Calculation of the Elevation Constant .A 0.200 m aqueous solution of a drug gave a boiling point elevation of 0.103◦C. Calculate the approximate molal elevation constant for the solvent, water.

Substituting into equation yields

$$\Delta T_b = K_b m$$

where T_b is known as the *boiling point elevation* and K_b is called the *molal elevation constant* or the *ebullioscopic constant*. K_b has a characteristic value for each solvent,

$$K_b = \frac{\Delta T_b}{m} = \frac{0.103}{0.200} = 0.515 \text{ deg kg/mole}$$

Freeze Point Depression

The normal freezing point or melting point of a pure compound is the temperature at which the solid and the liquid phases are in equilibrium under a pressure of 1 atm. Equilibrium here means that the tendency for the solid to pass into the liquid state is the same as the tendency for the reverse process to occur, because both the liquid and the solid have the same escaping tendency. If a solute is dissolved in the liquid at the triple point, the escaping tendency or vapor pressure of the liquid solvent is lowered below that of the pure solid solvent. The temperature must drop to reestablish equilibrium between the liquid and the solid. Because of this fact, the freezing point of a solution is always lower than that of the pure solvent the boiling point elevation, and the freezing point depression is proportional to the molal concentration of the solute.

The equation is

$$\Delta T_f = K_f m$$

or

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

T_f is the freezing point depression, and K_f is the molal depression constant or the cryoscopic constant, which depends on the physical and chemical properties of the solvent.

Example1

What is the freezing point of a solution containing 3.42 g of sucrose and 500 g of water? The molecular weight of sucrose is 342. In this relatively dilute solution, K_f is approximately equal to 1.86.We have.

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

$$\Delta T_f = 1.86 \times \frac{1000 \times 3.42}{500 \times 342}$$

$$\Delta T_f = 0.037^\circ\mathrm{C}$$

Therefore, the freezing point of the aqueous solution is −0.037◦C.

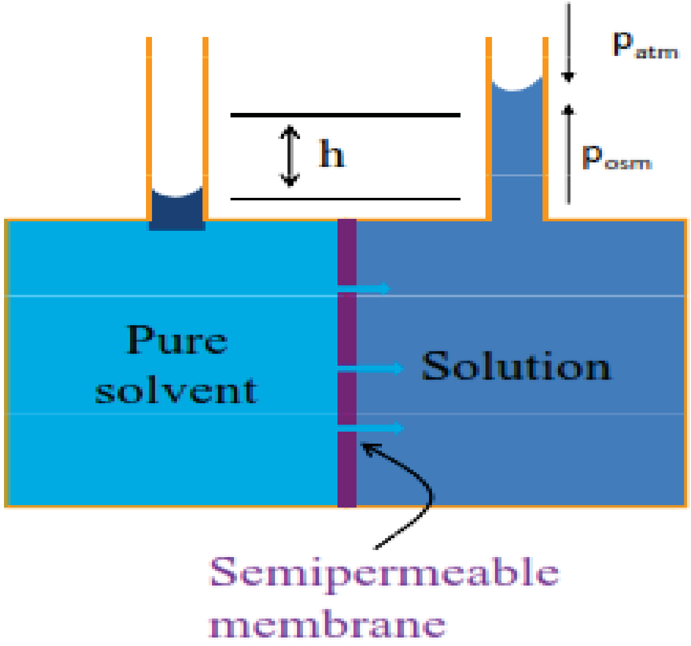
Example2

What is the freezing point depression of a 1.3 m solution of sucrose in water? the cryoscopic constant at this concentration is about 2.1. Thus, the calculation becomes

$$\Delta T_\mathrm{f} = K_\mathrm{f} \times m = 2.1 \times 1.3 = 2.73^\circ\mathrm{C}$$

➢ Osmotic Pressure

If cobalt chloride is placed in a parchment sac and suspended in a beaker of water, the water gradually becomes red as the solute diffuses throughout the vessel. In this process of diffusion, both the solvent and the solute molecules migrate freely. On the other hand, if the solution is limited in a membrane permeable only to the solvent molecules, the phenomenon known as osmosis (Greek: “a push or impulse”) occurs, and the barrier that permits only the molecules of one of the components (usually water) to pass through is known as a semipermeable membrane.



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

$$\pi = m\,R\,T$$

π: Osmotic pressure in atmospheres
R: Gas constsant (0.082 L.atm/mol.deg)
T: Absolute temperature
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.

Example

One gram of sucrose, molecular weight 342, is dissolved in 100 mL of solution at 25◦C. What is the osmotic pressure of the solution? We have.

$$\pi V = nRT$$

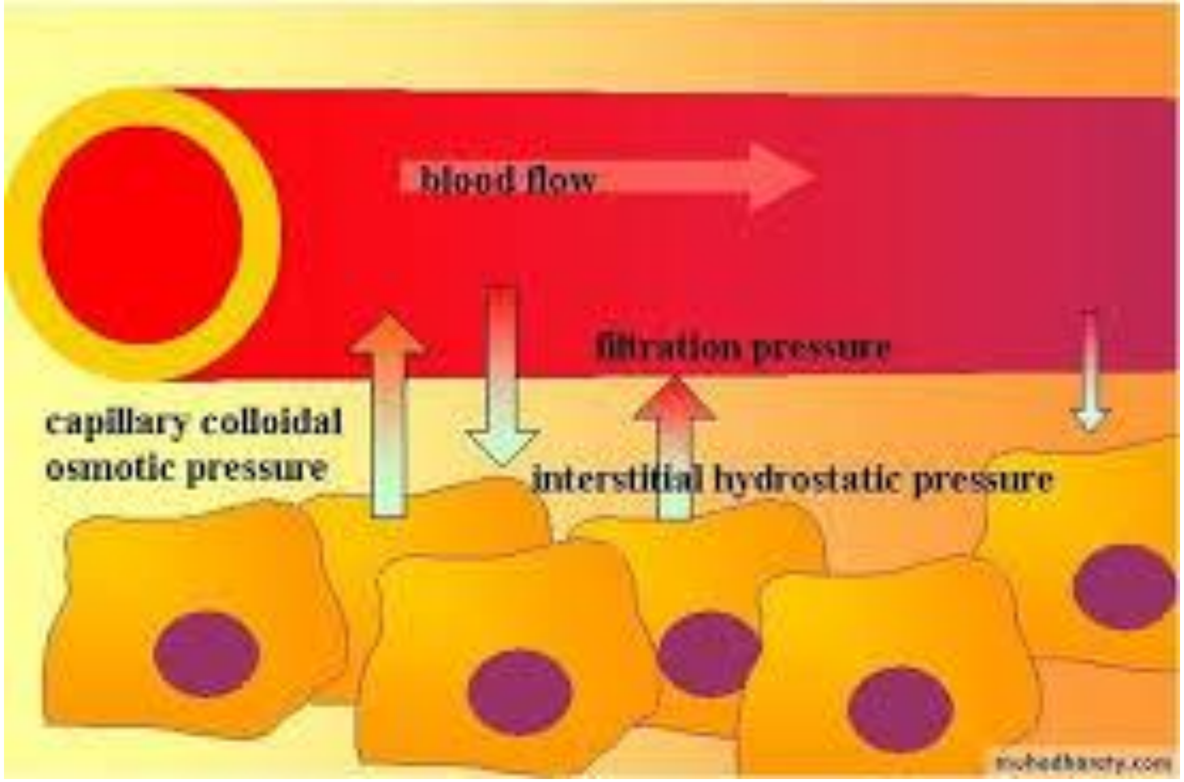
$$\text{Moles of sucrose} = \frac{1.0}{342} = 0.0029$$

$$\pi \times 0.10 = 0.0029 \times 0.082 \times 298$$

$$\pi = 0.71\ \text{atm}$$

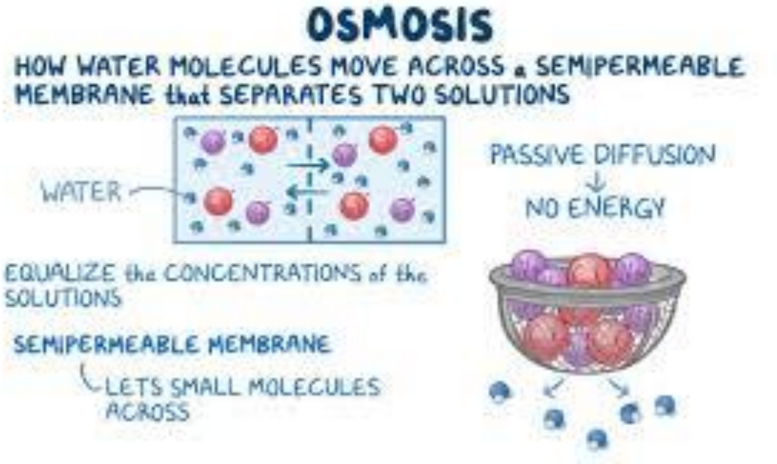
Osmotic pressure of body fluids

Biological cell membrane acts as the semipermeable cell membrane and osmotic pressure is an important factor regulating the intra-cellular fluid volume. Osmotic pressure of a series of body fluids, CSF, peritoneal, pleural, pericardial, synovial fluids has been measured and are found to have the same osmolarity as that of blood serum



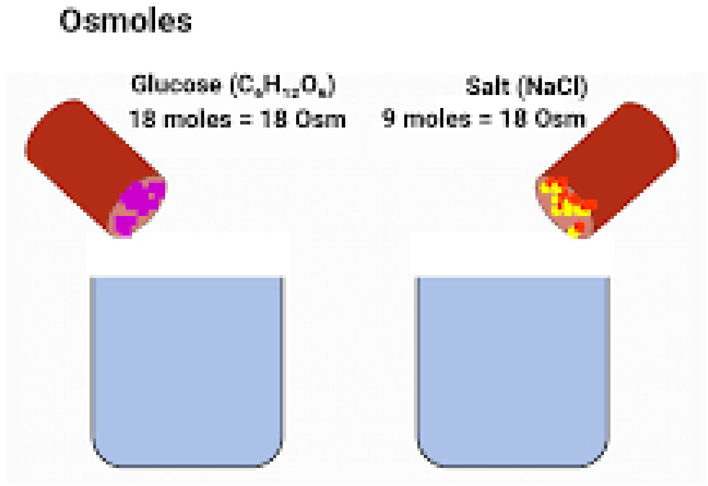
Iso-osmosis

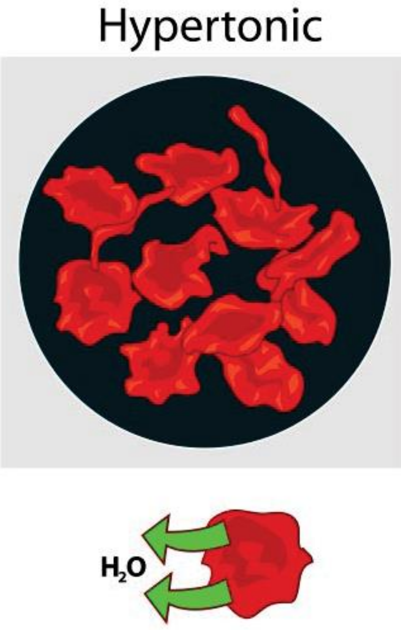
When osmotic equilibrium is reached, there will be no net movement of solvent molecules across the semipermeable membrane between two solutions, and the two solutions are said to be iso-osmotic .Aqueous solutions (e.g. injections, eye-drops) are said to be iso osmotic with blood serum and lachrymal secretions (tears) when they have a freezing point depression of 0.52 °C. The measurement of osmotic pressure of solutions is difficult and time consuming .The preferred method is the measurement of freezing point depression because the FD required for solution iso osmotic with all body fluids is 0.52 °C .Aqueous solutions having 308 m Osm/L are said to be iso osmotic with body fluids

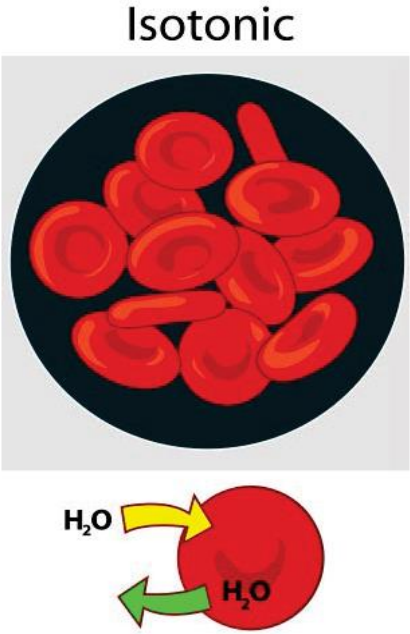


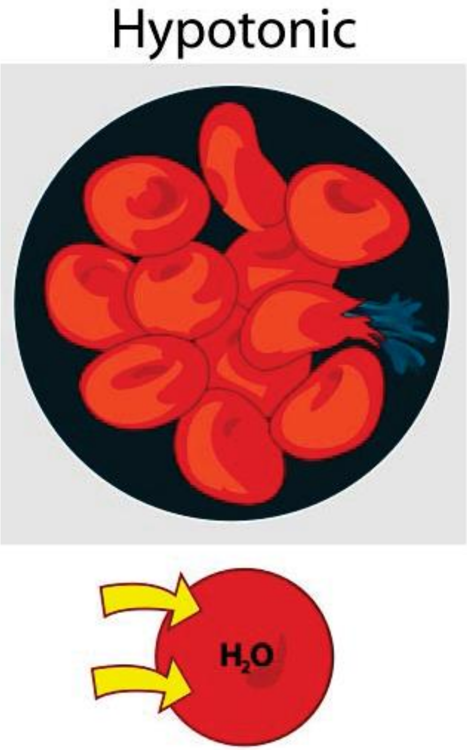
Osmole concentration

Solutions containing osmotically active particles is commonly expressed in terms of osmoles (Osm) or milliosmoles (mOsm) per kilogram of solvent (Osmolality) or liter of solution (Osmolarity) Osmole (Osm) is the number of moles of solute that contribute to the osmotic pressure of a solution. Glucose does not dissociate and thus 1 mole of this solute gives 1 osmole of particles .NaCl dissociates to form 2 ions and thus 1 mole of solute gives 2 osmole of osmotically active particles









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

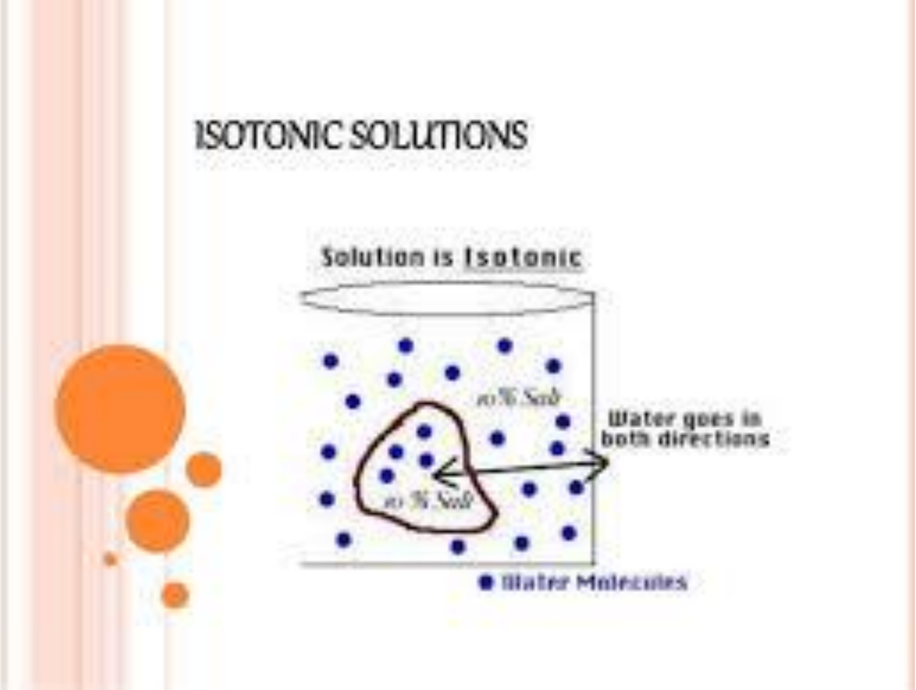
Isotonic solutions cause no net flow of water into or out of the red blood cell and do not adversely affect the red blood cell membrane They have the same osmotic pressure as blood serum (iso-osmotic)

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

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.



ISOTONIC SOLUTIONS

Molecular weight determination

The molecular weight of the solute can be calculated by the following methods

- ☐ Vapor pressure lowering:

$$M_2 = \frac{w_2 M_1 p_1^\circ}{w_1 \Delta p}$$

- ☐ Boiling point elevation: Can be only used for non-volatile solutes

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

- ☐ Freezing point depression :Can be used for both volatile and non-volatile solutes

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

- ☐ Osmotic pressure:

(where C_g: concentration in g/L)

$$M_2 = \frac{C_g RT}{\pi}$$


thank you