

COLLIGATIVE PROPERTIES OF SOLUTIONS

Nature of Solute

Non-electrolytic are substances that do not form ions and do not conduct electricity when placed in water.

An electrolyte is a substance that, when dissolved in water form ions, as results a solution can conduct electricity:



SOLUTION OF

Nonelectrolyte – solution that does not conduct electricity

- solute is dispersed but does not dissociate

Example: sugar (dissolves but does not dissociate), organic acids (contain carboxyl groups)

Solute such as sugar is dissolved in a given volume of solvent (water) to form a sugar solution, it changes the set of properties of the pure solvent entirely. In this regard, the set of properties such as freezing point, boiling point, vapor pressure, and osmotic pressure of a solvent are affected by the presence of the solute particles in the solution.

Electrolyte – solution that conducts electricity

- ionic compounds in polar solvents dissociate (break apart) in solution to make ions

- may be strong (100% dissociation) or weak (less than 100%)

Strong Electrolyte – all or almost all of compound dissociates; example: strong acids (H_2SO_4 , HNO_3 , HClO_4 , HCl , HBr , HI)

Weak Electrolyte – small amount of compound dissociates; example – weak acids (HF , CH_3COOH , H_3PO_4)

COLLIGATIVE PROPERTIES

Colligative properties are the set of properties that depend only on the concentration of solute particles (ions or molecules) in the solution and not the type.

COLLIGATIVE PROPERTIES:

1) Vapor Pressure Lowering (1st Raoult's Law)

- *Related to boiling point*

2) Freezing Point Depression

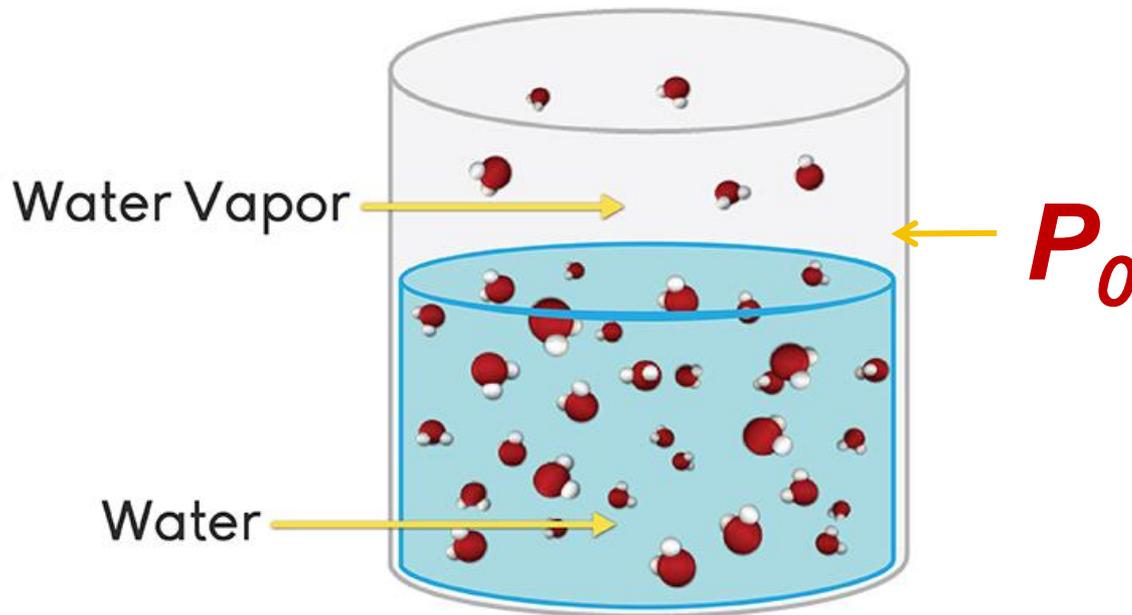
- *Salt on the road*
- *Anti-freeze in your radiator*

And Boiling Point Elevation (2nd Raoult's Law)

3) Osmotic Pressure (Van't Hoff's Law)

- *Membrane diffusion*

Vapor Pressure Lowering (1st Raoult's Law)



When $\uparrow t$, $\uparrow p_0$ H_2O :
0°C – 4,6 mm Hg
20°C – 17,4 mm Hg
100°C – 760 mm Hg

A solvent's vapor pressure will lower when a solute is added. This happens because of the displacement of solvent molecules by the solute. This means that some of the of solvent molecules at the surface of the liquid are replaced by the solute; it can occur in both electrolytic and non-electrolytic solutions. The lower number of solvent molecules at the surface means that fewer will evaporate, and thus the vapor pressure is lowered. For the vapor pressure to equal the atmospheric pressure, a higher temperature is required, and a higher boiling point is observed.

The vapor pressure of water (P_0) is the pressure at which water vapor is in thermodynamic equilibrium with its condensed state.

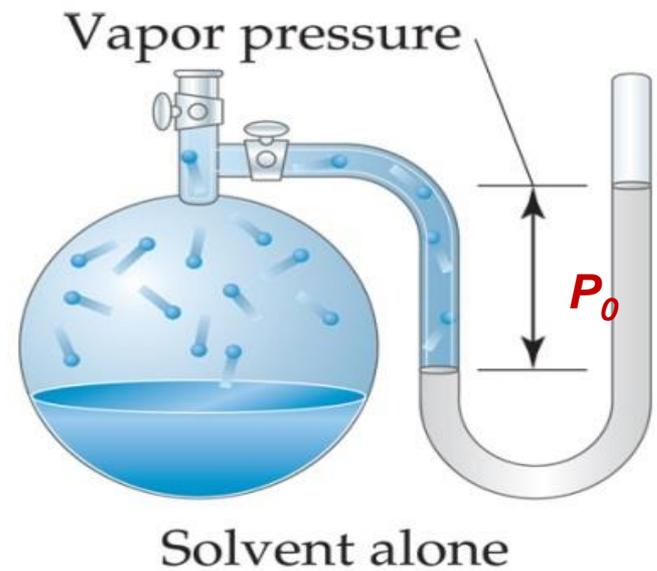
Vapor pressure depends on various factors:

- the nature of the liquid,**
- the presence of dissolved substances in the liquid or solid.**

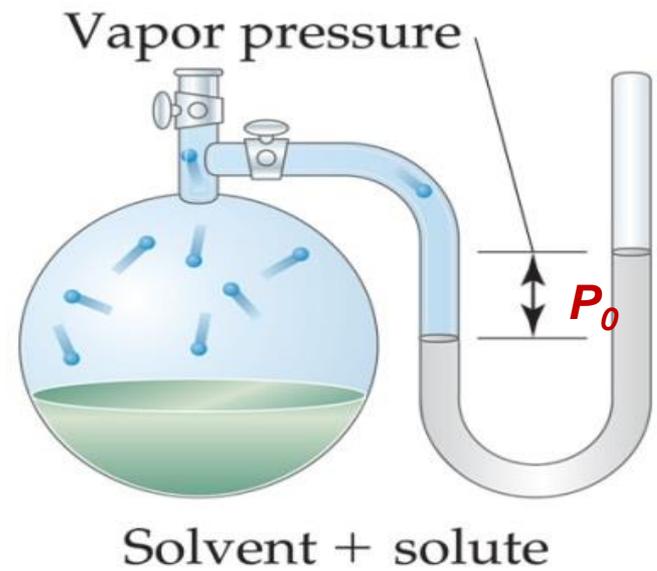
According to Raoult's law, the vapor pressure of a pure liquid or solid is lowered by the addition of a solute.

As solute molecules are added to a solution, the solvent becomes less volatile (=decreased vapor pressure).

Solute-solvent interactions contribute to this effect.

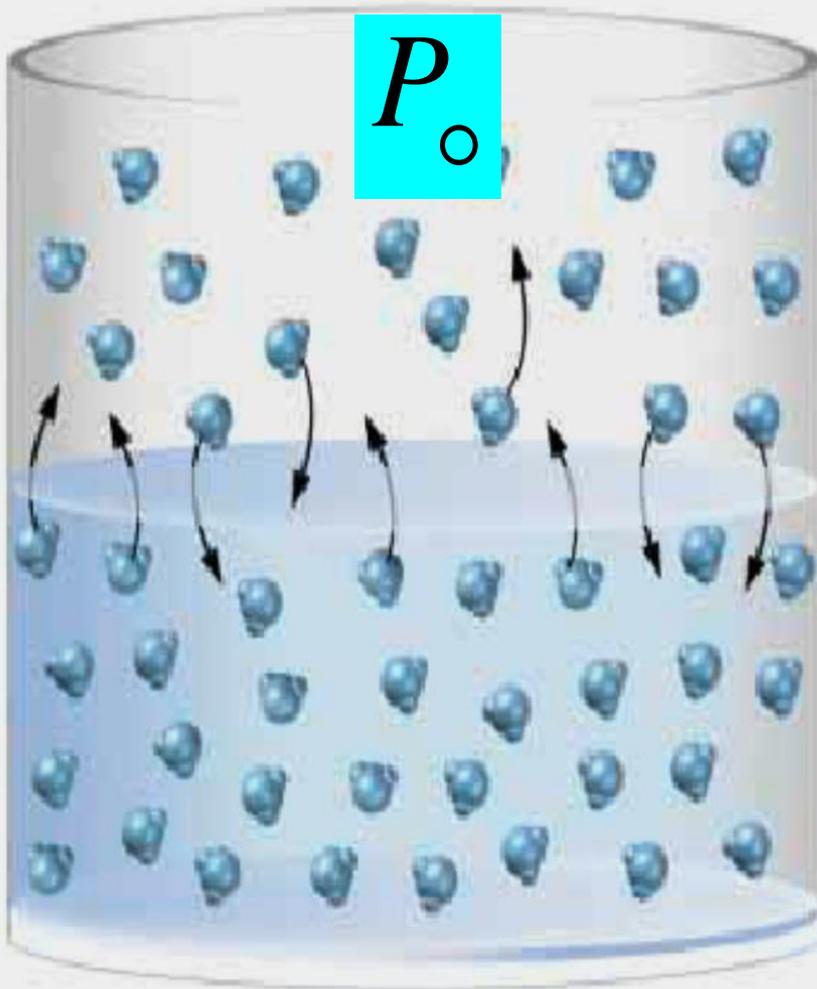


(a)

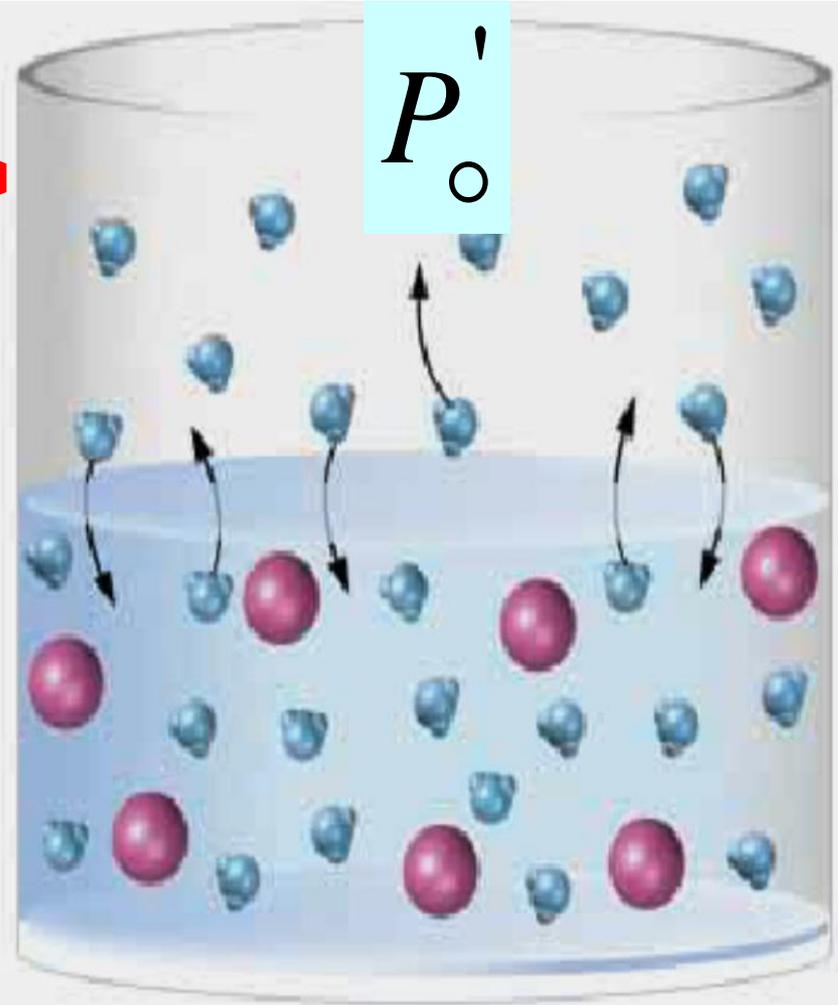


(b)

VAPOR PRESSURE LOWERING



P_o



P'_o

Pure water

**Aqueous solution of
nonvolatile solute**



Used to represent $C_{12}H_{22}O_{11}$, sucrose



Used to represent H_2O , water

The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration. This was discovered by French chemist Francois Raoult (1830-1907).

1st Raoult's law states that for non-electrolyte solutions, the partial vapor pressure of a solvent over a solution (P_1) is equal to the vapor pressure of the pure solvent (P_0) multiplied by the mole fraction of the solute (X_2). This law is mathematically expressed as:

$$\frac{P^\circ - P^1}{P^\circ} = N_{X_2}$$

$$N_{X_2} = \frac{n_{X_2}}{n_{X_1} + n_{X_2}}$$

N_{X_2} — the mole fraction

n_{X_1} — the number of dissolving solute moles

n_{X_2} — the number of solvent mole

The temperature at which vapor pressure is equal to the atmospheric pressure ($p_0 = p_{\text{atm}}$) is called ***boiling point***

The temperature at which vapor pressure of solvent in its liquid and solid phase become equal is called ***freezing point***

- at 0°C water is ***freezing***,
- and at 100°C water is ***boiling***

**Freezing Point
Depression and Boiling
Point Elevation
(2nd Raoult's Law)**

The 2nd Raoult's Law

One consequence of Raoult's law is that the boiling point of a solution made of a liquid solvent with a nonvolatile solute is greater than the boiling point of the pure solvent. The boiling point of a liquid or is defined as the temperature at which the vapor pressure of that liquid equals the atmospheric pressure. For a solution, the vapor pressure of the solvent is lower at any given temperature. **This pattern applies to the freezing point of the solution. Therefore, a higher temperature is required to boil the solution and a low temperature – to freeze the solution than the pure solvent.**

The boiling temperature of non-electrolytes solution

$$t_{\text{boil solution}} = t_{\text{boil solvent}} + \Delta t_{\text{boil}}$$

If solvent is a water: $t_{\text{boil H}_2\text{O}} = 100^\circ \text{C}$

$$\Delta t_{\text{boil}} = C_m \cdot E_{\text{svt}}$$

$E_{\text{H}_2\text{O}} = 0,52^\circ \text{C}$ **ebulioscopic constant of solvent**

$$C_m = \frac{v_{s-te} \cdot 1000}{m_{\text{svt}}} = \frac{m_{s-te} \cdot 1000}{M_{s-te} \cdot m_{\text{svt}}} = \frac{C\% \cdot 1000}{M_{s-te} \cdot (100 - C\%)}$$

$$M_{\text{unknown solute}} = \frac{m_{s-te} \cdot 1000 \cdot E_{\text{svt}}}{m_{\text{svt}} \cdot \Delta t_{\text{boil}}} \quad \text{ebulioscopic method}$$

The change in boiling point is proportional to the molality of the solution:

$$\Delta t_{boil} = C_m \cdot E_{svt}$$

$$E_{H_2O} = 0,52^\circ C$$

where E_{svt} is boiling point elevation constant, equivalent to $0.52^\circ C/m$ for aqueous solutions.

This means that, for example, 1 mole of sugar (non-electrolyte) in 1 kilogram of water will increase the boiling point from $100^\circ C$ to $100,52^\circ C$. And C_m is the molal concentration of solute.

It is also important to note that Δt_{boil} is a positive quantity and should be added to the boiling point of pure solvent (water), which is $100^\circ C$.

The freezing temperature of non-electrolytes solution

$$t_{\text{freez solution}} = t_{\text{freez solvent}} - \Delta t_{\text{freez}}$$

If solvent is a water: $t_{\text{freez H}_2\text{O}} = 0^\circ \text{C}$

$$\Delta t_{\text{freez}} = C_m \cdot K_{\text{svt}} = \frac{m_{s-te} \cdot 1000 \cdot K_{\text{svt}}}{M_{s-te} \cdot m_{\text{svt}}}$$

$K_{\text{H}_2\text{O}} = 1,86^\circ \text{C}$ **krioscopic constant of solvent**

$$M_{\text{unknown solute}} = \frac{m_{s-te} \cdot 1000 \cdot E_{\text{svt}}}{m_{\text{svt}} \cdot \Delta t_{\text{freez}}} \quad \text{brioscopic method}$$

The change in freezing point can be found similarly:

$$\Delta t_{\text{freez}} = C_m \cdot K_{\text{svt}}$$

$$K_{\text{H}_2\text{O}} = 1,86^\circ \text{C}$$

where K_{svt} is the freezing point depression constant equivalent to $-1,86^\circ \text{C}/m$ for aqueous solutions.

Again, for example, 1 mole of sugar (non-electrolyte) in 1 kilogram of water will decrease the freezing point from 0°C to $-1,86^\circ \text{C}$.

And since we have already established that the freezing point of the solution is less than that of the pure solvent, then Δt_{freez} is a negative quantity and should be subtracted from the freezing point of pure solvent (water), which is 0°C .

In both equations, ΔT does not depend on what the solute is, but only on how many particles are dissolved.

Some common values for K_{freez} and E_{boil} respectively, are:

Solvent	K_{freez}	E_{boil}
Water	1.86	0.512
Acetic acid	3.90	3.07
Benzene	5.12	2.53
Phenol	7.27	3.56

CASE PROBLEM

Determine the boiling point and freezing point of a solution containing 1 g of nitrobenzene in 10 g of benzene. $E (\text{C}_6\text{H}_6) = 2.57$, $K (\text{C}_6\text{H}_6) = 5.1$. The boiling point of pure benzene is $80.2\text{ }^\circ\text{C}$, the freezing point is $5.4\text{ }^\circ\text{C}$.

CASE PROBLEM

Determine the boiling point and freezing point of a solution containing 1 g of nitrobenzene in 10 g of benzene. E (C_6H_6) = 2.57, K (C_6H_6) = 5.1. The boiling point of pure benzene is $80.2\text{ }^{\circ}C$, the freezing point is $5.4\text{ }^{\circ}C$.

Boil = кип
Freez = зам
Solvent = р-ля

<p>Дано: $m(C_6H_6NO_2) = 1\text{ г}$ $m(C_6H_6) = 10\text{ г}$ $E(C_6H_6) = 2,57$ $K(C_6H_6) = 5,1$ $t_{кип} = 80,2^{\circ}C$ $t_{зам} = 5,4^{\circ}C$ $M(C_6H_6NO_2) = 123\text{ г/моль}$</p>	<p>Решение: $C_m = m(X) \times 1000 / (M(X) \times m(\text{р-ля}))$ $C_m(C_6H_6NO_2) = 1 \times 1000 / (123 \times 10) = 0,813$ (МОЛЬ/КГ) $\Delta T_{кип} = E \cdot C_m$ $T_{зам} = K \cdot C_m$ $\Delta T_{кип} = 2,57 \cdot 0,813 = 2,09\text{ К}$ $\Delta T_{зам} = 5,1 \cdot 0,813 = 4,15\text{ К}$ $t_{кип} = 80,2 + 2,09 = 82,29^{\circ}C$ $t_{зам} = 5,4 - 4,15 = 1,25^{\circ}C$</p>
<p>$t_{кип}(\text{р-ра}) = ?$ $t_{зам}(\text{р-ра}) = ?$</p>	<p>Ответ: $82,29^{\circ}C$; $1,25^{\circ}C$</p>

CASE PROBLEM

The boiling point of a solution containing 4 g of a substance in 110 g of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is 78.62°C . Determine the molar mass of the solute. E ($\text{C}_2\text{H}_5\text{OH}$) = 1.22, boiling point of ethanol 78.3°C .

CASE PROBLEM

The boiling point of a solution containing 4 g of a substance in 110 g of ethanol (C_2H_5OH) is $78.62^\circ C$. Determine the molar mass of the solute. $E(C_2H_5OH) = 1.22$, boiling point of ethanol $78.3^\circ C$.

Дано: $m(\text{в-ва}) = 4 \text{ г}$ $m(C_2H_5OH) = 110 \text{ г}$ $E(C_2H_5OH) = 1,22$ $t_{\text{кип}} = 78,3^\circ \text{ C}$	Решение: $\Delta T_{\text{кип}} = 78,62 - 78,3 = 0,32$ $\Delta T_{\text{кип}} = E \cdot C_m = E \times m(X) \times 1000 / (M(X) \times m(\text{р-ля}))$ $M(\text{в-ва}) = E \times m(\text{в-ва}) \times 1000 / (\Delta T_{\text{кип}} \times m(C_2H_5OH)) = 1,22 \times 4 \times 1000 / (0,32 \times 110) = 138,64 \text{ (г/МОЛЬ)}$	Boil = кип Solute = в-ва
$M(\text{в-ва}) = ?$	Ответ: 138,64 г/МОЛЬ	

CASE PROBLEM (HOMETASKS)

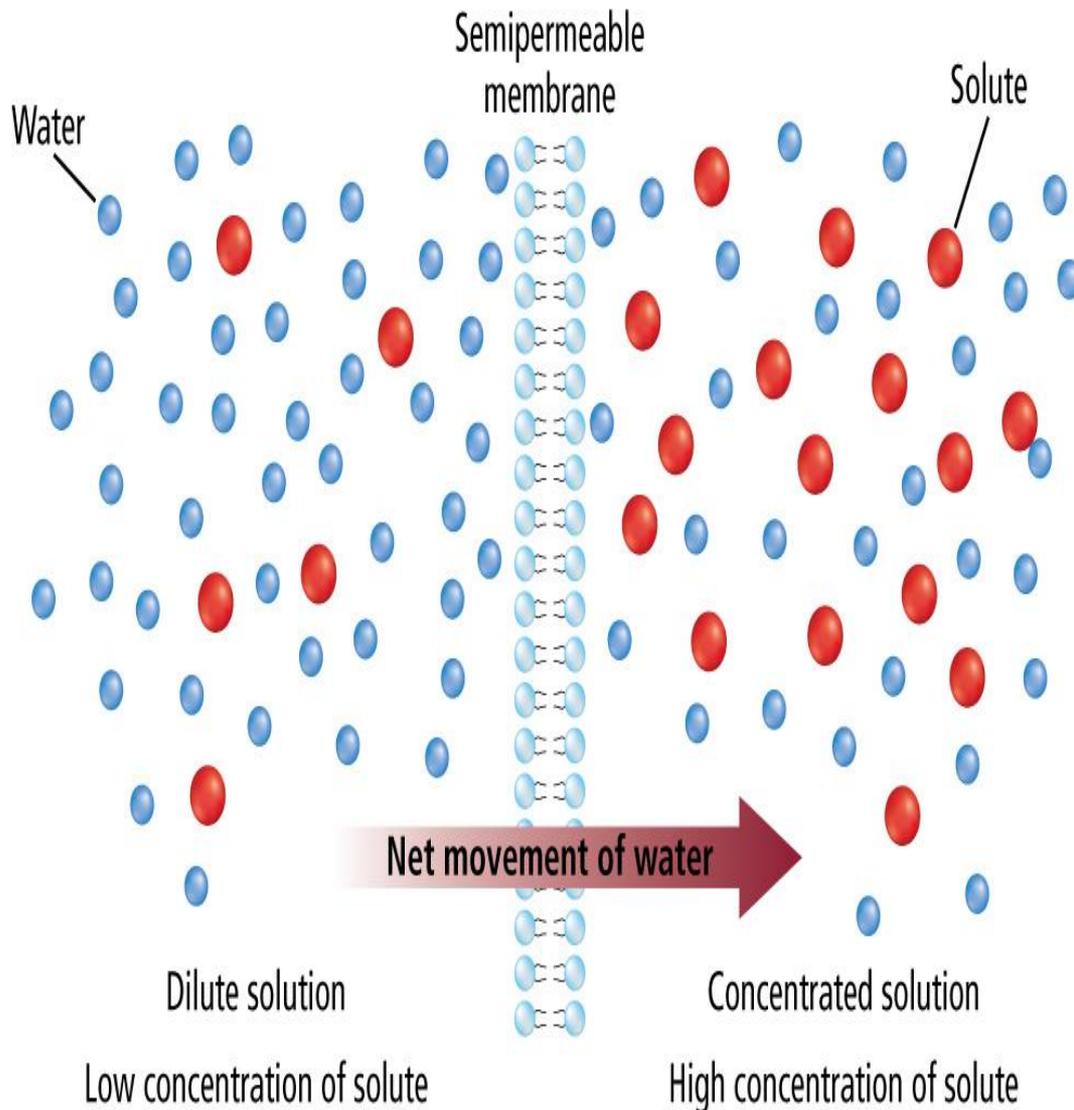
Blood plasma begins to freeze at -0.59°C . What is the osmolality (molal concentration of all particles) of blood plasma and its osmotic pressure at 37°C ? Cryoscopic constant $K(\text{H}_2\text{O}) = 1.86$

When 2.76 g of nonelectrolyte was dissolved in 200 g of water, the freezing point of the solution dropped by 0.279°C . Calculate the molar mass of the non-electrolyte. Cryoscopic constant $K(\text{H}_2\text{O}) = 1.86$

Osmotic Pressure (Van't Hoff's Law)

In 1784, the French physicist Jean Antoine Nollet discovered that a pig's bladder filled with a concentrated solution of alcohol in water expanded when it was immersed in water. The bladder acted as a *semipermeable membrane*, which allowed water molecules to enter the solution, but kept alcohol molecules from moving in the other direction. Movement of one component of a solution through a membrane to dilute the solution is called **osmosis**, and the pressure this produces is called the **osmotic pressure (π)**.

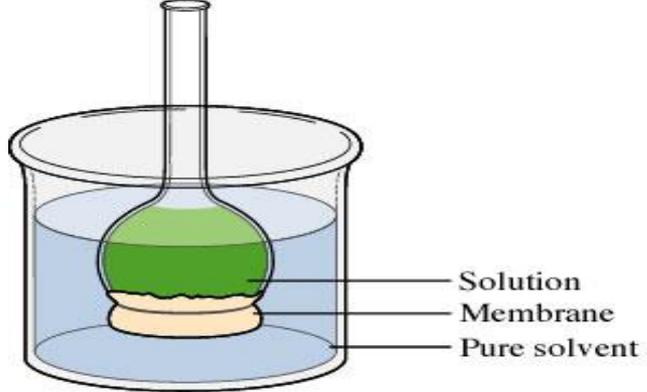
Osmotic pressure can be demonstrated with the apparatus shown in the figure below. A semipermeable membrane is tied across the open end of a thistle tube. The tube is then partially filled with a solution of sugar or alcohol in water and immersed in a beaker of water. Water will flow into the tube until the pressure on the column of water due to the force of gravity balances the osmotic pressure driving water through the membrane.



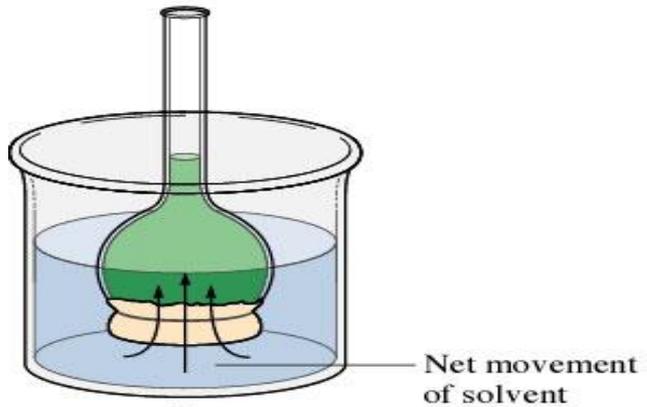
During osmosis pure solvent diffuses through a membrane but solutes do not.

Osmosis is defined as the flow of water/solvent molecules through a semipermeable membrane from a region of low to high solute concentration, until equilibrium is established.

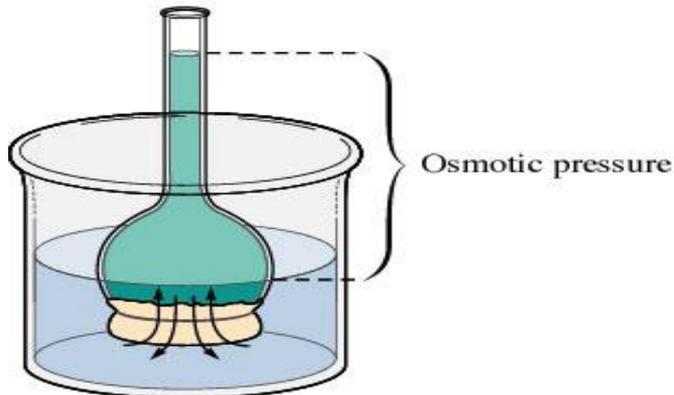
Jean-Antoine Nollet first documented observation of osmosis in 1748.



Time



Time



(at equilibrium)

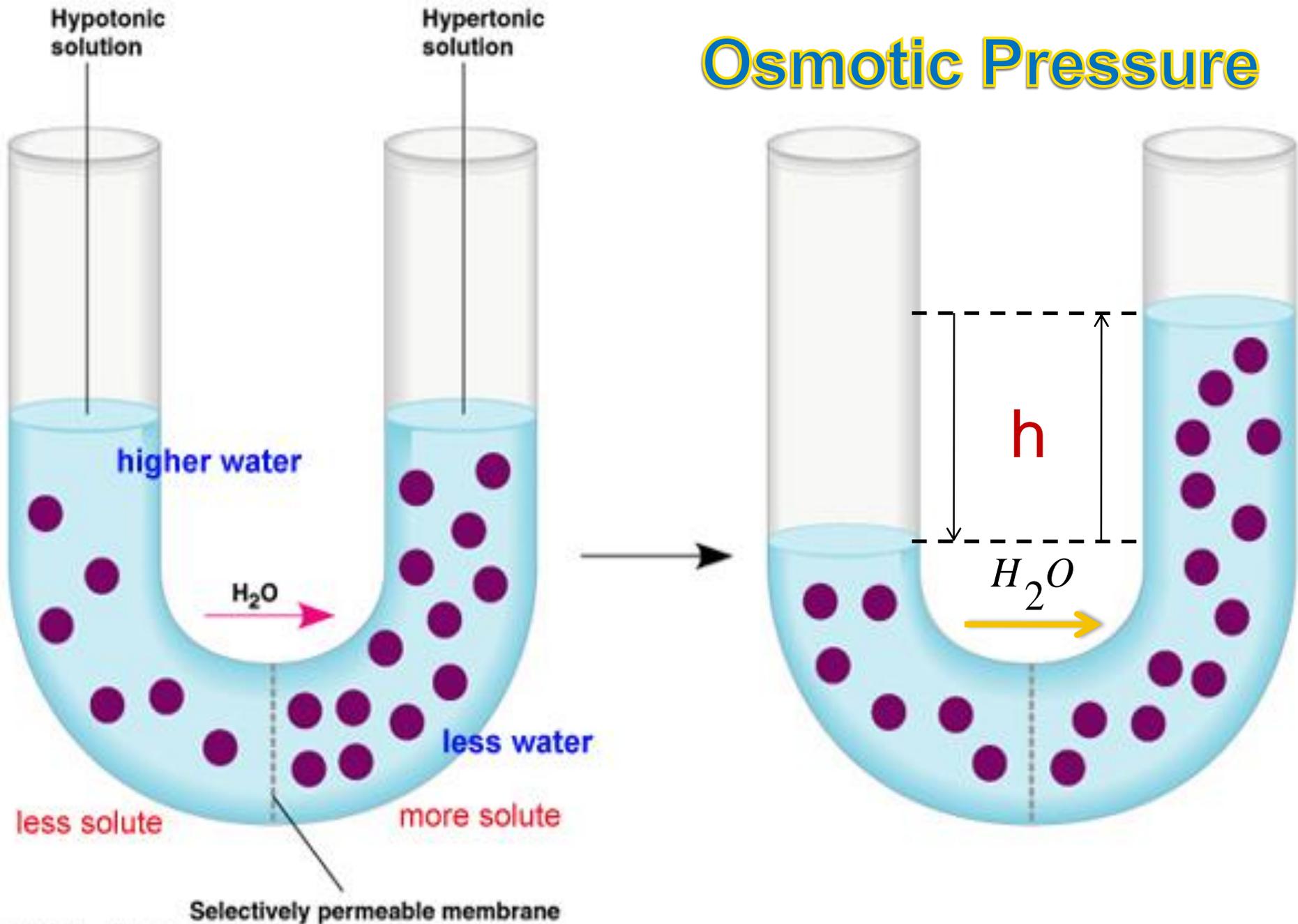
Net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions.

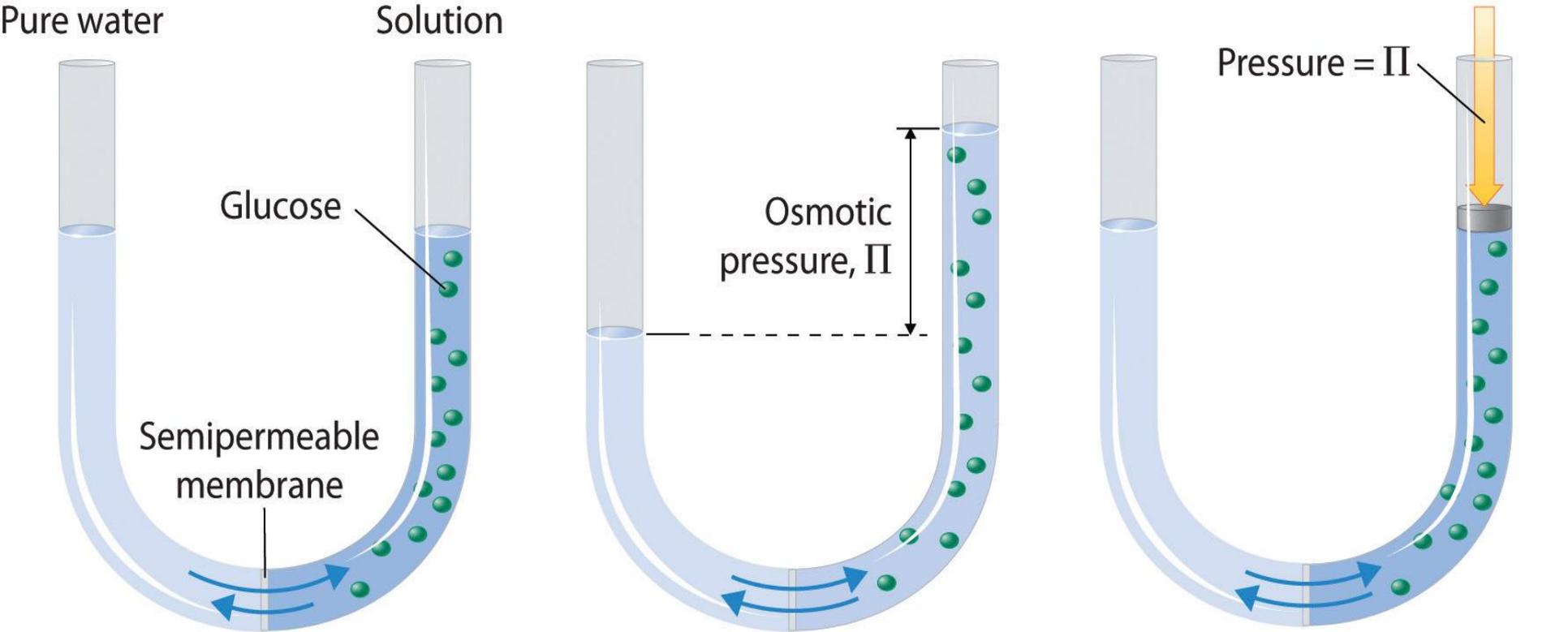
Because the liquid level for the solution is higher, there is greater hydrostatic pressure on the solution than on the pure solvent .

Osmotic Pressure:

The excess hydrostatic pressure on the solution compared to the pure solvent.

Osmotic Pressure





(a) Initial state

(b) Equilibrium

(c) External pressure applied

(a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

The osmotic pressure of a solution is the pressure required to stop osmosis. The osmotic pressure of the solution is given by:

$$P_{osm} = C_M \cdot R \cdot T$$

Van't Hoff's equation

$$C_M = \frac{V_{s-te}}{V_{sln(l)}} = \frac{m_{s-te}}{M \cdot V_{sln(l)}}$$

$$P \cdot V = \frac{m}{M} \cdot R \cdot T$$

Mendeleev Clapeyron equation

where C_M is the molarity of solution, R the gas constant (8, 31 J*mol/ K), and T the absolute temperature (in Kelvins +273).

The osmotic pressure is expressed in atm. As with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles.

CASE PROBLEM

Calculate the osmotic pressure of a solution containing 135 g of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ in 1.5 liters at 0°C .

CASE PROBLEM

Calculate the osmotic pressure of a solution containing 135 g of glucose $C_6H_{12}O_6$ in 1.5 liters at $0^\circ C$.

<p>Given:</p> <p>$V(s) = 1,5 \text{ л}$</p> <p>$m(C_6H_{12}O_6) = 135 \text{ г}$</p> <p>$t^0 = 0^\circ C$.</p> <p>$T = t^0 + 273 = 273 \text{ К}$</p>	<p>Decision:</p> <p>1) $C_M(\text{solution}) = \frac{m(C_6H_{12}O_6)}{M(C_6H_{12}O_6) \times V}$</p> <p>$130 / (180 \times 1,5) = 0,5 \text{ (моль/л)}$</p> <p>2) $P_{osm} = C_M RT = 0,5 \times 8,31 \times 273 = 1134,315 \text{ (кПа)}$</p>
<p>$P_{osm} = ?$</p>	<p>Ans.: 1134,315 кПа</p>

CASE PROBLEM

Determine the molar mass of a substance if 5L of its solution contains 25 g of a substance. The osmotic pressure of the solution is 230 kPa at 20⁰ C.

CASE PROBLEM

Determine the molar mass of a substance if 5L of its solution contains 25 g of a substance. The osmotic pressure of the solution is 230 kPa at 20° C.

Given: $V(\text{solution}) = 5 \text{ л}$ $P_{\text{osm}} = 0,23 \times 10^5 \text{ Pa}$ or 230 kPa $t^0 = 20 \text{ }^\circ\text{C.}$ $T = t^0 + 273 = 293 \text{ K}$	Decision: 1) $C_M = P/RT = 230/(8,31 \times 293) = 0,0945$ (mol/L) 2) $M(\text{substance}) = m/(C_M V) = 25/(0,0945 \times 5) = 52,9$ g/mol
$M(\text{substance}) = ?$	Ans.: 52,9 g/mol

CASE PROBLEM (HOMETASKS)

Calculate the osmotic pressure of a 3.5% aqueous solution of hemoglobin ($M = 70\,000\text{ g/mol}$) at $22\text{ }^{\circ}\text{C}$, $\rho = 1.06\text{ g/ml}$.

Calculate the osmotic pressure of a 0.02% aqueous carbohydrate solution ($M = 180\text{ g/mol}$) at 20°C , $\rho \approx 1.05\text{ g/ml}$.

Types of Solutions Based on Solute Concentration...

- ✓ **Hypotonic** (lower solute concentration) to the solution
- ✓ **Hypertonic** (higher solute concentration) to the solution
- ✓ **Isotonic** solutions are ***equal*** in their solute concentrations. We say that they are isotonic to each other.

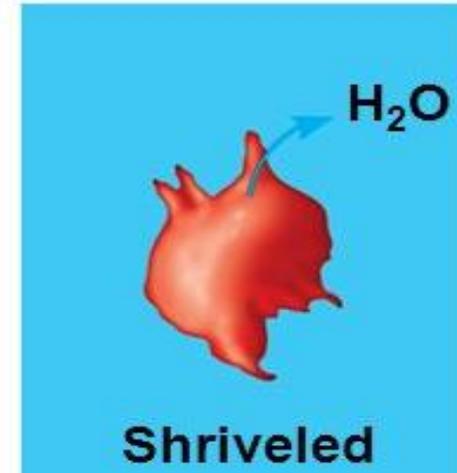
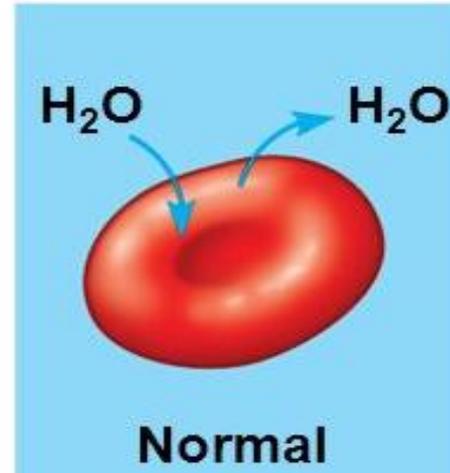
Types of Solutions Based on Solute Concentration

Hypotonic solution

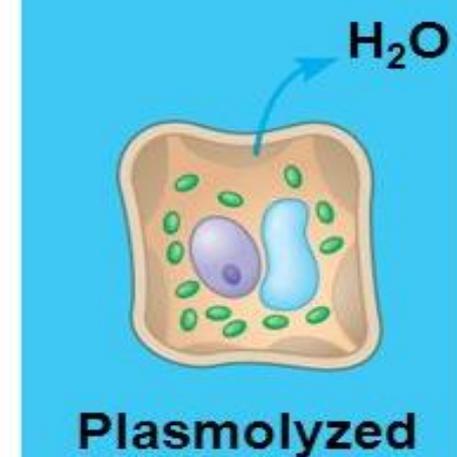
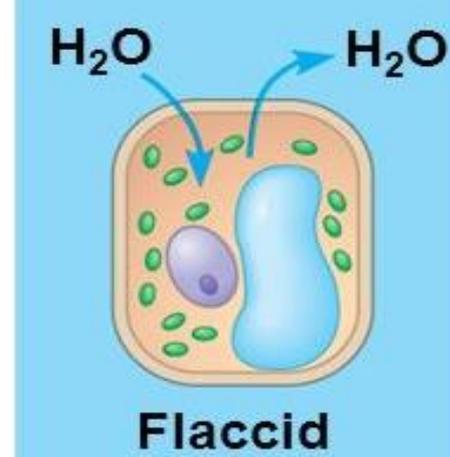
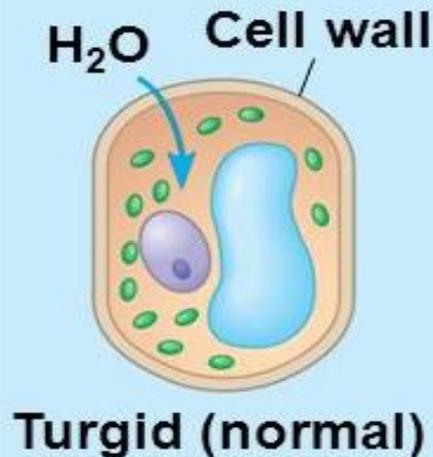
Isotonic solution

Hypertonic solution

(a) Animal cell



(b) Plant cell



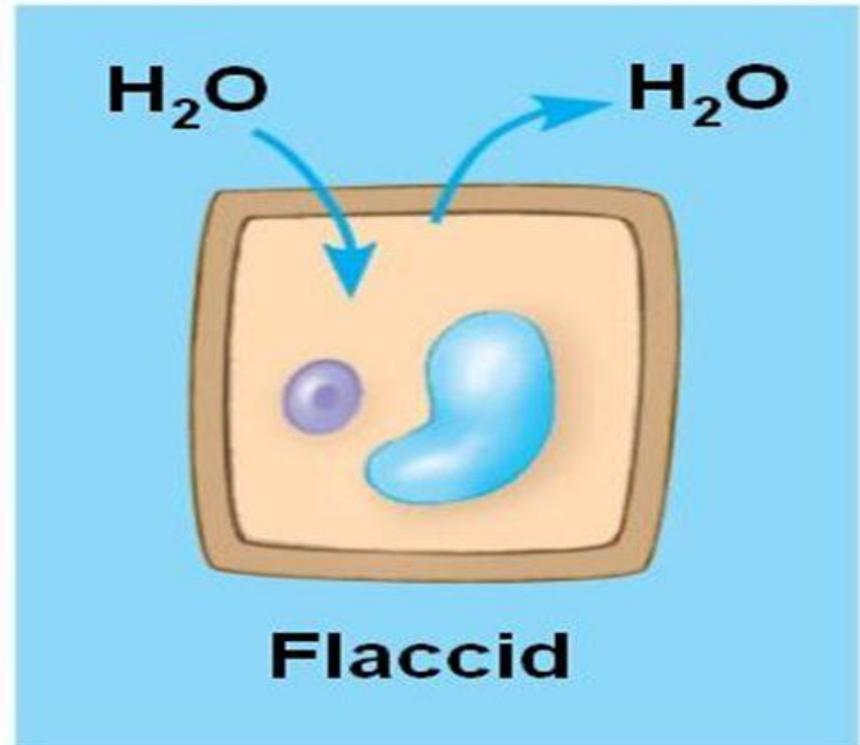
Types of Solutions Based on Solute Concentration

(c) Isotonic solution



No net loss or gain

Isotonic solution



Isotonic solution = SAME concentration as the cytoplasm of the cell. H₂O diffuses (osmosis) IN & OUT of the cell at the same rate. The cell stays the same size.

PHYSIOLOGICAL SOLUTIONS

Solutions that are ***isotonic*** to human fluids are also called ***physiological***.

In modern medicine, the use of saline is quite widespread. It is used to rehydrate, detoxify, dilute medications, wash wounds, etc.

PHYSIOLOGICAL SOLUTIONS

There are many solutions that can be called physiological, but the most common is sodium chloride NaCl solution at a concentration of 0.9%. This solution contains nothing but salt (sodium chloride) and water. It is a colorless transparent liquid with slightly salty taste.



PHYSIOLOGICAL SOLUTIONS

Also in medical practice, the following physiological solutions are used:

- **Ringer's solution.** This solution contains several salt components, in addition to distilled water, it includes sodium chloride, potassium chloride, calcium chloride. Due to the multicomponent base, Ringer's solution is more similar in electrolyte composition to blood plasma than a simple aqueous solution of sodium chloride 0.9%

PHYSIOLOGICAL SOLUTIONS

- **Ringer-Locke's solution.** This solution is a modification of Ringer's solution, added to the known composition: glucose and sodium bicarbonate. This solution regulates not only the water-salt balance, but also the acid-base balance.
- **Ringer-Krebs solution.** This solution is a modification of Ringer's solution, added to the known composition: sodium dihydrogen phosphate, magnesium chloride, sodium bicarbonate, glucose. This solution regulates not only the water-salt balance, but also the acid-base balance.

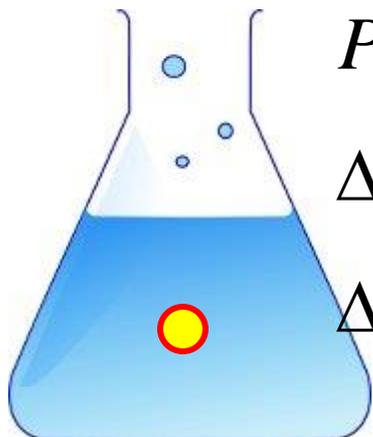
PHYSIOLOGICAL SOLUTIONS

- **Ringer-Tyrode solution.** This solution is similar in chemical composition to the Ringer-Locke solution, however, the salts included in its composition are taken in a slightly different concentration.
- **Acesol, Disol, Trisol, etc.** These solutions are based on an aqueous solution of sodium chloride, to which some types of salts are added: potassium chloride, sodium bicarbonate, sodium acetate, etc.

All these solutions are isotonic to human blood plasma, so they can be called physiological solutions.

COLLIGATIVE PROPERTIES FOR ELECTROLYTES

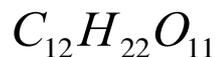
Non-electrolyte: 1 M sugar solution



$$P_{osm\ non-el\ s\ ln}$$

$$\Delta T_{boil\ non-el\ s\ ln}$$

$$\Delta T_{freez\ non-el\ s\ ln}$$

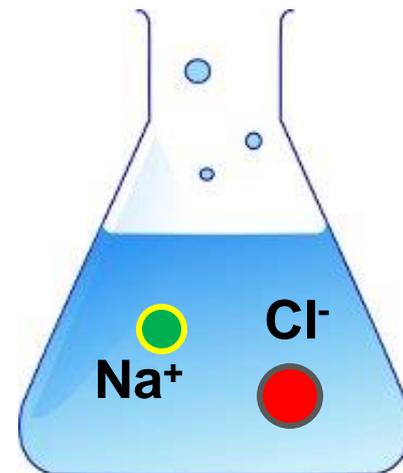


1 mole solute

i

< <

Electrolyte: 1 M NaCl salt solution



$$P_{osm\ el\ s\ ln}$$

$$\Delta T_{boil\ el\ s\ ln}$$

$$\Delta T_{freez\ el\ s\ ln}$$



1 mole of salt gives \rightarrow 2 moles ions

where *i* is the Van't Hoff factor, named after Jacobus Henricus Vant' Hoff (1852-1911), who won the very first Nobel Prize in chemistry in 1901 for his work on colligative properties of solution.

The *i* factor gives the number of particles per formula unit of the solute.

Since these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.

For Electrolyte Solution:

$$P_{osm} = i \cdot C_M \cdot R \cdot T$$

$$\Delta t_{boil} = i \cdot C_m \cdot E_{svt}$$

$$\Delta t_{freez} = i \cdot C_m \cdot K_{svt}$$

The degree of dissociation is associated with an isotonic factor by next ratio:

$$\alpha = \frac{i - 1}{n - 1} \quad \Rightarrow \quad i = \alpha \cdot (n - 1) + 1$$



$$n = 2 \text{ cation} + 3 \text{ anion} = 5$$

CASE PROBLEM (HOMETASKS)

Calculate the isotonic coefficient of a substance if it is known that its 0.02 molar solution at $t = 19^{\circ}\text{C}$ is isotonic with blood plasma. $P_{\text{osm}}(\text{blood}) = 740\text{-}780 \text{ kPa}$.

A solution containing 0.9 mol of the substance and 1000 g of water boils at $t = 100.8^{\circ}\text{C}$. Calculate the isotonic coefficient of this substance. $E(\text{H}_2\text{O}) = 0.51$.

SUMMARY OF FACTS AND CONCEPTS

1. Colligative properties (or collective properties) are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.

2. The four colligative properties of a solution are vapor pressure, osmotic pressure, boiling point and freezing point.

3. The change in vapor pressure where the solute is less volatile than the solvent is regulated by Raoult's law, which states that the vapor pressure of a solvent over a solution is equal to the mole fraction of the solvent times the vapor pressure of pure solvent.

4. The osmotic pressure of a solution is the pressure required to stop osmosis.

5. The freezing point of the solution is always less than the freezing point of the pure solvent.

7. In electrolyte solutions, the interaction between ions leads to the formation of ion pairs. The Van't Hoff factor (i) provides a measure of the extent of dissociation of electrolytes in solution.

8. Solutions can be classified as hypertonic, hypotonic or isotonic depending on the concentration of solute inside and outside the cell.

9. A hypertonic solution has a higher concentration of particle than the cell causing the cell to shrink.

10. A hypotonic solution has a lower concentration of particles than the cell causing the cell to swell.

11. An isotonic solution has the same osmotic strength on both sides of the semipermeable membrane.

12. Osmosis is the spontaneous net movement of solvent molecules through a semi-permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides.

Colligative properties of solutions

