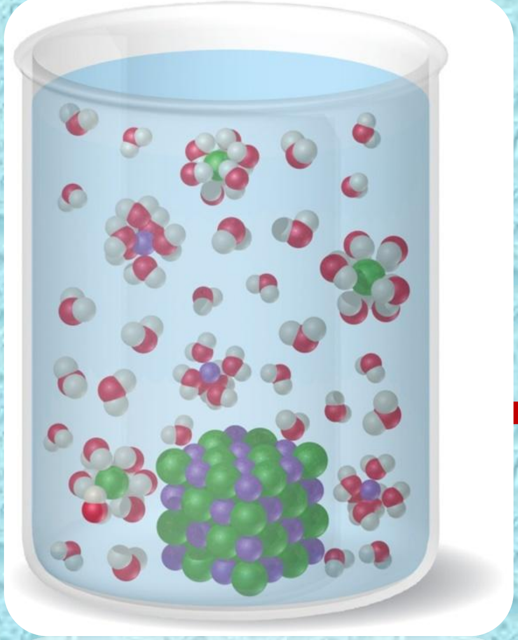


LECTURE Nº5

COLLIGATIVE PROPERTIES OF SOLUTIONS

QUIZ ME

1 What is it a true solution?

○ a heterogeneous mixture

○ a homogeneous mixture

○ a pure substances in water

○ compounds in water

NEX

QUIZ ME

2 The amount of a solute dissolved in a given amount of solvent is represented by the …

○ **Mass of the solution**

○ **Volume of the solution**

○ **Mass of the solute**

○ **Concentration of the solute**

NEX

QUIZ ME

3 What is the molar concentration of solution?

- ○ the gram of a solute per 1 milliliter of solution
- ○ the number of moles of solute per 1 kilogram of solvent
- ○ the number of equivalent-moles of solute per 1 liter of solution
- ○ the number of moles of solute per 1 liter of solution

QUIZ ME

4 What is the molality of solution?

○ the gram of a solute per 1 milliliter of solution

○ the number of moles of solute per 1 kilogram of solvent

○ the number of equivalent-moles of solute per 1 liter of solution

○ the number of moles of solute per 1 liter of solution

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:

$$\mathrm{NaCl} \Rightarrow \underset{\text{cation}}{\mathrm{Na}^{+}} + \underset{\text{anion}}{\mathrm{Cl}^{-}}$$

SOLUTION OF

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)

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)

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.

In other words, it doesn't matter if it is salt, sugar, gasoline, or tennis balls – it will behave the same way!

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)

  - *Anti-freeze in your radiator*

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

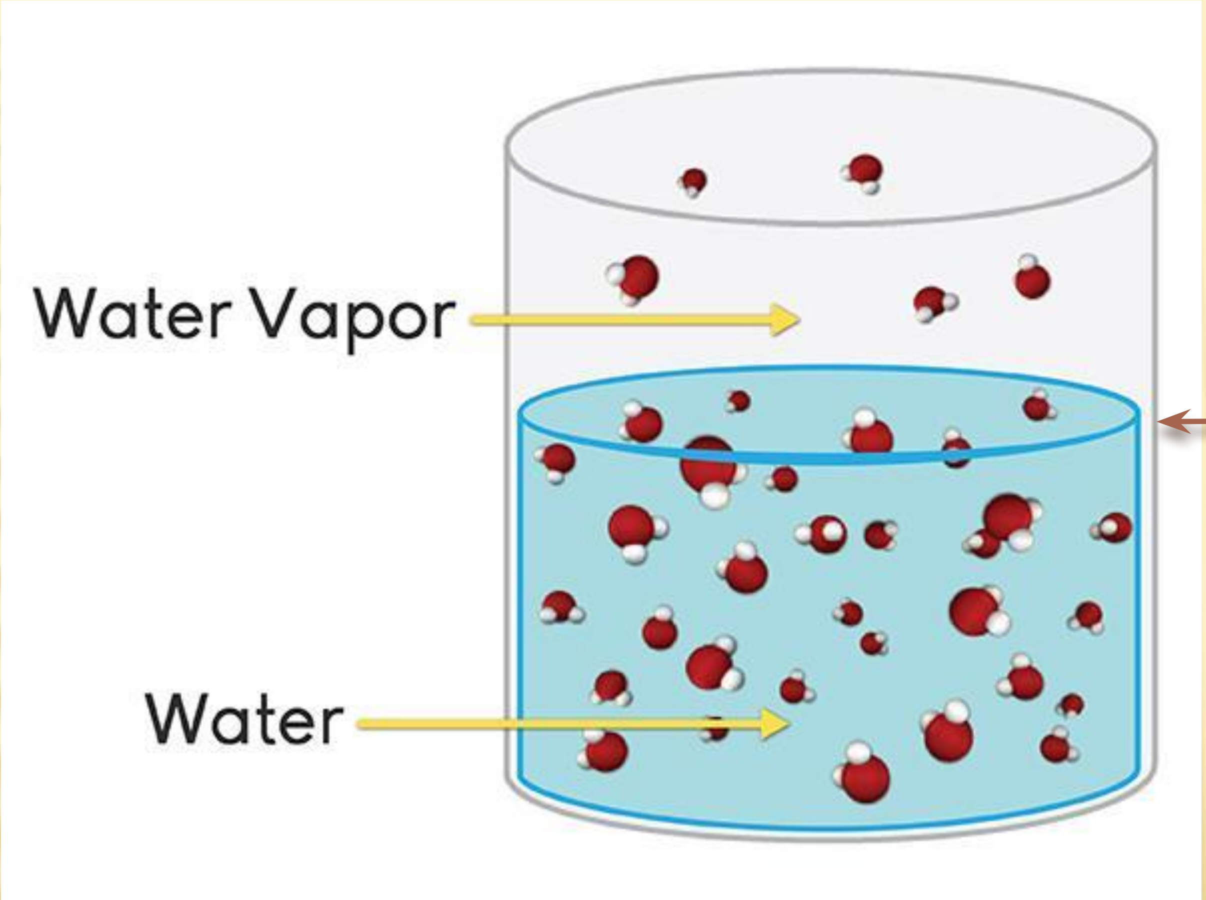
  - *Membrane diffusion*
  - *The Great Sugar Fountain*

When ↑t , ↑p_0 H_2O:

0^0C – 4,6 mm Hg

20^0C – 17,4 mm Hg

100^0C – 760 mm Hg



P_0

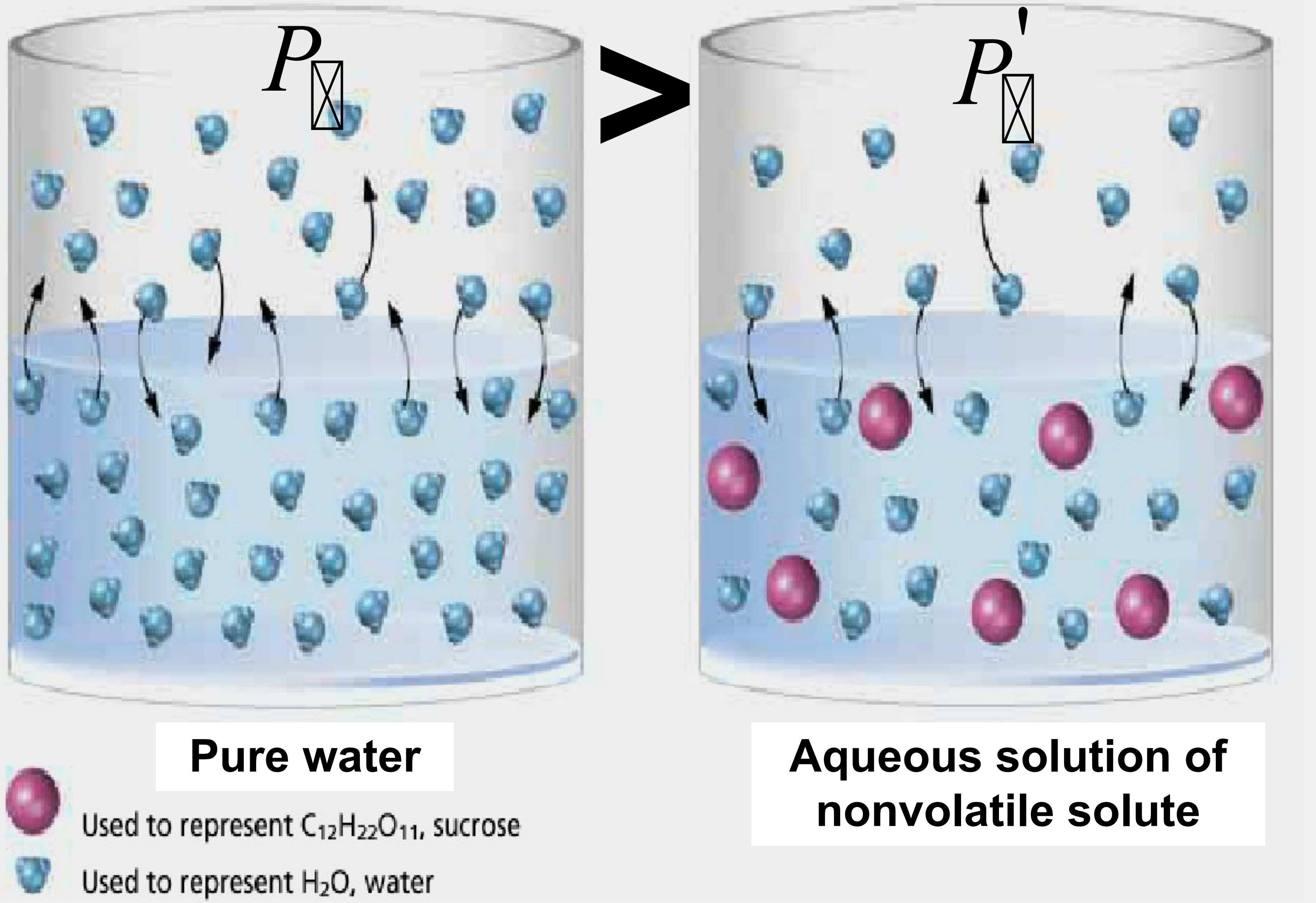
The vapor pressure of water (P_0) is the pressure at which water vapor is in thermodynamic equilibrium with its condensed state.

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.

VAPOR PRESSURE LOWERING



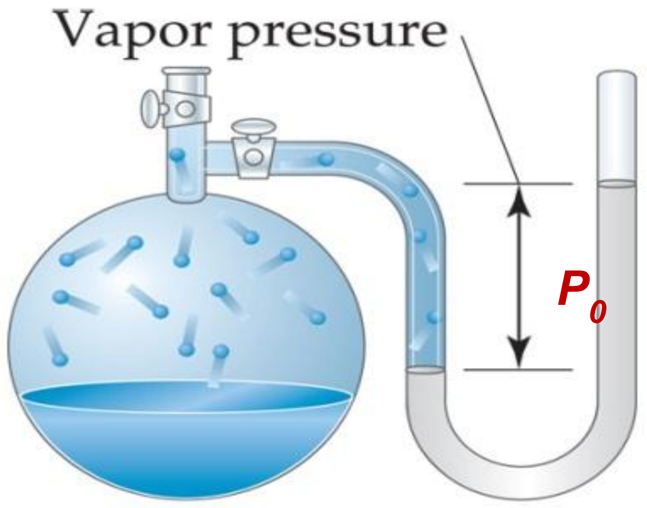
$P_{\boxtimes}$ > $P'_{\boxtimes}$

Pure water

Aqueous solution of nonvolatile solute

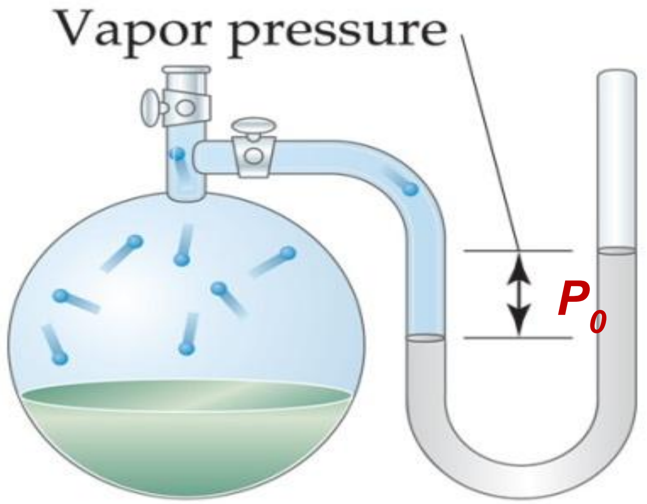
As solute molecules are added to a solution, the solvent become less volatile (=decreased vapor pressure).

Solute-solvent interactions contribute to this effect.



Solvent alone

(a)



Solvent + solute

(b)

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:

$$\frac{P^{0} - P^{1}}{P^{0}} = N_{X_2} \qquad N_{X_2} = \frac{n_{X_2}}{n_{X_1} + n_{X_2}}$$

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 ($p_0 = p_{atm}$) 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 0^0C water is ***freezing***,
- and at 100^0C water is ***boiling***

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

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

$$If\ solvent\ is\ a\ water:\ t_{boil\ H_2O} = 100^{\circ}C$$

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

$$E_{H_2O} = 0{,}52^{\circ}C$$ **ebulioscopic constant of solvent**

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

$$M_{unknown\ solute} = \frac{m_{s-te} \cdot 1000 \cdot E_{svt}}{m_{svt} \cdot \Delta t_{boil}}$$ **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°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°C to 100,52°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°C.

The freezing temperature of non-electrolytes solution

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

$$If\ solvent\ is\ a\ water:\ t_{freez\ H_2O} = 0^{\circ}C$$

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

$$K_{H_2O} = 1{,}86^{\circ}C$$

krioscopic constant of solvent

$$M_{anknown\ \ solute} = \frac{m_{s-te} \cdot 1000 \cdot E_{svt}}{m_{svt} \cdot \Delta t_{freez}}$$

krioscopic method

The change in freezing point can be found similarly:

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

$$K_{H_2O} = 1{,}86^{\circ}C$$

where ***K_{svt} is the freezing point depression constant equivalent to -1,86°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°C.

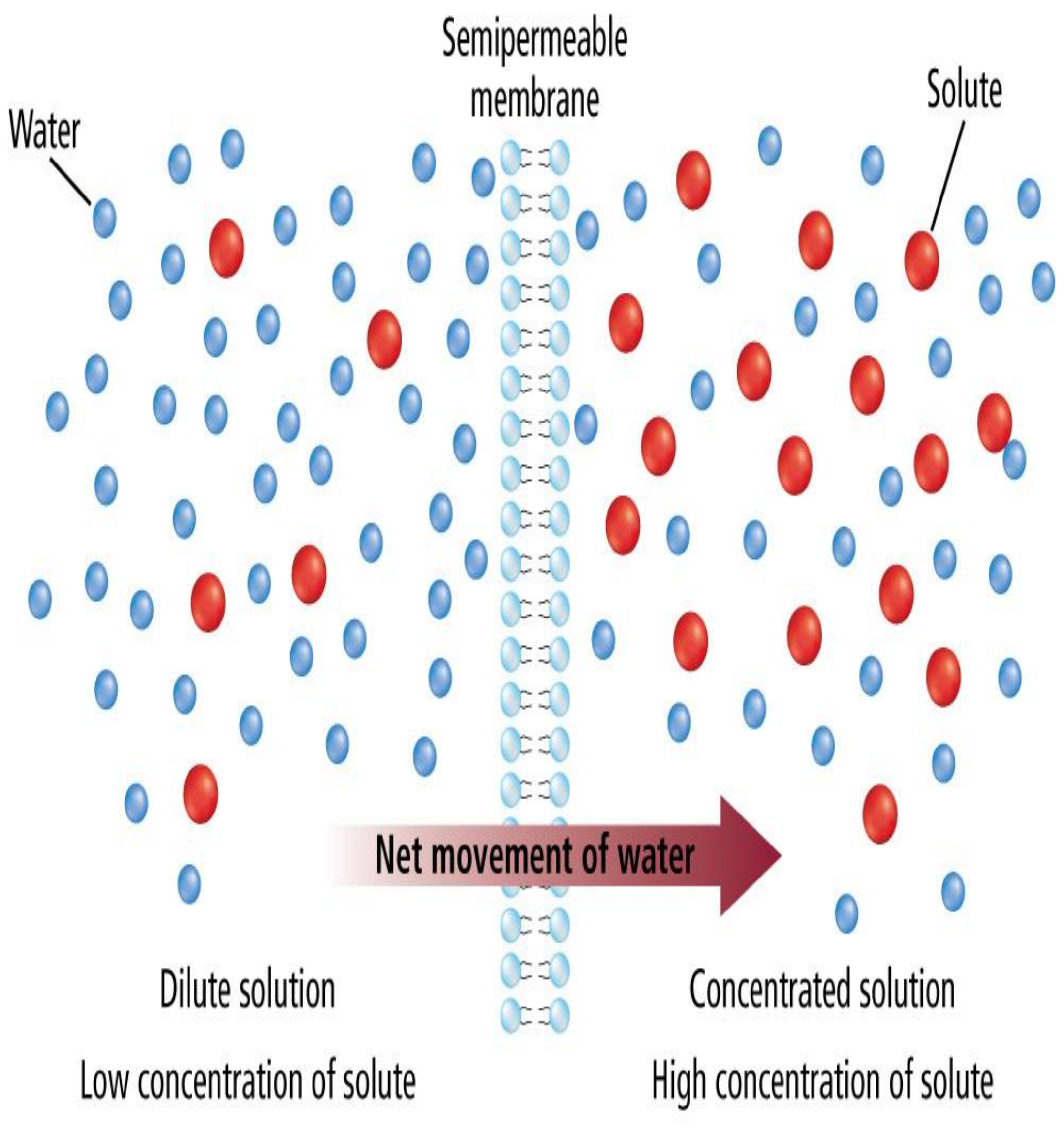
And since we have already established that the freezing point of the solution is less than that of the pure solvent, then Δt_{freez} is a negative quantity and should be subtracted from the freezing point of pure solvent (water), which is 0° C.

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

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)**.

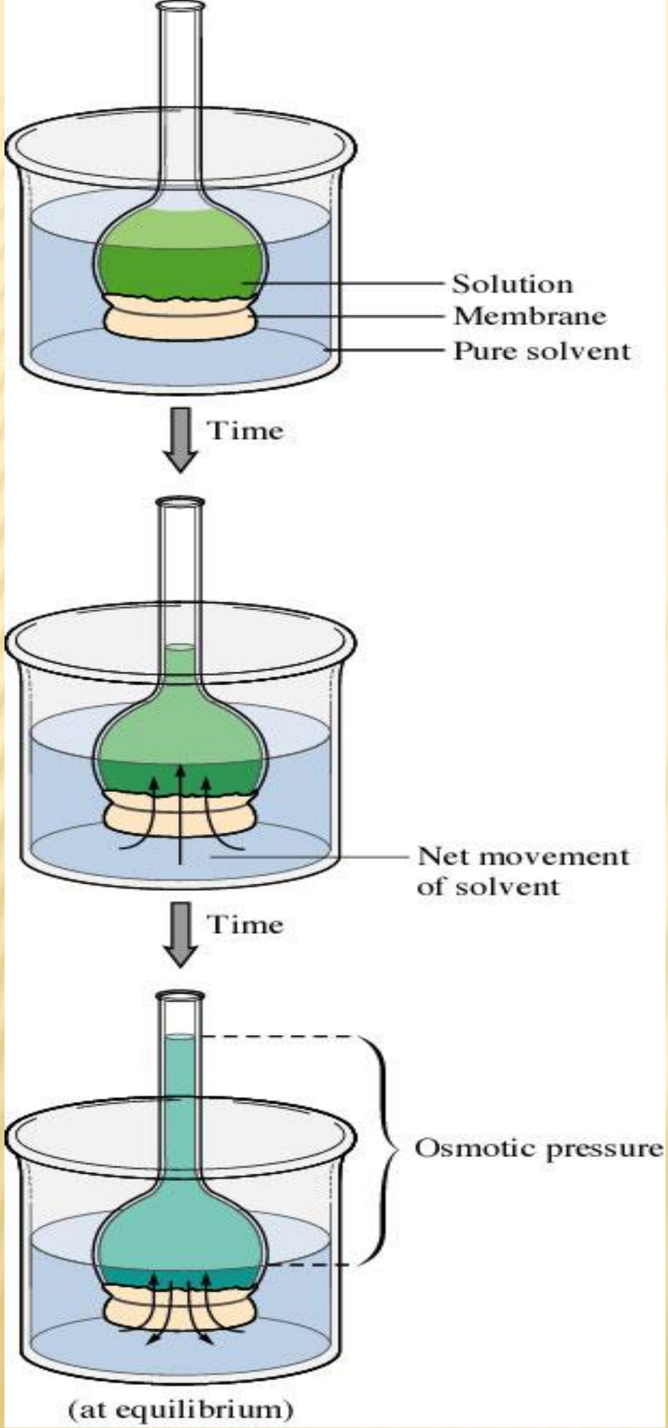
Osmotic pressure can be demonstrated with the apparatus shown in the figure below. A semipermeable membrane is tied across the open end of a thistle tube. The tube is then partially filled with a solution of sugar or alcohol in water and immersed in a beaker of water. Water will flow into the tube until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



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

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.**

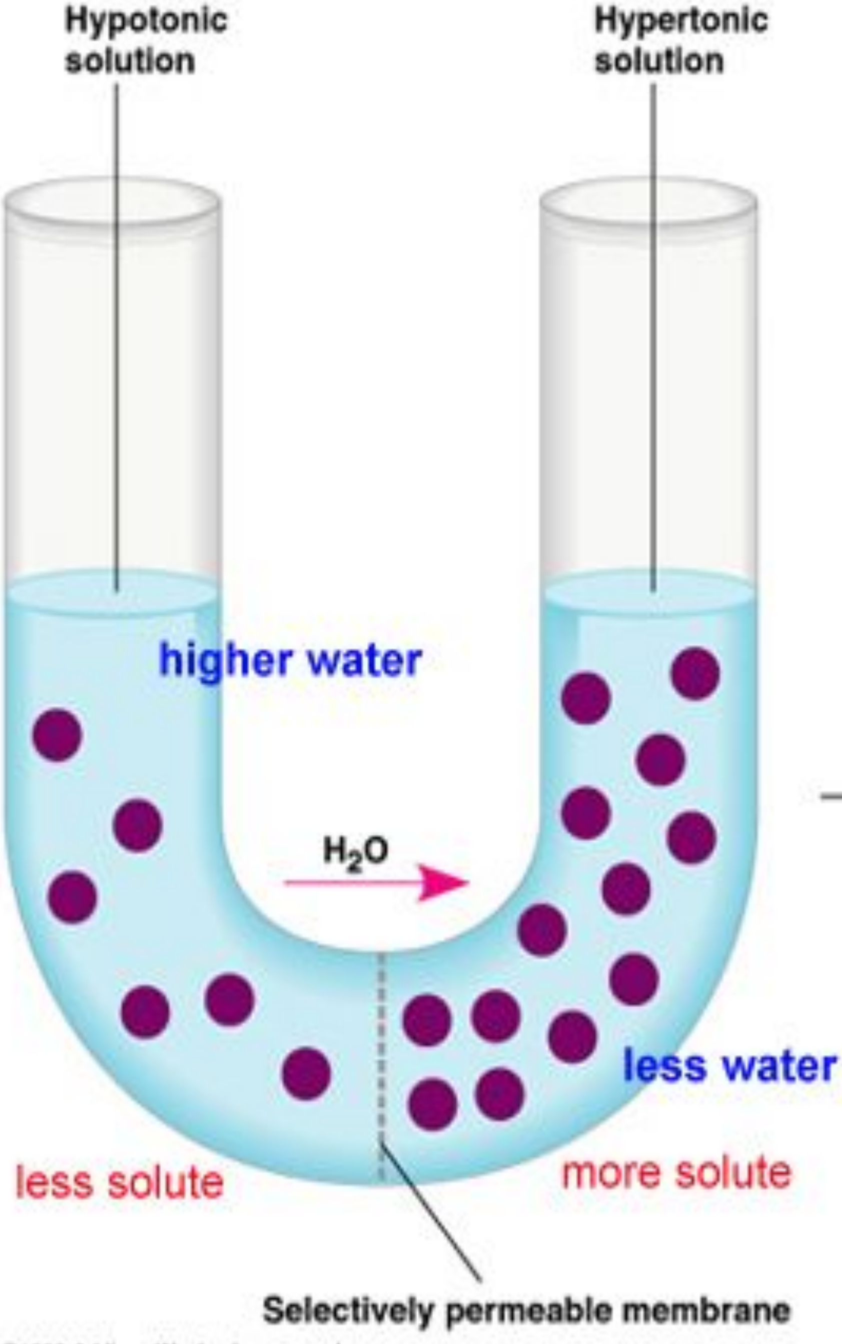


Net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions.

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



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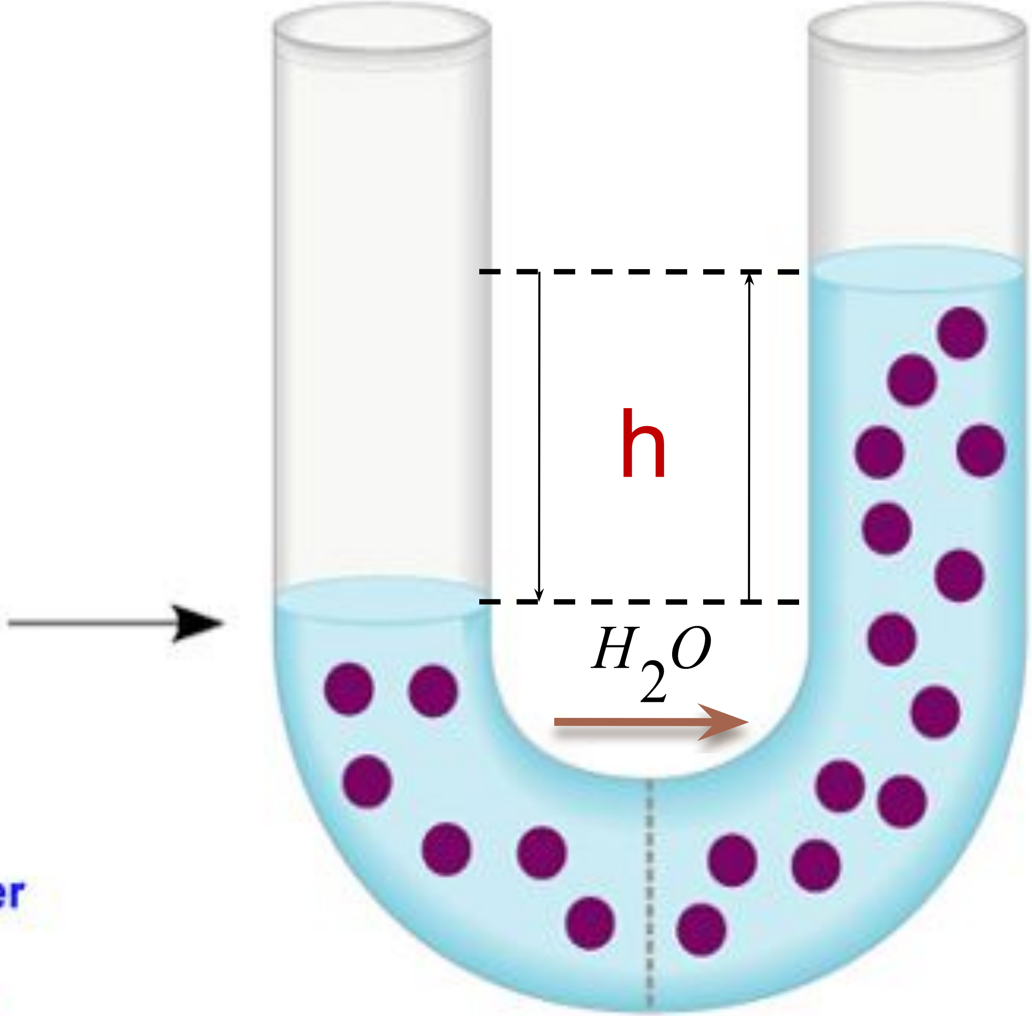
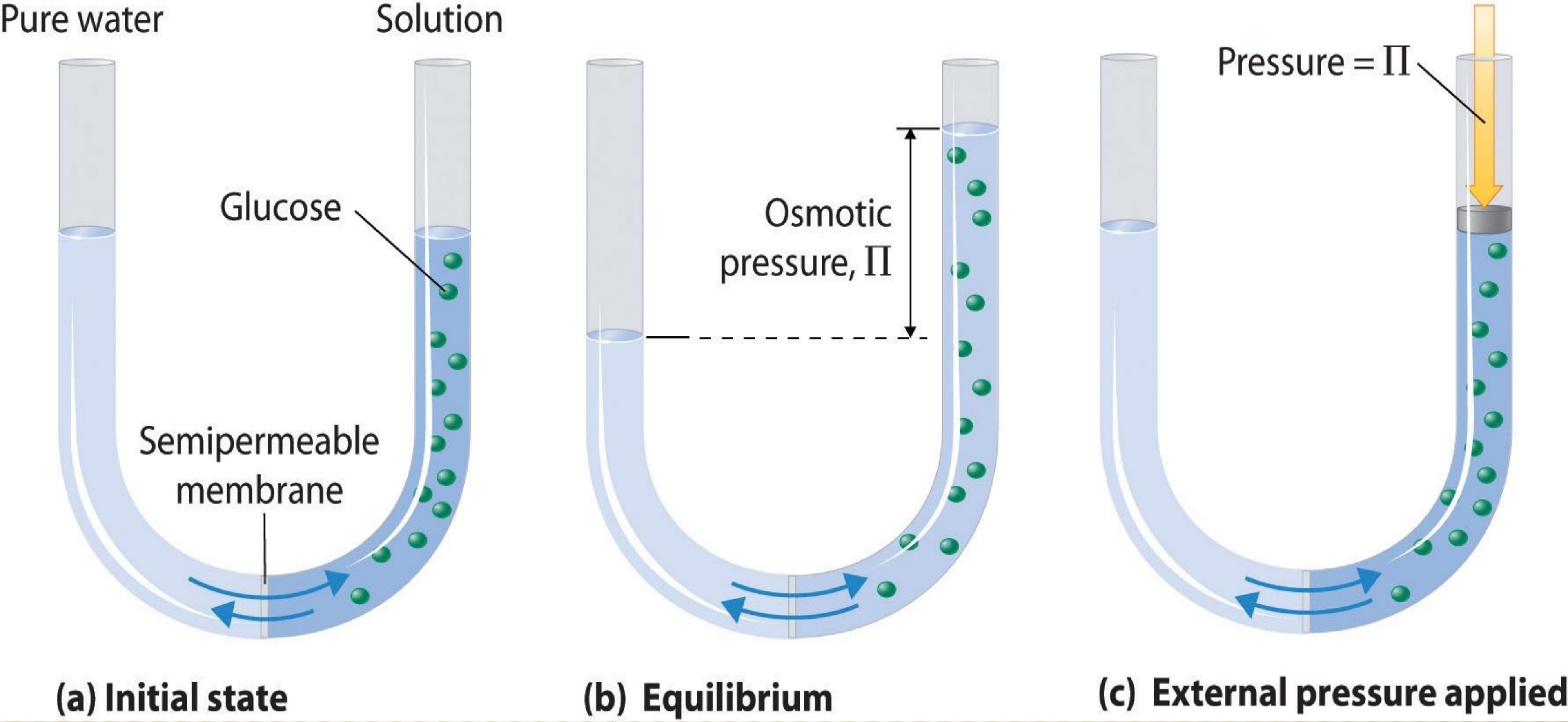


$$\pi_{osm} = g \cdot h \cdot \rho$$



(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 (Πsoln), 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

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

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

Mendeleev Clapeyron equation

where C_M is the molarity of solution, R the gas constant (0.0821 L . atm / K . mol), and T the absolute temperature (in Kelvins).

The osmotic pressure is expressed in atm.

QUIZ ME

Molarirty units are most appropriate in calculating which of the following?

A) freezingpoint depression

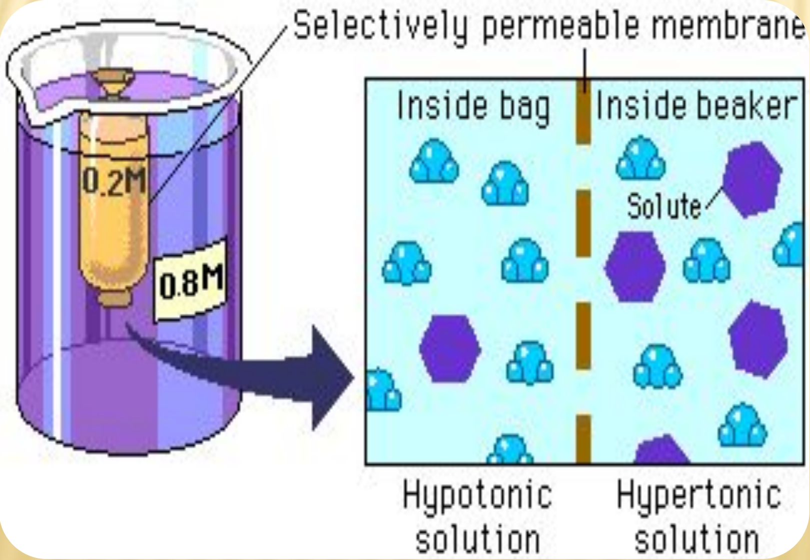
B) vapor pressure

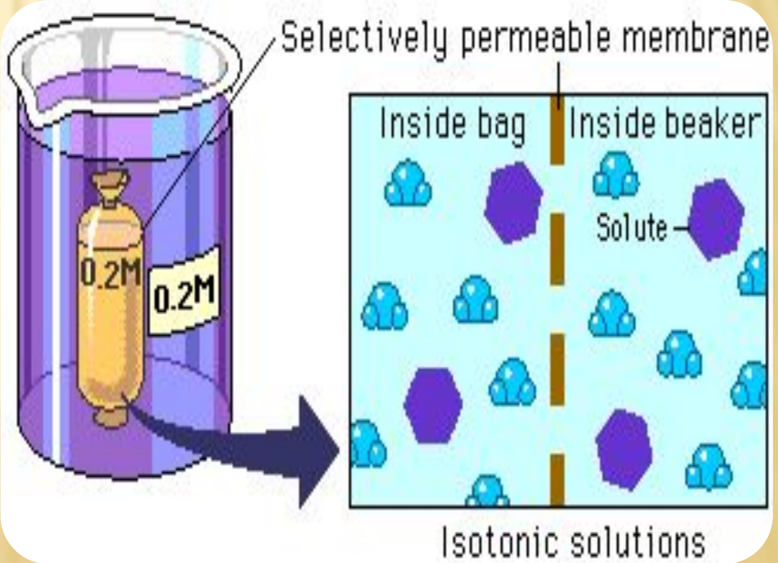
C) boilingpoint evaluation

D) osmotic pressure

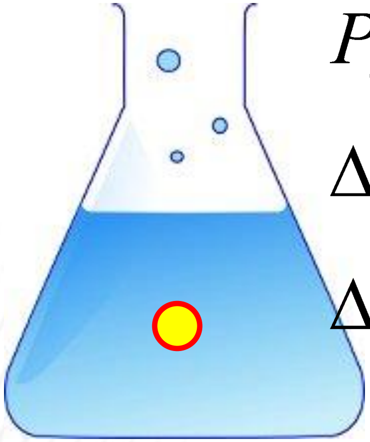
Types of Solutions Based on Solute Concentration…

- **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.





Non-electrolyte:
1 M sugar solution



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

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

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

$$C_{12}H_{22}O_{11}$$

$$1\ mole\ solute$$

$$i$$

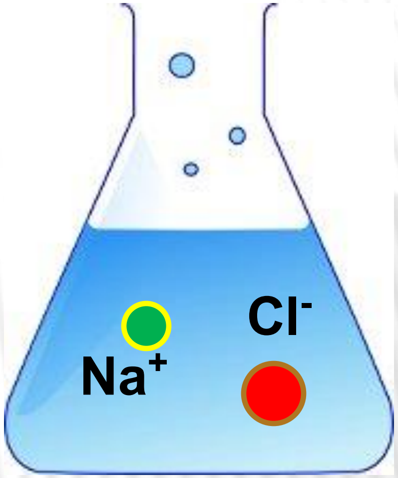
$$<<$$

Electrolyte:
1 M NaCl salt solution

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

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

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



$$NaCl \rightarrow Na^{+} + Cl^{-}$$

$$1\ mole\ of\ salt\ gives \rightarrow 2\ moles\ ions$$

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.*

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:

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

$$Al_2(SO_4)_3 \Leftrightarrow 2Al^{3+} + 3SO_4^{2-}$$

$$n = 2 \ \ cation + 3 \ \ anion = 5$$

QUIZ ME

If equal numbers of moles of each of the following are dissolved in 1 kg of distilled water, the one with the lowest boiling point will be:

A) NaI

B) $AlCl_3$

C) $Mg(NO_3)_2$

D) CH_3COOH

E) $C_6H_{12}O_6$

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.

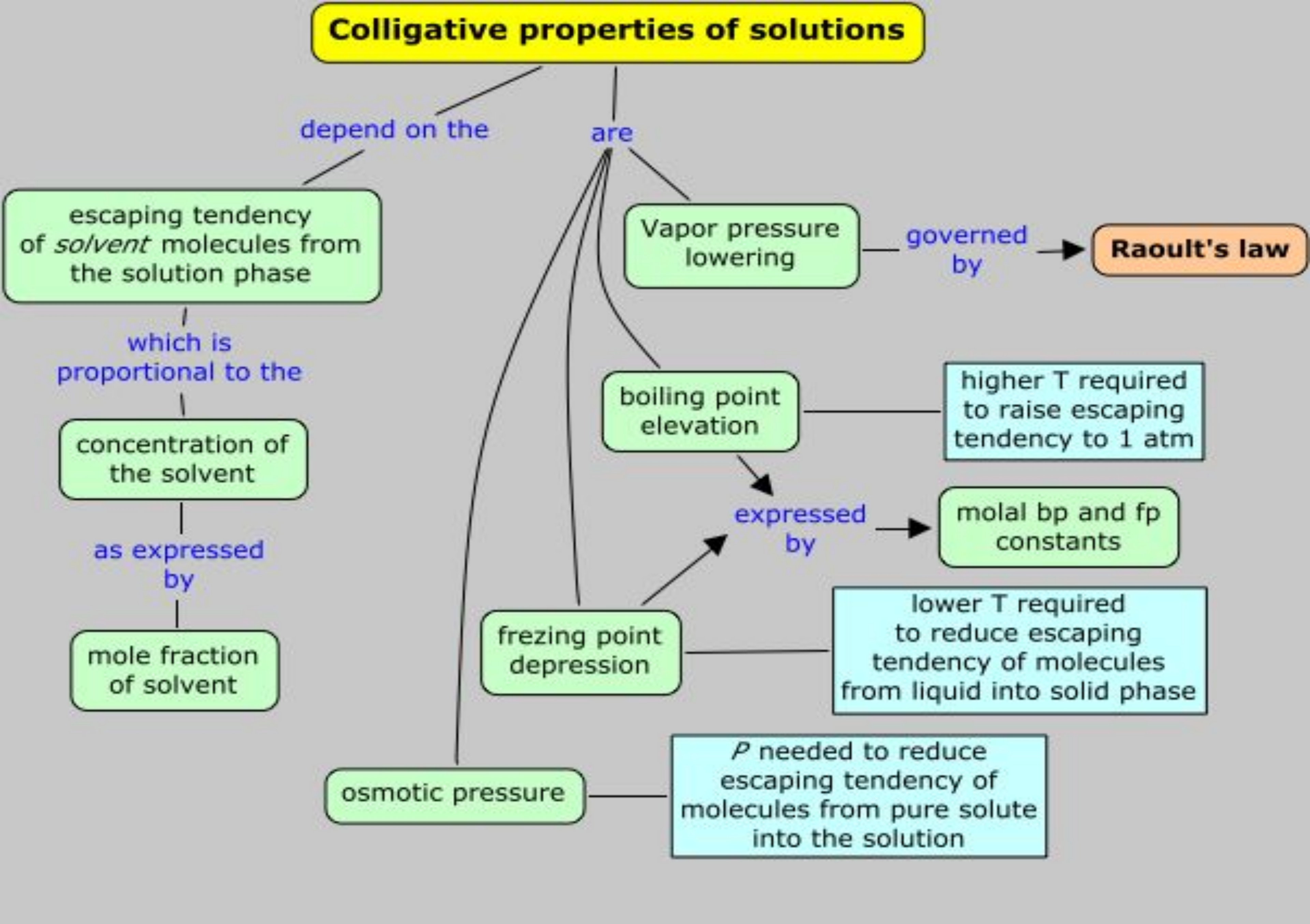
9. A hypertonic solution has a higher concentration of particle than the cell causing the cell to shrink.

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



depend on the

escaping tendency of *solvent* molecules from the solution phase

which is proportional to the

concentration of the solvent

as expressed by

mole fraction of solvent

are

Vapor pressure lowering

governed by

Raoult's law

boiling point elevation

higher T required to raise escaping tendency to 1 atm

expressed by

molal bp and fp constants

frezing point depression

lower T required to reduce escaping tendency of molecules from liquid into solid phase

osmotic pressure

P needed to reduce escaping tendency of molecules from pure solute into the solution

Stephen Lower