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Physical Pharmacy

Non-electrolytes 4

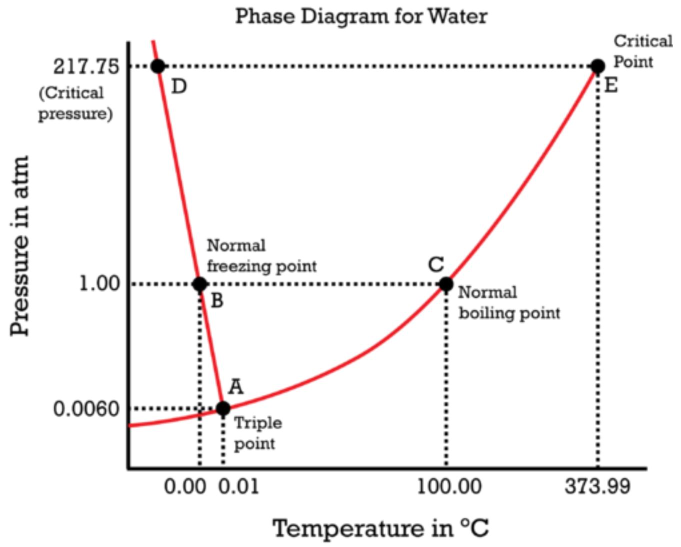
Nonelectrolytes

Elevation of the Boiling Point (ΔTb)

- It is well known that, there is a direct relationship between temperature and vapor pressure of a liquid

- 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.

- Addition of nonvolatile solute to a solution raises the boiling point of the solution above that of pure solvent (solution will boil at a higher temperature than will the pure solvent).



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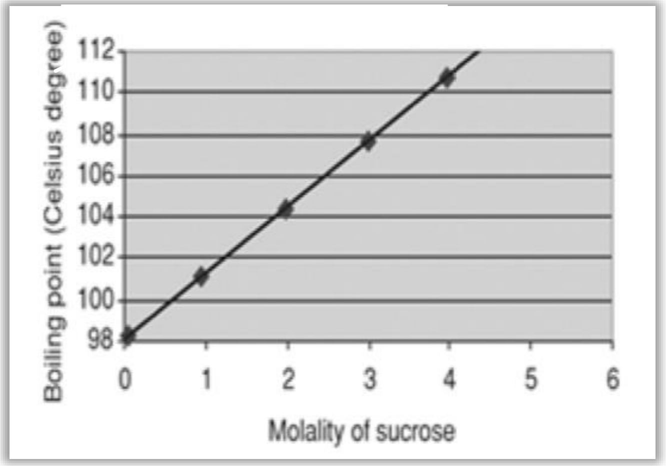
Elevation of the Boiling Point (ΔTb)

- The more of the solute that is dissolved, the greater is the effect.
- Because the solute will lower the vapor pressure of the solvent, so the temp, of the solution must be raised to make the solution's vapor pressure equal to the atmospheric pressure



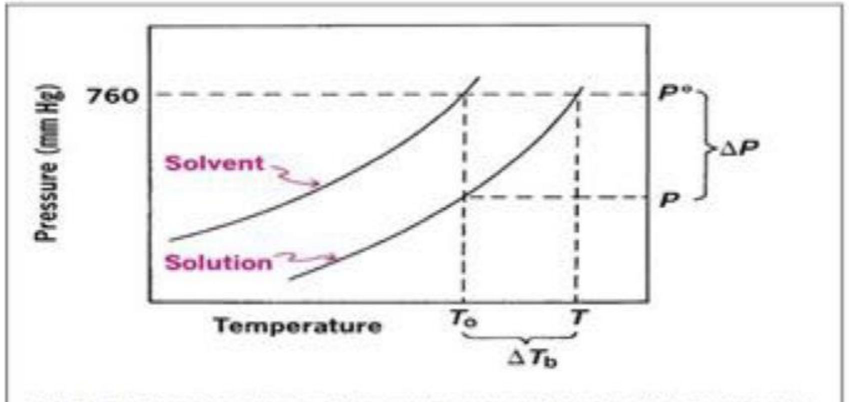
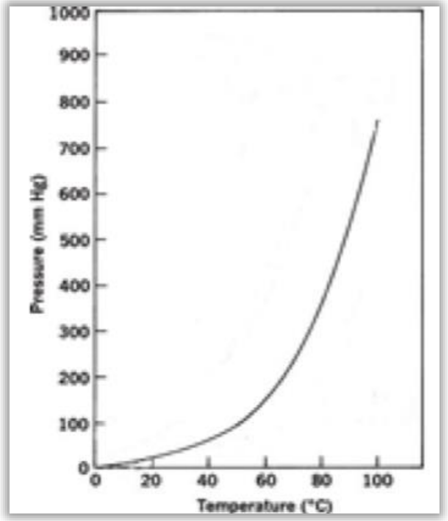


Fig. 5-6. Boiling point elevation of the solvent due to addition of a solute (not to scale).



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Elevation of the Boiling Point (ΔTb)

- $\Delta T_b = T_{b\ solution} - T_{b\ solvent}$

  To prove that ΔT_b is a colligative property :

  $\Delta T_b \propto \Delta P$

  Since P° for a solvent is constant at constant temp.

  Therefore $\Delta T_b \propto \Delta P / P°_1$

  $\Delta Tb = K \frac{\Delta P}{P°_1}$ As we know $\Delta P / P°_1 = X_2$

  Therefore $\Delta T_b = K X_2$

- Since boiling point elevation (ΔT_b) depends on the no. of particles (X_2) .. So it is a colligative property

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Elevation of the Boiling Point (ΔTb)

- To find the relationship between **ΔT_b** and molality of the solution we continue the derivation as follow: Since from last lecture we conclude that :

$$X_2 = m.\ \frac{Mwt_1}{1000}$$

Therefore by substitution

$$\Delta T_b = K \frac{Mwt_1}{1000} m$$ **Since K, Mwt1 are constants**

- Therefore we can consider that $K.\ \frac{Mwt_1}{1000}$ is constant value .

- This constant has a symbol known as K_b

- So **$\Delta T_b = K_b$** m (K_b is known as molal elevation constant with units of °C/mole)

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Elevation of the Boiling Point (ΔTb) : Example

A 0.2 m aqueous solution of a drug gave a boiling point elevation of 0.103°C, Calculate the approximate molal elevation constant (K_b) and the boiling point of the solution

Answer

$\Delta T_b = K_b\, m$

$0.103 = K_b\, 0.2$

$K_b = 0.515$ °C/mole

$\Delta T_b = T_{b\ solution} - T_{b\ solvent}$

As we know the boiling point of water = 100°C

$0.103 = T_{b\ solution} - 100$

$T_{b\ solution} = 100.103$ °C (Elevation)

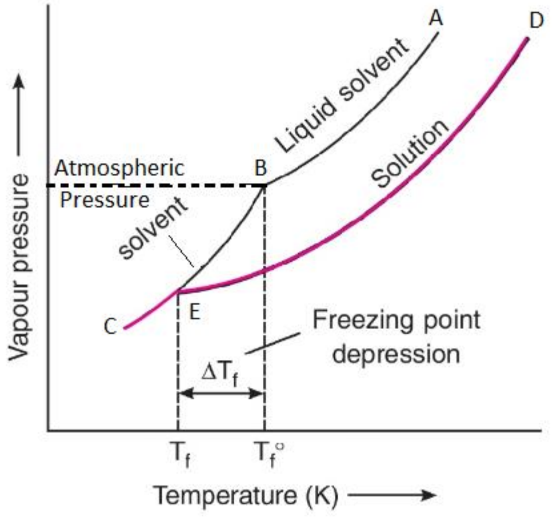
Nonelectrolytes

Depression of the Freezing Point (Δ Tf)

- 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.



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Depression of the Freezing Point (Δ Tf)

- 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.

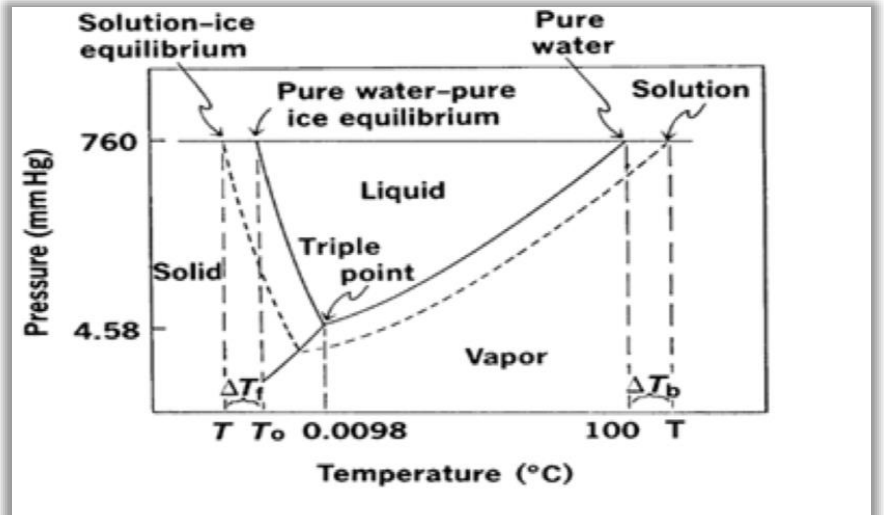

Fig. 5-8. Depression of the freezing point of the solvent, water, by a solute (not to scale).

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Depression of the Freezing Point (ΔT_f)

$$\Delta T_f = T_{f\,solvent} - T_{f\,solution}$$

- To prove that ΔT_f is a colligative property :

  $$\Delta T_f \propto \Delta P$$

- Since P° for a solvent is constant at constant temp.

  Therefore $\Delta T_f \ \alpha \ \frac{\Delta P}{P°_1}$ $\quad \Delta T_f = K \frac{\Delta P}{P°_1}$

  As we know $x_2 = \frac{\Delta P}{P_1^{\circ}}$

  Therefore $\Delta T_f = K X_2$

- Since freezing point depression (**ΔT_f**) depends on the no. of particles (**X_2**) .. So it is a colligative property

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Depression of the Freezing Point (Δ Tf)

- To find the relationship between **Δ T_f** and molality of the solution we continue the derivation as follow: **As mentioned previously**

$$X_2 = m.\ \frac{Mwt_1}{1000}$$

Therefore by substitution

$$\Delta T_f = K\ \frac{Mwt_1}{1000}\ m$$ **Since K, Mwt1 are constants**

- **Therefore we can consider that** $K.\ \frac{Mwt_1}{1000}$ **is constant value**
- **This constant has a symbol known as K_b**
- **So Δ T_f = K_f m (Kf is known as molal depression constant with units of °C/mole)**

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Depression of the Freezing Point (ΔT_f): Example

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, Kf is approximately equal to 1.86°C/mole

Answer

$\Delta T_f = T_{f\ solvent} - T_{f\ solution}$

$\Delta T_f = K_f\ m$

M = Wt / Mwt x 1000/ Wt of solvent

m = 3.42 / 342 x 1000/ 500 =0.02

$\Delta T_f = 1.86 \times 0.02 = 0.037°C$

As we know the freezing point of water = zero°C

$\Delta T_f = T_{f\ solvent} - T_{f\ solution}$

$0.037 = \text{zero} - T_{f\ solution}$

= - 0.037°C (Depression)

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Depression of the Freezing Point (ΔT_f): Example

What is the freezing point depression of a 1.3 m solution of sucrose in water? If you know that cryoscopic constant (K_f) at this concentration is about 2.1

Answer

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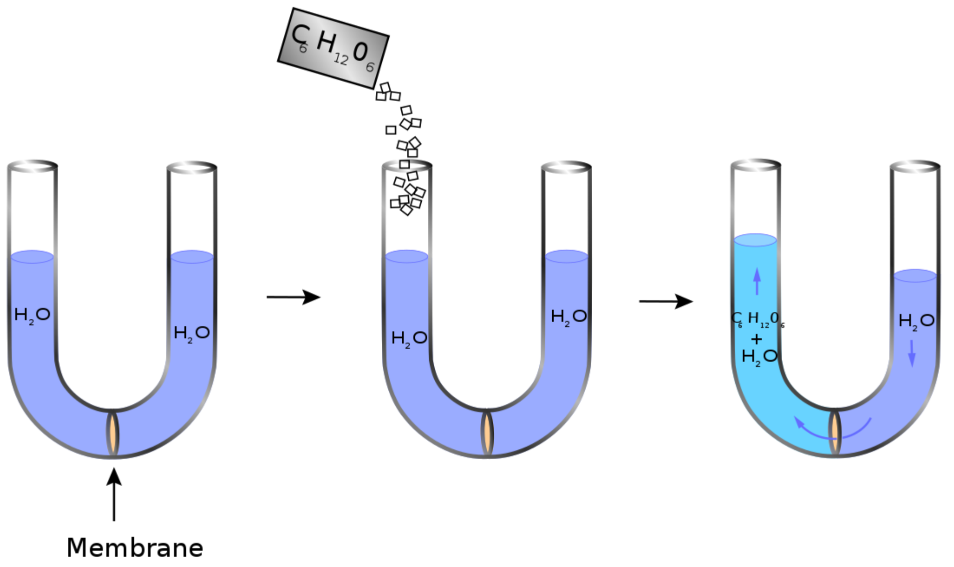
Osmotic Pressure (π)

- Osmosis (**Greek: “a push or impulse”**): is defined as the passage of the solvent into a solution through a semipermeable membrane.

- It takes place when a concentrated solution is separated from a less concentrated solution by a semipermeable membrane



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Semipermeable membrane:

- is a membrane that allows the passage of solvent molecules but blokes the passage of solute molecules

- The addition of a nonvolatile solute to the solvent forms a solution in which the vapor pressure of the solvent is reduced (Raoult's law).

- If pure solvent is now placed adjacent to the solution but separated from it by a semipermeable membrane, solvent molecules will pass through the membrane into the solution in an attempt to dilute out the solute and raise the vapor pressure back to its original value (namely, that of the original solvent)

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Semipermeable membrane:

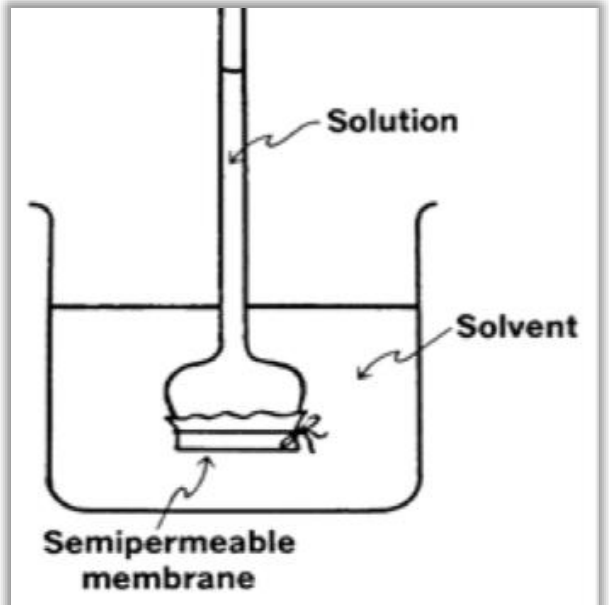
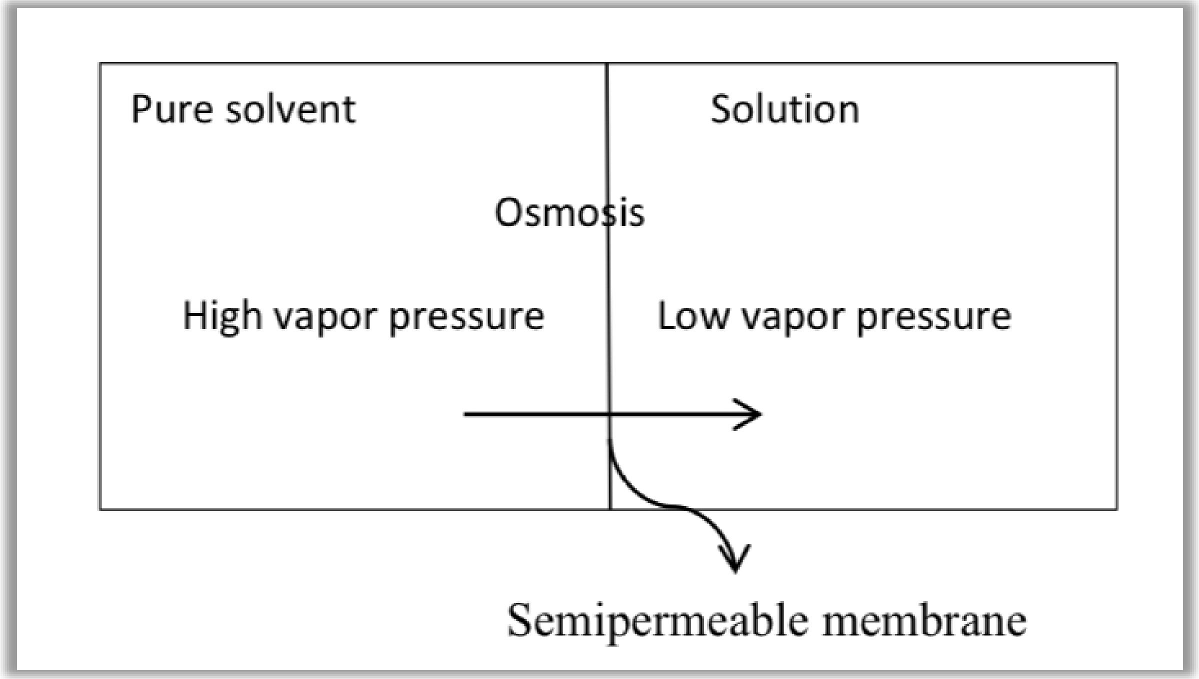


Fig. 5-10. Apparatus for demonstrating osmosis.



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Osmotic pressure

- Is the minimum pressure which needs to be applied to a solution toprevent the inward flow of its pure solvent across a semipermeable membrane.

- The osmotic pressure thus obtained is proportional to the reduction in vapor pressure brought about by the concentration of solute present as shown below

$$\pi \ \alpha \ \Delta P$$

$$\pi \ \alpha \ \Delta P / P_1^o \longrightarrow \pi \alpha X_2$$

- Therefore, osmotic pressure is a colligative property.

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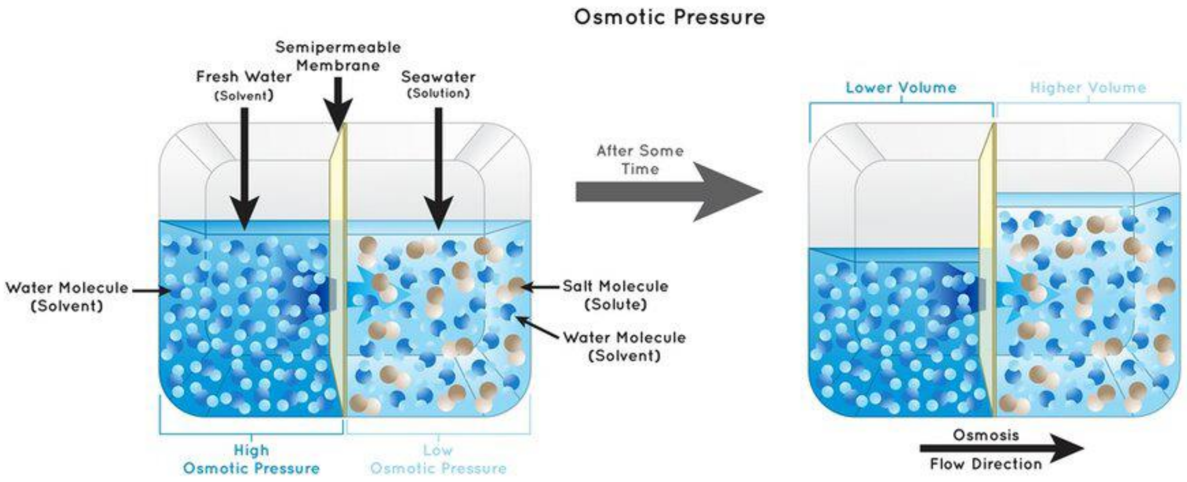
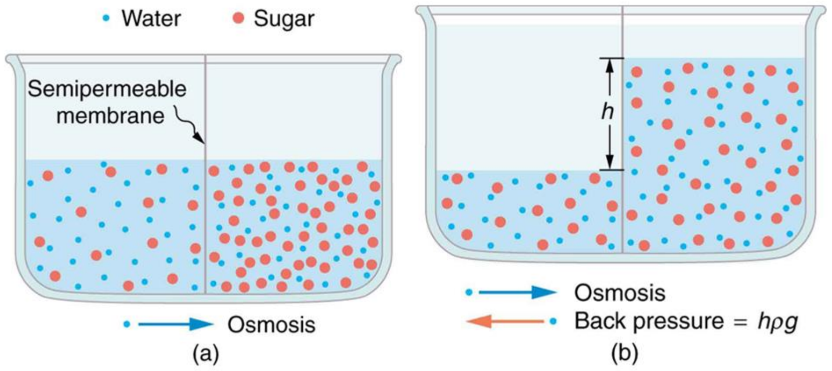
Osmotic pressure





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van't Hoff and Morse Equations for Osmotic Pressure

- In a dilute solution it was concluded that there is proportionality between osmotic pressure, concentration, and temperature corresponded to the equation for an ideal gas

- As follow :

PV=nRT (ideal gas)

R is gas constant = 0.082 atm.L/ mole .deg. , T is the absolute temp (°C+273)

π V=nRT (Osmotic pressure equation) ..... van't Hoff equation

$$\pi = \frac{n}{v} RT \longrightarrow \pi = cRT$$ **... van't Hoff equation**

- where c is the concentration of the solute in moles/liter (molarity).

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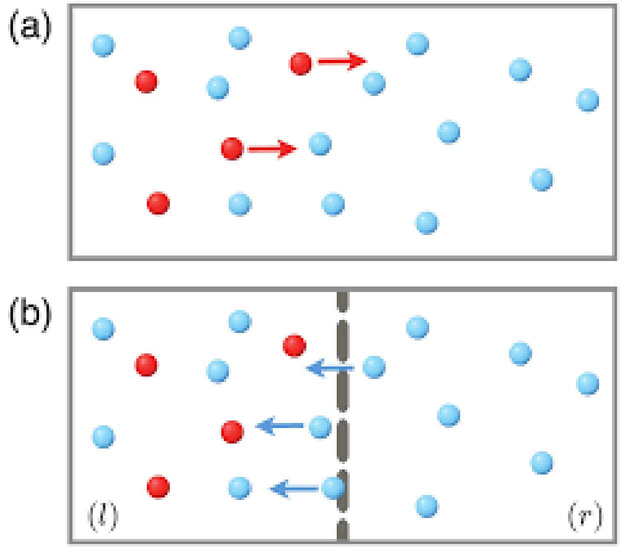
van't Hoff and Morse Equations for Osmotic Pressure

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

- The Morse equation is :

  $\pi = RTm$ .... Morse Equation



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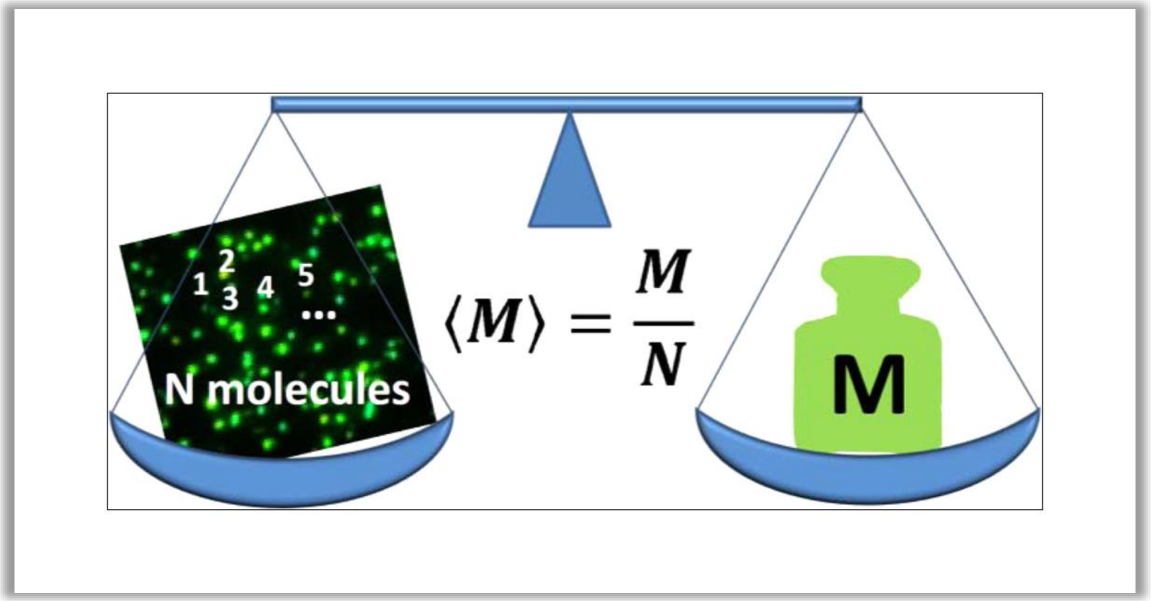
Molecular Weight Determination

- The four colligative properties that have been discussed (vapor pressure lowering, freezing point lowering, boiling point elevation, and osmotic pressure) can be used to calculate the molecular weights of nonelectrolytes present as solutes in a solution.



Molecular Weight Determination: Example(17)

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? (K_b of water = 0.51)

Answer

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Molecular Weight Determination: Example(18)

The freezing point depression of a solution of 2 g of 1,3-dinitrobenzene in 100 g of benzene was determined and was found to be 0.6095°C. Calculate the molecular weight of 1,3-dinitrobenzene if you know that the K_f of benzene is 5.12

Answer

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Molecular Weight Determination: Example(19)

Fifteen grams of a new drug dissolved in water to yield 1000 mL of solution at 25°Cwas found to produce an osmotic pressure of 0.6 atm , What is the molecular weight of the solute?

Answer

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Thank You !

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