

Properties of Solutions

Z Ch 17.1-17.4

Almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the nonliving surface of the earth, ... take place between substances in solution."

Friedrich Wilhelm Ostwald, 1890

(Nobel Prize for Chemistry in 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction".)

**Exam II – everything from last exam – Ch 5,
13, 16 (selected sections), 17**

17.4 Vapor Pressures of Solutions

17.5 Boiling Point Elevation/Freezing Point Depression

17.6 Osmotic Pressure

17.7 Electrolyte Solutions

17.8 Colloids (omit)

**midterm grades available
tomorrow morning
myuic.edu**

Colligative Properties

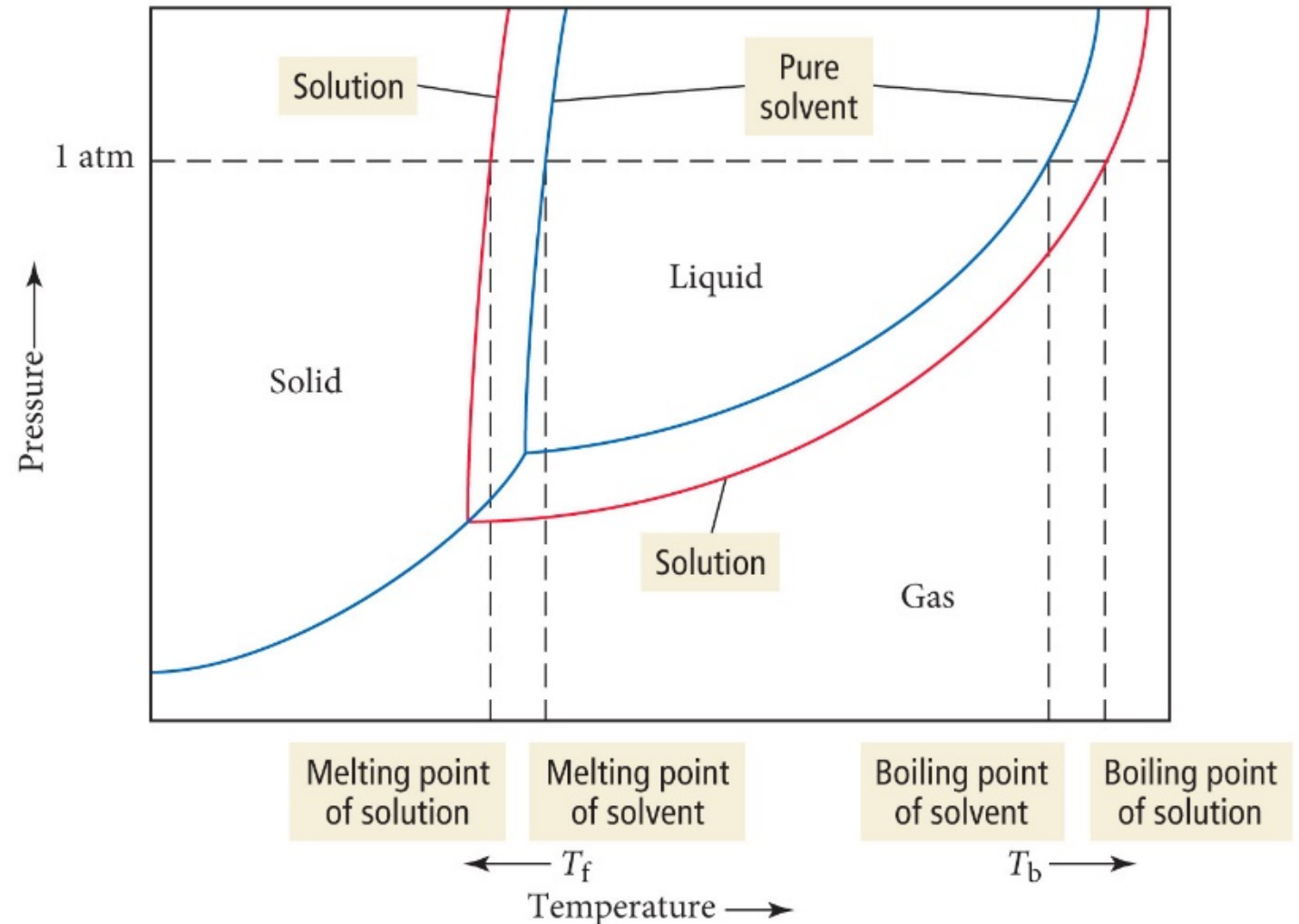
depend on relative number of dissolved solute particles
classification

seen on phase diagram

1. vapor pressure lowering
2. boiling point elevation
3. freezing point depression

not on phase diagram

4. osmosis



Solution Composition

homogeneous mixture of two or more components in a single phase

composition

solute - substance being dissolved, usually minor component

solvent - dissolving medium, generally major component

expressing composition

mass percent – (mass of solute) / (mass of solvent) × 100

molarity, M – (moles of solute) / (1 L of solution)

mole fraction, χ_A – **for two component solution A, B** $\chi_A = n_A / (n_A + n_B)$

molality, m – (moles of solute) / (1 kg of solvent) – independent of temperature, unlike molarity

Molarity and Molality

EX 2. A 5.50 weight percent sulfuric acid ($M = 98.0778$) solution has a density of 1.0352 g cm^{-3} .

a) What is the molarity of the solution?

$$M = n / L = (5.50 \text{ g} / 100 \text{ g sol'n}) (1 \text{ mol} / 98.0778 \text{ g}) (1.0352 \text{ g sol'n} / \text{mL}) \\ \times (1000 \text{ mL} / \text{L}) = \mathbf{0.581 \text{ M}}$$

b) What is the molality of the solution?

$$m = n / \text{kg} = [5.50 \text{ g} / (100 - 5.50 \text{ g water})] (1 \text{ mol} / 98.0778 \text{ g}) (1000 \text{ g} / \text{kg})$$

Vapor Pressure and Raoult's Law

The vapor pressure of the solvent above a solution containing a nonvolatile solute is proportional to the mole fraction of the solvent present

Raoult's Law: $P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$ (linear function)

EX 3. The vapor pressure of water at 90°C is 525.8 mm Hg. If a solution of 651 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is dissolved in 1.50 kg of water, what is the solution vapor pressure at 90°C? ($M_{\text{H}_2\text{O}} = 18.02$, $M_{\text{C}_2\text{H}_6\text{O}_2} = 62.07$ g/mol)

$$P_1 = \chi_1 P^{\circ}_1 = (1500/18.002) / (1500/18.02 + 651/62.07) \times 525.8$$

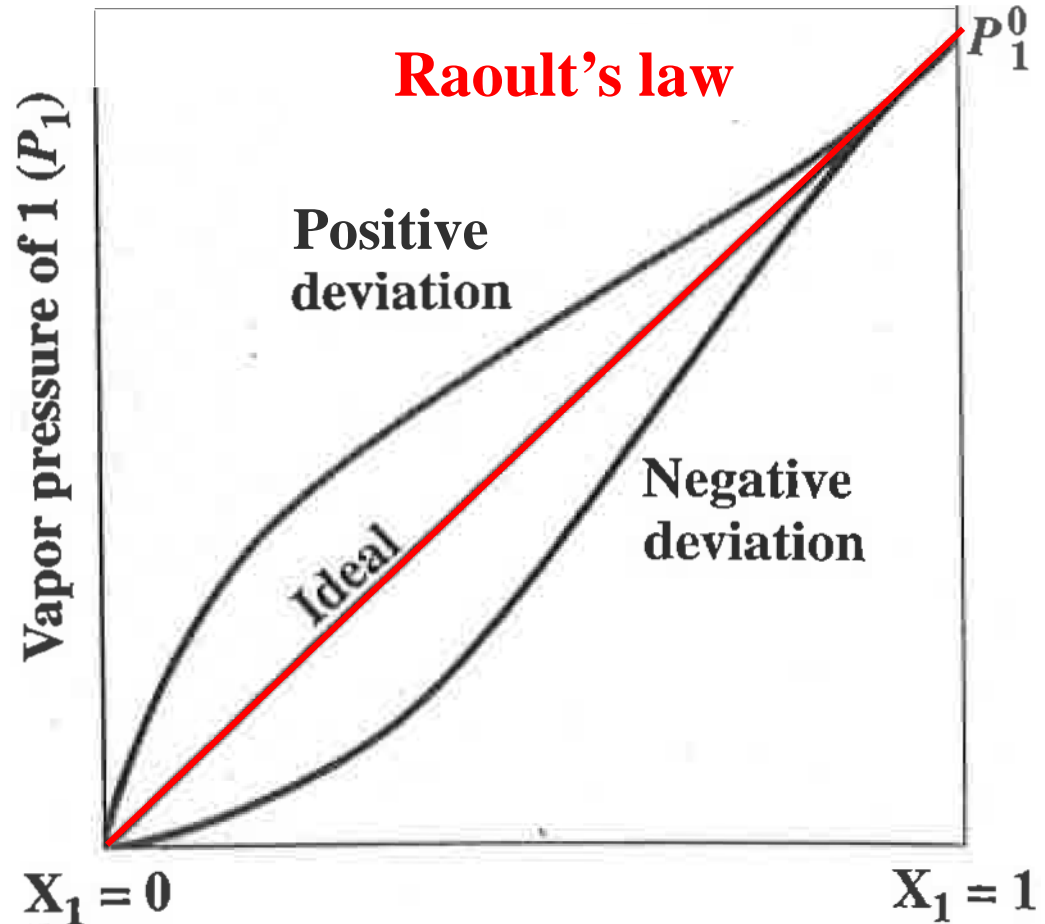
Deviations of Raoult's Law

Nonideal solutions show deviations from Raoult's law

negative deviations – strong solute/solvent interactions

positive deviations – weak solute/solvent interactions (weaker than pure liquids)

$$P_{\text{solvent}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$



Raoult's Law for Determining Molar Mass

1 solvent, 2 solute

EX 4. 20.0 g of urea is dissolved in 125 g of water ($M_{\text{H}_2\text{O}} = 18.0148$) at 25°C. The vapor pressure of the solution was observed to be 22.67 mm Hg. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the molar mass of urea?

$$M = \text{mass} / n \quad P_1 = \chi_1 P_1^\circ \Rightarrow \chi_1 = P_1 / P_1^\circ = n_1 / (n_1 + n_2)$$

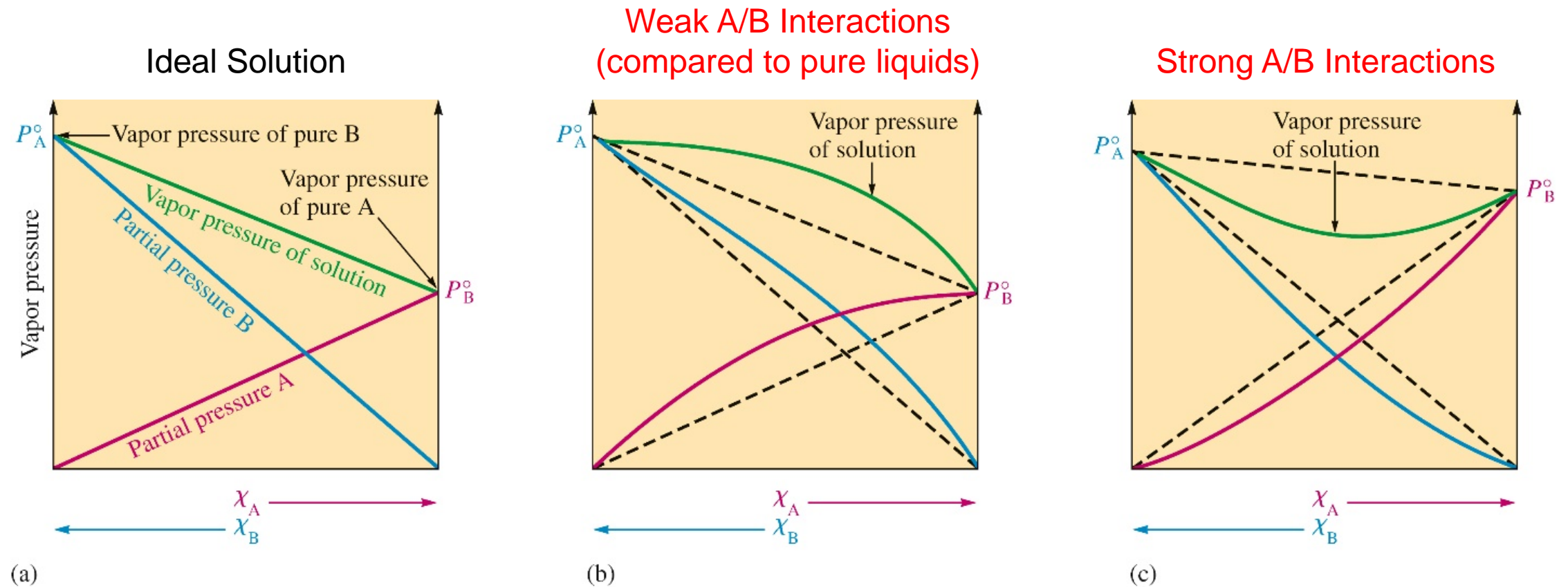
$$n_1 P_1^\circ = (n_1 + n_2) P_1 \text{ or } n_1 P_1^\circ - n_1 P_1 = n_2 P_1 \Rightarrow$$

$$n_2 = \text{mass} / M = n_1 (P_1^\circ - P_1) / P_1$$

$$M = (\text{mass}) P_1 / [n_1 (P_1^\circ - P_1)] = 20.0 (22.67) / [(125/18.0148)(23.76 - 22.67)] = \mathbf{59.9 \text{ g/mol}}$$

Deviations from Raoult's Law Ideal Behavior

$$P_{\text{total}} = P_A + P_B = \chi_A P_A^\circ + \chi_B P_B^\circ$$



Henry's Law (for Solutes)

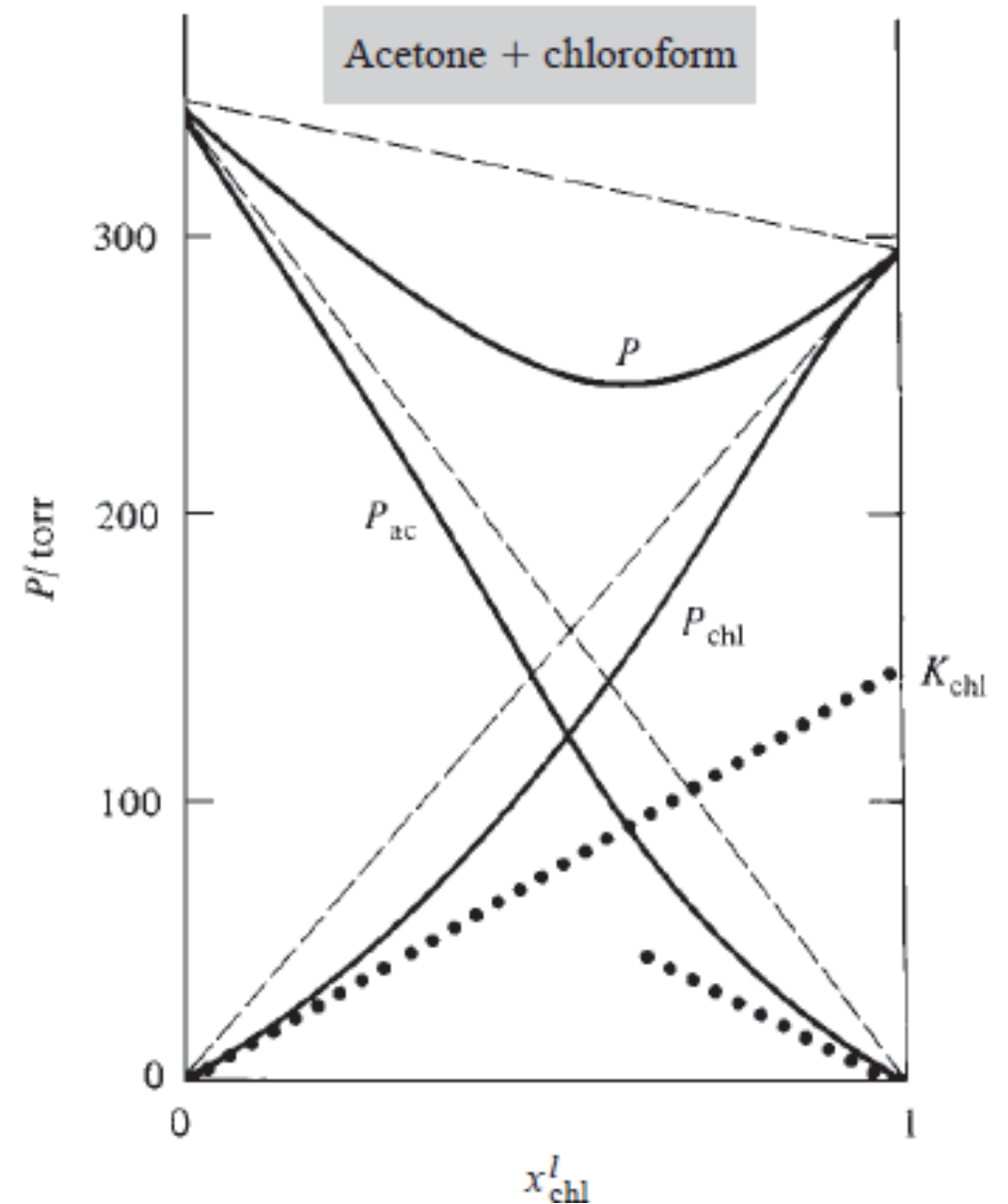
It is experimentally found that in the limiting case of a solution very dilute in the solute 2, the partial pressure of 1 in the vapor is directly proportional to the mole fraction of 2 in the liquid.

$$P = \chi_{\text{gas}} k_{\text{H}}$$

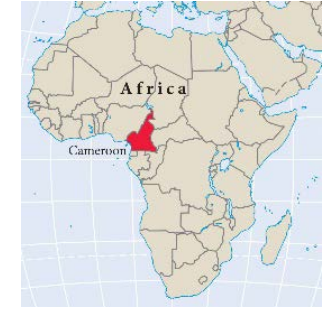
where k_{H} is the Henry's law constant for the solution.

$$P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

Note: this is not Raoult's law behavior where the linear relationship is with the mole fraction of the solvent, 1.



Henry's Law (for Solutes)



1,750 people^[3] and 3,500 livestock suffocated

Lake Nyos, Cameroon



Table 17.3

The Values of Henry's Law Constants for Several Gases Dissolved in Water at 298 K

Gas	k_H (atm)
CH ₄	4.13×10^2
CO ₂	1.64×10^3
O ₂	4.34×10^4
CO	5.71×10^4
H ₂	7.03×10^4
N ₂	8.57×10^4

Raoult's Law and a Binary Solution

For an ideal binary solution of A and B the partial pressure of each component above the solution obeys Raoult's law and Dalton's law

$$P_{\text{total}} = P_A + P_B = \chi_A P_A^{\circ} + \chi_B P_B^{\circ}$$

Since both the liquid and gas compositions can be given in terms of mole fractions it is helpful to distinguish between them. The following equations are useful for dealing with binary solutions

$$P_A = \chi_A^L P_A^{\circ} (\chi^{\text{liquid}}) \quad P_A = \chi_A^V P_{\text{tot}} (\chi^{\text{vapor}}) \quad P_{\text{tot}} = P_A + P_B (\text{vapor}) \quad \chi_A + \chi_B = 1$$

(liquid/vapor)

Raoult's Law for Binary Solution (Upstairs/Downstairs)

EX 5. A mixture of hexane ($P^{\circ}_1 = 0.198$) and heptane ($P^{\circ}_2 = 0.060$) obeys Raoult's law. If the mole fraction of heptane is 0.600, what is the composition of the vapor above the solution?

Strategy:

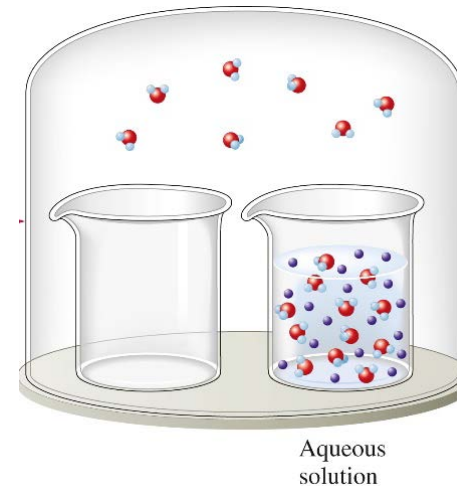
DOWNSTAIRS

use Raoult's law to find vapor pressure of each component

UPSTAIRS

sum to get total vapor pressure

use Dalton's law to get vapor composition



UPSTAIRS

$$P_{\text{tot}} = P_A + P_B$$

$$P_A = \chi_A^V P_{\text{tot}} \quad (\chi^{\text{vapor}})$$

DOWNSTAIRS

$$P_A = \chi_A^L P^{\circ}_A \quad (\chi^{\text{liquid}})$$

BOTH

$$\chi_A + \chi_B = 1$$

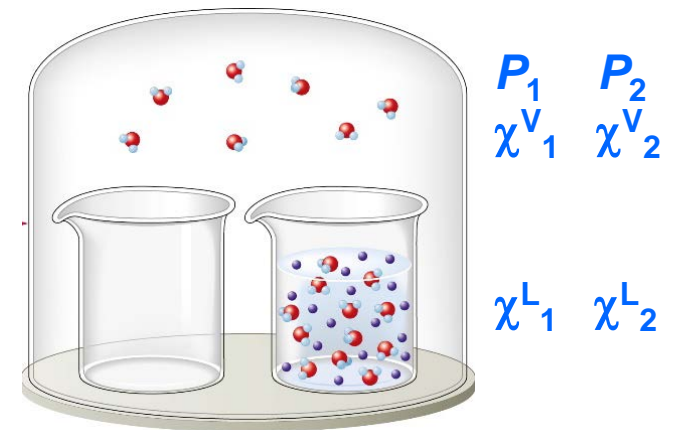
Raoult's Law for Binary Solution (Upstairs/Downstairs)

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$$P_1 = \chi^L_1 P^{\circ}_1 = (0.400) (0.198) = 0.0792$$

$$P_2 = \chi^L_2 P^{\circ}_2 = (0.600) (0.060) = 0.0360$$

$$P_{\text{tot}} = 0.0792 + 0.0360 = 0.1152$$



in gas phase

$$P_1 = \chi^V_1 P_{\text{tot}} \Rightarrow \chi^V_1 = P_1 / P_{\text{tot}} = 0.0792 / 0.1152 = \mathbf{0.688}$$

$$\chi^V_2 = 1.00 - 0.688 = \mathbf{0.312}$$

Boiling Point Elevation and Freezing Point Depression

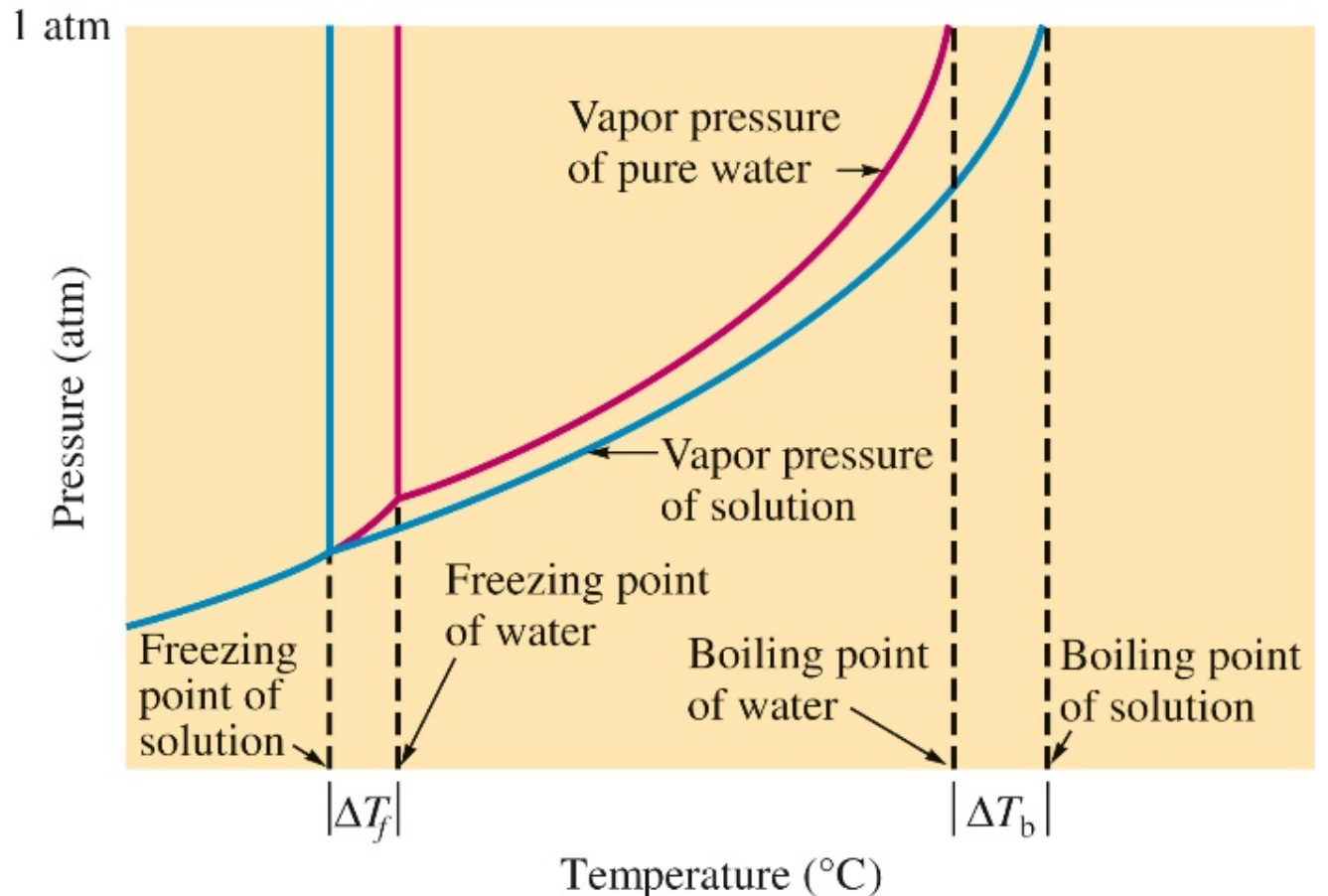
A nonvolatile solute elevates the boiling point of a solution

$$\Delta T = K_b m_{\text{solute}}$$

and depresses the freezing point

$$\Delta T = -K_f m_{\text{solute}}$$

Consider the solvent with a nonvolatile dissolved solute (volatility immaterial for freezing point depression). For freezing point depression assume that the solute does not freeze out of solution. Only the pure solid solvent freezes out when it is cooled to its freezing point.



Boiling Point Elevation for Molar Mass

EX 6. A solution prepared from 1.25 g of oil of wintergreen (methyl salicylate) in 99.0 g of benzene ($T_b = 80.10^\circ\text{C}$, $K_b = 2.3 \text{ K kg mol}^{-1}$) has a boiling point of 80.31°C . Determine the molar mass of the compound.

$$\Delta T = K_b m_{\text{solute}}$$

$$(80.31 - 80.10) = (2.3 \text{ K kg mol}^{-1})[(1.25 \text{ g} / M) / 99.0 \text{ g}] \times 1000 \text{ g} / \text{kg}$$

$$0.21 = 2.3 [(1.25/M) / 99.0] (1000)$$

$$\Rightarrow M = 150 \text{ g/mol}$$

Boiling Point Elevation / Freezing Point Depression

$$\Delta T_b = K_b m_{\text{solute}}$$

$$\Delta T_f = -K_f m_{\text{solute}}$$

molality

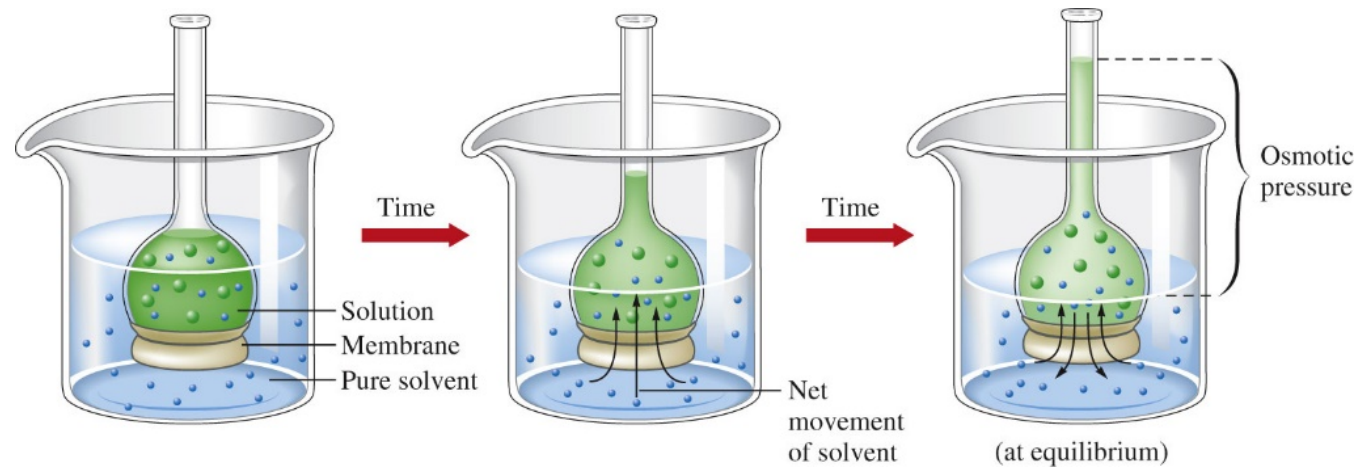
Table 17.5

Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C kg/mol)	Freezing Point (°C)	K_f (°C kg/mol)
Water (H ₂ O)	100.0	0.51	0.	1.86
Carbon tetrachloride (CCl ₄)	76.5	5.03	-22.99	30.
Chloroform (CHCl ₃)	61.2	3.63	-63.5	4.70
Benzene (C ₆ H ₆)	80.1	2.53	5.5	5.12
Carbon disulfide (CS ₂)	46.2	2.34	-111.5	3.83
Ethyl ether (C ₄ H ₁₀ O)	34.5	2.02	-116.29	1.79
Camphor (C ₁₀ H ₁₆ O)	208.0	5.95	179.8	40.

Osmotic Pressure

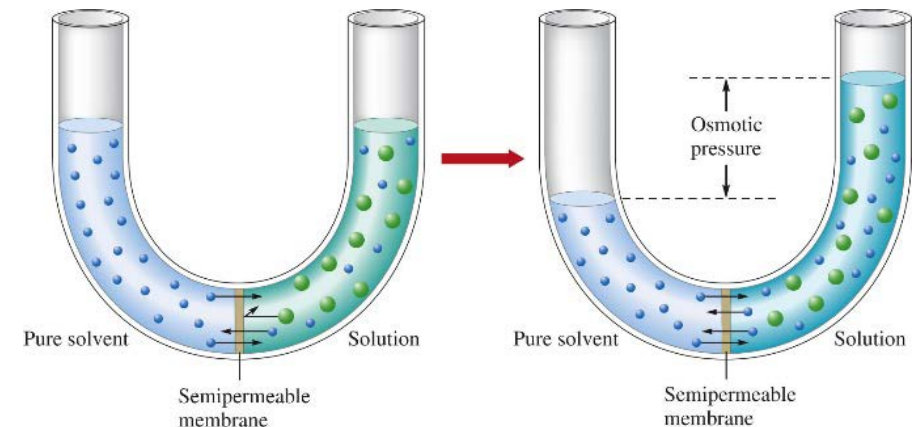
The movement of solvent through a barrier (semipermeable membrane) into a solution containing a solute creates a pressure, P , called the osmotic pressure. This pressure is the extra pressure that must be applied to the solution to maintain equilibrium between the solutions on either side of the barrier.



height proportional to osmotic pressure

$$\Pi = MRT$$

A tube with a bulb on the end is covered by a semipermeable membrane. The solution inside the tube is surrounded by pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions and equilibrium is reached.



Osmotic Pressure

EX 7. 1.00×10^{-3} g of a protein is dissolved in 1.00 mL of water. The osmotic pressure of the solution is found to be 1.12 mm Hg at 25°C. What is the molar mass of the protein?

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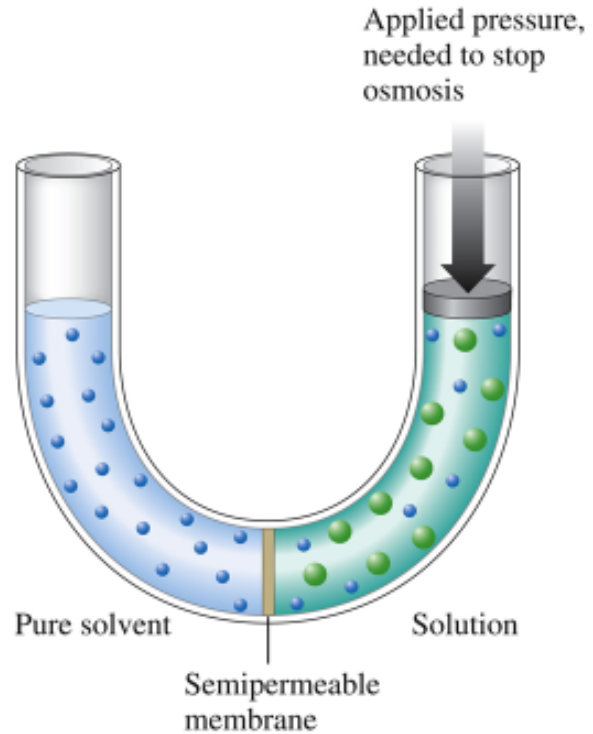
$$\begin{aligned} \Pi &= MRT \Rightarrow \Pi V = nRT & n &= \text{mass} / M & (\text{M molarity,} \\ & & & & M \text{ molar mass}) \\ & & & = \text{mass } RT / M & \end{aligned}$$

$$M = \text{mass } RT / \Pi V$$

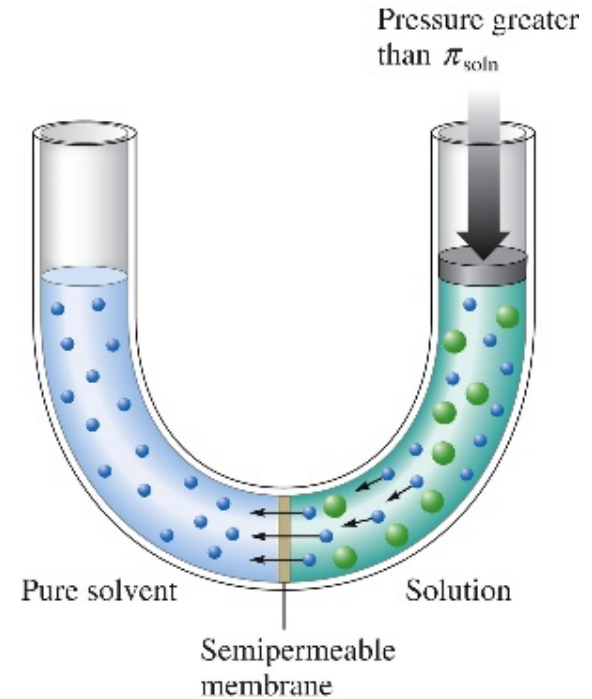
$$= (1.00 \times 10^{-3} \text{ g}) (0.08206) (298.15) / (1.12 / 760) (1.00 \times 10^{-3} \text{ L})$$

$$= \mathbf{1.66 \times 10^4 \text{ g/mol}}$$

Osmotic Pressure



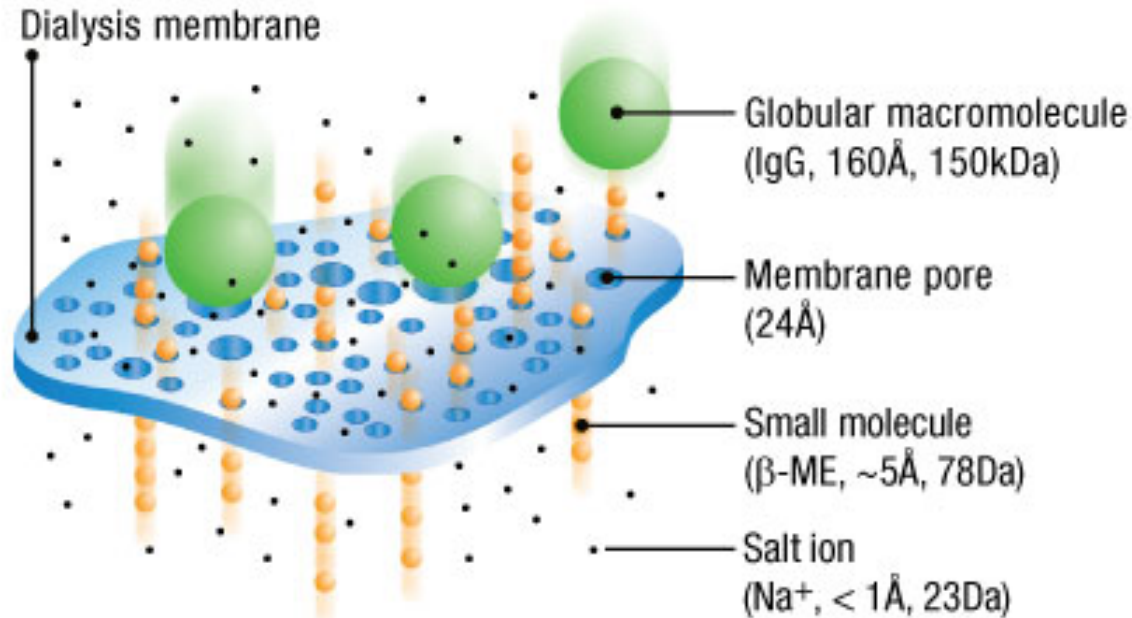
Normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. Minimum pressure required to stop osmosis is equal to the osmotic pressure of the solution.



Reverse osmosis. Pressure greater than the osmotic pressure of the solution applied, which causes a net flow of solvent (blue) from the solution to the pure solvent leaving solute molecules (green) behind.

Dialysis

Osmosis is a critical property of solvents in biology. It keeps a balance between the interior and exterior of cells and other biological systems. Since the cell wall is semipermeable it behaves as a semipermeable membrane. Small molecules and water can pass through the cell wall but large molecules (such as DNA and proteins) generally cannot. Therefore there is a higher concentration of particles inside the cell (colligative effect).



A typical dialysis membrane has a pore size of about 24 angstroms which excludes large macromolecules but allows water and small molecules to pass through.

Biological Solutions

Consider a transfusion or even administration of a saline solution. One needs to input a solution of similar osmotic properties (*isotonic*) to avoid having too dilute a solvent (*hypotonic*) which will go into the cell and raise pressure and cause rupture or too concentrated a solution (*hypertonic*) which extracts the solvent and collapses the cell.

