

Properties of Solutions

Z Ch 17.1-17.7

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".)

activity – Week 10

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

Week 10 (next week) – makeup lab week, be sure to tell your TA beforehand what lab(s) you would like to makeup

Please check your grades on Blackboard

- 6. Osmotic Pressure**
- 7. Electrolyte Solutions**
- 8. Colloids (omit)**

Colligative Properties

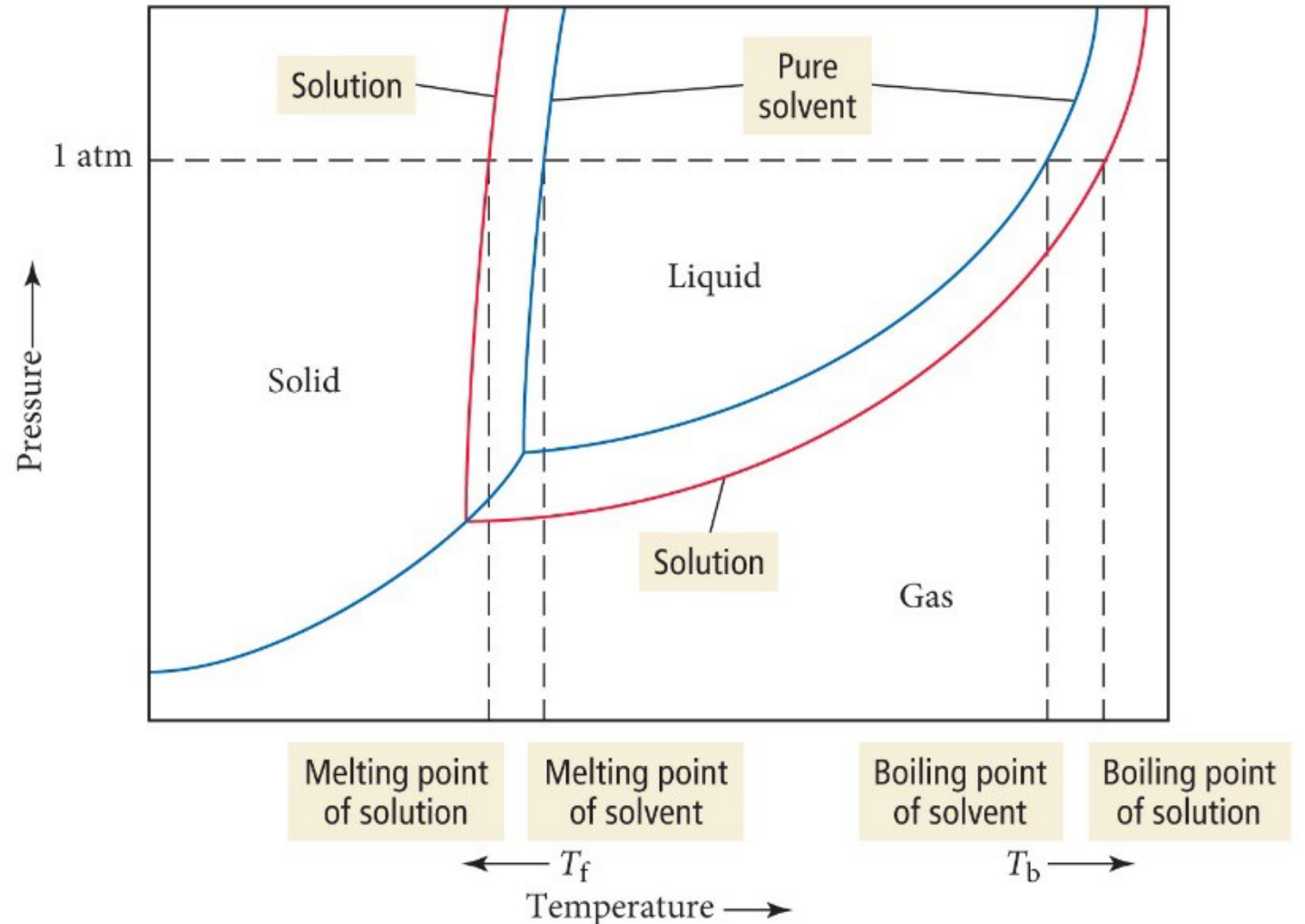
depend on relative number of dissolved solute particles
classification

seen on phase diagram

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

not on phase diagram

4. osmosis



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:

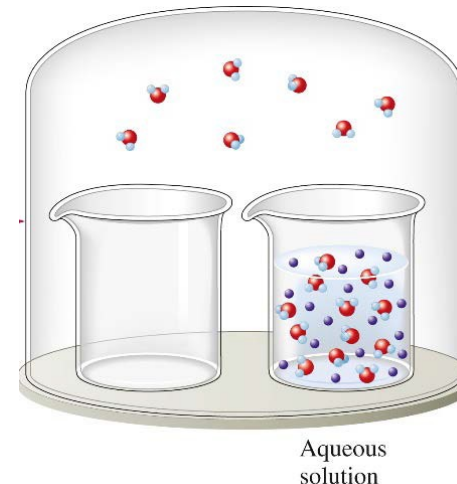
DOWNSTAIRS

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

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

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

DOWNSTAIRS

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

BOTH

$$\chi_A + \chi_B = 1$$

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?

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

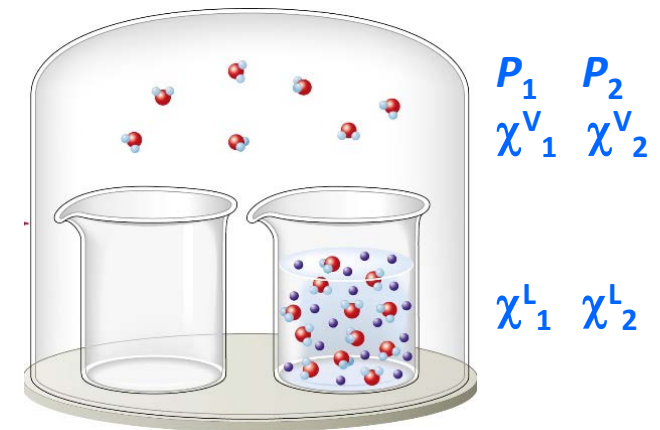
$$P_2 = \chi^L_2 P^{\circ}_2 = (0.600) (0.060) = 0.0360$$

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

in gas phase

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

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



Henry's Law (for Solutes)

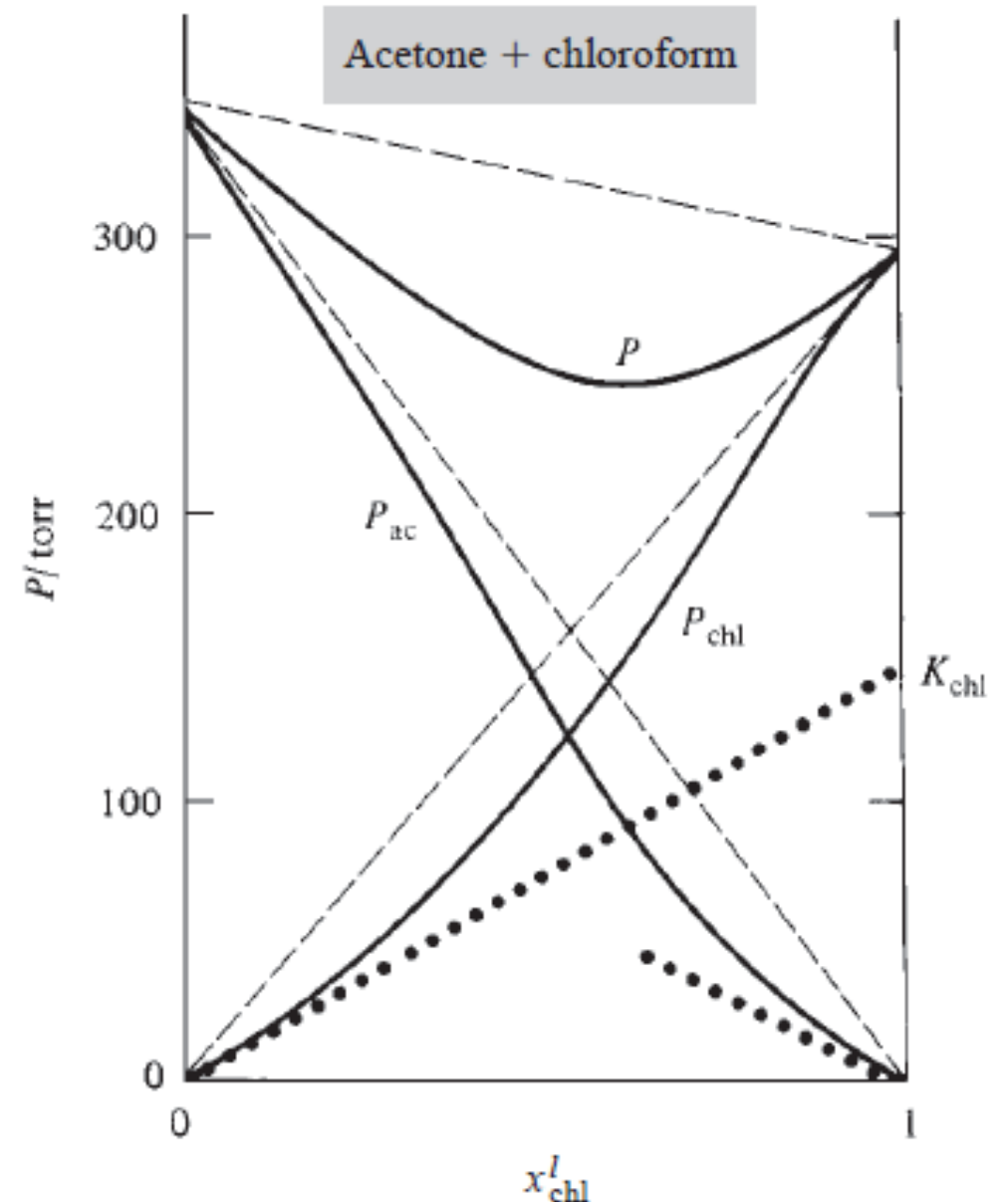
It is experimentally found that in the limiting case of a solution very dilute in the solute 2, the partial pressure of 1 in the vapor is directly proportional to the mole fraction of 2 in the liquid.

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

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

$$P_{\text{A}} = \chi_{\text{A}}^{\text{L}} P_{\text{A}}^{\text{o}}$$

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



Boiling Point Elevation and Freezing Point Depression

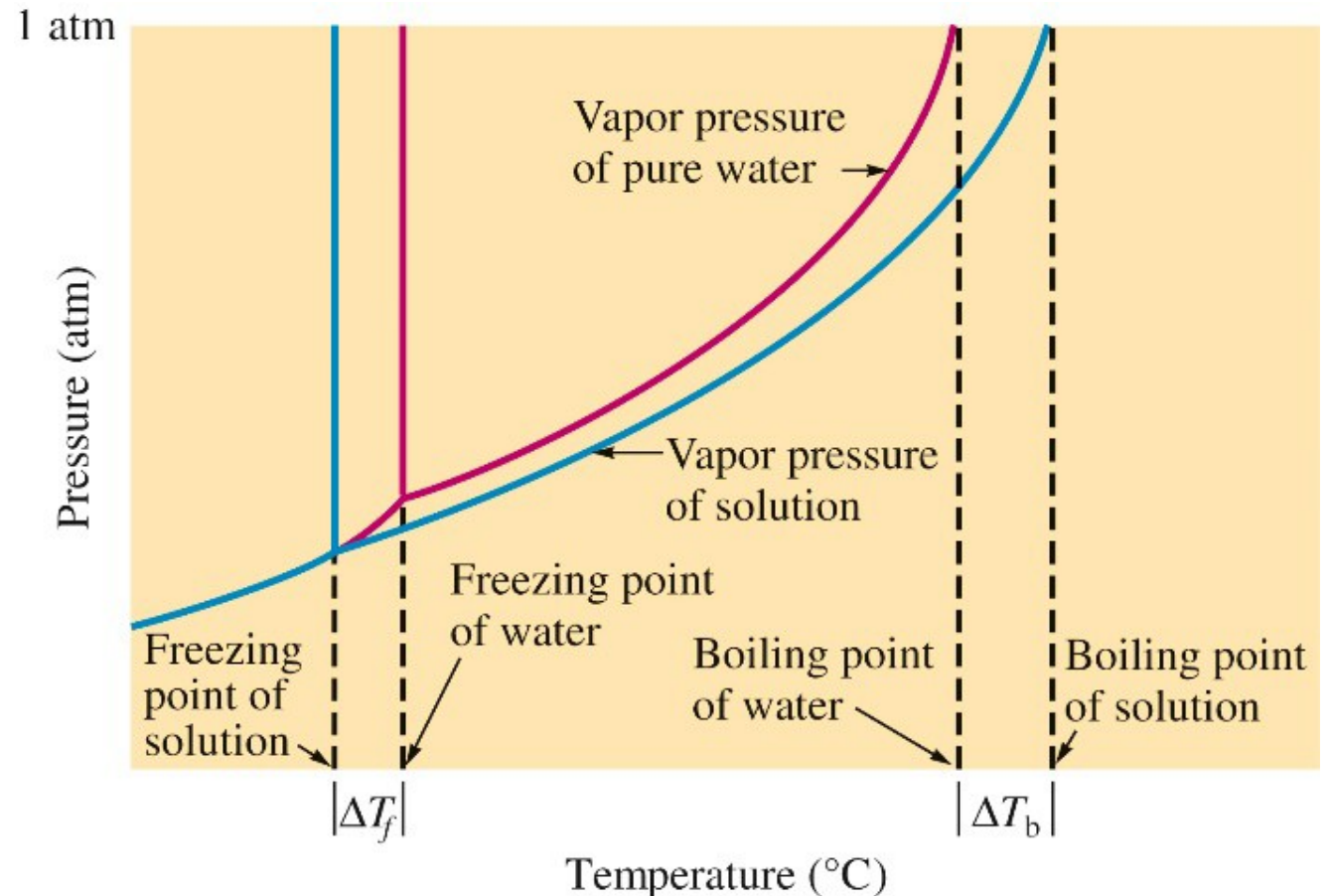
A nonvolatile solute elevates the boiling point of a solution

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

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 / Freezing Point Depression

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

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

molality

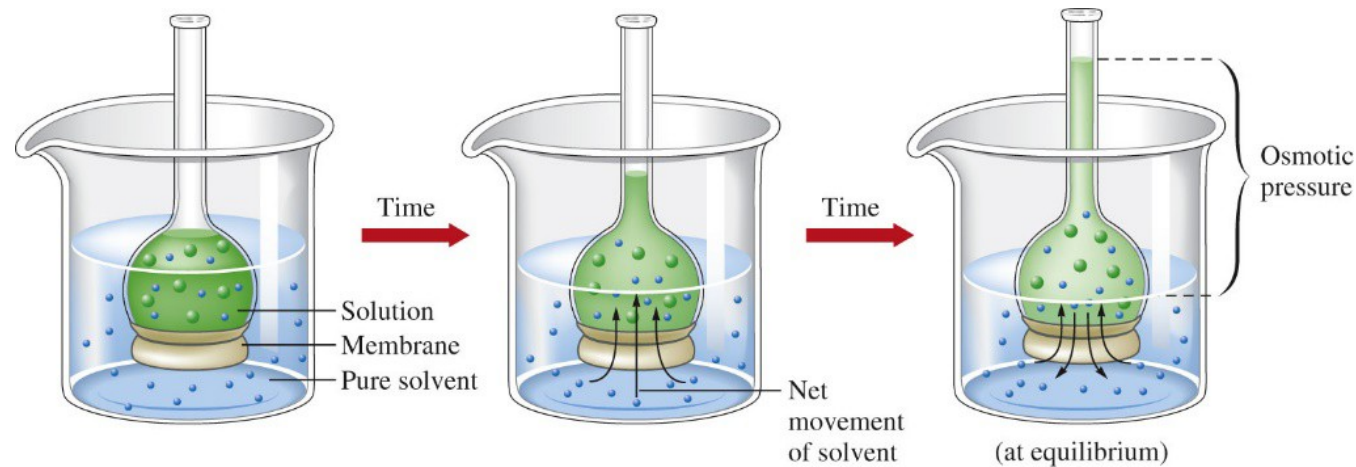
Table 17.5

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

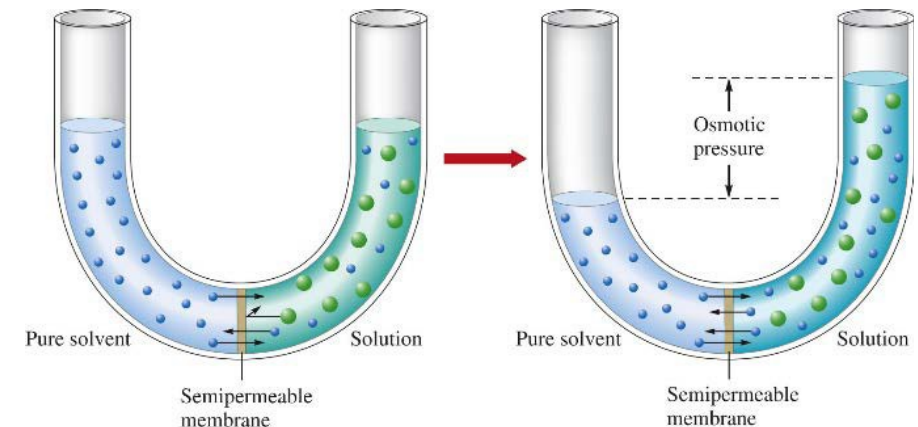
The movement of solvent through a barrier (semipermeable membrane) into a solution containing a solute creates a pressure, P , called the osmotic pressure. This pressure is the extra pressure that must be applied to the solution to maintain equilibrium between the solutions on either side of the barrier.



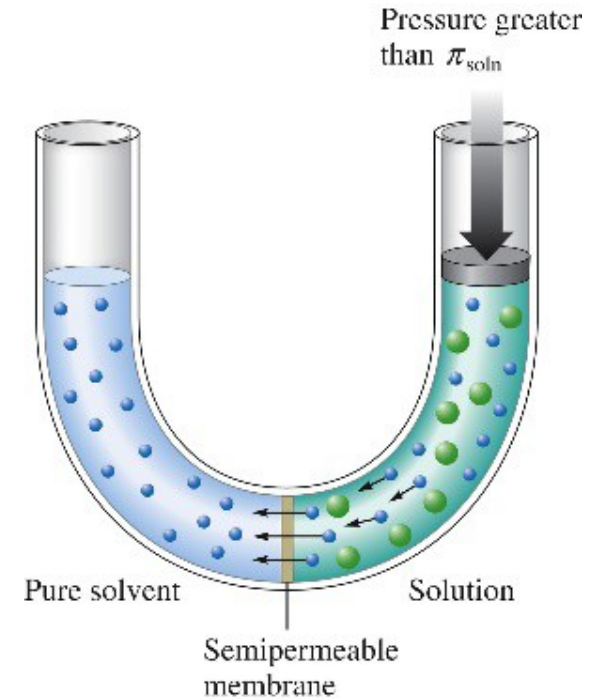
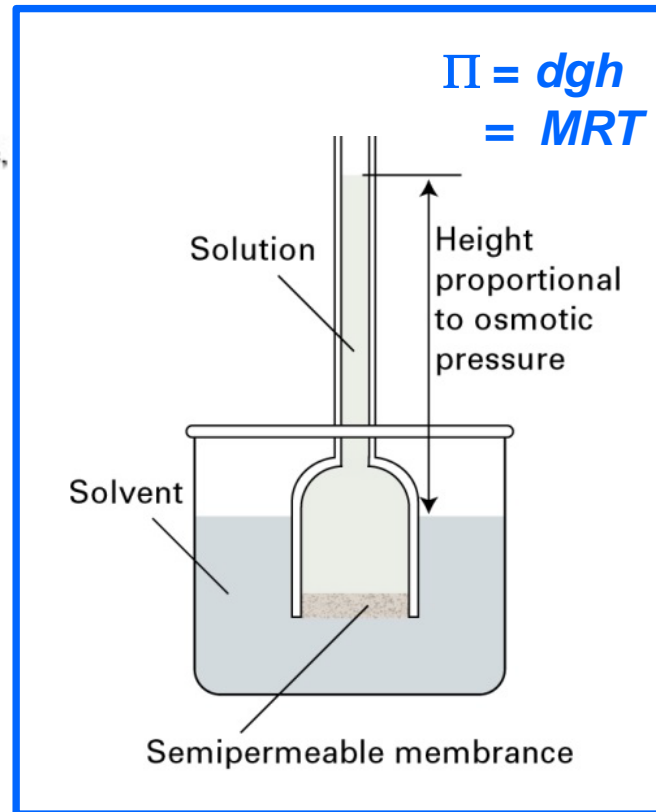
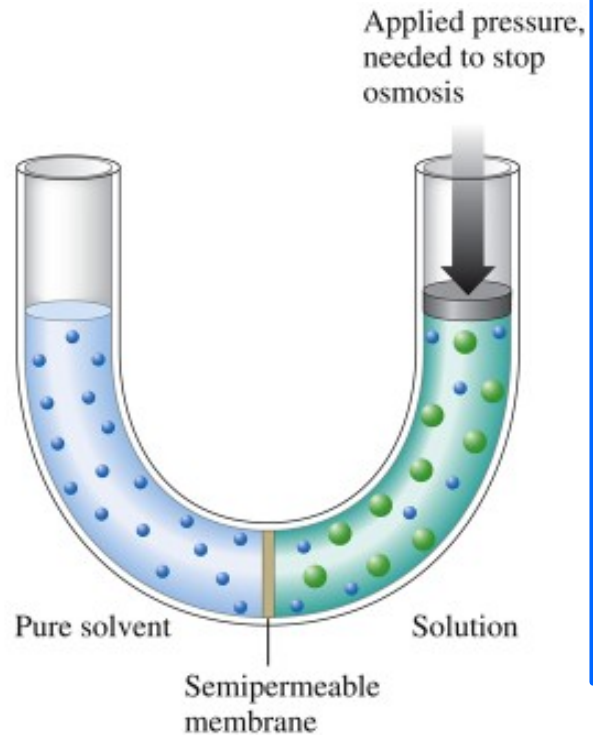
height proportional to osmotic pressure

$$\Pi = MRT$$

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

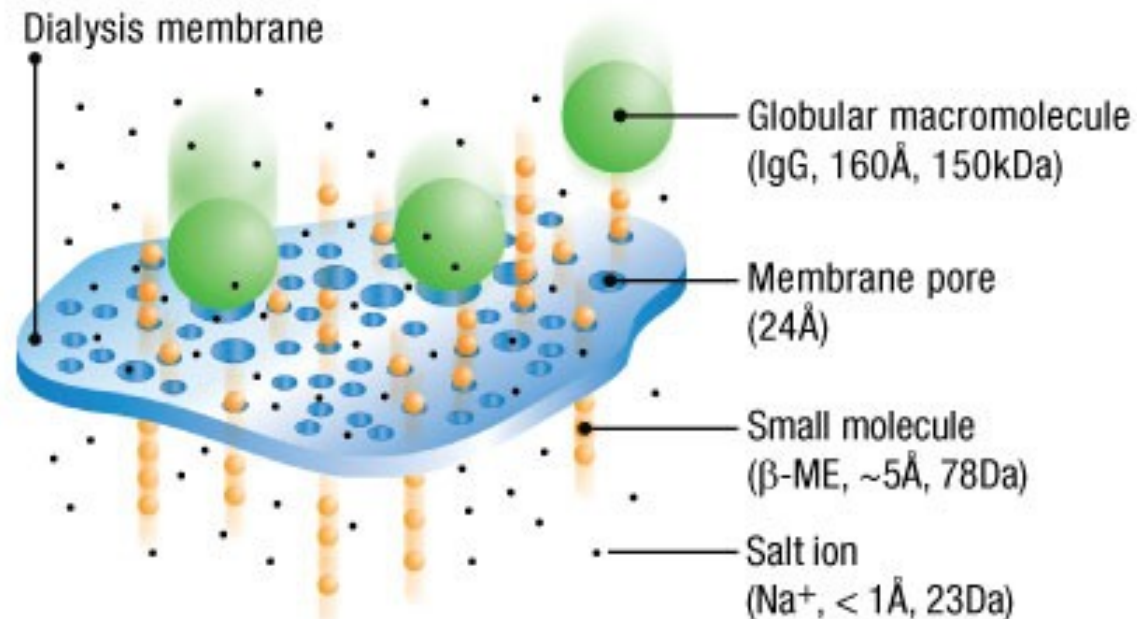


Normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. Minimum pressure required to stop osmosis is equal to the osmotic pressure of the solution.

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

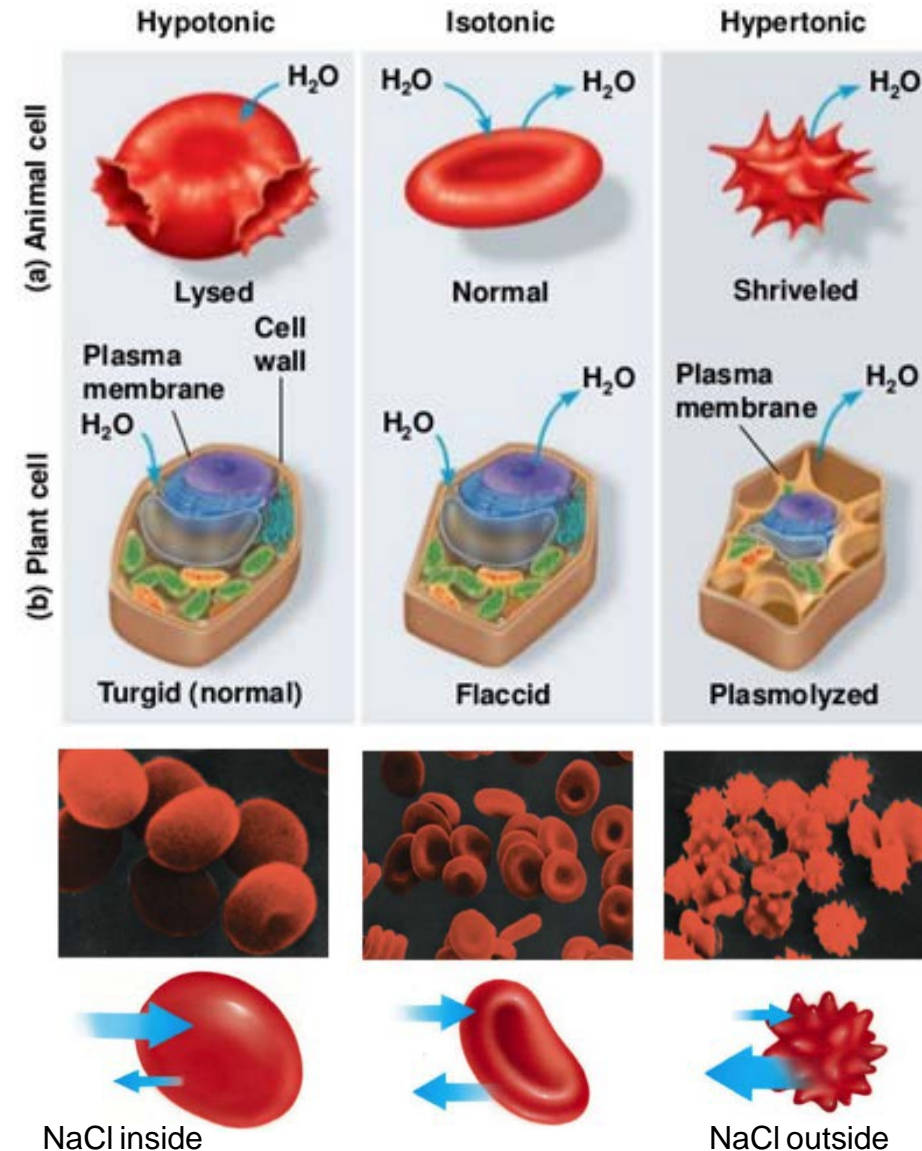
Osmosis is a critical property of solvents in biology. It keeps a balance between the interior and exterior of cells and other biological systems. Since the cell wall is semipermeable it behaves as a semipermeable membrane. Small molecules and water can pass through the cell wall but large molecules (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.



Colligative Properties of Electrolyte Solutions

A solute which dissociates into ions has more "particles" in solution. Colligative property formulas account for dissociation by insertion of the **van't Hoff i factor**:

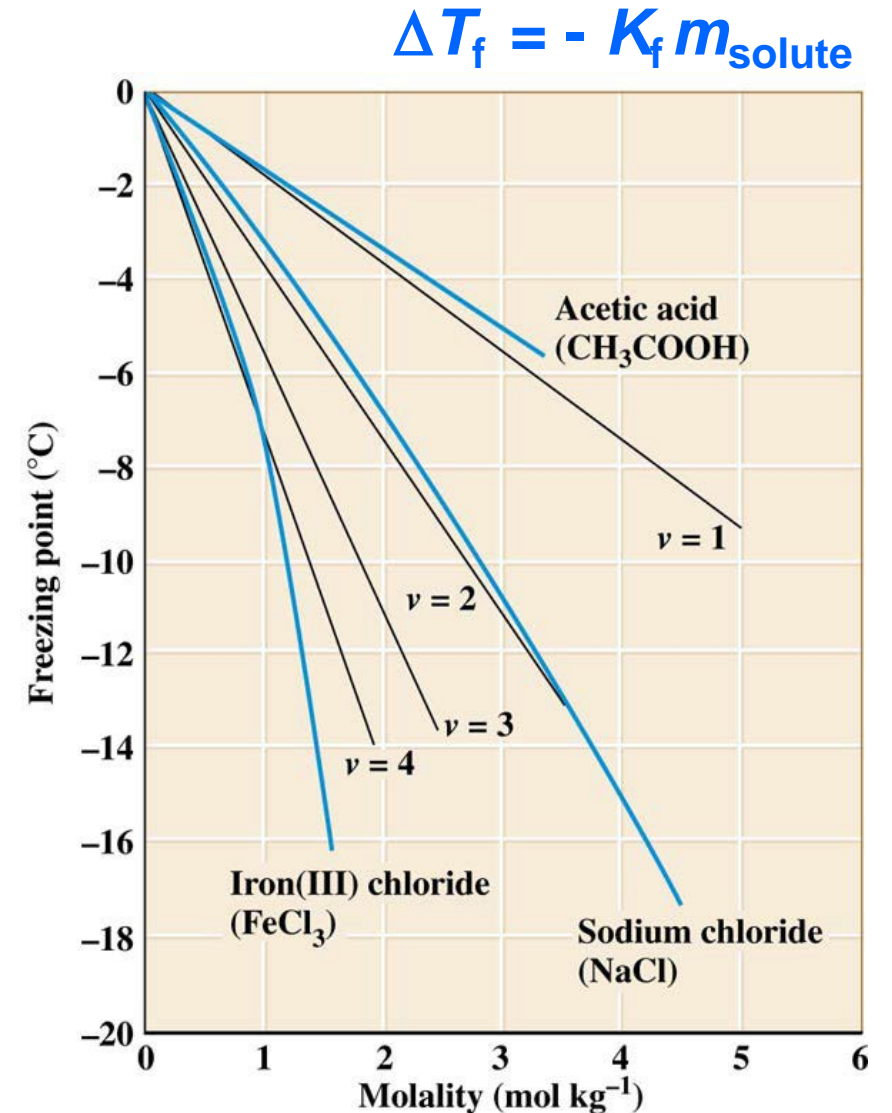
$$P = iMRT$$

An aqueous NaCl solution



theoretically has $i = 2$ for complete dissociation.

Freezing point depressions for different molalities of four solutes in water. Blue curves are the experimental depressions and black from our colligative property formulas.



Electrolyte Solutions: Osmosis

EX 8. What concentration of NaCl in water gives the same osmotic pressure as that of blood (7.70 atm at 25°C)?

$$\Pi = MRT \Rightarrow \Pi = iMRT$$

so

$$M = \Pi / iRT$$

$$= 7.70 / 2 (0.0820574) (298.15) = \mathbf{0.157 \text{ M}}$$

0.315 M (no *i*)

Electrolyte Solutions: Finding van't Hoff i

EX 9. When 2.02 g NaHCO_3 ($M = 84.0059$) is dissolved in 200 g water ($K_f = 1.86$), the freezing point is -0.396°C . What is the solution's van't Hoff i factor?

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

$$m_{\text{solute}} = (2.02 / 84.0059) / 0.200 = 0.120 \text{ m}$$

$$i = -\Delta T_f / K_f m$$

$$= -(-0.396) / (0.120)(1.86)$$

$$= 1.77 \sim \mathbf{2}$$



Electrolyte Solutions: Finding Freezing Point

EX 10. Assuming complete dissociation, calculate the freezing point of 525 g of water ($K_f = 1.86$) that contains 25.0 g of NaCl ($M = 58.443$).

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

$$= - 2 (1.86) (25.0 / 58.443) / (0.525 - 0.025)$$

$$= - 3.182$$

$$\Rightarrow - 3.18^\circ\text{C}$$

Chapter 13 (Bonding, Lewis, VSEPR)

omit 13.5 – 13.8, hyperconjugation

Bonding

ionic

covalent

polar covalent

Periodic Trends

ionization energy

size

electron affinity

electronegativity

acidity/basicity

electronegativity/size effect

acidity

Lewis Structures (obtain the “best” structure)

resonance

formal charge

valence shell expansion

Valence Shell Electron Pair Repulsion (VSEPR)

electronic geometry

molecular geometry (shape)

repulsions: BP/BP < BP/LP < LP/LP

Polarity

bond dipoles

molecular dipoles

Chapter 5 (Gases, Kinetic Theory, Real Gases)

omit 5.12

How Barometer Works

Gas Laws (don't memorize)

combine with $PV = nRT$

absolute zero

density and molar mass

Dalton's law of partial pressures

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

$$P_A = \chi_A P_{\text{tot}}$$

Real Gases

attractive forces

repulsive forces

van der Waals (gives phase transition)

compare ideal / real / van der Waals

Kinetic Theory

$$PV = nRT = \frac{1}{3} Nm \langle u^2 \rangle$$

kinetic energy / mol only depends upon T

$$u_{\text{rms}} = \sqrt{(3RT / M)} \text{ (work with)}$$

Maxwell Boltzmann

effect of mass

effect of temperature

Graham's law of effusion

collisions (work with equations)

$$\text{with wall: } Z_W = (N / V) A \langle u \rangle$$

$$\text{intermolecular: } Z = (N / V) \pi d^2 \sqrt{2} \langle u \rangle$$

$$\text{mean free path: } \lambda = \langle u \rangle / Z$$

Chapter 16 (Intermolecular Forces, Phase Diagrams)

omit 16.3-16.9, 16.12, equation on p. 689

Intermolecular Forces

types

ion/ion – NaCl(s)

ion/dipole – NaCl(aq)

hydrogen bond – H₂O(l)
(strong dipole/dipole)

dipole/dipole – HCl(g)

ion/induced dipole -

dipole/induced dipole – O₂(g)/H₂O(l)

induced dipole/ induced dipole – He(g)
(dispersion, London)

van der Waals forces (no ions)

effect on melting / boiling points

Vapor Pressure

Phase Transitions

sublimation

vaporization

fusion

Phase Diagrams

coexistence (equilibrium) lines

solid / liquid

solid / gas

liquid / gas

triple point

critical point

Chapter 17 (Solutions, Colligative Properties)

omit 17.2-17.3, 17.8

Solution Composition

descriptions

mass percent

mole fraction

molarity

molality

conversion between

use of density

Colligative Properties

relation to phase diagram

vapor pressure lowering

Raoult's law: $P_A = \chi_A^L P_A^0$

binary solutions (not colligative prop)

nonideal and deviations

Henry's law: $P = \chi_{\text{gas}} k_H$

freezing point depression: $\Delta T_f = -K_f m_{\text{solute}}$

boiling point elevation: $\Delta T_b = K_b m_{\text{solute}}$

osmotic pressure: $\Pi = MRT$

electrolyte solutions

van't Hoff i factor

$\Delta T_f = -iK_f m$, $\Delta T_b = iK_b m$, $\Pi = iMRT$

Equation Sheet

$$PV = nRT = Nk_{\text{B}}T = \frac{1}{3} Nm\langle u^2 \rangle$$

$$P = \chi P_{\text{TOT}}$$

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$u_{\text{rms}} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}}$$

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}}$$

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

$$Z_{\text{molecular collisions}} = \frac{N}{V} \pi d^2 \sqrt{2} \langle u \rangle$$

$$\lambda = \frac{\langle u \rangle}{Z}$$

$$Z_{\text{wall}} = \frac{N}{V} A \frac{1}{4} \langle u \rangle$$

$$P = \chi P^0$$

$$\Delta T_{\text{b}} = imK_{\text{b}}$$

$$\Delta T_{\text{f}} = -imK_{\text{f}}$$

$$\pi = iMRT$$

$$N_{\text{o}} = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ Pa} = 1 \text{ Nt m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\text{K} = ^{\circ}\text{C} + 273.15$$