

PROPERTIES OF SOLUTIONS _____ Z Ch17

"Almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the non-living 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".)

17.1 Solutions - homogeneous mixture of two or more components;

composition

solute - substance being dissolved, usually minor component

solvent - dissolving medium, generally major component

expressing composition

mass percent – (mass of solute) / (mass of solvent) $\times 100$

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

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

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

EX 1. A solution is prepared from 18.0 g of water ($M = 18.0148$) and 23.0 g of ethanol ($M = 46.0684$).

- What is the mole fraction of ethanol?
- What is the molality of the solution assuming water to be the solvent?
- What is the molality of the solution assuming ethanol to be the solvent?

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

- What is the molarity of the solution?
- What is the molality of the solution?

Colligative Properties

depend on relative **number** of dissolved solute particles

classification

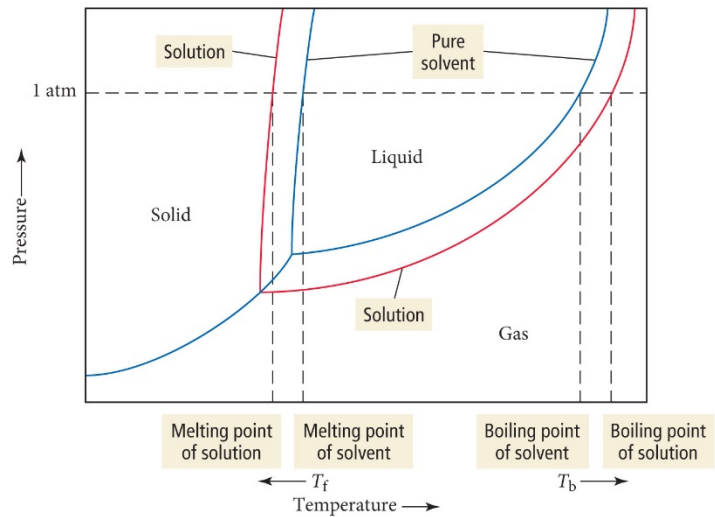
seen on phase diagram

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

not on phase diagram

4. osmosis

FIG I. Generic phase diagram of a pure solvent with a nonvolatile solute added



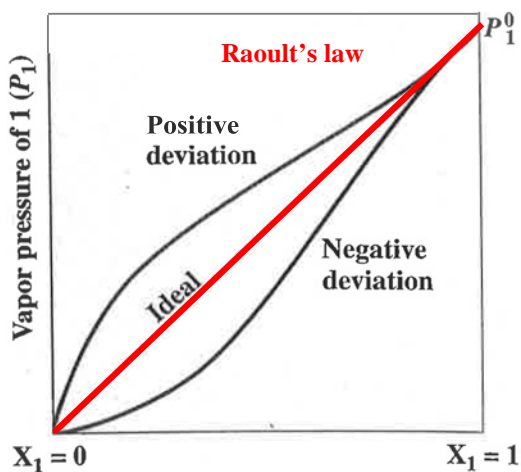
17.4 The Vapor Pressures of Solutions

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:

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

EX 3. The vapor pressure of water at 90°C is 525.8 mm Hg. If a solution of 651 g of ethylene glycol ($C_2H_6O_2$) is dissolved in 1.50 kg of water, what is the solution vapor pressure at 90°C? ($M_{H_2O} = 18.02$, $M_{C_2H_6O_2} = 62.07$ g/mol)



Nonideal solutions show deviations from Raoult's law

negative deviations – strong solute/solvent interactions

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

Raoult's law is useful for molar mass determination

EX 4. 20.0 g of urea is dissolved in 125 g of water at 25°C. The vapor pressure of the solution was observed to be 22.67 mm Hg while the vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the molar mass of urea?

Binary Solutions

Ideal solutions are analogous to mixtures of ideal gases. Unlike an ideal gas however, they can have interactions. In an ideal solution of two components A and B, the interactions A-A, A-B, and B-B are all the same. 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

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

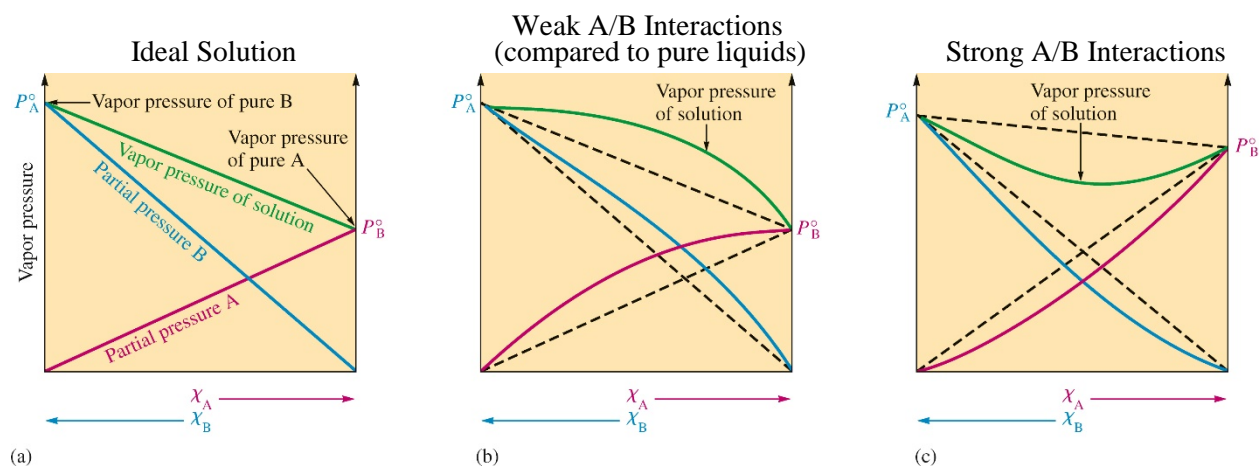
Since both the liquid and gas compositions can be given in terms of mole fractions it is helpful to distinguish between them. The following equations are useful for dealing with binary solutions

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

EX 5. A mixture of hexane ($P_1^{\circ} = 0.198$) and heptane ($P_2^{\circ} = 0.060$) obeys Raoult's law. If the mole fraction of heptane is 0.600, what is the composition of the vapor above the solution?

Strategy:

- 1) use Raoult's law to find vapor pressure of each component
- 2) sum to get total vapor pressure
- 3) use Dalton's law to get vapor composition



Henry's Law

It is experimentally found that in the limiting case of a solution very dilute in the solute B, the partial pressure of B in the vapor is directly proportional to the mole fraction of B in the liquid. Note: this is not Raoult's law behavior where the linear relationship is with the mole fraction of the solvent, A.

The pressure of a gas above a solution is proportional to the amount of gas dissolved in the solution:

$$P = \chi_{\text{gas}} k_H$$

where k_H is the Henry's law constant for the solution.

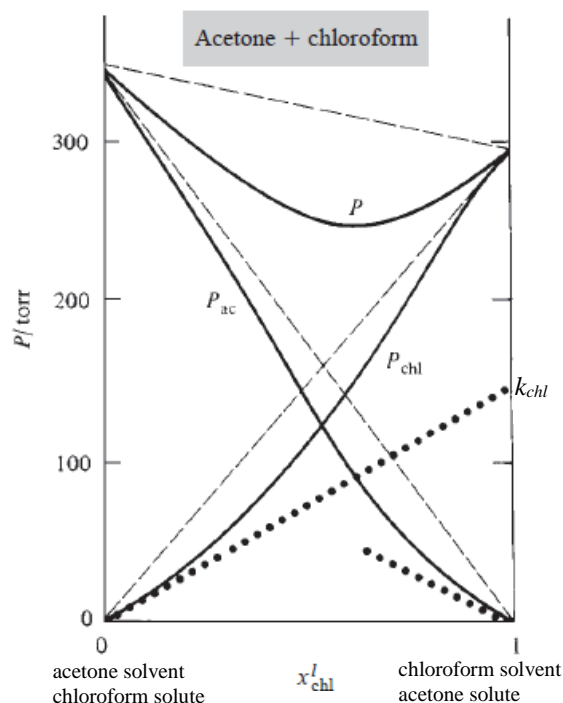
Table 17.3

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



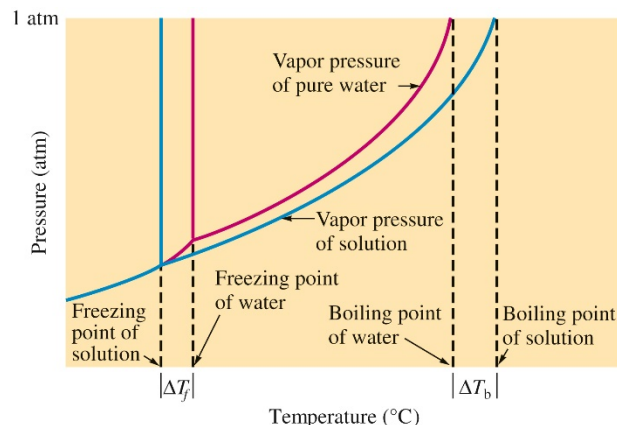
Lake Nyos in Cameroon, West Africa – a fatal example of Henry's law



Common Equilibrium Shared by Colligative Properties

Freezing point depression is the decrease in the freezing point of the solution, compared to pure solvent at the same temperature. Boiling point elevation is the increase in the boiling point of a solution containing a nonvolatile solute, compared to pure solvent at the same temperature. Vapor pressure lowering is the decrease in vapor pressure of a solution containing a nonvolatile solute compared to the vapor pressure of pure solvent at the same temperature. Osmotic pressure is the increase in the pressure of a solution that places the solvent in transfer equilibrium (e.g., though a membrane) with pure solvent at the same temperature and pressure as the original solution. All four properties are defined by an equilibrium between the liquid solution containing the dissolved solute and a gas, solid, or liquid phase of the pure solvent.

17.5 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

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

Note use of molality.

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

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

Freezing Point Depression

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

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.

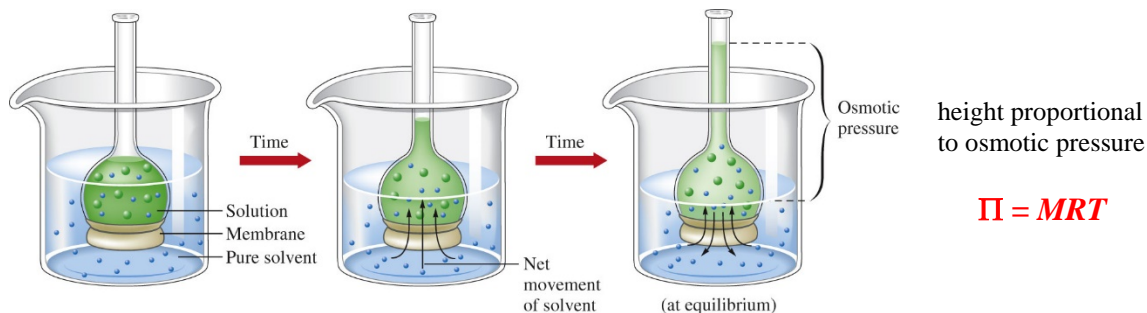
The boiling-point elevation constant, K_b , and the freezing-point depression constant, K_f , both have units of K (or °C) kg mol⁻¹ and are constant for a given solvent. For the boiling point elevation consult the liquid \rightleftharpoons gas equilibrium line on the phase diagram of the solvent. For the freezing point depression consult the solid \rightleftharpoons liquid equilibrium line on the phase diagram of the solvent

Both are useful for molar mass determination

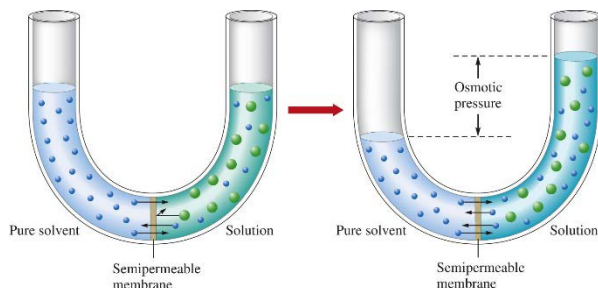
EX 6. A solution prepared from 1.25 g of oil of wintergreen (methyl salicylate) in 99.0 g of benzene ($T_b = 80.10^\circ\text{C}$, $K_b = 2.3 \text{ K kg mol}^{-1}$) has a boiling point of 80.31°C . Determine the molar mass of the compound.

17.6 Osmotic Pressure

The movement of solvent through a barrier (semipermeable membrane) into a solution containing a solute creates a **pressure, Π** , 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.



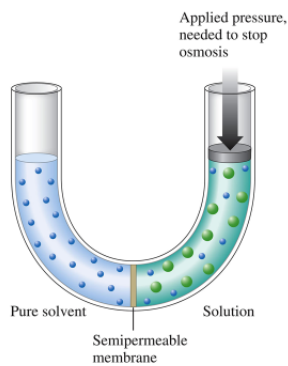
A tube with a bulb on the end is covered by a semipermeable membrane. The solution inside the tube is surrounded by pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions and equilibrium is reached.



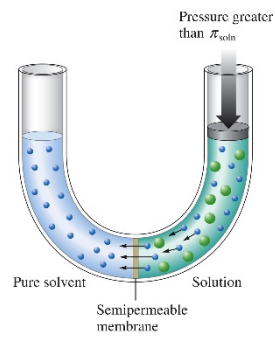
Another viewpoint

Pure solvent and its solution (with a nonvolatile solute) separated by a semipermeable membrane through which solvent (blue) can pass but solute (green) cannot. Rate of solvent transfer greater from solvent to solution than from solution to solvent. On the right is the system at equilibrium, where the rate of solvent transfer is equal.

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?



Considering osmotic pressure as the pressure required to stop osmosis leads to the concept of reverse osmosis when the pressure exceeds that of the osmotic pressure driving out pure solvent.

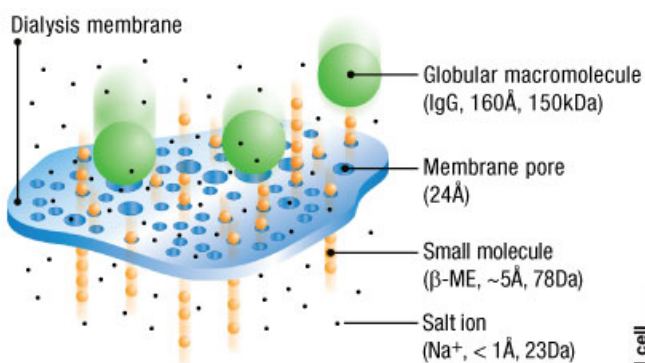


Normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. Minimum pressure required to stop osmosis is equal to the osmotic pressure of the solution.

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.

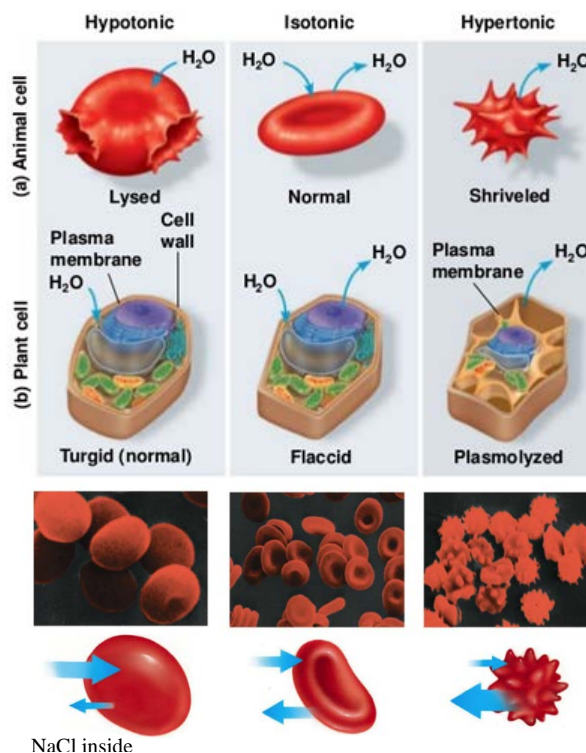
Dialysis

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

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.



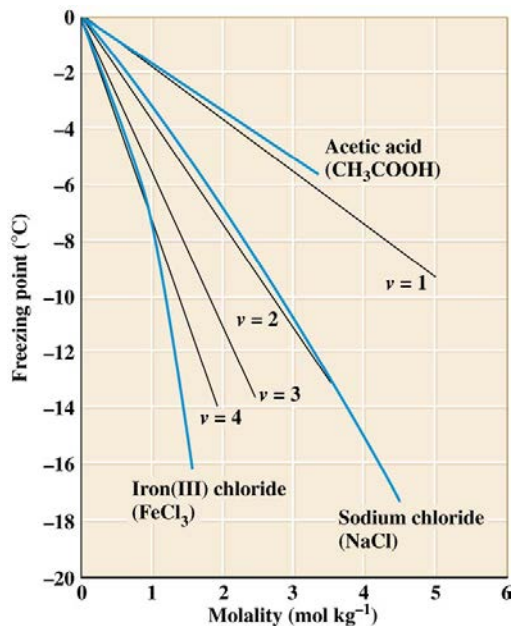
17.7 Colligative Properties of Electrolyte Solutions

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:

$$\Pi = iMRT$$

For example an aqueous NaCl solution $[\text{NaCl}(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)]$ theoretically has $i = 2$ if there is complete dissociation.

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



Freezing point depressions observed for different molalities of four different solutes in water. The blue curves are the experimentally observed depressions and the black lines are from our colligative property formulas.

EX 9. When 2.02 g NaHCO₃ ($M = 84.0059$) 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?

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 ($M = 58.443$).