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Ninth
Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 13: Solutions and Their Physical Properties

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➤ *Focus On Chromatography*

13-1 Types of Solution: Some Terminology

- ◆ Solutions are *homogeneous* mixtures.
 - Uniform throughout.
- ◆ Solvent.
 - Determines the state of matter in which the solution exists.
 - Is the largest component.
- ◆ Solute.
 - Other solution components said to be dissolved in the solution.

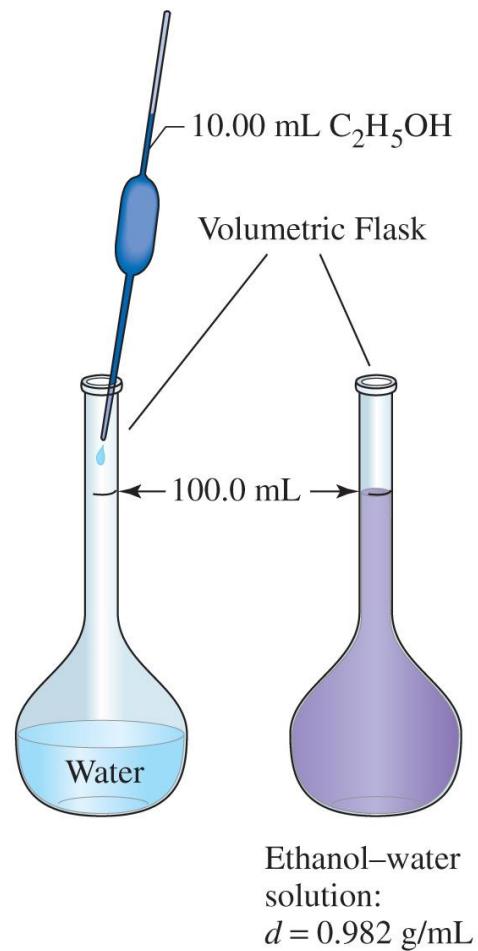
TABLE 13.1 Some Common Solutions

Solution	Components
Gaseous solutions	
Air	N_2 , O_2 , and several others
Natural gas	CH_4 , C_2H_6 , and several others
Liquid solutions	
Seawater	H_2O , NaCl , and many others
Vinegar	H_2O , $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid)
Soda pop	H_2O , CO_2 , $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose), and several others
Solid solutions	
Yellow brass	Cu , Zn
Palladium–Hydrogen	Pd , H_2

13-2 Solution Concentration.

- ◆ Mass percent. (m/m)
 - ◆ Volume percent. (v/v)
 - ◆ Mass/volume percent. (m/v)
-
- ◆ Isotonic saline is prepared by dissolving 0.9 g of NaCl in 100 mL of water and is said to be:
- 0.9% NaCl (*mass/volume*)**

10% Ethanol Solution (v/v)



ppm, ppb and ppt

- ◆ Very low solute concentrations are expressed as:

ppm: parts per million $(\mu\text{g/g}, \text{mg/L})$

ppb: parts per billion $(\text{ng/g}, \mu\text{g/L})$

ppt: parts per trillion $(\text{pg/g}, \text{ng/L})$

note that $1.0 \text{ L} \times 1.0 \text{ g/mL} = 1000 \text{ g}$

ppm, ppb, and ppt are properly m/m or v/v.

Mole Fraction and Mole Percent

$$\chi = \frac{\text{Amount of component } i \text{ (in moles)}}{\text{Total amount of all components (in moles)}}$$

$$\chi_1 + \chi_2 + \chi_3 + \dots \chi_n = 1$$

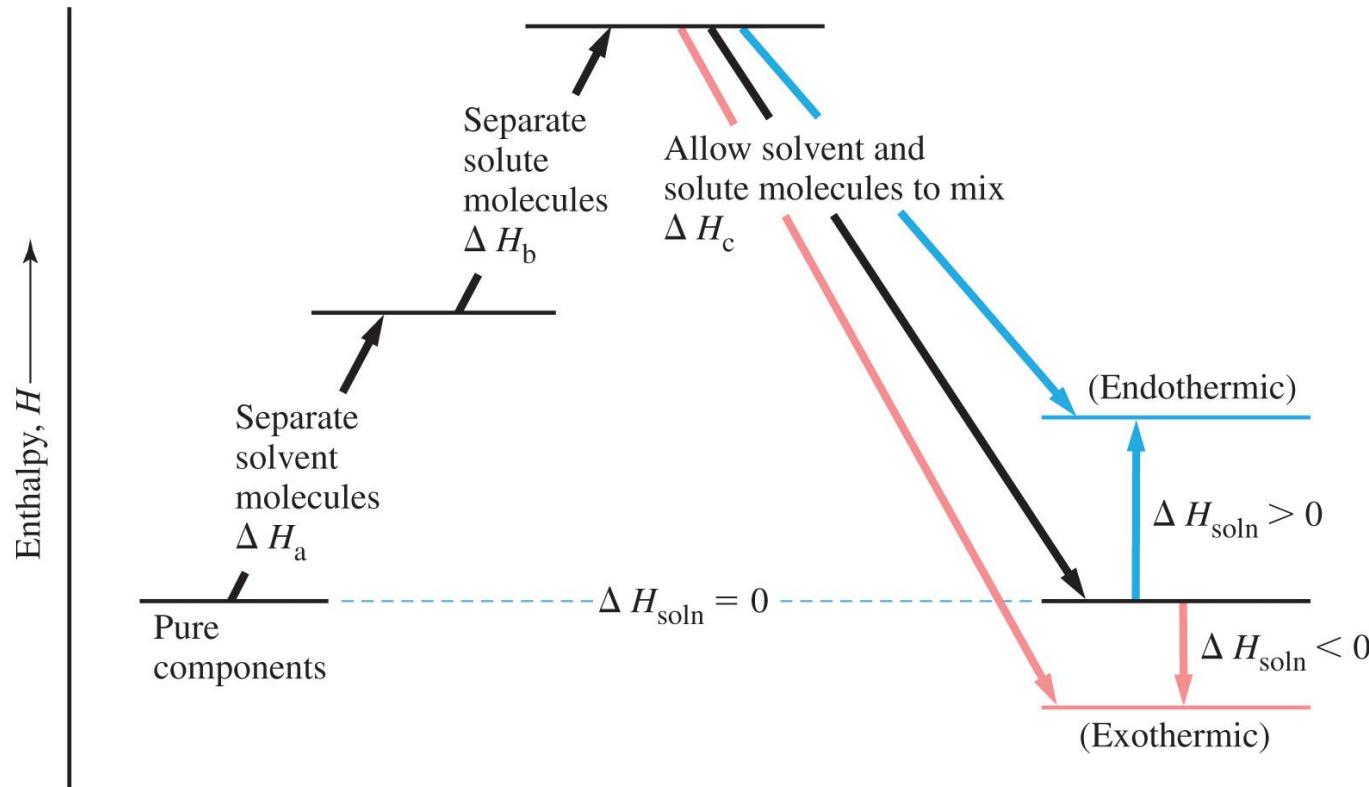
$$\text{Mole \% } i = \chi_i \times 100\%$$

Molarity and Molality

$$\text{Molarity (M)} = \frac{\text{Amount of solute (in moles)}}{\text{Volume of solution (in liters)}}$$

$$\text{Molality (m)} = \frac{\text{Amount of solute (in moles)}}{\text{Mass of solvent (in kilograms)}}$$

13-3 Intermolecular Forces and the Solution Process

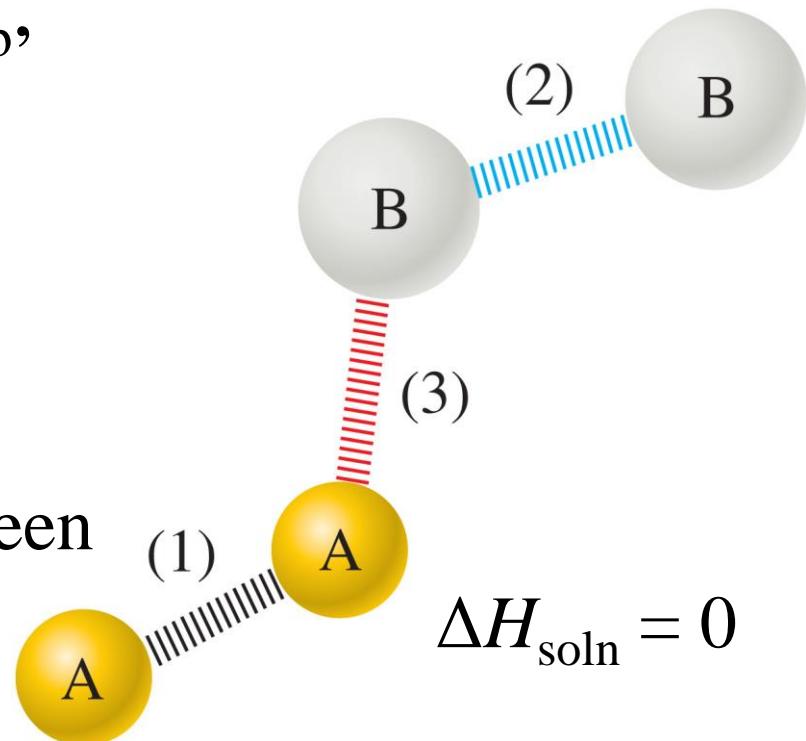


Intermolecular Forces in Mixtures

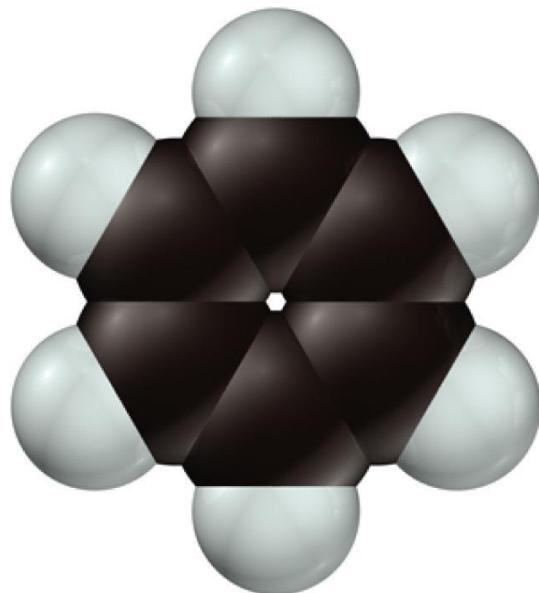
- ◆ Magnitude of ΔH_a , ΔH_b , and ΔH_c depend on intermolecular forces.

- ◆ Ideal solution

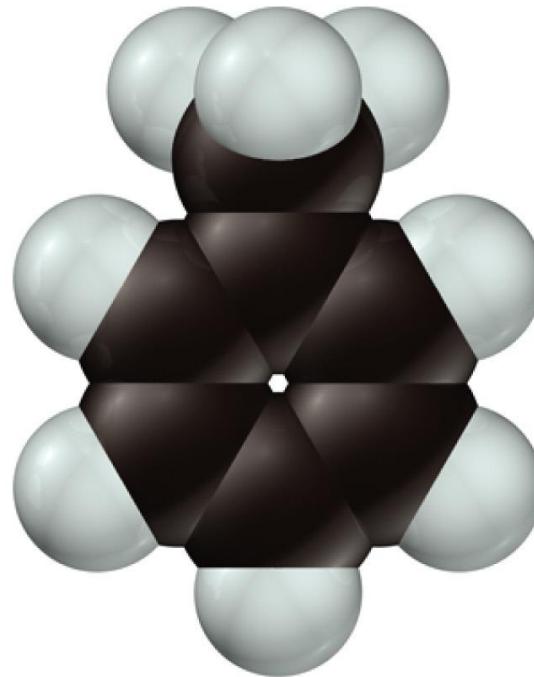
- Forces are similar between all combinations of components.



Ideal Solution



(a)

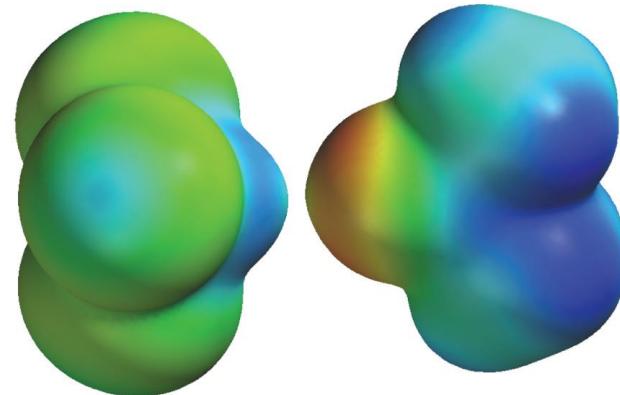
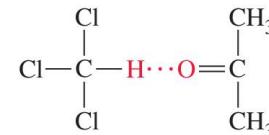
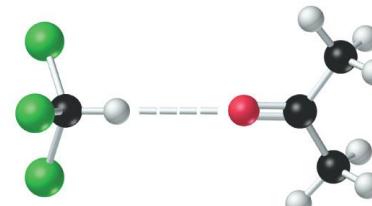


(b)

Non-ideal Solutions

- ◆ If adhesive forces greater than cohesive forces.

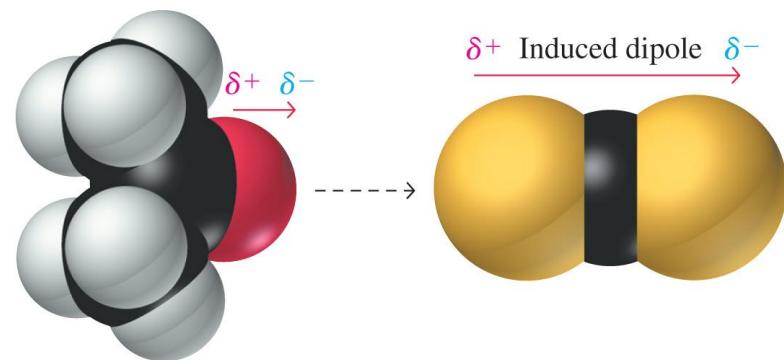
$$\Delta H_{\text{soln}} < 0$$



Non-ideal Solutions

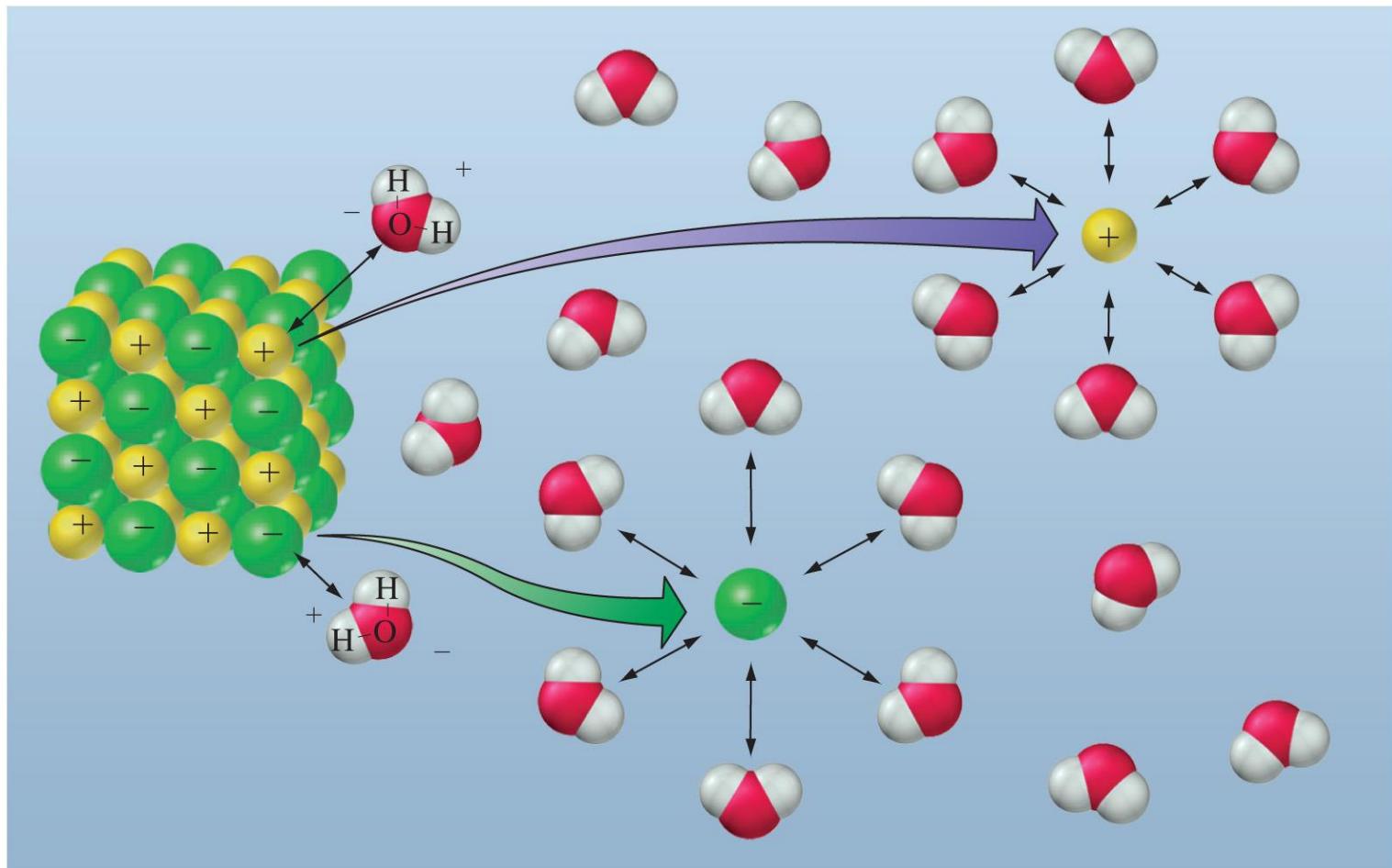
- ◆ If adhesive forces are less than cohesive forces.

$$\Delta H_{\text{soln}} > 0$$



- ◆ At the limit these solutions are heterogeneous.

Ionic Solutions

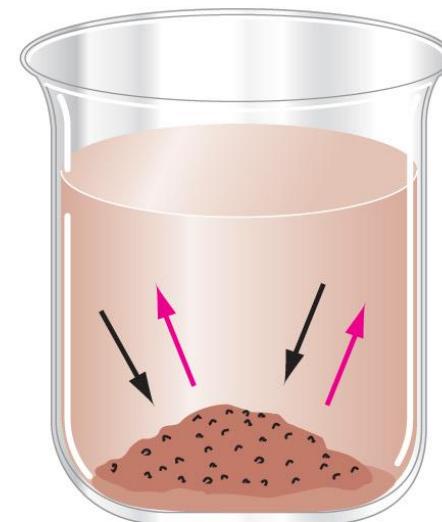
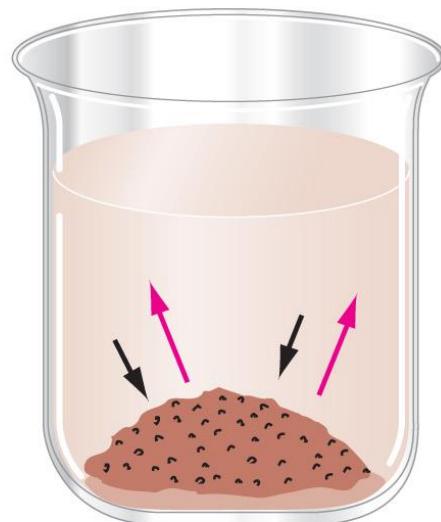
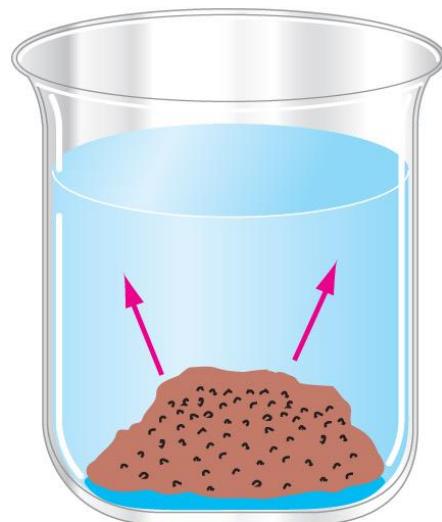


Hydration Energy

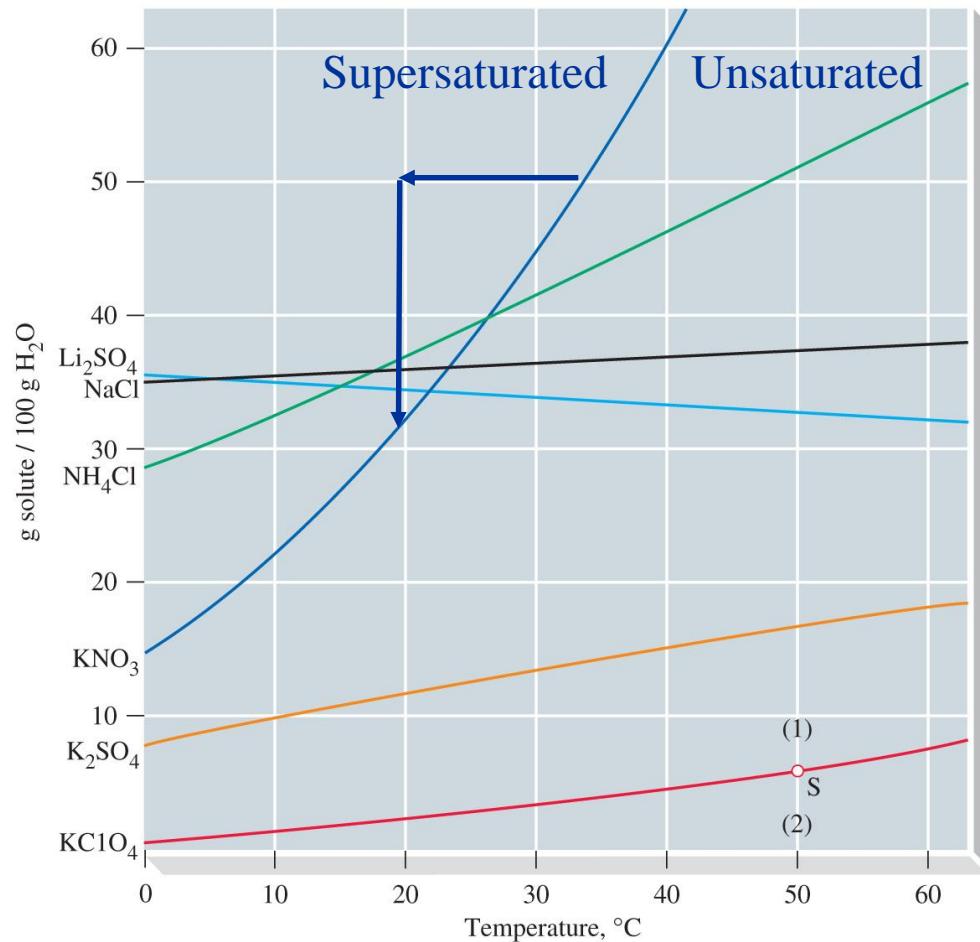


$$\Delta H_{\text{soln}} > 0 \text{ but } \Delta G_{\text{solution}} < 0$$

13-4 Solution Formation and Equilibrium



Solubility Curves



13-5 Solubility of Gases



- ◆ Most gases are less soluble in water as temperature increases.
- ◆ In organic solvents the reverse is often true.

Henry's Law

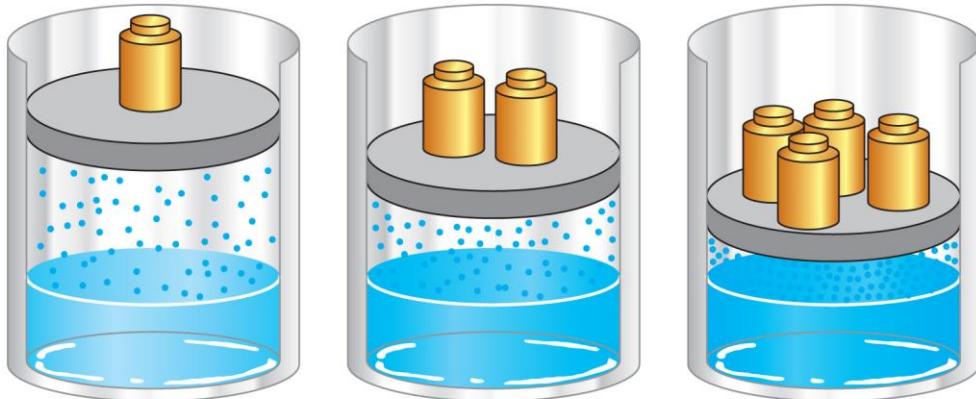
- ◆ Solubility of a gas increases with increasing pressure.

$$C = kP_{\text{gas}}$$

$$k = \frac{C}{P_{\text{gas}}} = \frac{23.54 \text{ mL}}{1.00 \text{ atm}} = 23.54 \text{ ml N}_2/\text{atm}$$

$$P_{\text{gas}} = \frac{C}{k} = \frac{100 \text{ mL}}{23.54 \text{ ml N}_2/\text{atm}} = 4.25 \text{ atm}$$

Henry's Law



13-6 Vapor Pressures of Solutions

◆ Roault, 1880s.

- Dissolved solute *lowers* vapor pressure of solvent.
- The partial pressure exerted by solvent vapor above an ideal solution is the product of the mole fraction of solvent in the solution and the vapor pressure of the pure solvent at a given temperature.

$$P_A = \chi_A P_A^\circ$$

EXAMPLE 13-6

Predicting vapor pressure of ideal solutions. The vapor pressures of pure benzene and toluene at 25°C are 95.1 and 28.4 mm Hg, respectively. A solution is prepared in which the mole fractions of benzene and toluene are both 0.500. What are the partial pressures of the benzene and toluene above this solution? What is the total vapor pressure?

$$P_{\text{benzene}} = \chi_{\text{benzene}} P^{\circ}_{\text{benzene}} = (0.500)(95.1 \text{ mm Hg}) = 47.6 \text{ mm Hg}$$

$$P_{\text{toluene}} = \chi_{\text{toluene}} P^{\circ}_{\text{toluene}} = (0.500)(28.4 \text{ mm Hg}) = 14.2 \text{ mm Hg}$$

$$P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 61.8 \text{ mm Hg}$$

EXAMPLE 13-7

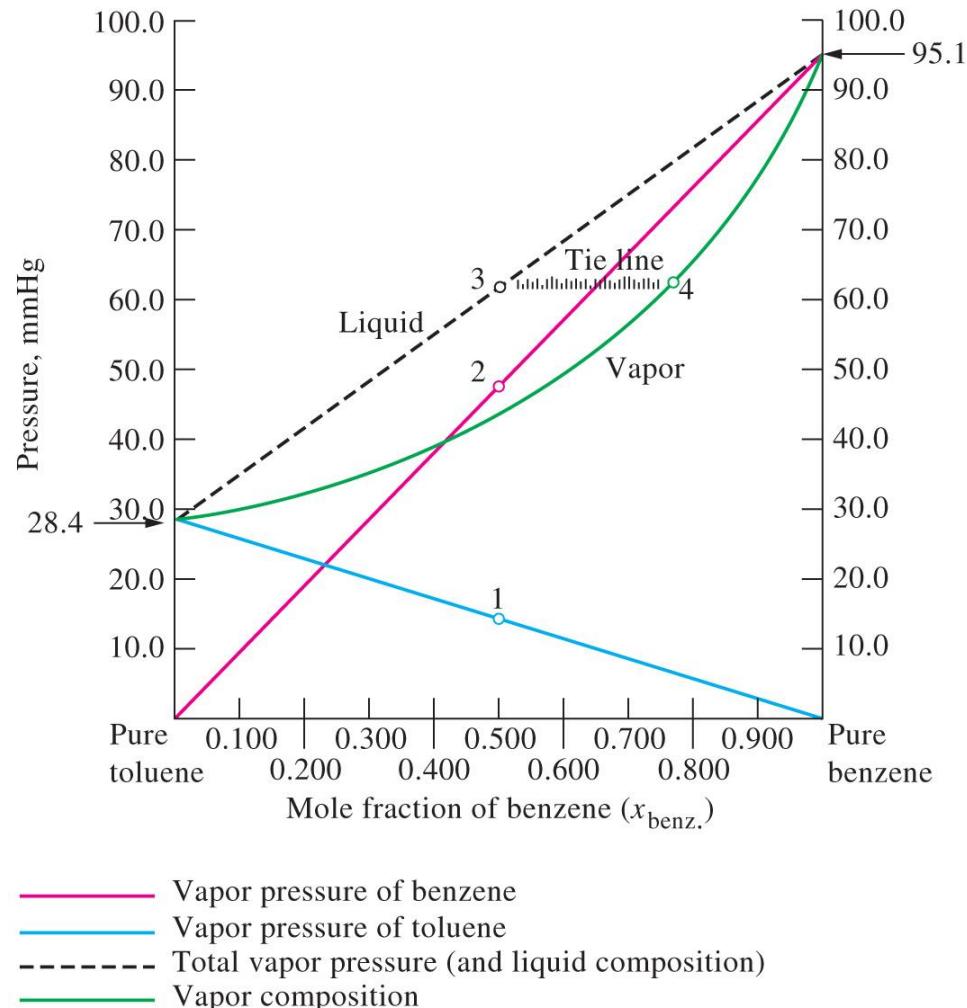
Calculating the Composition of Vapor in Equilibrium with a Liquid Solution. What is the composition of the vapor in equilibrium with the benzene-toluene solution?

Partial pressure and mole fraction:

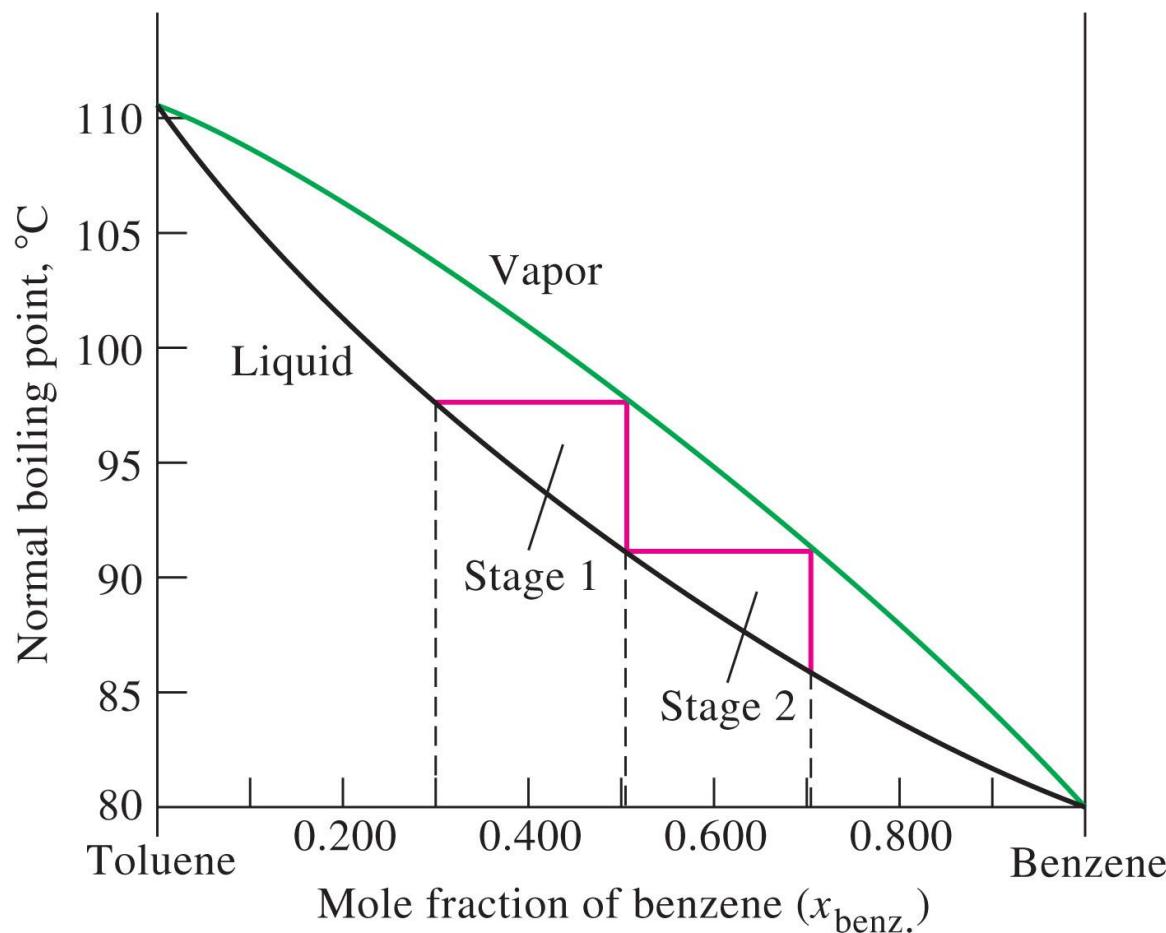
$$\chi_{\text{benzene}} = P_{\text{benzene}}/P_{\text{total}} = 47.6 \text{ mm Hg}/61.89 \text{ mm Hg} = 0.770$$

$$\chi_{\text{toluene}} = P_{\text{toluene}}/P_{\text{total}} = 14.2 \text{ mm Hg}/61.89 \text{ mm Hg} = 0.230$$

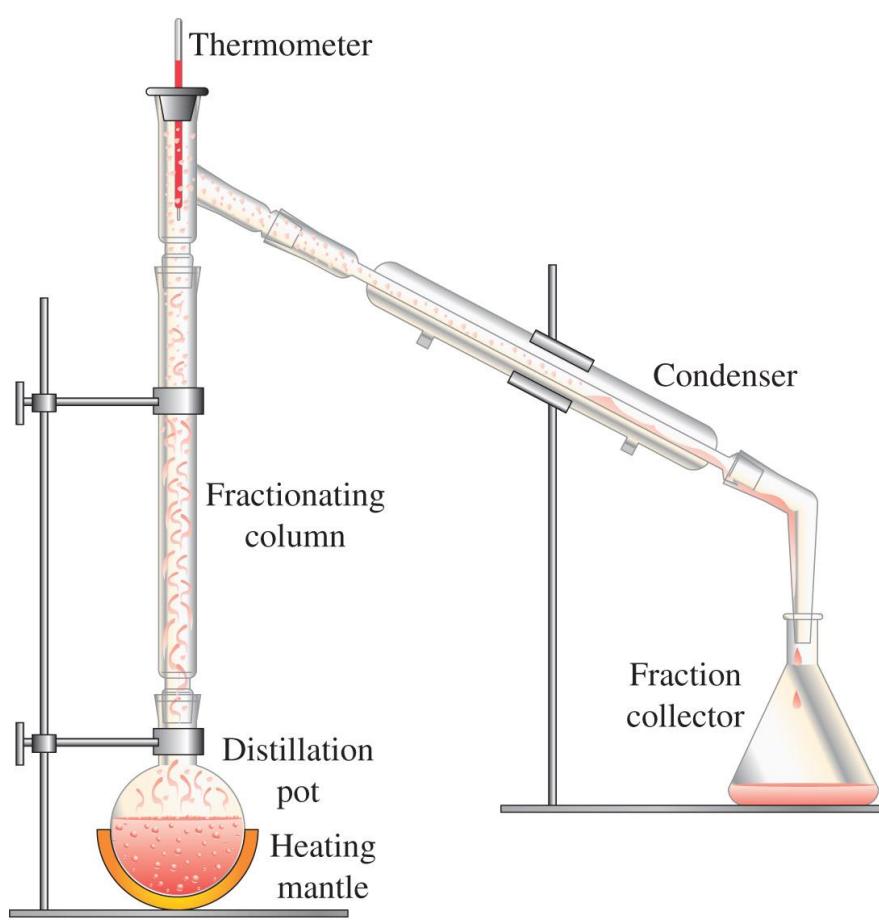
Liquid-Vapor Equilibrium



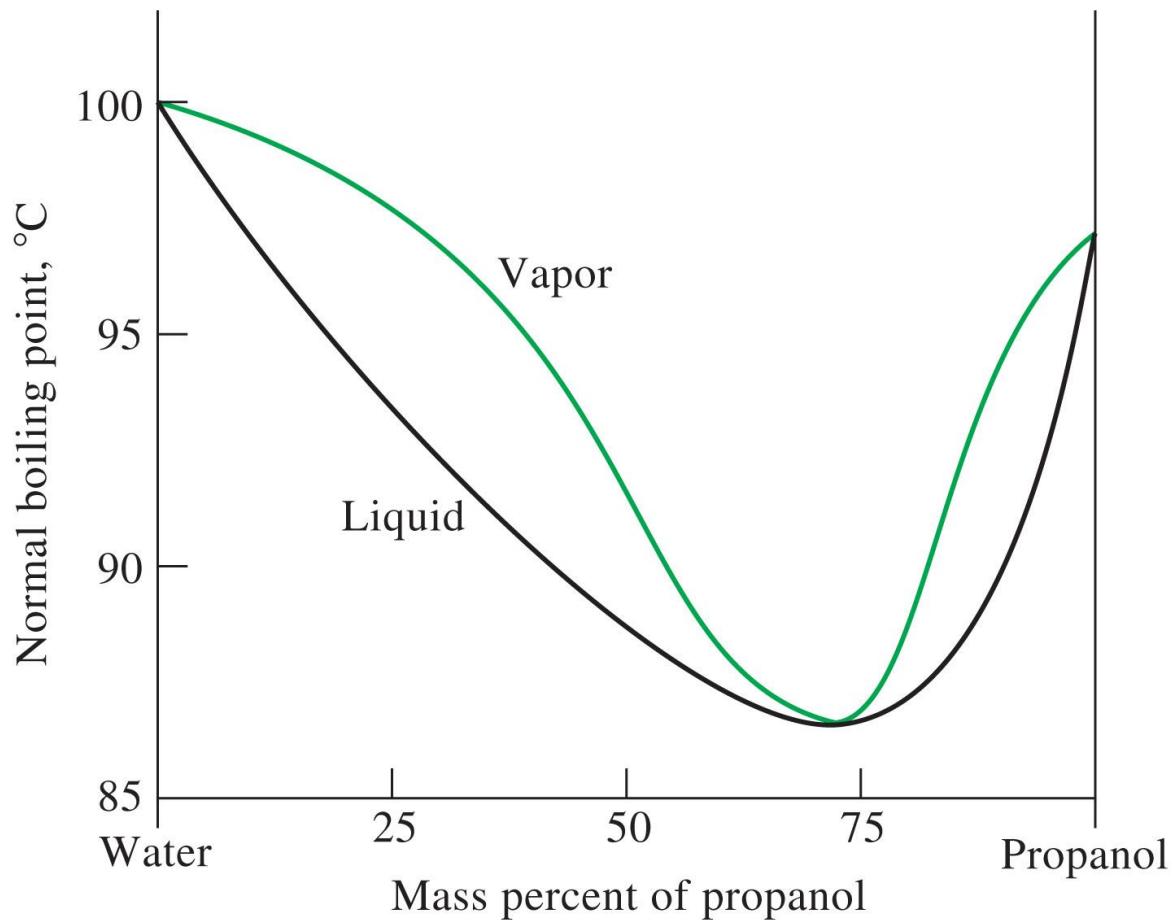
Fractional Distillation



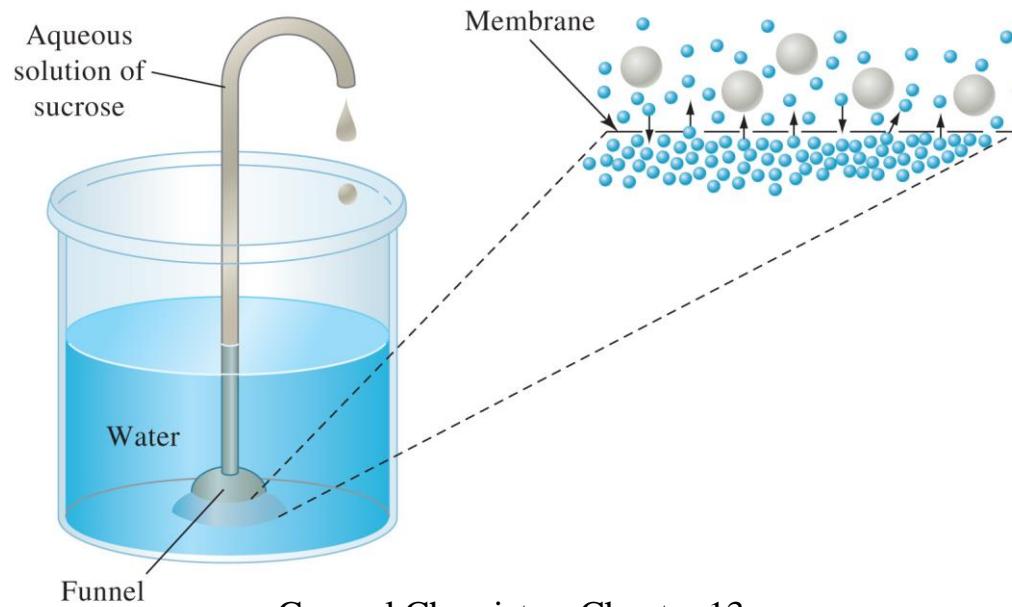
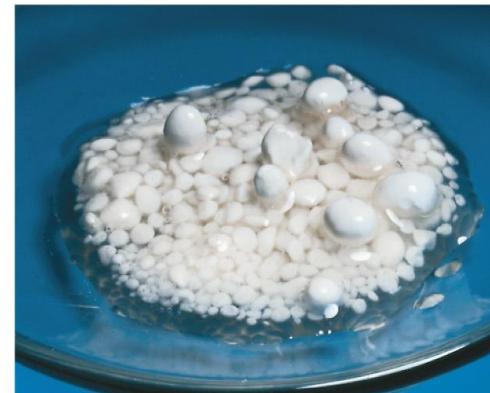
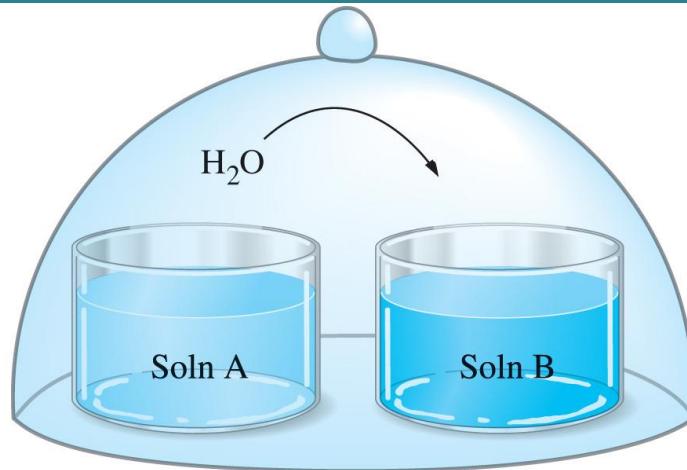
Fractional Distillation



Non-ideal behavior



13-7 Osmotic Pressure



Osmotic Pressure

For dilute solutions of electrolytes:

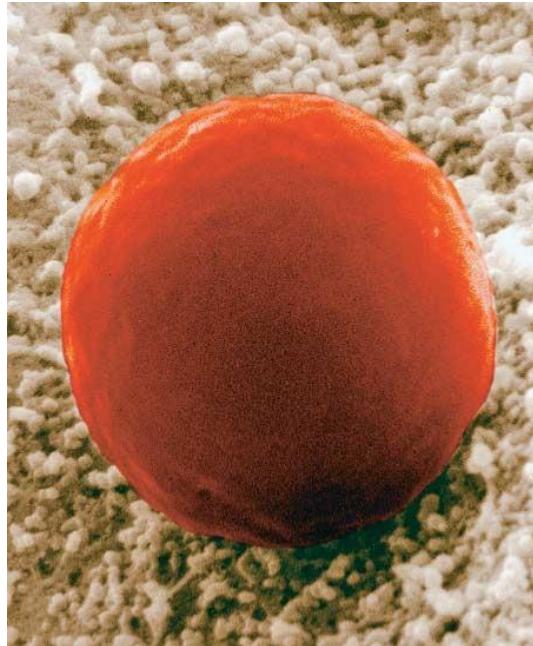
$$\pi V = nRT$$

$$\pi = \frac{n}{V} RT = MRT$$

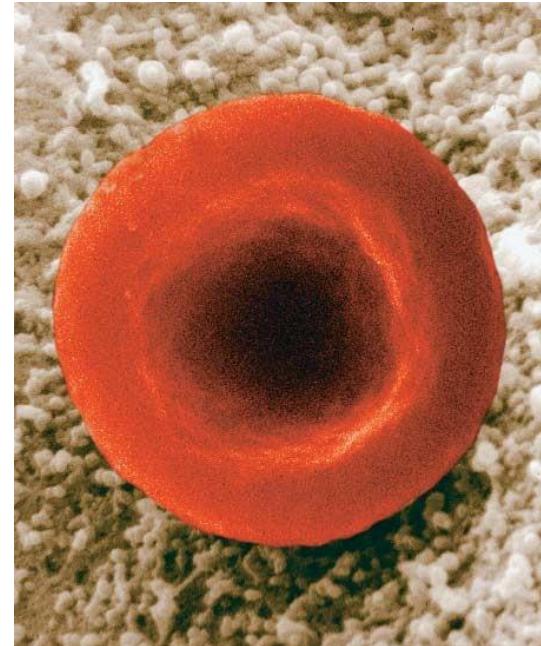
Osmotic Pressure



Hypotonic
 $< 0.92\% \text{ } m/V$
rupture

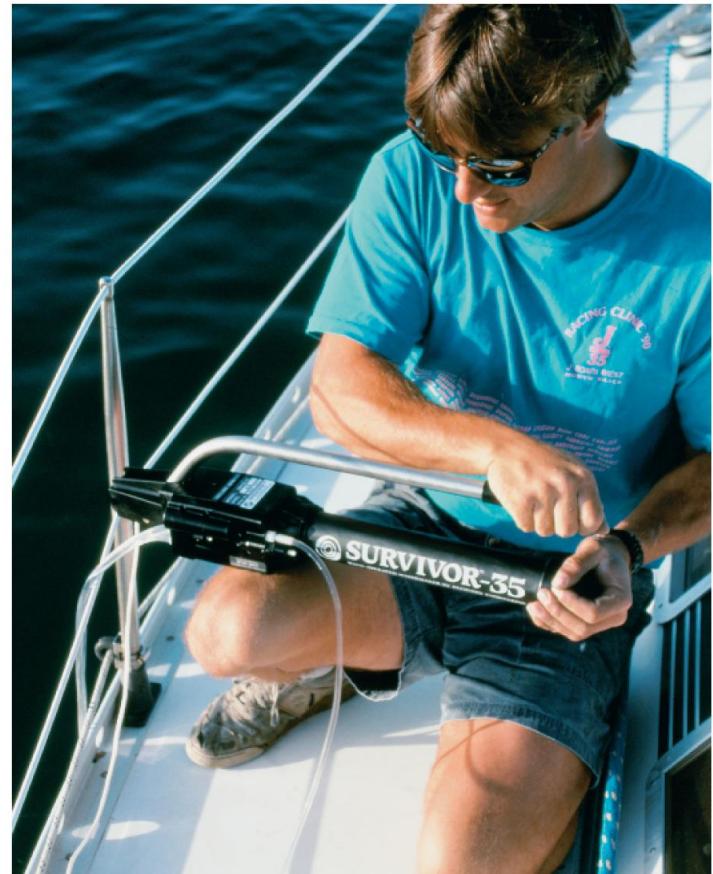
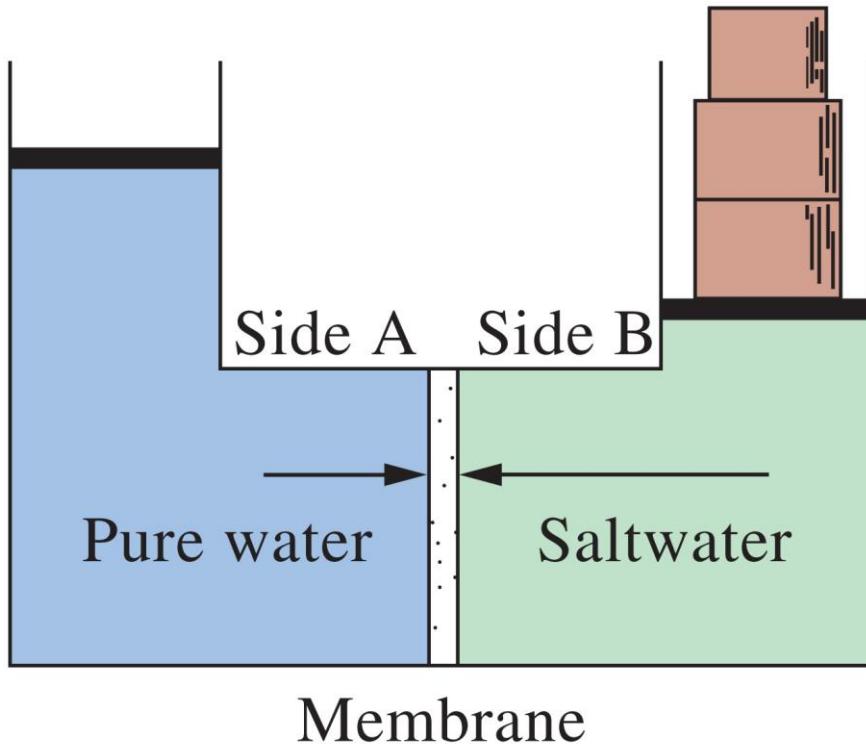


Isotonic Saline
 $0.92\% \text{ } m/V$



Hypertonic
 $> 0.92\% \text{ } m/V$
crenation

Reverse Osmosis - Desalination

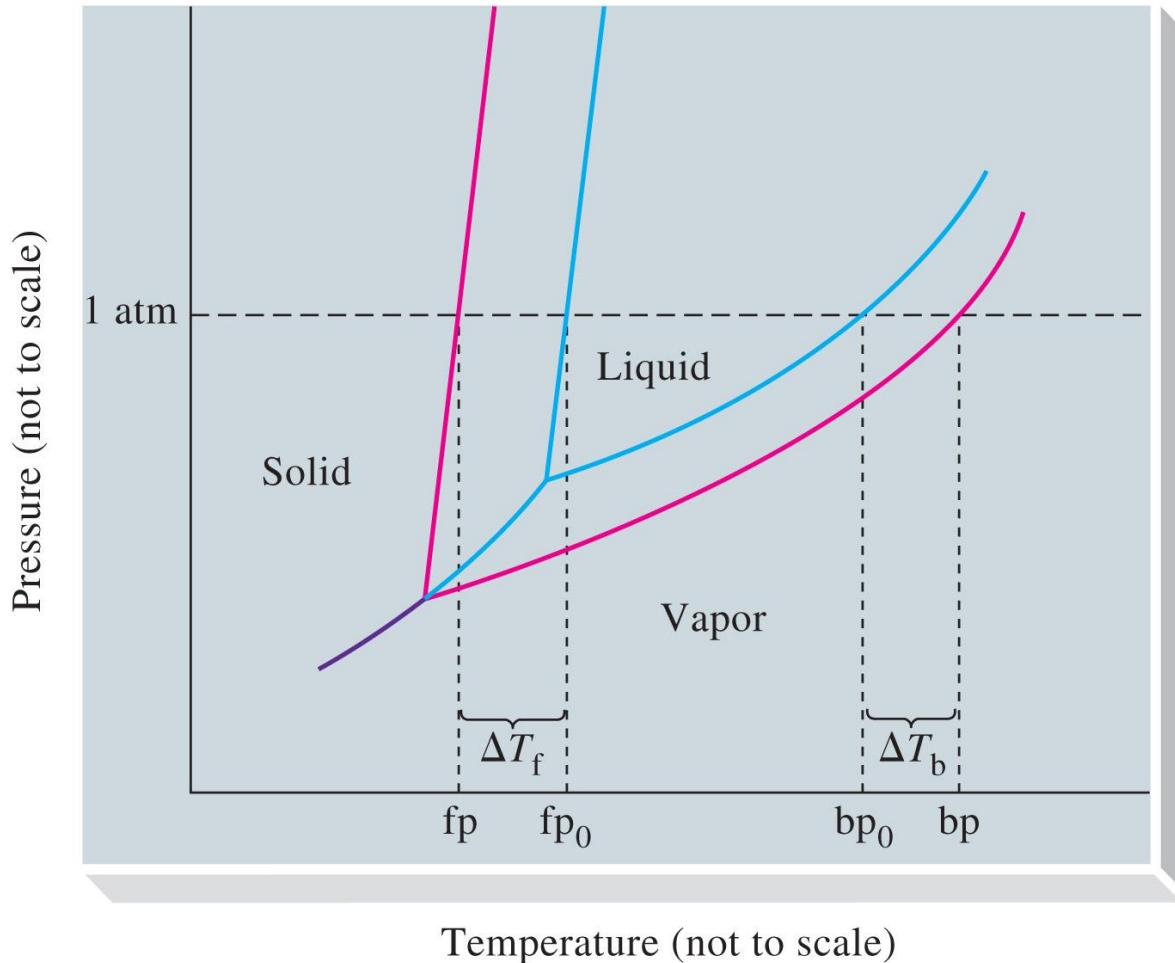


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13-8 Freezing-Point Depression and Boiling Point Elevation of Nonelectrolyte Solutions

- ◆ A Colligative property.
 - Depends on the number of particles present.
- ◆ Vapor pressure is lowered when a solute is present.
 - This results in boiling point elevation.
 - Freezing point is also effected and is lowered.

Vapor Pressure Lowering



$$\Delta T_f = -K_f \times m$$

$$\Delta T_b = -K_b \times m$$

TABLE 13.2 Freezing-Point Depression and Boiling-Point Elevation Constants^a

Solvent	Normal Freezing Point, °C	$K_f, \text{ } ^\circ\text{C } m^{-1}$	Normal Boiling Point, °C	$K_b, \text{ } ^\circ\text{C } m^{-1}$
Acetic acid	16.6	3.90	118	3.07
Benzene	5.53	5.12	80.10	2.53
Nitrobenzene	5.7	8.1	210.8	5.24
Phenol	41	7.27	182	3.56
Water	0.00	1.86	100.0	0.512

^aValues correspond to freezing-point depressions and boiling-point elevations, in degrees Celsius, due to 1 mol of solute particles dissolved in 1 kg of solvent in an ideal solution.

$$\Delta T_f = -K_f \times m$$

$$\Delta T_b = -K_b \times m$$

Practical Applications



13-9 Solutions of Electrolytes

◆ Svante Arrhenius

- Nobel Prize 1903.
- Ions form when electrolytes dissolve in solution.
- Explained anomalous colligative properties.

Compare 0.0100 m aqueous urea to 0.0100 m NaCl (aq)

$$\Delta T_f = -K_f \times m = -1.86^\circ\text{C m}^{-1} \times 0.0100 \text{ m} = -0.0186^\circ\text{C}$$

Freezing point depression for NaCl is -0.0361°C .

van't Hoff

$$i = \frac{\text{measured } \Delta T_f}{\text{expected } \Delta T_f} = \frac{0.0361^\circ\text{C}}{0.0186^\circ\text{C}} = 1.98$$

$$\pi = -i \times M \times RT$$

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

$$\Delta T_b = -i \times K_b \times m$$

Interionic Interactions

- ◆ Arrhenius theory does not correctly predict the conductivity of concentrated electrolytes.

TABLE 13.3 Variation of the van't Hoff Factor, i , with Solution Molality

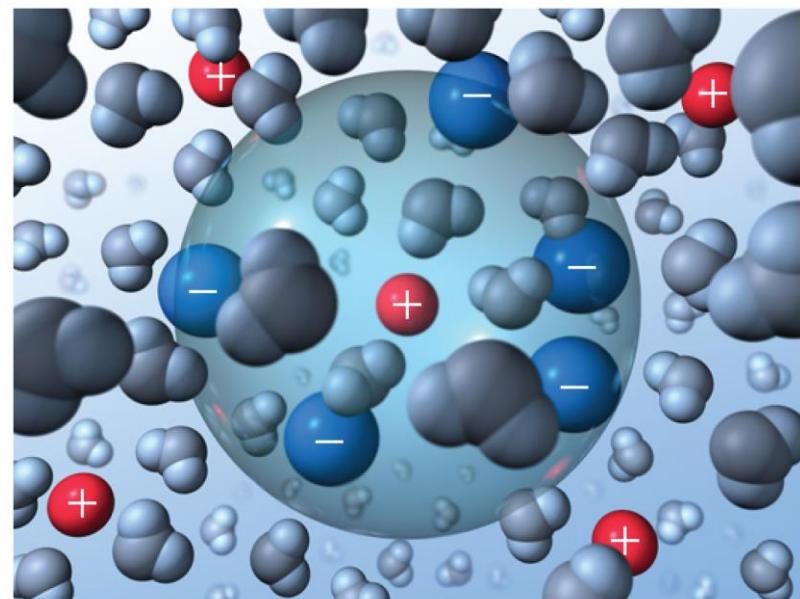
Solute	Molality, m					
	1.0	0.10	0.010	0.0010	...	Inf. dil. ^a
NaCl	1.81	1.87	1.94	1.97	...	2
MgSO ₄	1.09	1.21	1.53	1.82	...	2
Pb(NO ₃) ₂	1.31	2.13	2.63	2.89	...	3

^aThe limiting values: $i = 2, 2$, and 3 are reached when the solution is infinitely dilute. Note that a solute whose ions are singly charged (for example, NaCl) approaches its limiting value more quickly than does a solute whose ions carry higher charges. Interionic attractions are greater in solutes with more highly charged ions.

Debye and Hückel

◆ 1923

- Ions in solution do not behave independently.
- Each ion is surrounded by others of opposite charge.
- Ion mobility is reduced by the *drag* of the *ionic atmosphere*.
- The magnitudes of colligative properties are reduced.

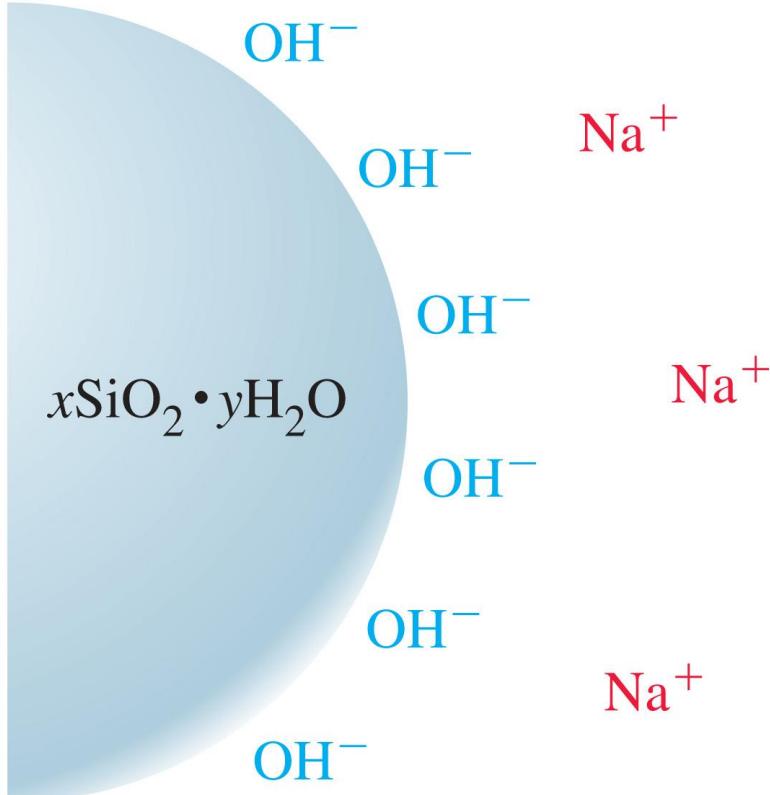


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13-10 Colloidal Mixtures



Colloids



Particles of 1-1000 nm size.

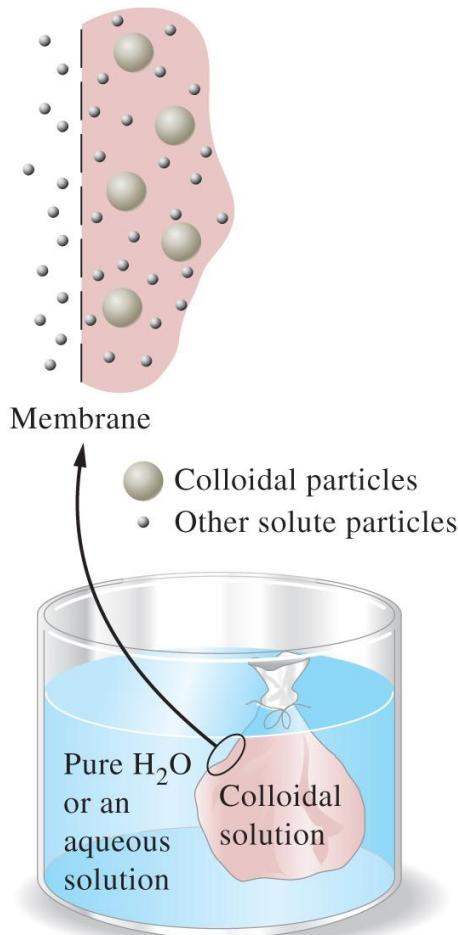
- *Nanoparticles* of various shapes: rods, discs, spheres.
- Particles can remain suspended indefinitely.
 - Milk is colloidal.

Increasing ionic strength can cause precipitation.

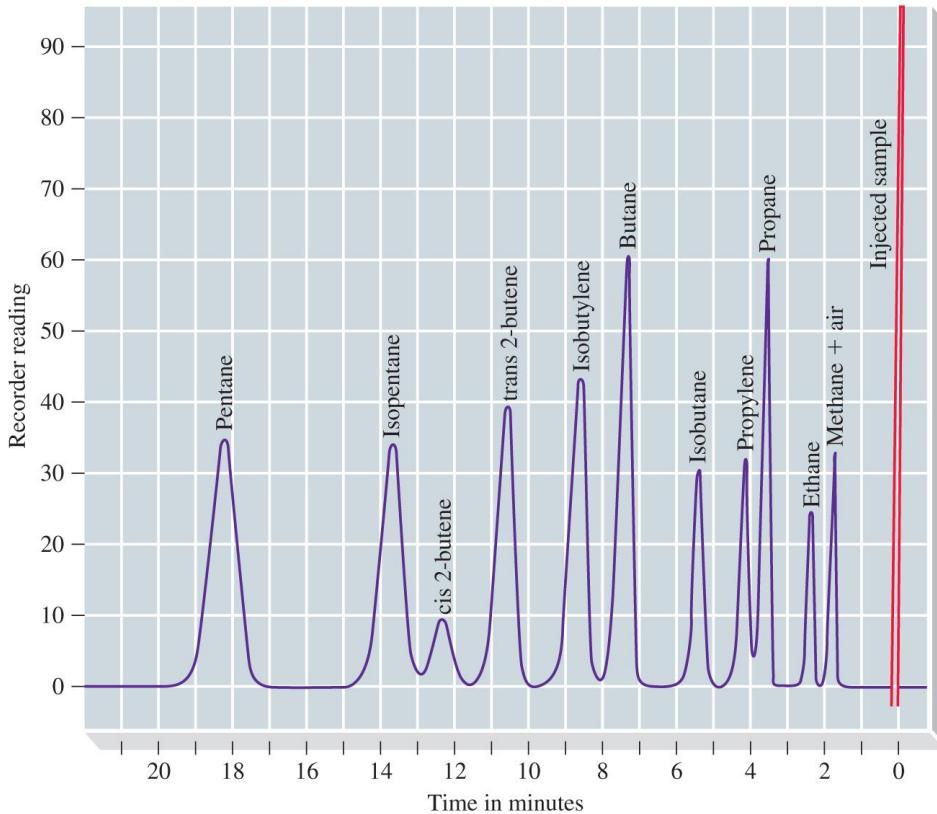
Precipitation by Increasing Ionic Strength



Dialysis



Focus on Chromatography



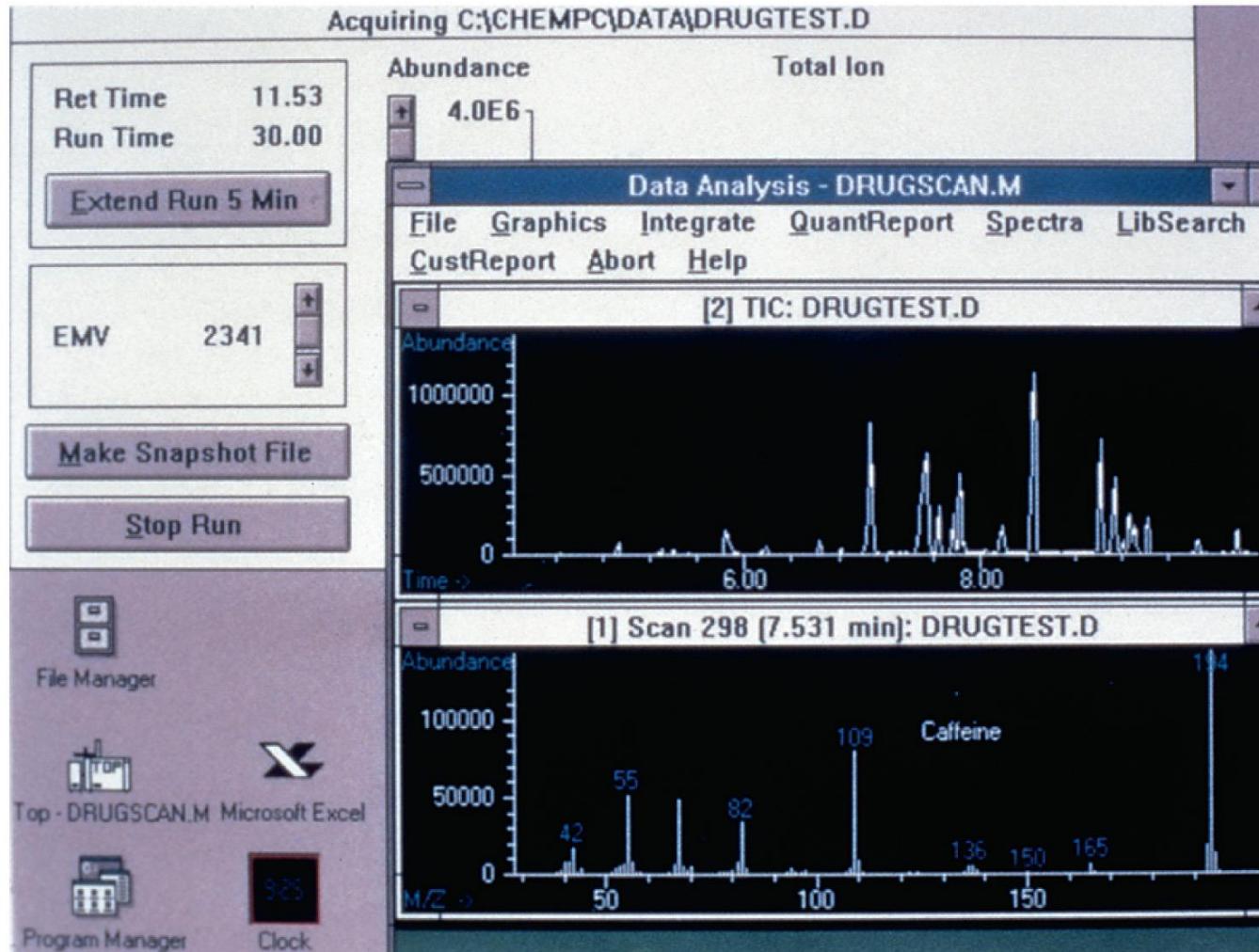
Stationary Phase

- silicon gum
- alumina
- silica

Mobile Phase

- solvent
- gas

Chromatography



End of Chapter Questions

- ◆ Mathematical errors are lethal to a solution.
 - Use estimation in your head to check your calculations (don't trust your calculator).
 - Shortcuts or tricks are unreliable.
 - Limit the number of operations that you perform in each step.
 - You must be able to read the solution later and not struggle to figure out what you did.