CHEMISTRY XL-14A

PHYSICAL EQUILIBRIUM

August 13, 2011   Robert Iafe

Chapter Overview

- Phases and Phase Transitions

- Solubility

- Colligative Properties

- Binary Liquid Mixtures

Phases and Phase Transitions

- Vapor Pressure
- Volatility
  - Intermolecular Forces (Chapter 4)
    - Ion-Dipole Forces
    - Dipole-Dipole Forces
    - Londen Forces
    - Hydrogen Bonding
- Variation of Vapor Pressure with Temperature
- Boiling
- Freezing and Melting
- Phase Diagrams
- Critical Properties

Origin of Intermolecular Forces

- Intermolecular forces are responsible for phases of matter
- Phase: form of matter that is uniform in both chemical composition and physical state
  - Gas
  - Liquid
  - Solid
- All intermolecular interactions can be traced back to the coulombic interaction between charges

Intermolecular interaction

0

Potential energy

Ionic and covalent bonding

0

Internuclear separation, r
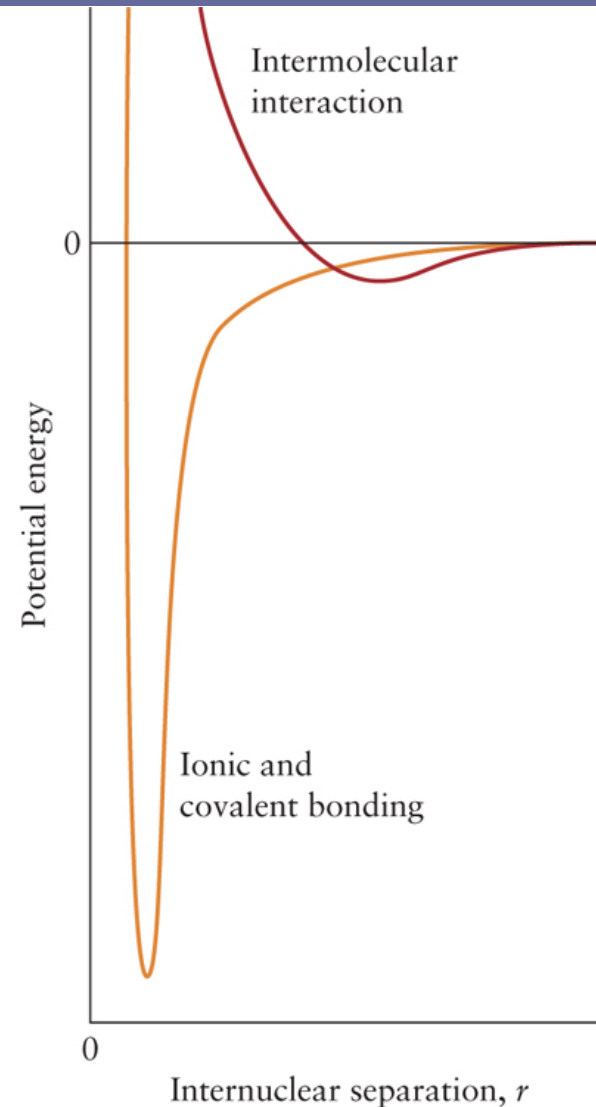
Origin of Intermolecular Forces

- Coulombic interaction

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_o r}$$

- Deep well indicates a bond between atoms

- Shallow well shows small attractive forces between molecules, even though no bonds are formed

Intermolecular interaction

0

Potential energy

Ionic and covalent bonding

0

Internuclear separation, r
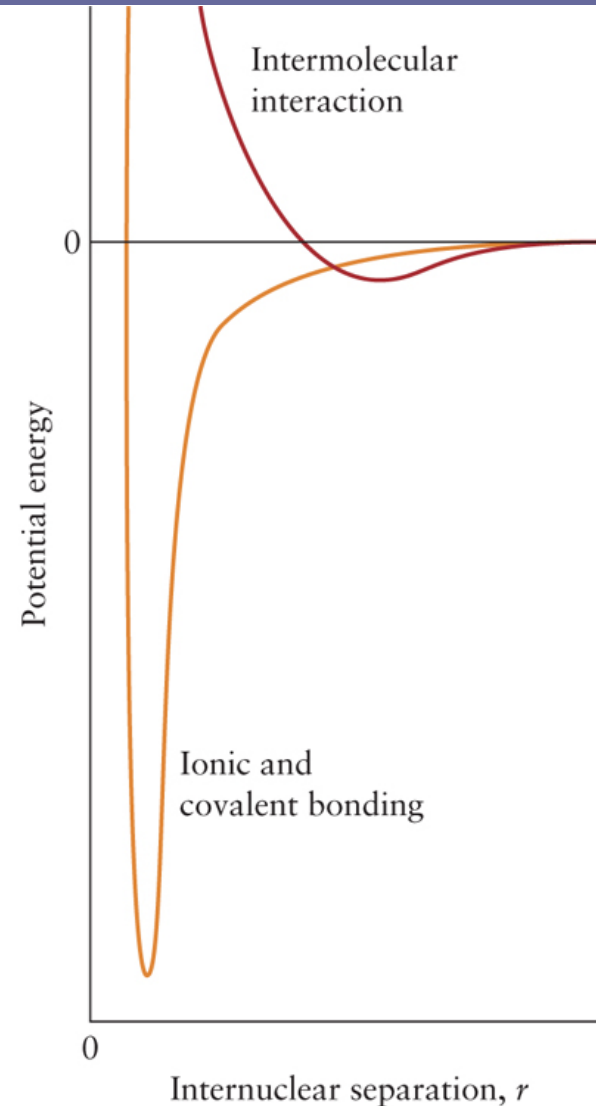
Ion-Dipole Forces

- Ionic solids dissolve in water when water molecules become attached to each ion and separate it from the other ions

- Hydration due to dipole of water

- Partial positive interacts with anion

- Partial negative interacts with cation

- Ion-Dipole interaction
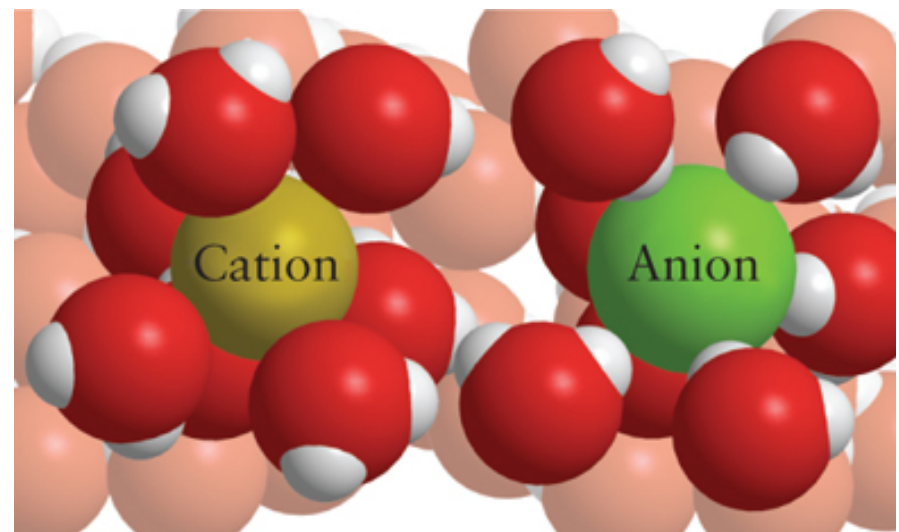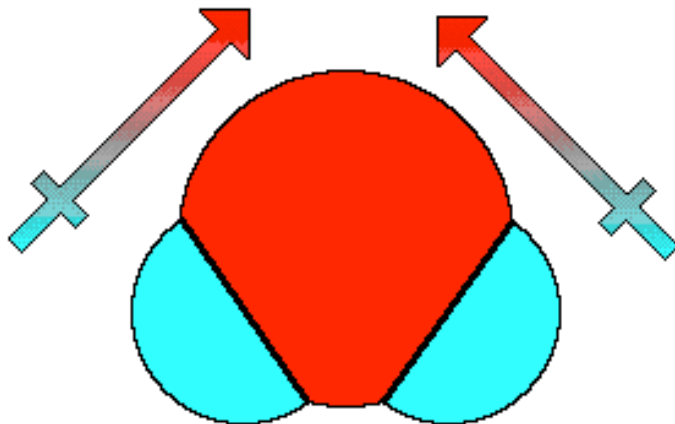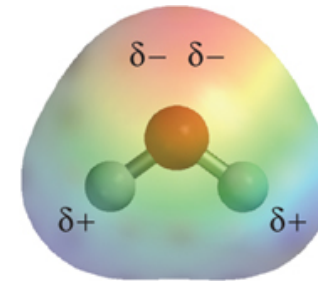
Potential Energy

☐ Potential energy for the interaction of a full charge and partial charges

☐ Potential energy is lowered by interaction with polar solvent

☐ Distance of the ion and dipole play a larger role than distance between the two ions

☐ Results:

  ❑ Small cations are more extensively hydrated than large cations

  ❑ Smaller metals form hydrated salts

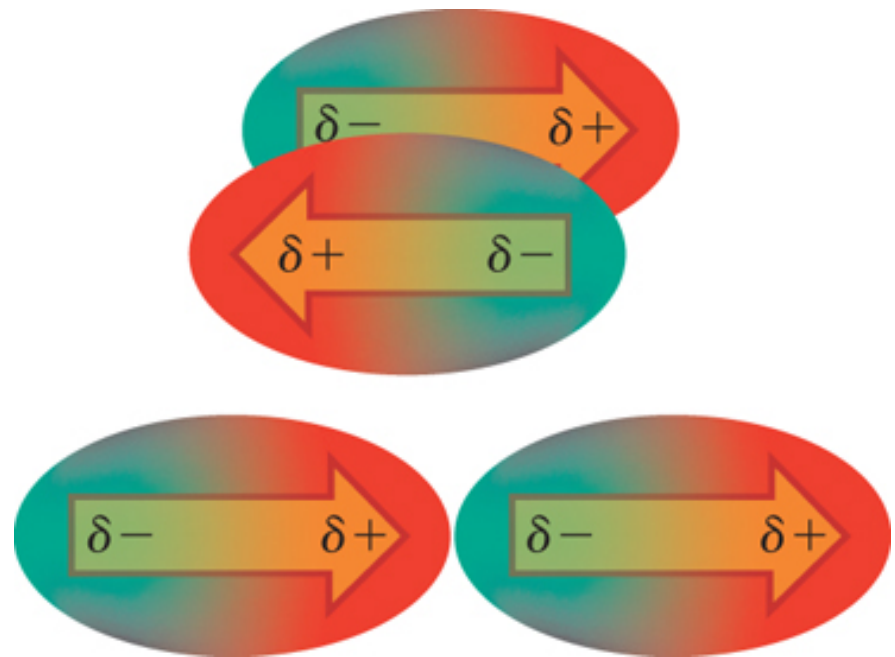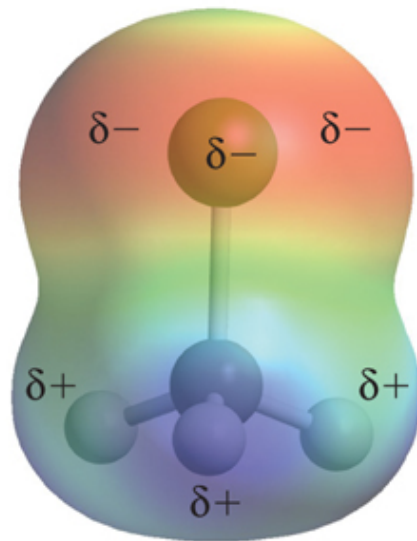 ❑ Larger charges on metals cause hydration

$$E_p \propto -\frac{|z|\mu}{r^2}$$

Dipole-Dipole Forces

- Polar molecules attract each other by the interaction between the partial charges of their electric dipoles
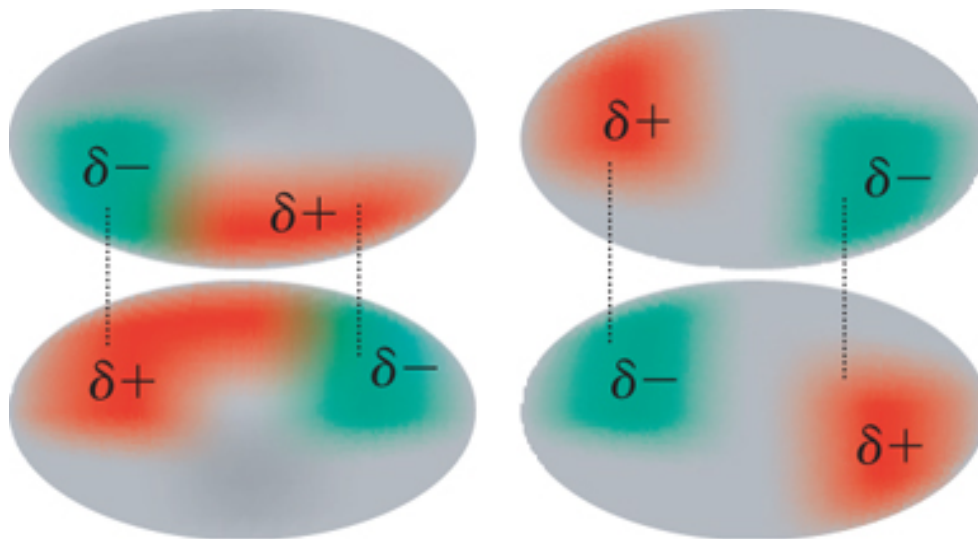
- Dipole-Dipole interaction

$$E_p \propto -\frac{\mu_1 \mu_2}{r^3}$$

London Forces

- Attractive interactions are also found in nonpolar molecules
- Evidence: noble gases can be liquefied even though they are nonpolar
- Electrons are not stationary
- Nonpolar molecules can have instantaneous dipoles
- Attractive interactions are called London interactions

London Forces

□ What determines strength of London interactions?

    □ Distance

    □ Polarizability (alpha)

    □ Shape

$$E_p \propto -\frac{\alpha_1 \alpha_2}{r^6}$$
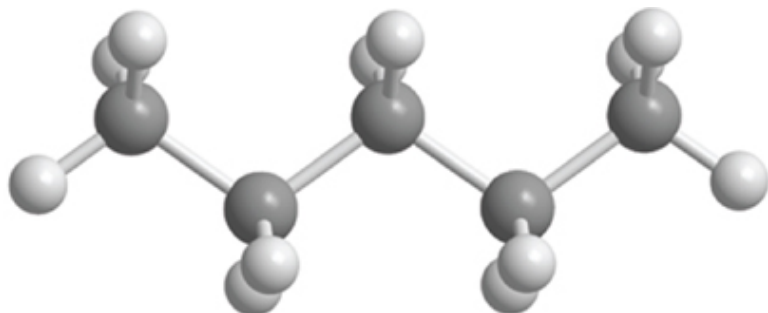
London Forces - Polarizability

More electrons = More polarizable

More polarizable = more stabilization

Substance	Melting point (°C)	Boiling point (°C)
Noble gases		
He	-270 (3.5 K)[†]	-269 (4.2 K)
Ne	-249	-246
Ar	-189	-186
Kr	-157	-153
Xe	-112	-108
Halogens		
F_2	-220	-188
Cl_2	-101	-34
Br_2	-7	59
I_2	114	184
Hydrogen halides		
HF	-93	20
HCl	-114	-85
HBr	-89	-67
HI	-51	-35

London Forces - Shape

Bp: 36 °C

8 Pentane, C_5H_{12}

$\delta-$ $\delta+$
$\delta+$ $\delta-$

(a)

$\delta-$ $\delta+$ $\delta-$ $\delta+$
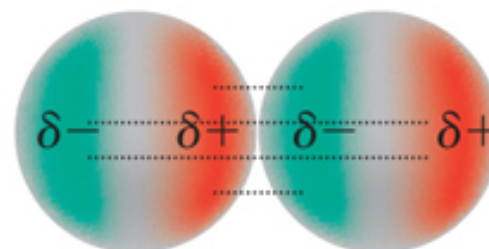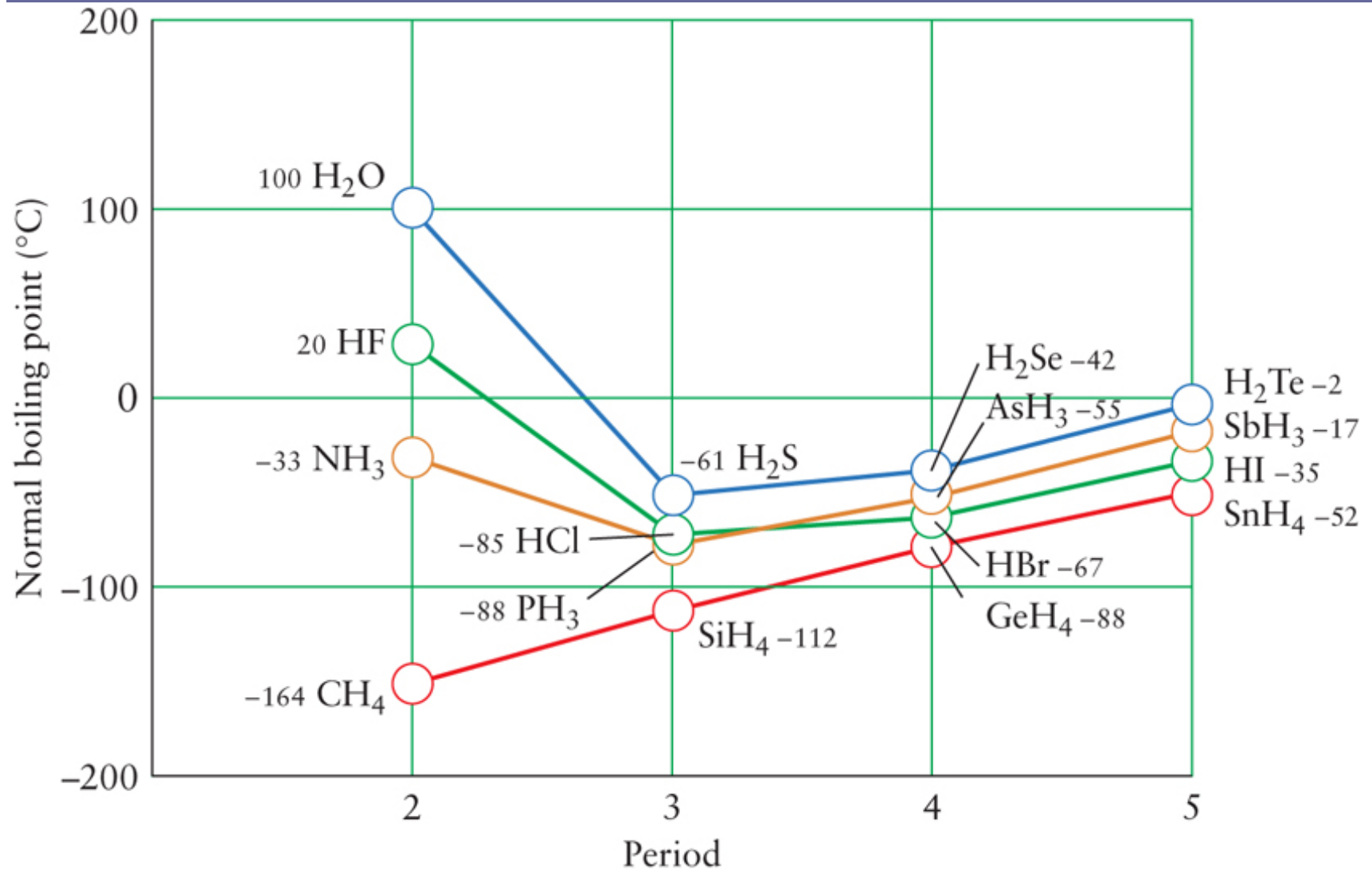
(b)
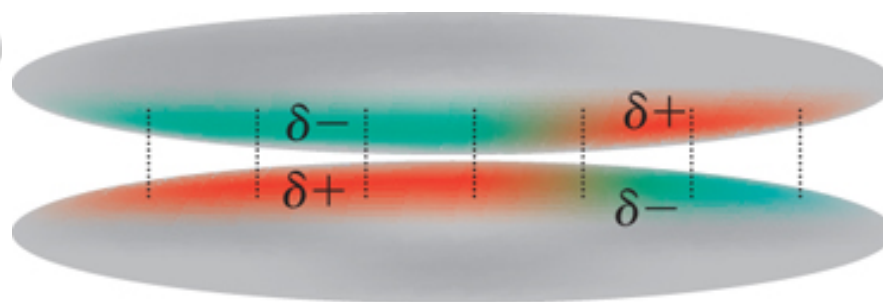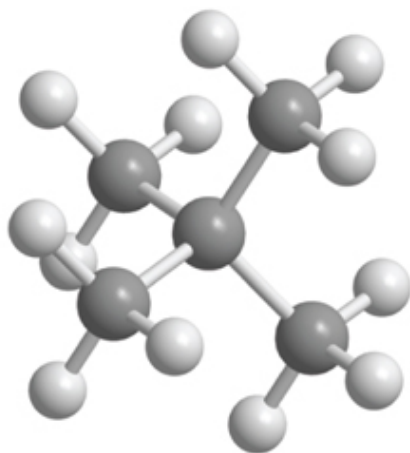
Bp: 10 °C

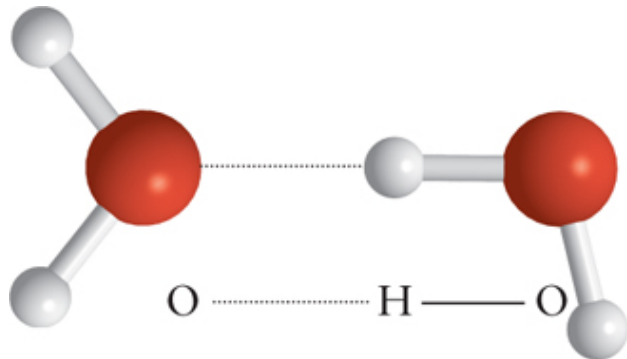9 2,2-Dimethylpropane, $C(CH_3)_4$
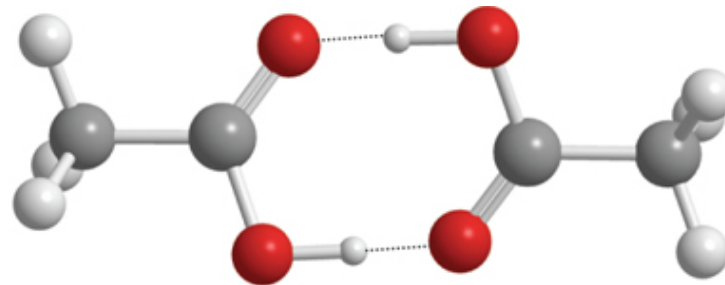
Trends in London Forces

Hydrogen Bonding

- Ammonia (NH_3), water (H_2O), and HF have abnormally high boiling points

- Strong attractive forces due to hydrogen bonding
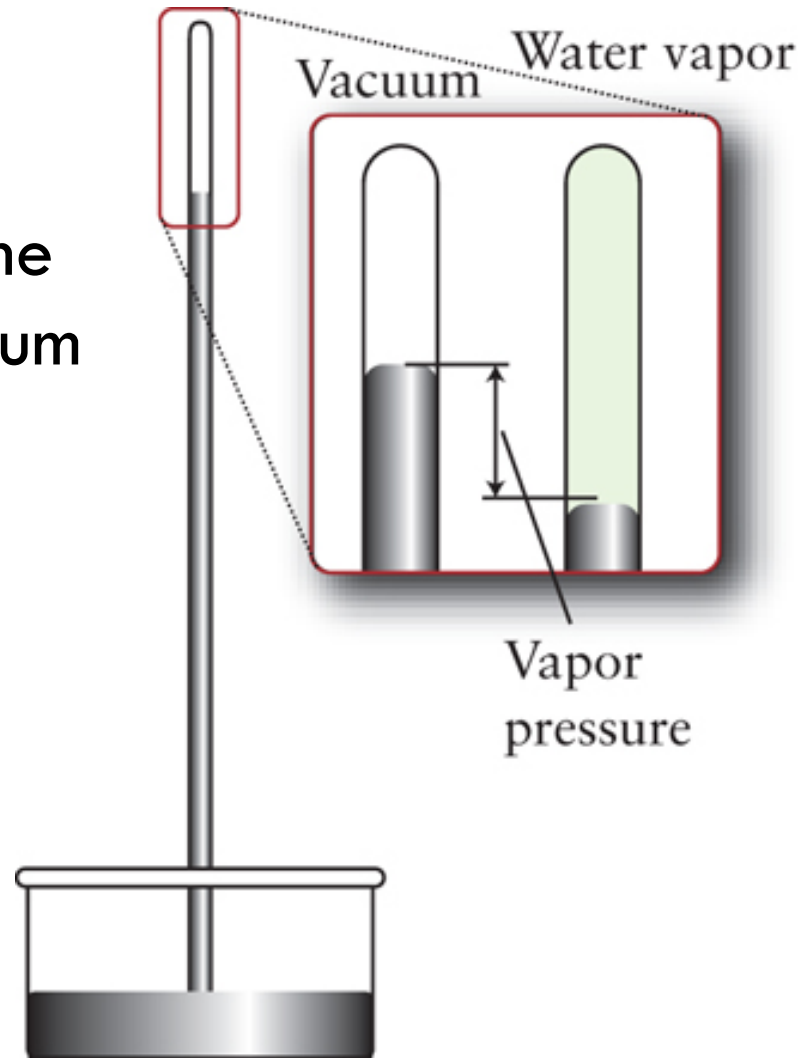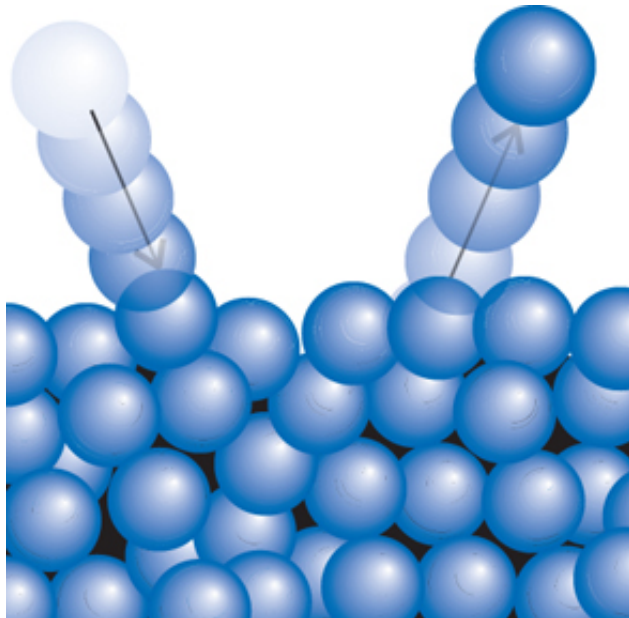

10   Hydrogen bond (in water)

12   Acetic acid dimer

- Hydrogen bonding **only** occurs with N-H, O-H, F-H

Vapor Pressure

- The vapor pressure of a substance is the pressure exerted by its vapor when the vapor is in dynamic equilibrium with the condensed phase

Vacuum

Water vapor

Vapor pressure

Vapor Pressure and IM

□ Intermolecular forces play a <u>large</u> role in physical properties of liquids and solids

□ General rule:

◘ Molecules with stronger intermolecular forces have lower vapor pressures (higher boiling points and melting points)

◘ Molecules with weaker intermolecular forces have higher vapor pressures (lower boiling points and melting points)

Type of interaction	Typical energy ($kJ \cdot mol^{-1}$)	Interacting species
ion–ion	250	ions only
ion–dipole	15	ions and polar molecules
dipole–dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole–induced-dipole	2	at least one molecule must be polar
London (dispersion)[†]	2	all types of molecules
hydrogen bonding	20	molecules containing an N—H, O—H, or F—H bond; a shared H atom links the molecules

Vapor Pressure and IM

Substance	Vapor pressure (Torr)
benzene	94.6
ethanol	58.9
mercury	0.0017
methanol	122.7
water*	23.8

*For values at other temperatures, see Table 9.3.

Vapor Pressure and Temperature

□ Vapor pressure increases with temperature

  ◻ Higher temperature = greater energy to overcome attractive forces of the liquid

Clausius-Clapeyron equation

$$\ln\frac{P_2}{P_1} = \frac{\Delta H^{\circ}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Temperature (°C)	Vapor pressure (Torr)
0	4.58
10	9.21
20	17.54
21	18.65
22	19.83
23	21.07
24	22.38
25	23.76
30	31.83
37*	47.08
40	55.34
60	149.44
80	355.26
100	760.00

*Body temperature.

Boiling

- Boiling occurs when the vapor pressure of a liquid is equal to the external (atmospheric) pressure
  - Normal boiling point = boiling point at 1 atm (760 torr)
- Boiling point is dependent on:
  - Intermolecular forces
  - External Pressure

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^{\circ}_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

  - Thinking questions
    - Does water boil at a higher or lower temperature on the top of Mt. Everest?
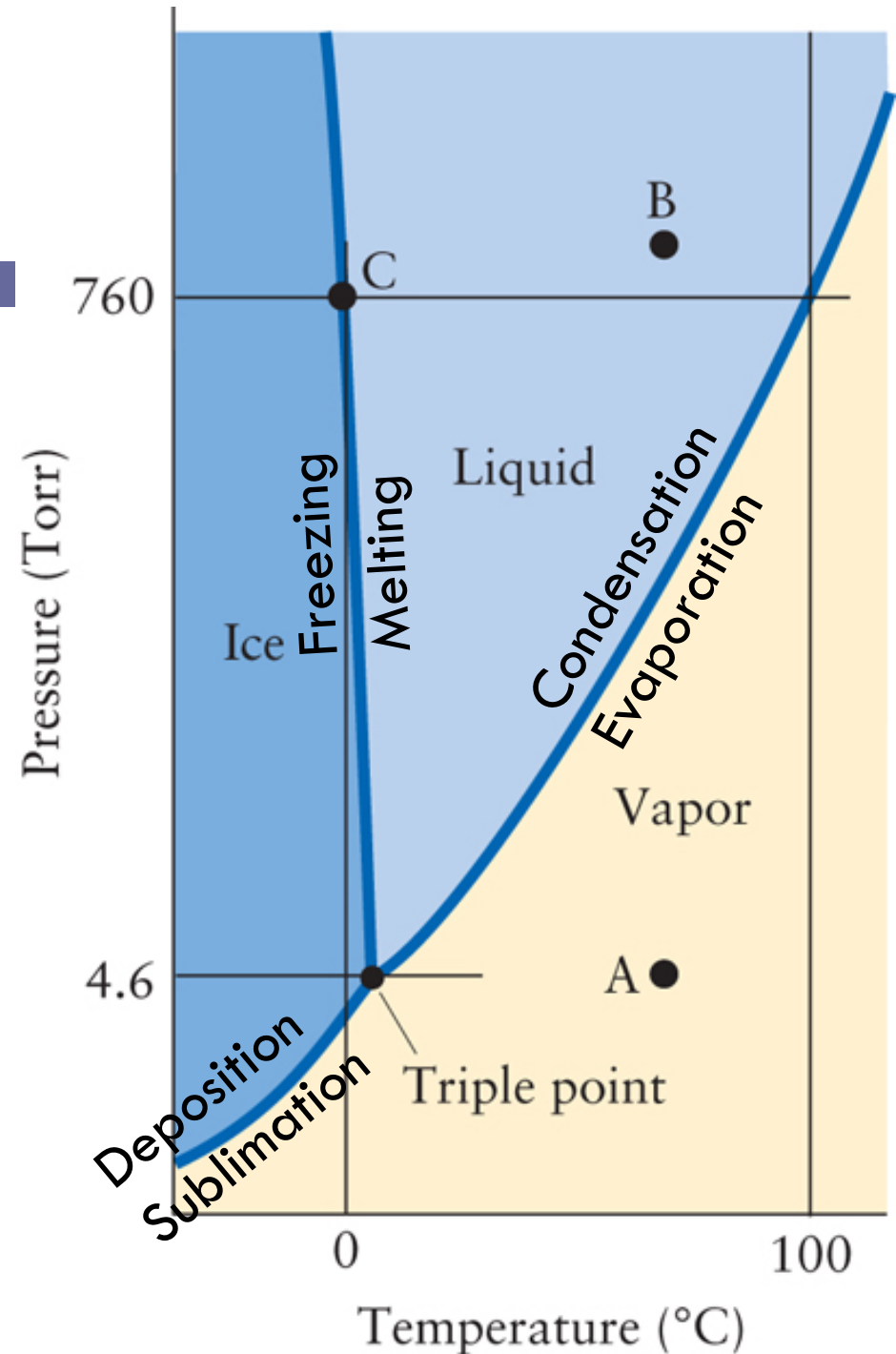   - How does a pressure cooker work?

Freezing and Melting

- Freezing temperature is the temperature at which the solid and liquid phase are in dynamic equilibrium with each other
  - Normal freezing point = freezing point at 1 atm (760 Torr)
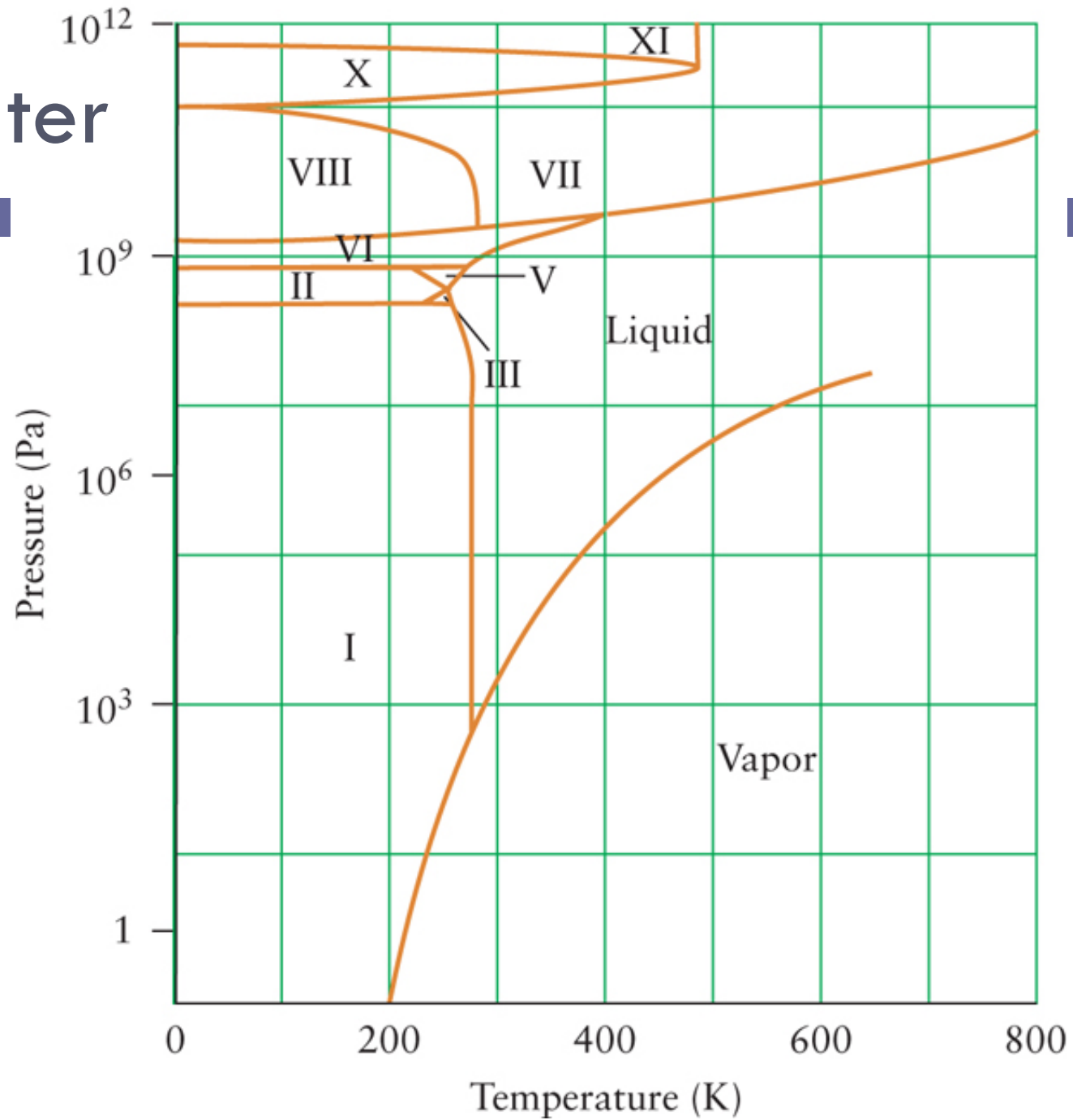- Supercooling = when a liquid exists beyond its freezing point

Phase Diagrams

- Phase diagram of water
- Phase boundaries
  - Equilibrium btwn phases
- Triple point
  - All 3 phases coexist
- Solid-liquid boundary
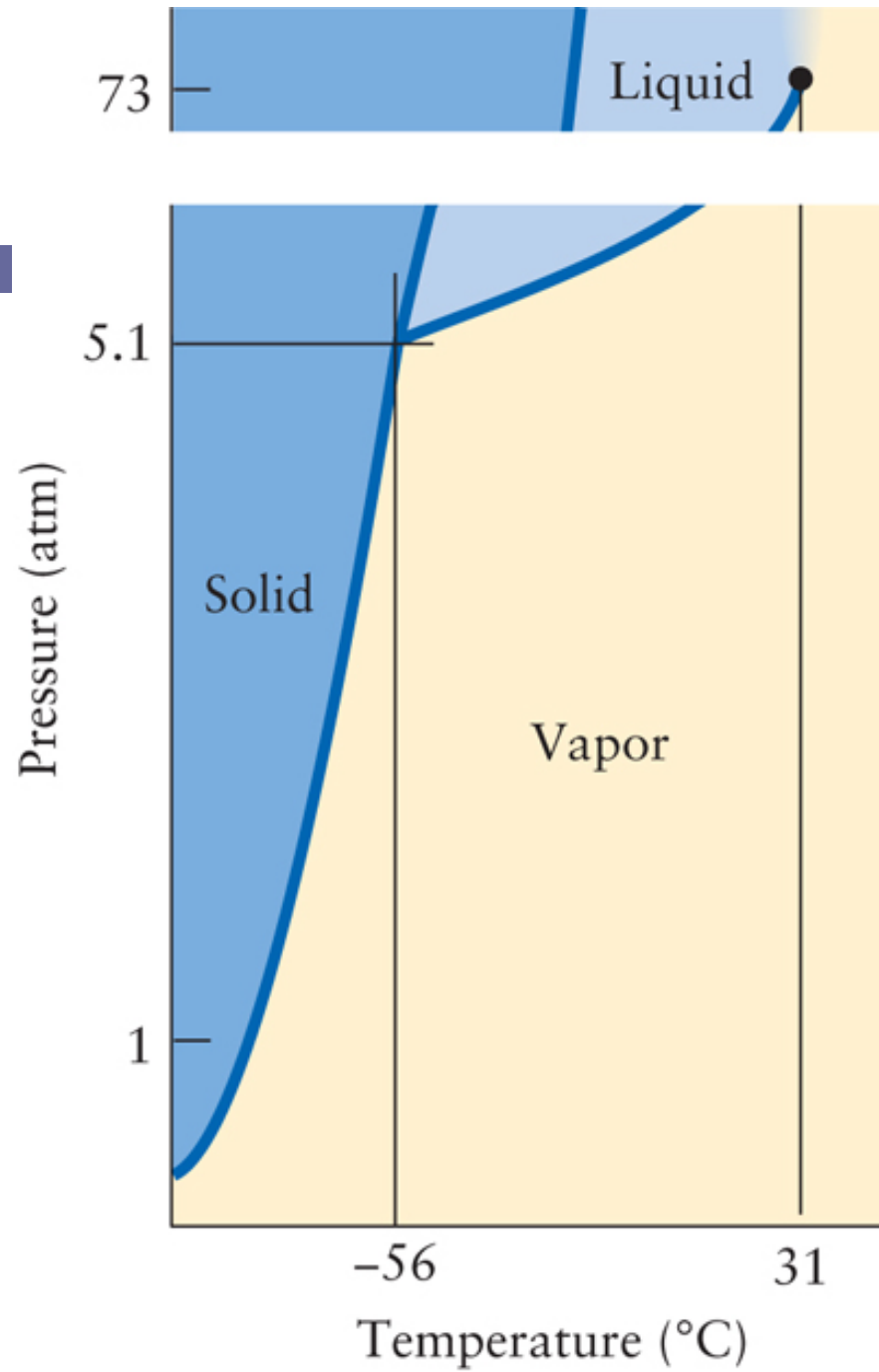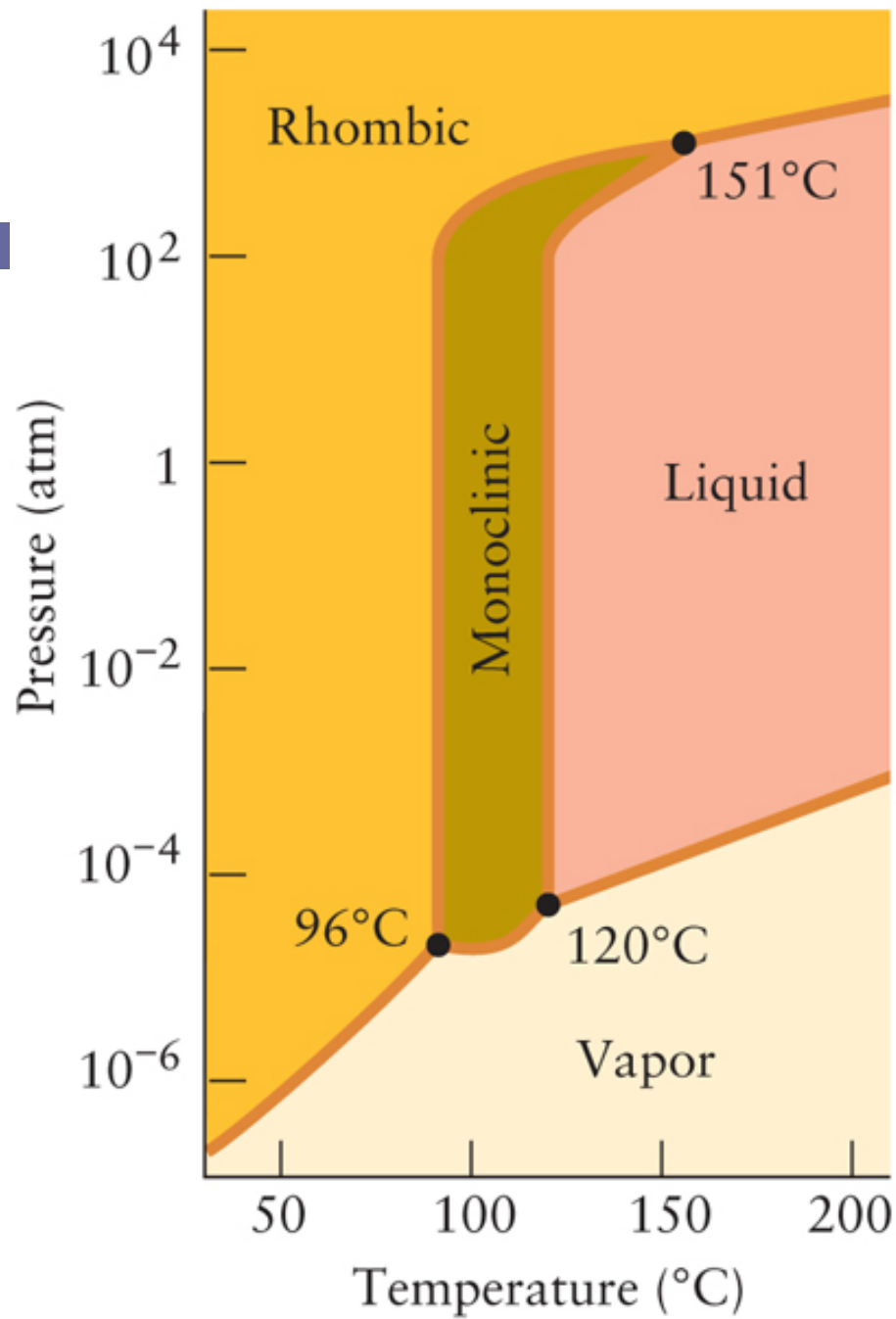 - Negative slope = solid is less dense than liquid (ice floats in water)

Water

Phase diagram of water showing pressure (Pa) versus temperature (K). Regions labeled: I, II, III, V, VI, VII, VIII, X, XI, Liquid, and Vapor.

CO_2

Sulfur

Critical Points

Solubility

- The Limits to Solubility

- The "Like-Dissolves-Like" Rule

- Pressure and Gas Solubility: Henry's Law

- Temperature and Solubility

Limits of Solubility

- Terms:
  - Solvent: the substance that dissolves
  - Solute: the substance that is dissolved
  - Saturated: the solvent has dissolved the maximum amount of solute it can, and undissolved solute remains
- Saturation is a dynamic equilibrium with the undissolved solute
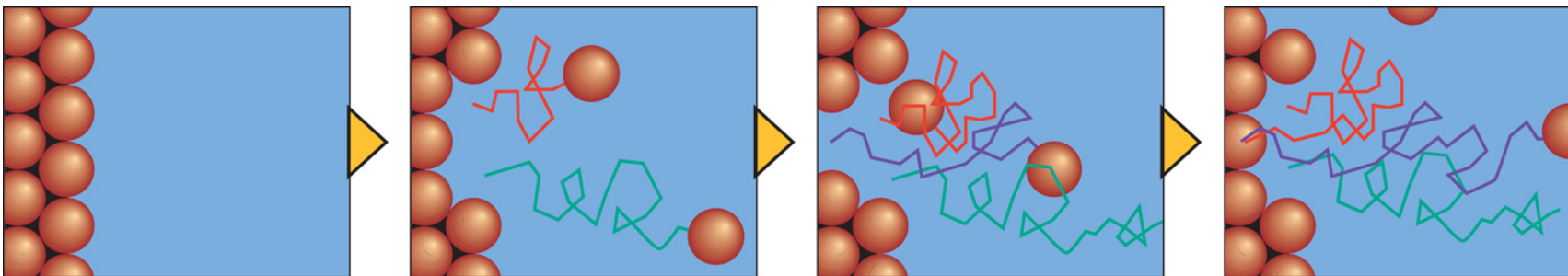
Like Dissolves Like

- Substances have attractive cohesion forces when the have the same intermolecular forces

- Rule: Like Dissolves Like

  - Polar solvents dissolve polar solutes

  - Nonpolar solvents dissolve nonpolar solutes

  - Polar liquids and nonpolar liquids are immiscible
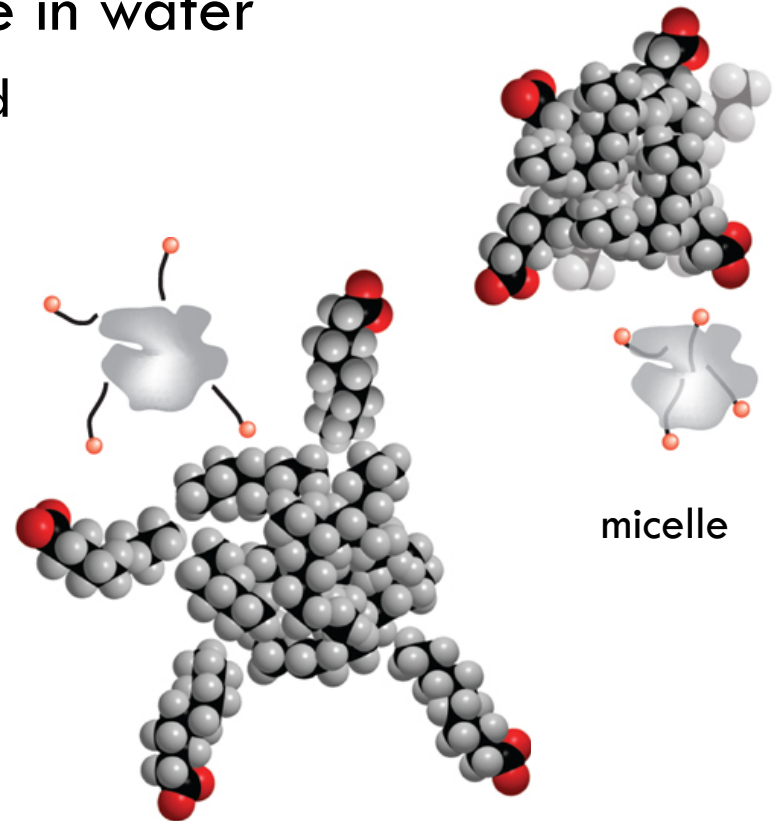
Detergents

☐ Detergents have a hydrophobic tail group and a hydrophilic head group

  ❑ Hydrophobic – does not dissolve in water

   ▪ 'hydro' = water; 'phobic' = afraid

  ❑ Hydrophilic – dissolved in water

   ▪ 'hydro' = water; 'philic' = loves

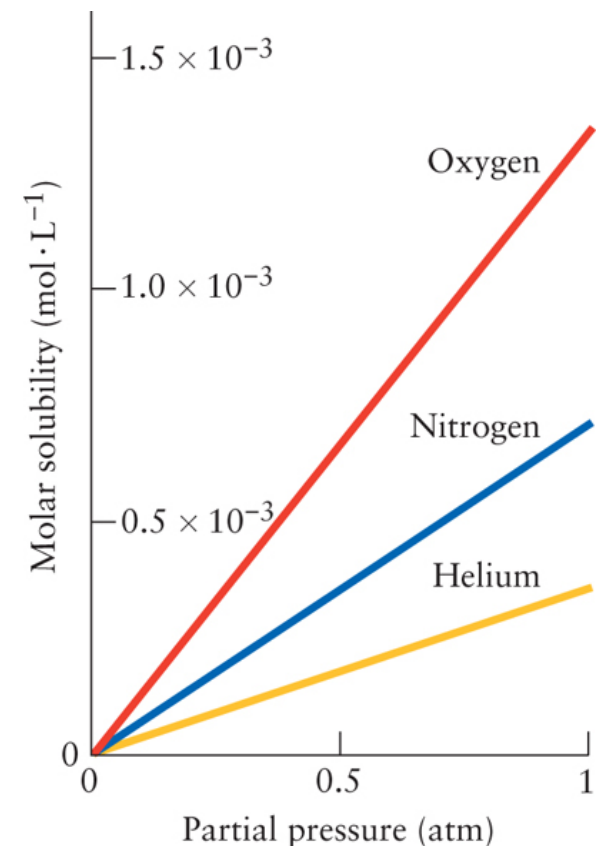Na^+
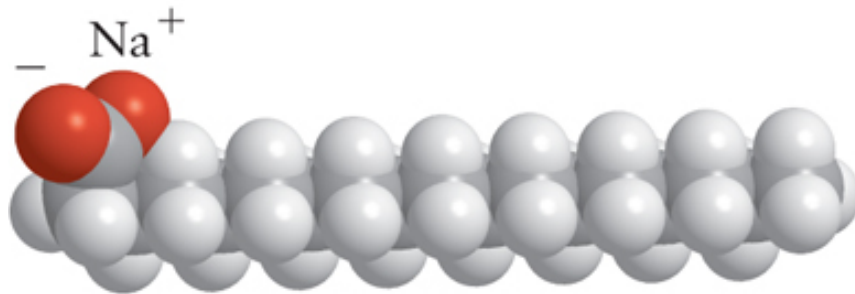
3 Sodium stearate, $NaCH_3(CH_2)_{16}CO_2$

micelle

Pressure and Gas Solubility: Henry's Law

- English chemist William Henry, 1801
- The solubility of a gas is directly proportional to its partial pressure, P
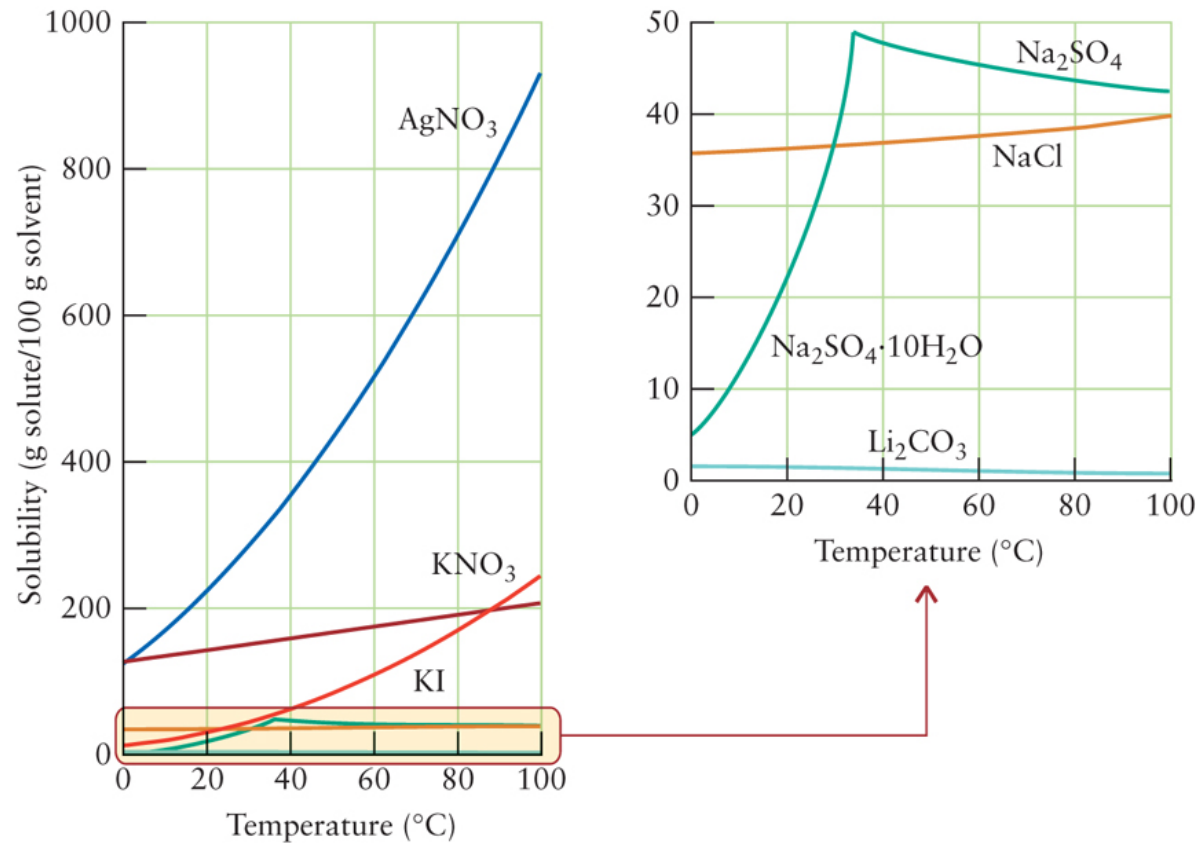- Henry's Law

$$s = k_H P$$

Gas	k_H (mol·L^{-1}·atm^{-1})
air	7.9×10^{-4}
argon	1.5×10^{-3}
carbon dioxide	2.3×10^{-2}
helium	3.7×10^{-4}

Temperature and Solubility

- Rate of dissolving, but not generally the solubility of a substance, increases at higher temperatures.
- Most gasses are less soluble in warm water than in cold water

Colligative Propreties

- Molality

- Vapor-Pressure Lowering

- Boiling-Point Elevation

- Freezing Point Depression

- Oxmosis

Molality

- Three measures of concentration
  - Mole fraction $$x_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$$
  - Molarity $$M = \frac{n_{solute}}{L_{solution}} = \frac{mol}{L}$$
  - Molality $$b_{solute} = \frac{n_{solute}}{m_{solvent}} = \frac{mol}{(kg)solvent}$$

- Molality and mole fraction are independent of temperature

Mole Fraction → Molality

What is the molality of benzene, C_6H_6, dissolved in toluene, $C_6H_5CH_3$, in a solution for which the mole fraction of benzene is 0.150?

- Step 1. Find the amount of solute molecules in a total of exactly 1 mol of solution molecules

$$n_{solute} = x_{solute} \times n_{total} = 0.150 \times 1mol = 0.150mol$$

- Step 2. Find the mass of solvent present and convert to kg

$$m_{solvent} = \{(1 - x_{solute})mol\} \times MM_{solvent}$$

$$m_{solvent} = \{(1 - 0.150)mol\} \times 92.13\frac{g}{mol} \times \frac{1kg}{1000g} = 0.0783kg$$

- Step 3. Calculate the molality

$$b_{solute} = \frac{n_{solute}}{m_{solvent}} = \frac{0.150mol}{0.0783kg} = 1.92\frac{mol}{kg}$$

Molarity → Molality

- Find the molality of sucrose, $C_{12}H_{22}O_{11}$, in 1.06 M $C_{12}H_{22}O_{11(aq)}$, which is known to have density 1.14g/mL

  - Step 1. Find the mass of exactly 1 L (10^3 mL) of solution

  $$m_{solution} = d \times (10^3\, mL) = 1.14 \times 10^3\, g$$

  - Step 2. Find the mass of solute in exactly 1 L of solution

  $$m_{sucrose} = n_{solute} MM_{solute} = c_{solute} \times (1L) \times MM_{solute}$$

  $$m_{sucrose} = 1.06 \frac{mol}{L} \times (1L) \times 342.3 \frac{g}{mol} = 363g$$

  - Step 3. Find the mass of water present in exactly 1 L of sol'n

  $$m_{water} = m_{solution} - m_{solute} = 1140 - 363g = 0.78kg$$

 - Step 4. Calculate molality.

  $$b_{(C_{12}H_{22}O_{11})} = \frac{1.06mol}{0.78kg} = 1.4 \frac{mol}{kg}$$

Vapor Pressure Lowering

- French scientist Francois-Marie Raoult
  - Spent most of his time measuring vapor pressure
- Vapor pressure of a solvent is proportional to its mole fraction in a solution
- Ideal solutions follow Raoult's law
- The vapor pressure of a solvent is reduced by the presence of a nonvolatile solute
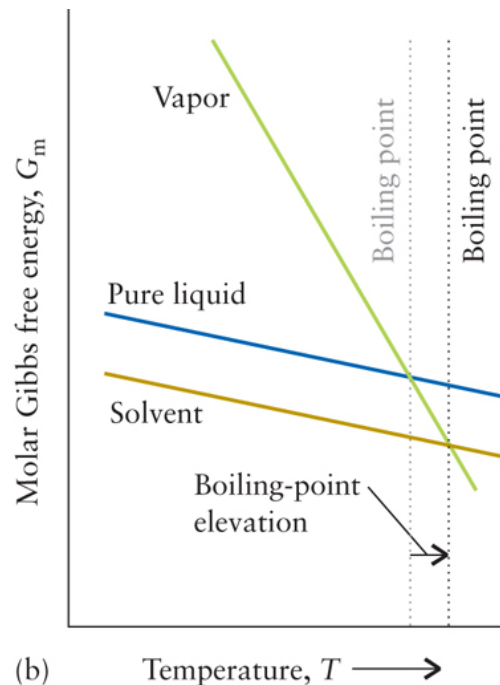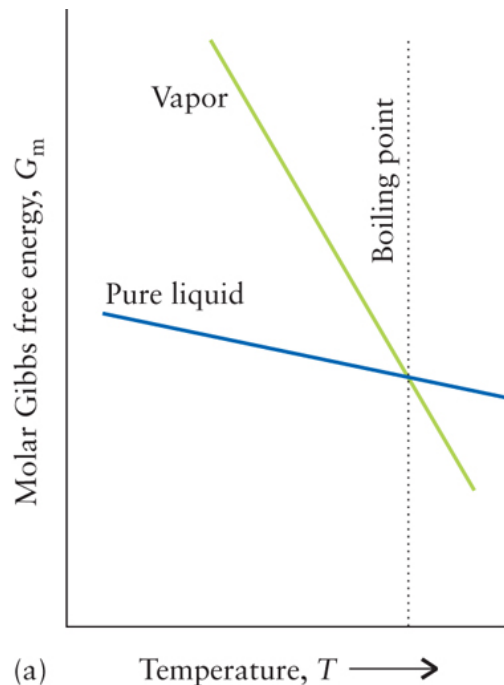
$$P = x_{solvent}P_{pure}$$

Mole fraction of solvent, x_A
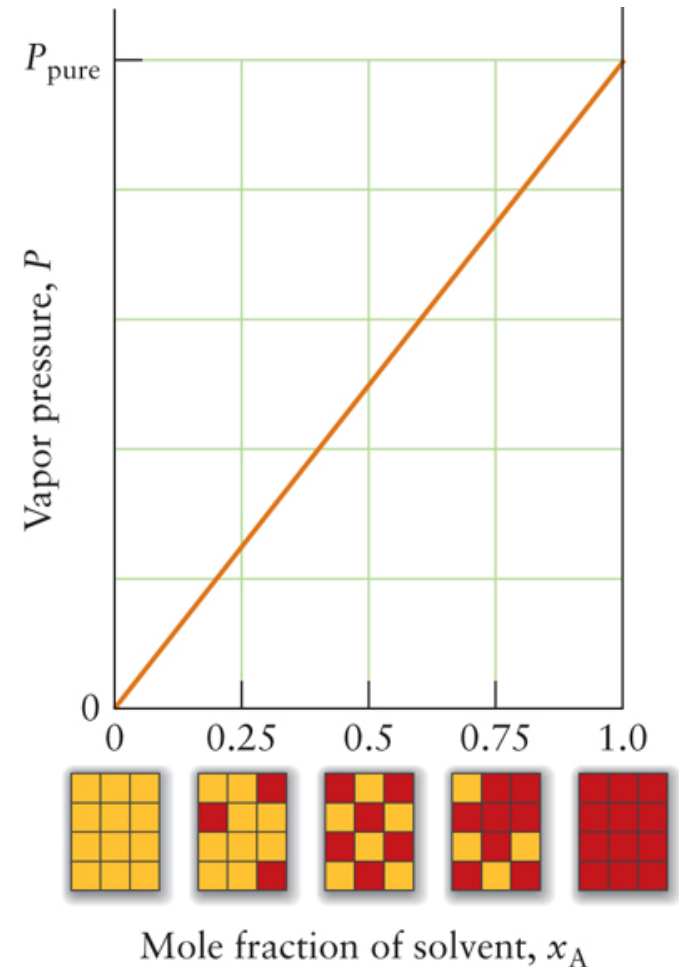
Boiling Point Elevation

□ Presence of nonvolative solutes raises the boiling point of pure liquids

$$\Delta T_b = ik_b \times b_{solute}$$

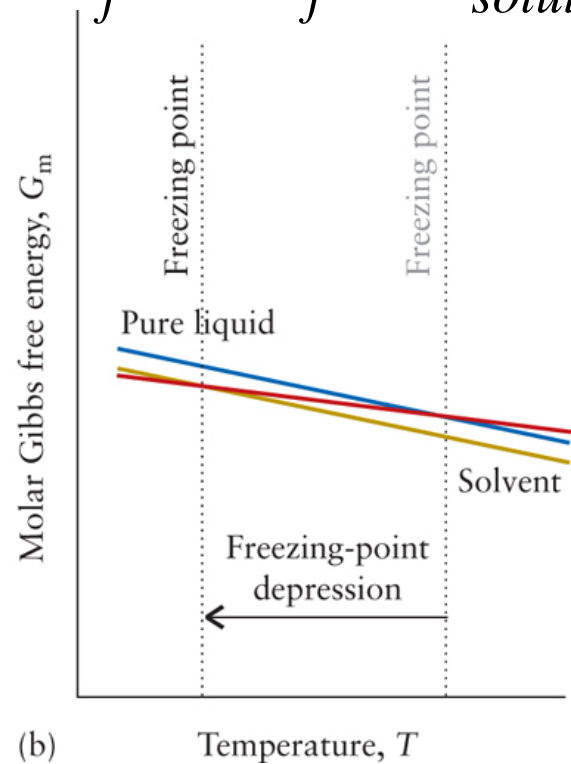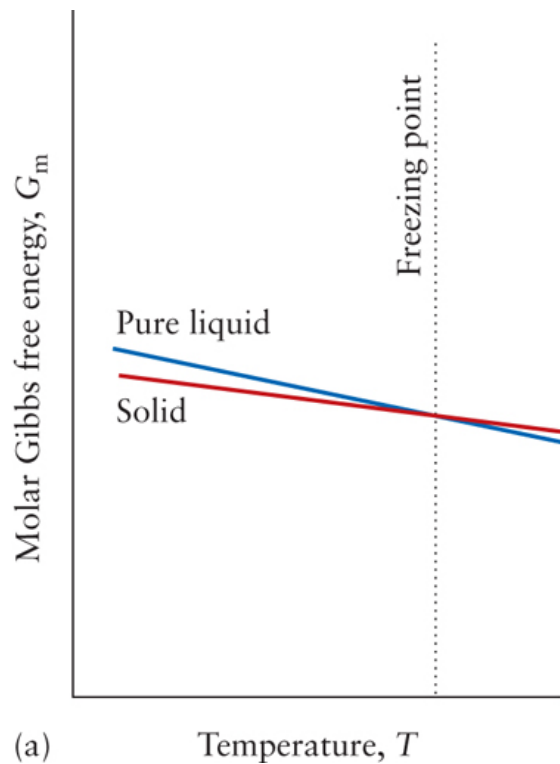i = van't Hoff i factor
(# of particles)

eg. NaCl = 2
$CaCl_2$ = 3
Sucrose = 1

(a) Vapor, Pure liquid, Boiling point, Molar Gibbs free energy, G_m, Temperature, T

(b) Vapor, Pure liquid, Solvent, Boiling-point elevation, Boiling point, Boiling point, Molar Gibbs free energy, G_m, Temperature, T

Freezing Point Depression

□ Presence of nonvolative solutes lowers the freezing point of pure liquids
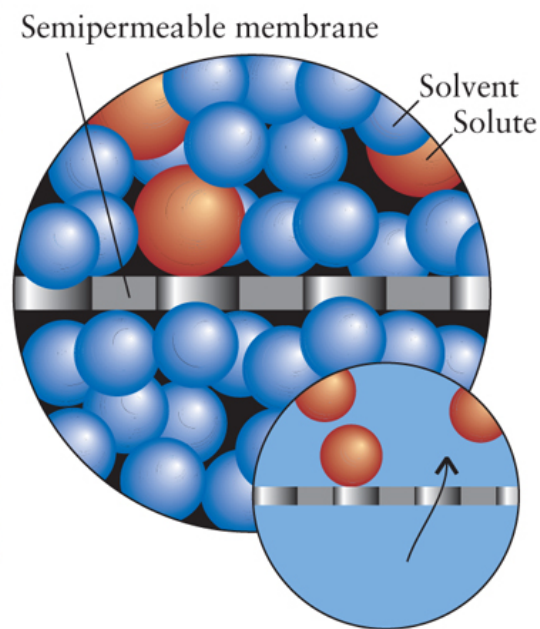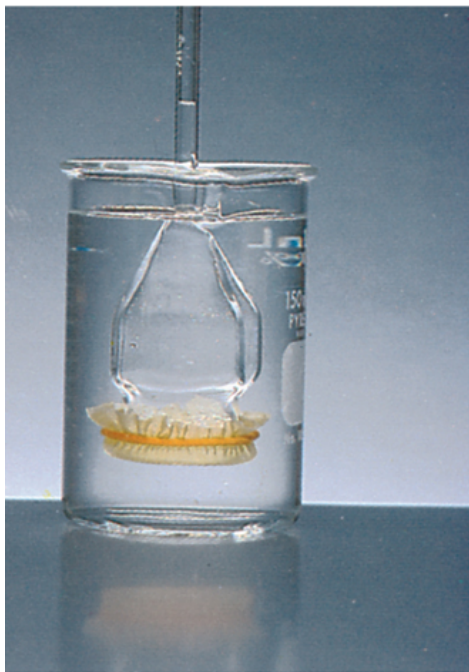
$$\Delta T_f = i k_f \times b_{solute}$$

i = van't Hoff i factor (# of particles)

eg. NaCl = 2
$CaCl_2$ = 3
Sucrose = 1

Osmosis

- Definition: the flow of solvent through a membrane into a more concentrated solution

Semipermeable membrane

Solvent
Solute

The pressure needed to stop the flow of solvent is called the osmotic pressure, Π

$$\Pi = iRTc_{solute}$$

Binary Liquid Mixtures

- Vapor Pressure of Binary Liquid Mixtures

- Distillation
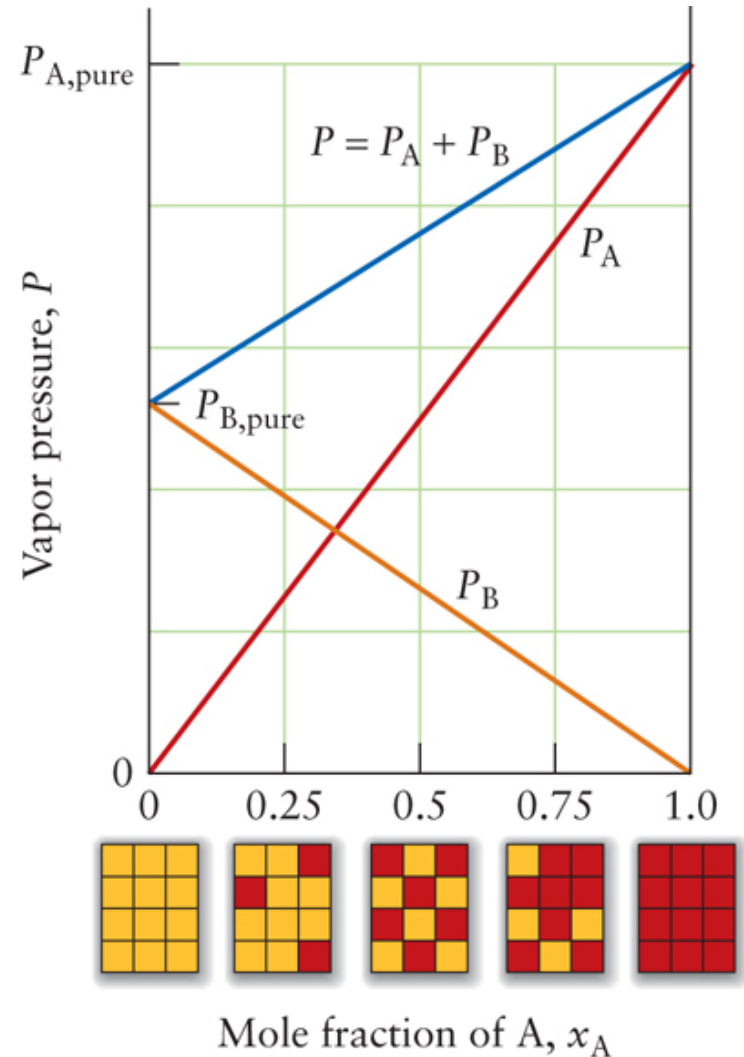
- Azeotropes

Vapor pressure of Binary Liquid Mixtures

- The vapor pressure of a mixture of two volatile liquids is the sum of their individual partial pressures
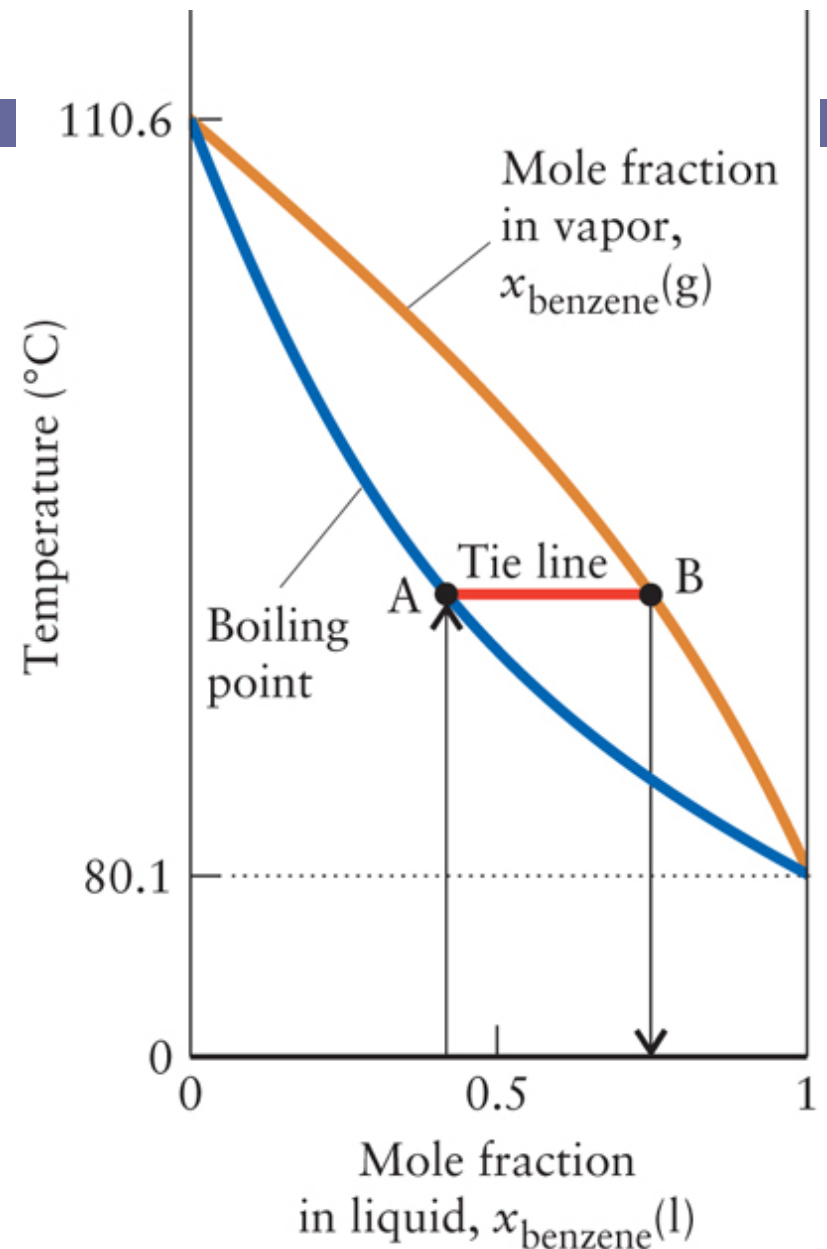
$$P_A = x_A(l)P_A^*$$

$$P_B = x_B(l)P_B^*$$

$$P = P_A + P_B$$

Distillation

- The vapor pressure of a binary mixture is intermediate between the 2 volatile liquids

- Temperature-composition diagram

- Upper curve = vapor composition

- Horizontal line = tie line

- Distillate = condensed vapor

Fractional Distillation
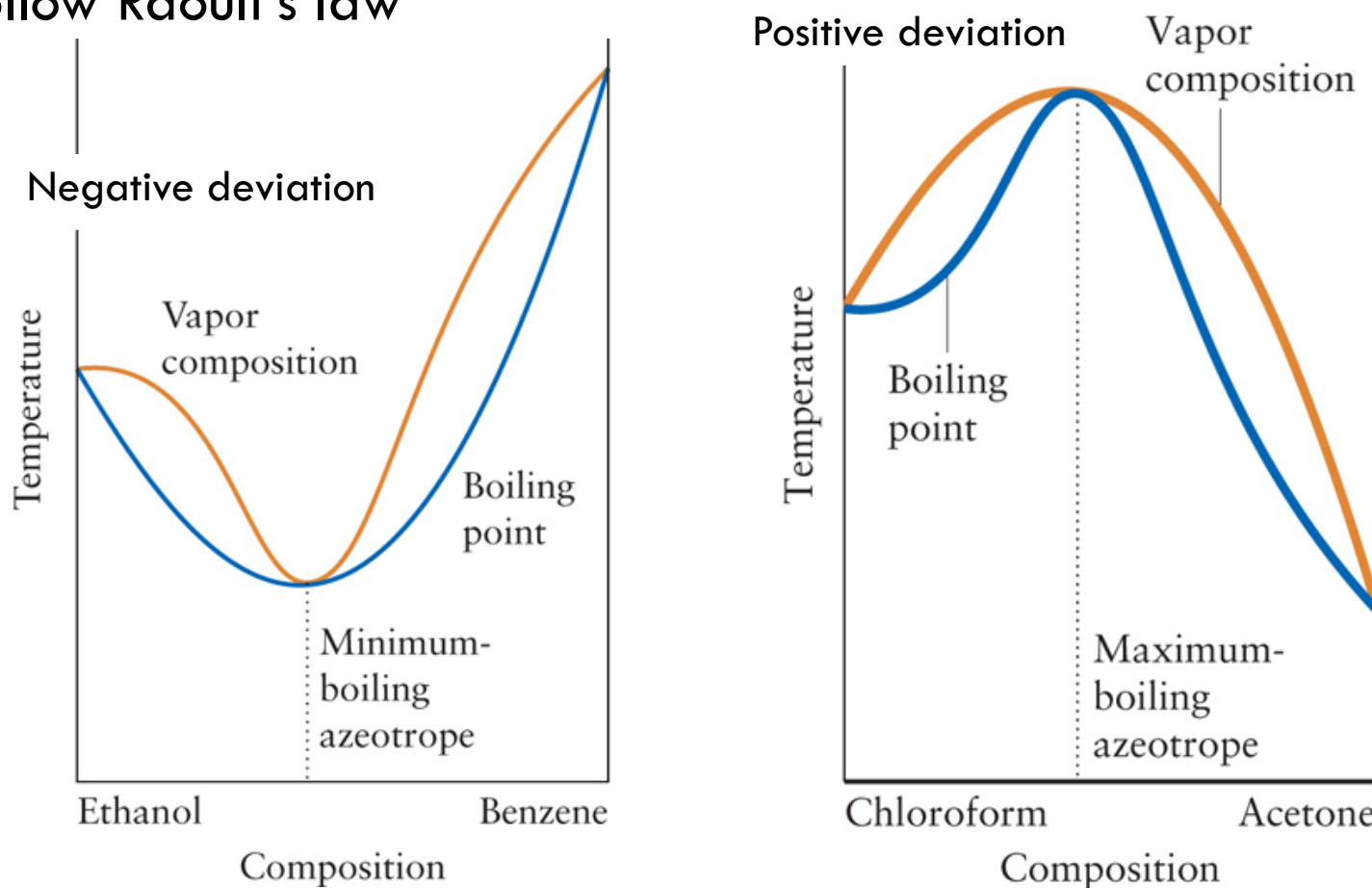
- Continuous redistillation leads to purer and purer distillate

- Becomes richers in the substance with the lower boiling point
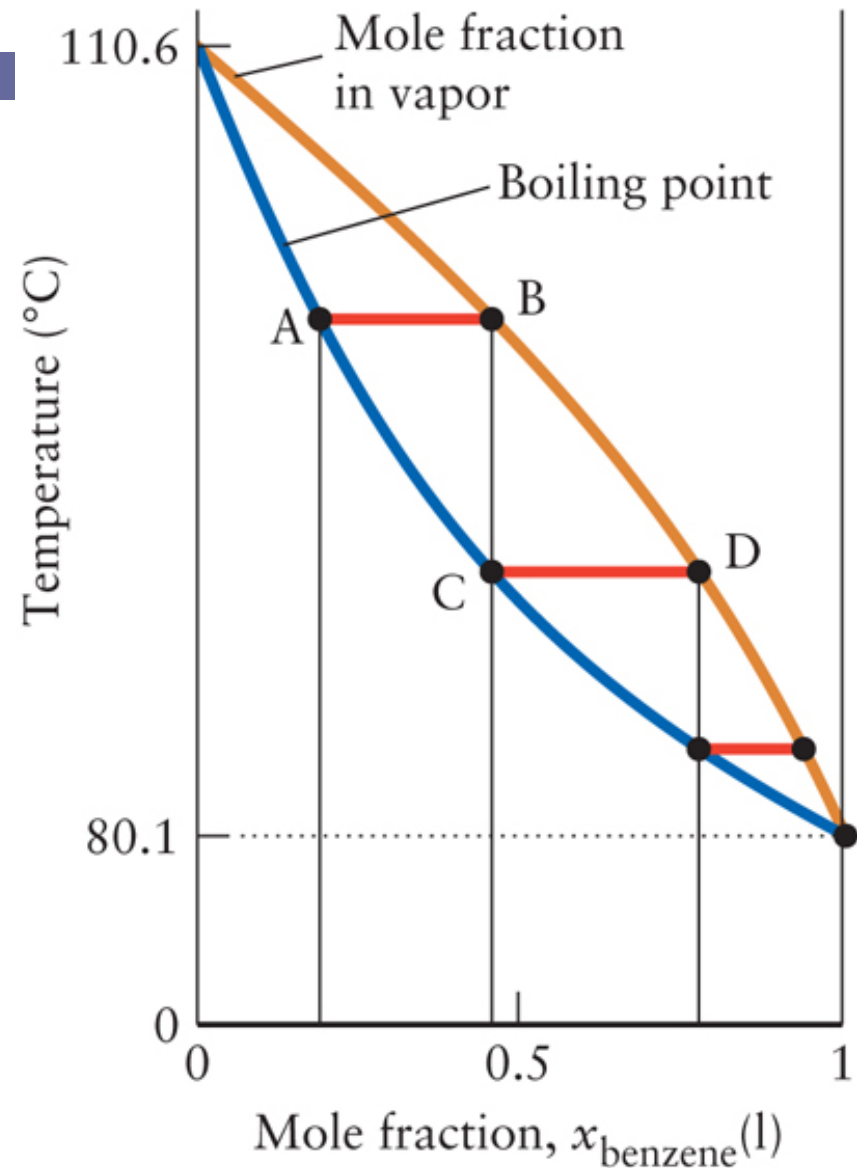
Azeotropes

☐ Most liquid mixtures are not ideal, so their vapor pressures do not follow Raoult's law

Impact on Biology and Materials

- Colloids

Colloids

- Colloid: a dispersion of large particles (1 nm to 1 μm in diameter) in a solvent

- Colloids have properties between those of a homogeneous solution and a heterogeneous mixture

Dispersed phase	Dispersion medium	Technical name	Examples
solid	gas	aerosol	smoke
liquid	gas	aerosol	hairspray, mist, fog
solid	liquid	sol or gel	printing ink, paint
liquid	liquid	emulsion	milk, mayonnaise
gas	liquid	foam	fire-extinguisher foam
solid	solid	solid dispersion	ruby glass (Au in glass); some alloys
liquid	solid	solid emulsion	bituminous road paving; ice cream
gas	solid	solid foam	insulating foam

Tyndall Effect

- Because colloids are a dispersion of many tiny particles in a solvent, we can see the Tyndall Effect
  - The beam reflects off each individual particle

Laser beam through silver solution