

# 화학 General Chemistry

## 034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45  
Building 028-302

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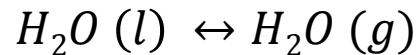
# Phase and Phase Transition

- **Phase:** a specific physical state of matter

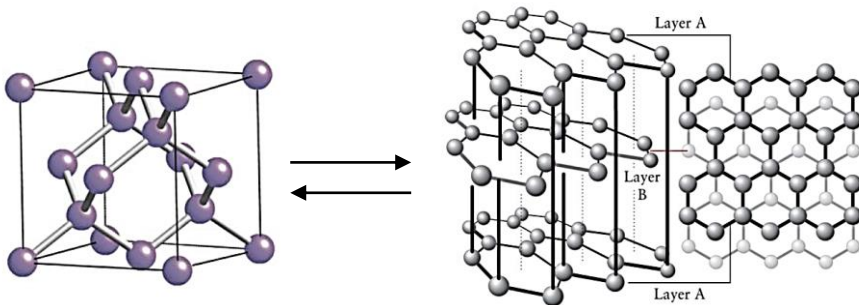
  - : Solids, liquids, and gases

- **Phase transition**

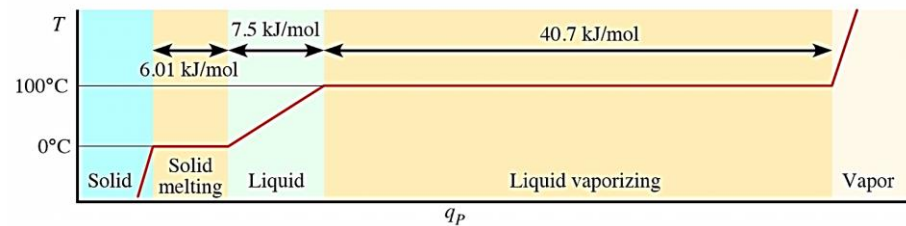
- Equilibrium (physical or chemical equilibrium):  $\Delta G = 0$ ;  $\Delta S_{\text{univ}} = 0$



- Liquid-vapor (gas) equilibrium



Diamond vs. Graphite



# Vapor pressure

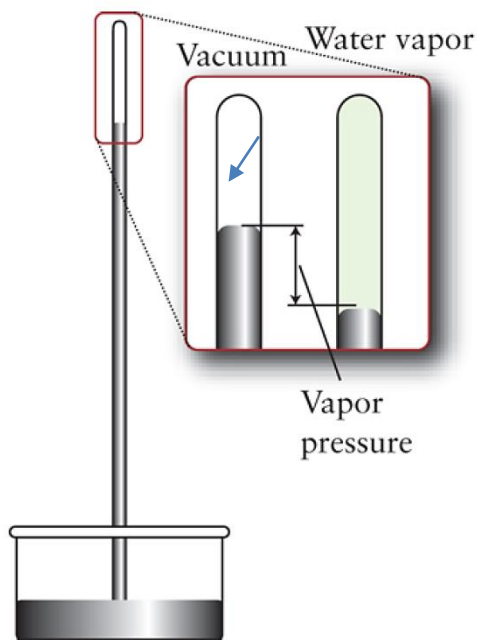
- Vapor pressure ( $P$  or  $P^{\text{sat}}$ )

: Characteristic pressure of a vapor above a confined liquid or solid in **dynamic equilibrium** (closed system)

- Vapor vs. condensed phase

- Vapor  $P$  is a function of temperature (rapidly increase with  $T$ )

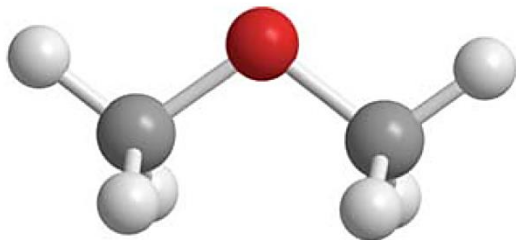
- Different vapor pressure for different matters ( $\text{H}_2\text{O}$  vs  $\text{EtOH}$ )



Substance	Vapor pressure (Torr)	at 25 °C
benzene	94.6	
ethanol	58.9	
mercury	0.0017	
methanol	122.7	
water*	23.8	

# Volatility and Intermolecular Forces

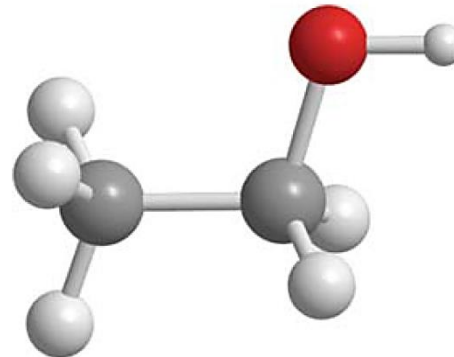
- the intermolecular forces in a liquid or solid
  - the **volatility**
  - the **vapor pressure** at a given temperature
- Effect of hydrogen bond (for example,  $C_2H_6O$ )



1 Dimethyl ether

Boiling point

VS



2 Ethanol

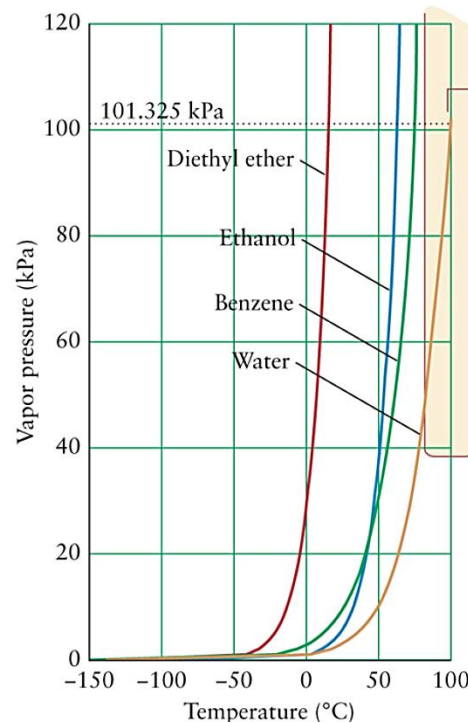
Boiling point

# Variation of Vapor Pressure with T

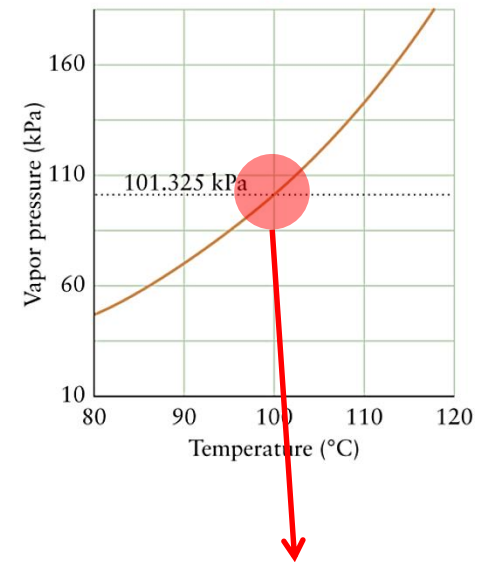
## - Boiling

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.



Atmosphere (atm) =  
 $1.01325 \times 10^5 \text{ Pa} =$   
 $1.01 \text{ bar}; 1 \text{ bar} = 10^5 \text{ Pa}$



Normal boiling point

- Boiling: vapor P of liquid = external P

→ rapid vaporization occurs throughout the entire liquid

- Boiling point: T at which the liquid begins to boil

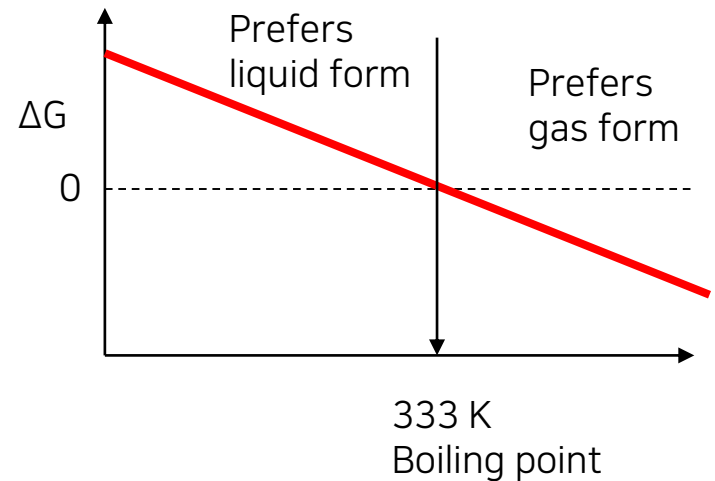
# Boiling Point



What is the normal boiling point?

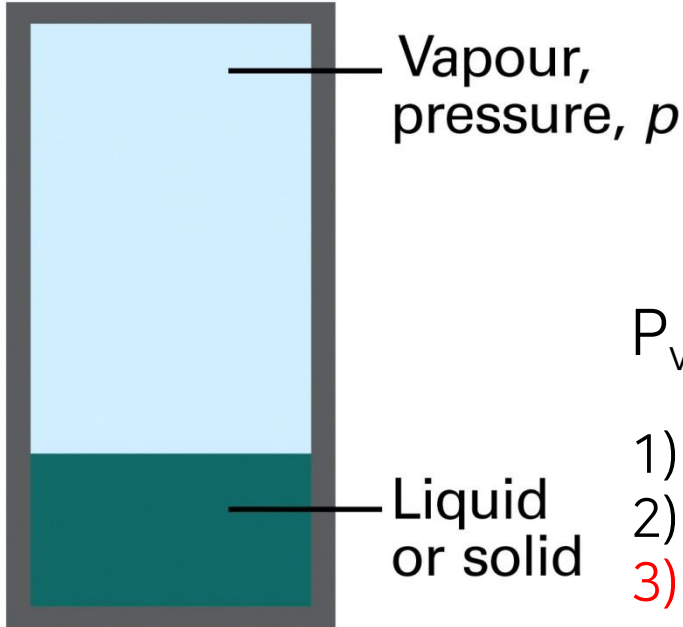
Soln)

At phase transition temperature, the process is reversible and  $\Delta G = 0$ .



# Vapor Pressure:

The pressure exerted by its vapor when the vapor is in dynamic equilibrium with the condensed phase.



$$P_{\text{vap}} = P_{\text{vap}} (X, T)$$

- 1) Dependent on the
- 2) Dependent on
- 3) **Independent** of solids

*of liquids and*

Figure 4-2  
Atkins Physical Chemistry, Eighth Edition  
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Closed container

# Free Energy and Pressure

$$G = G^o + RT \ln(P / P^o)$$

$G^o$  : Free energy at standard condition

Isothermal expansion:  $dG =$

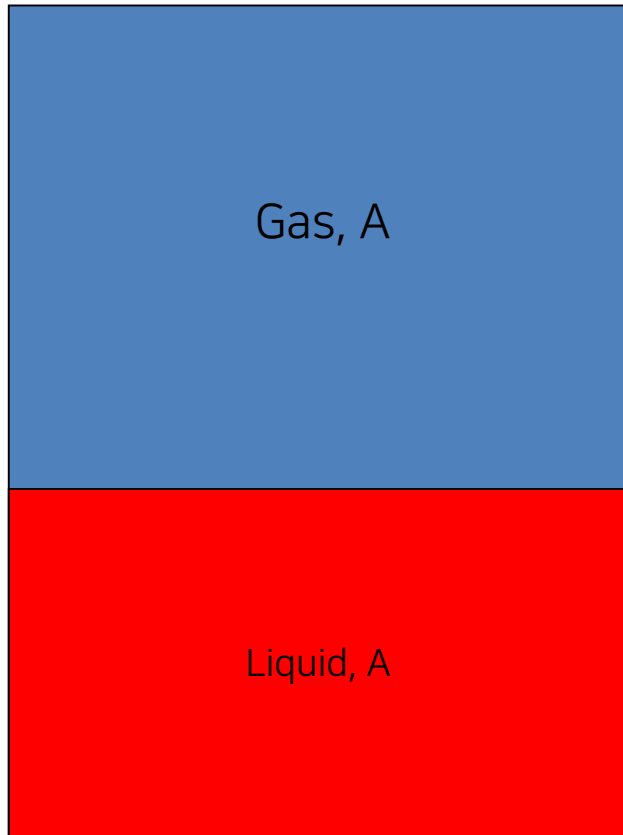
$$\Delta G = G(P_f) - G(P_i) = \int_{P_i}^{P_f} V dp = \int_{P_i}^{P_f} \frac{nRT}{P} dp =$$

$$G_m(P) = G_m^o + RT \ln\left(\frac{P}{P_0}\right)$$

*Standard state*: pure form at exactly 1 bar  
(for solute in a liquid solution: 1 M)



## $G_m$ of liquids and solids

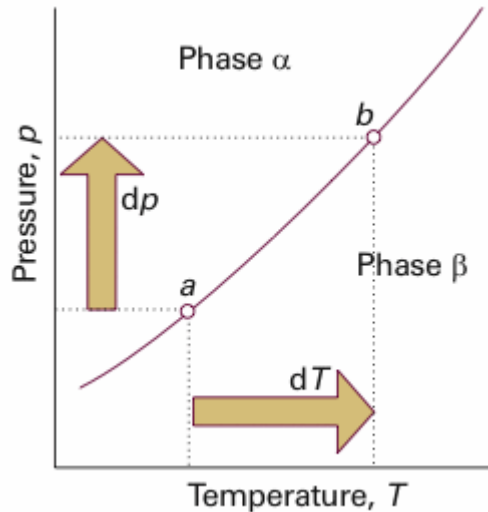


Consider a pure liquid A in equilibrium with its own vapor A. At equilibrium,  $G_m$  of A should be the same for liquid and gas. Therefore, we define the  $G_m$  of pure liquid A as:

$$G_{m,A}^*(l) = G_{m,A}^0(g) + RT \ln(p_A^* / p^0)$$

$p_A^*$  = vapor pressure of pure A(liq)

# Phase boundaries



$$\begin{aligned}\Delta G_{\text{vap}} &= G_m(g, P) - G_m(l, p) = \{G_m^\circ(g, P) + RT \ln(P/P^\circ)\} - G_m^\circ(l, p) \\ &= G_m^\circ(g, P) - G_m^\circ(l, p) + RT \ln(P/P^\circ) \\ &= \Delta G_{\text{vap}}^\circ + RT \ln(P/P^\circ)\end{aligned}$$

At equilibrium,  $\Delta G_{\text{vap}} = 0$ ;  $\Delta G_{\text{vap}}^\circ = -RT \ln(P/P^\circ)$

Therefore,  $\ln(P/P^\circ) = -\Delta G_{\text{vap}}^\circ / RT$ ,

where  $\Delta G_{\text{vap}}^\circ = \Delta H_{\text{vap}}^\circ - T \Delta S_{\text{vap}}^\circ$

$$\ln(P/P^\circ) = -\Delta H_{\text{vap}}^\circ / RT - \Delta S_{\text{vap}}^\circ / R$$

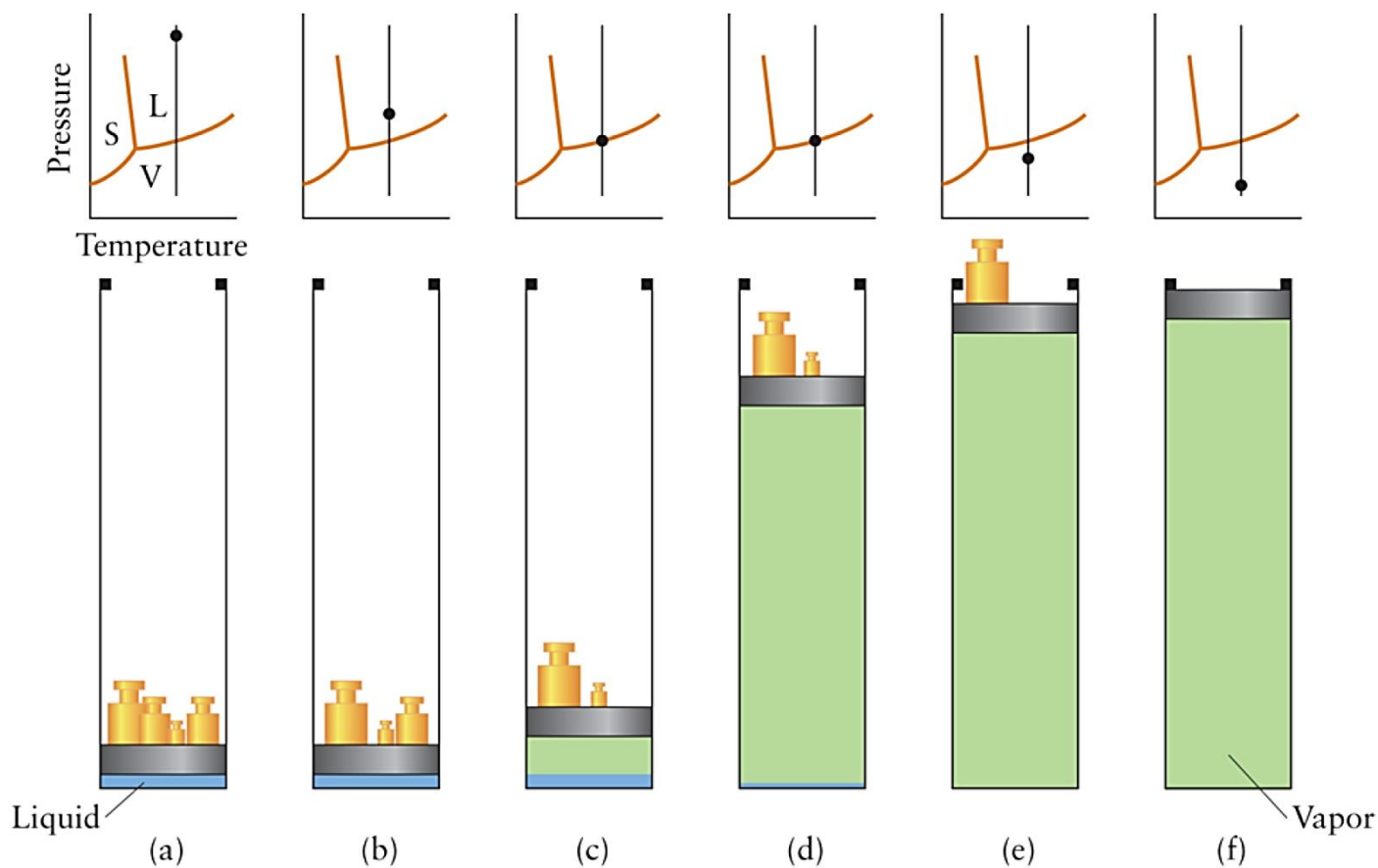
For the transition from  $T_1, P_1$  to  $T_2, P_2$ ,

$$\ln(P_1/P^\circ) = -\Delta H_{\text{vap}}^\circ / RT_1 - \Delta S_{\text{vap}}^\circ / R$$

$$\ln(P_2/P^\circ) = -\Delta H_{\text{vap}}^\circ / RT_2 - \Delta S_{\text{vap}}^\circ / R$$

$$\ln(P_1/P^\circ) - \ln(P_2/P^\circ) = -\Delta H_{\text{vap}}^\circ / RT_1 + \Delta H_{\text{vap}}^\circ / RT_2$$

**Clausius-Clapeyron Equation:** Vapor pressure for a liquid at two different temperature



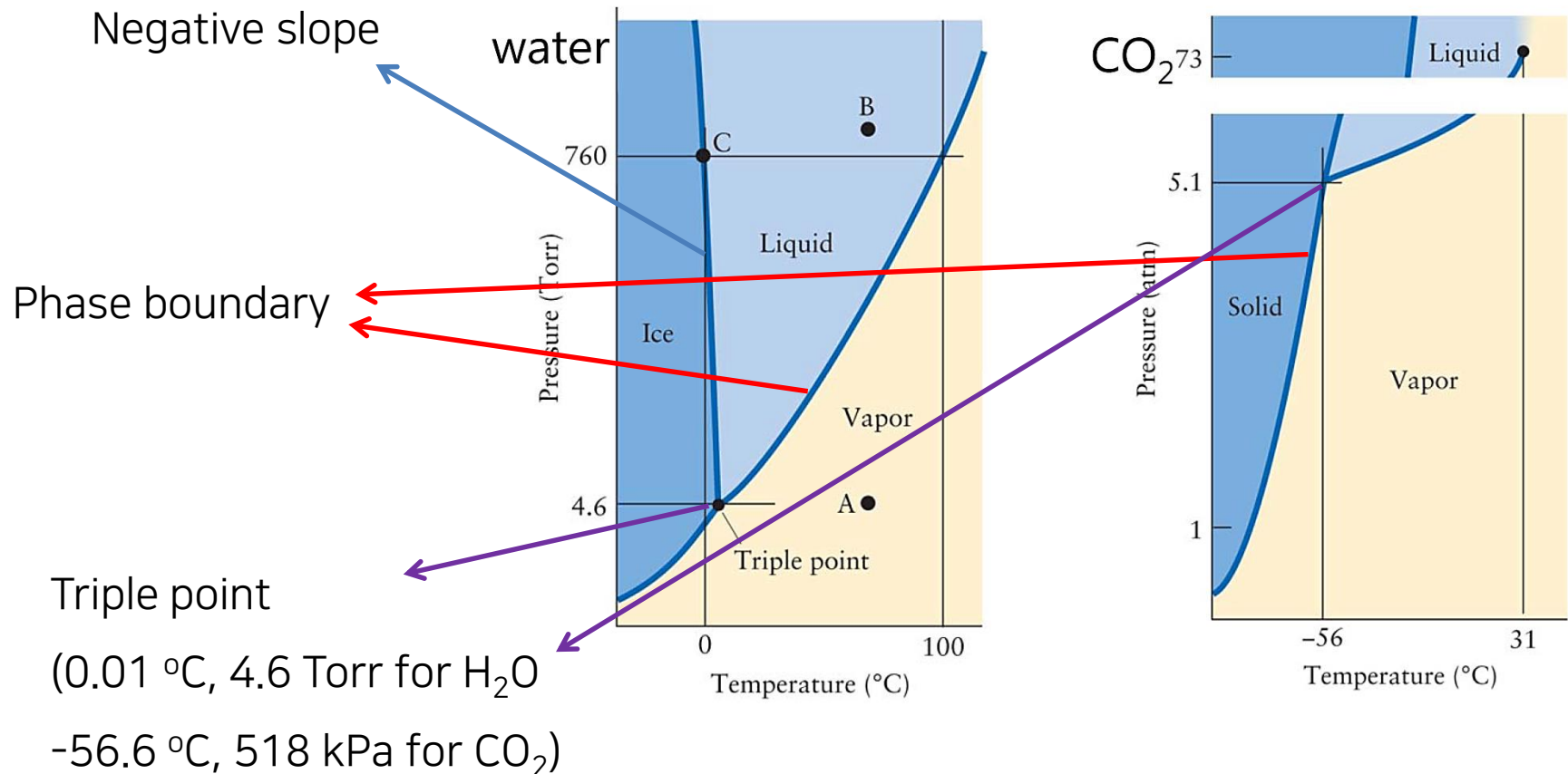
**FIGURE 9.11** The changes undergone by a liquid as its pressure is decreased at constant temperature. The large dot on the vertical line in the phase diagram traces the path taken by the system, which is described in the text. The blue region in the container is the liquid and the light green region above it is the vapor.

## 9.5. Freezing and Melting

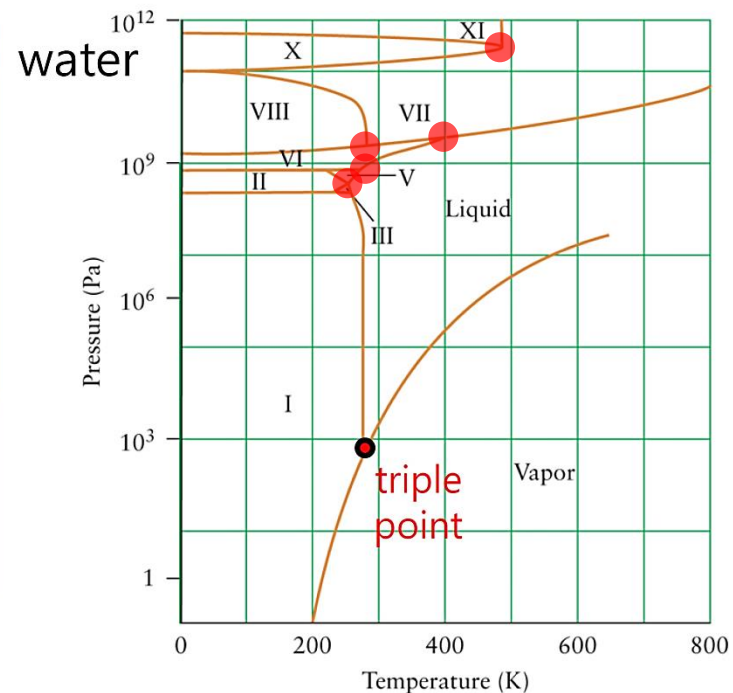
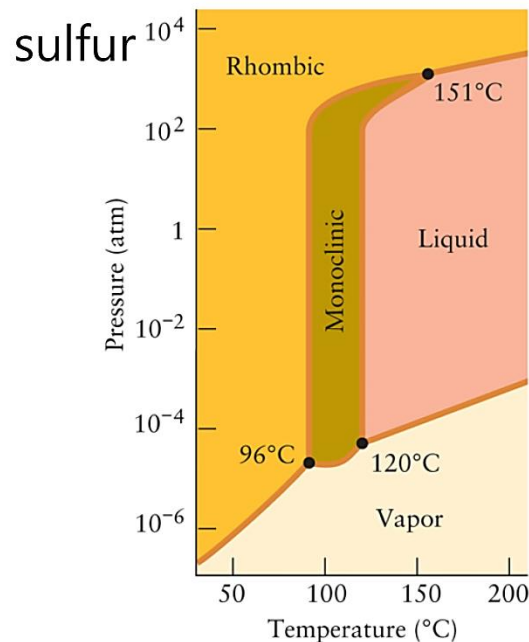
- Freezing (melting): solidification of a liquid (liquidation of a solid)
- Freezing (melting) point: T at which liquid freeze (solid melts)
- Normal freezing point: T at which solid begins to freeze at 1 atm
- Pressure dependence of the freezing point  
:  $T_f$  increases with pressure for most substances (exception:  $H_2O$  etc)

## 9.6. Phase Diagram

- **Phase diagram:** a map that shows which phase is the most stable at certain pressures and temperatures

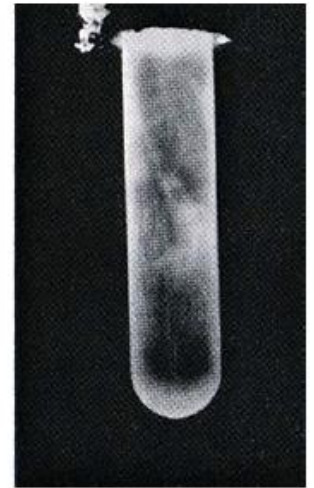
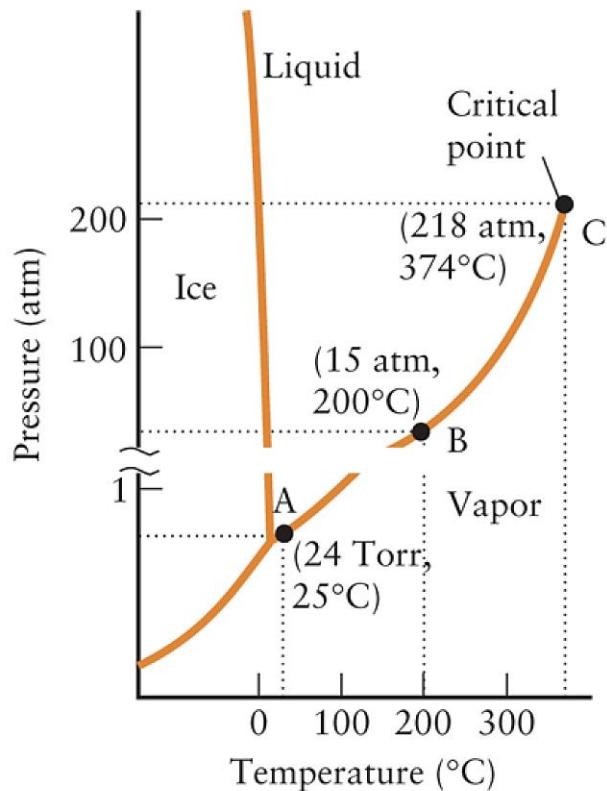


- **Phase boundary:** curves separating region on a phase diagram  
 → Represents a set of P and T values for which *2 phases coexist in dynamic equilibrium*
- **Triple point:** point where three phase boundaries intersect  
 → **a single value of P and T** for which *3 phases coexist in dynamic equilibrium*

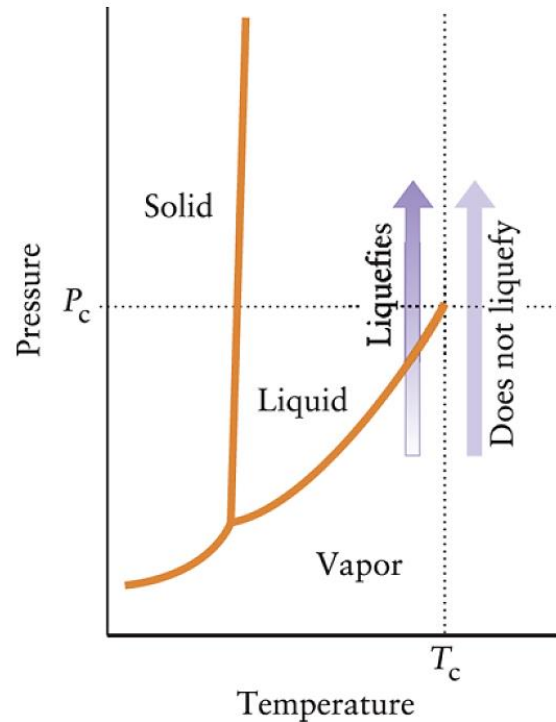


## 9.7. Critical Properties

- **Critical Point:** terminus of liquid-gas phase boundary
- Above the  $T_c$ , a gas cannot be liquefied by pressure.
- Super critical fluid: substance above its  $T_c$  and  $P_c$



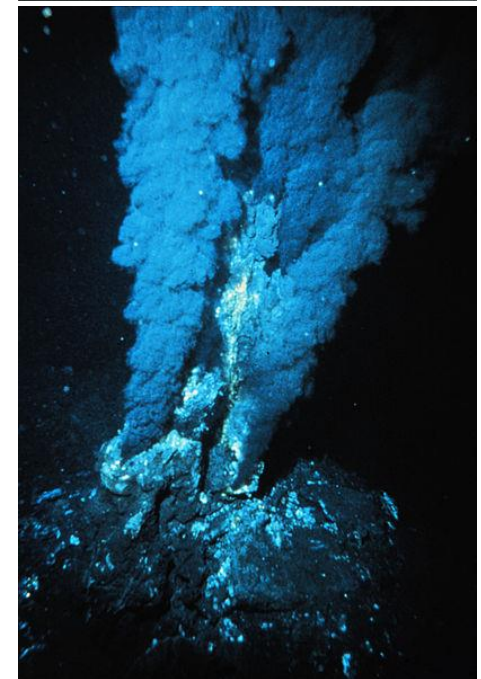
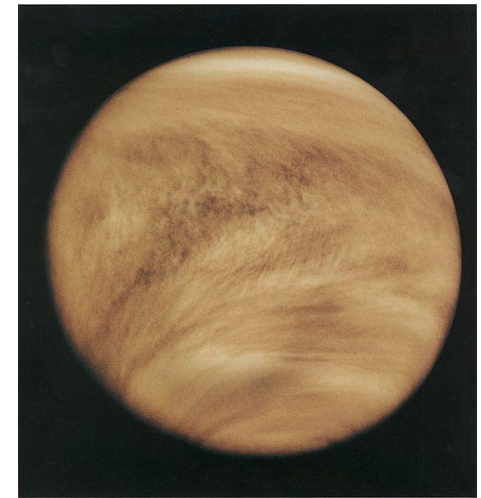
## - Supercritical region and supercritical fluid



Substance	Critical temperature (°C)	Critical pressure (atm)
He	-268 (5.2 K)	2.3
Ne	-229	27
Ar	-123	48
Kr	-64	54
Xe	17	58
H <sub>2</sub>	-240	13
O <sub>2</sub>	-118	50
H <sub>2</sub> O	374	218
N <sub>2</sub>	-147	34
NH <sub>3</sub>	132	111
CO <sub>2</sub>	31	73
CH <sub>4</sub>	-83	46
C <sub>6</sub> H <sub>6</sub>	289	49

### Comparison of Gases, Supercritical Fluids and Liquids

	Density (kg/m <sup>3</sup> )	Viscosity (μPa·s)	Diffusivity (mm <sup>2</sup> /s)
<b>Gases</b>	1	10	1–10
<b>Supercritical Fluids</b>	100–1000	50–100	0.01–0.1
<b>Liquids</b>	1000	500–1000	0.001

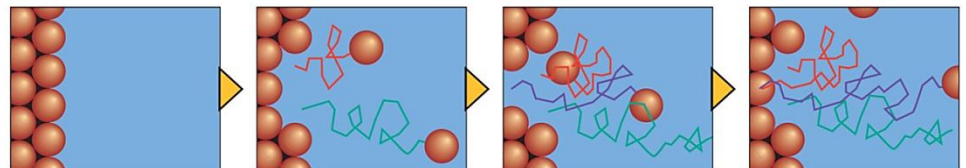
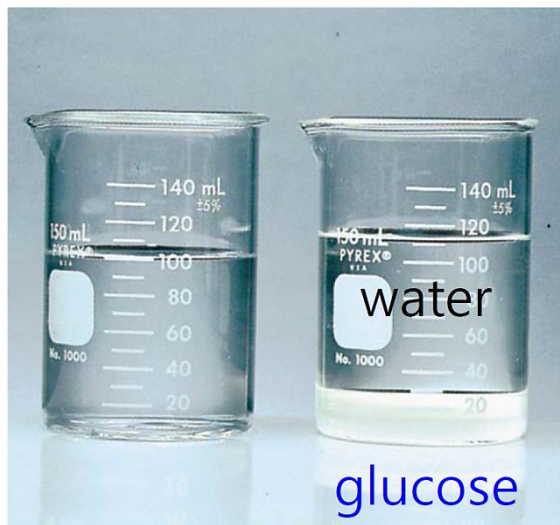




# Solubility

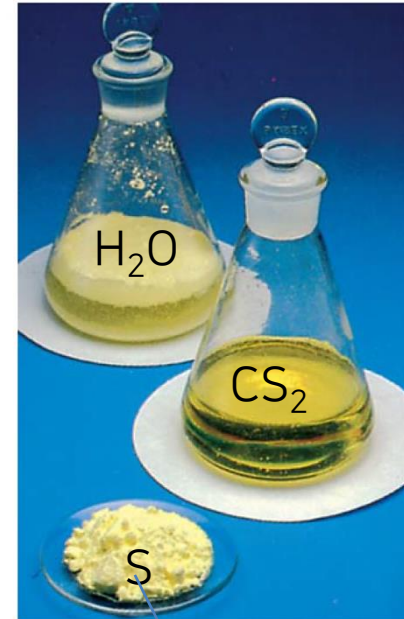
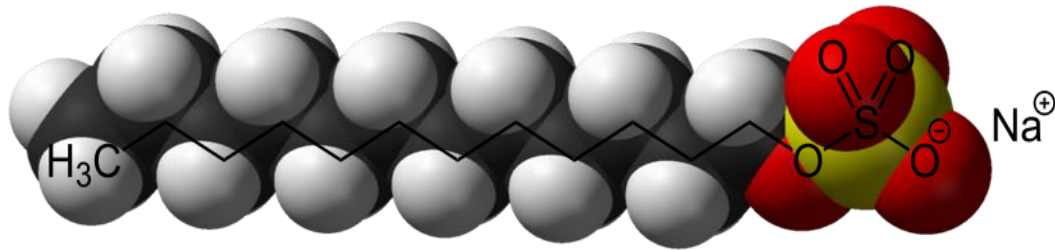
## 9.8. The Limits of Solubility

- Interactions in solutions
  - : solvent-solvent, solute-solute and solute-solvent
- solubility
- Saturated solution → dynamic equilibrium between the dissolved and undissolved solute

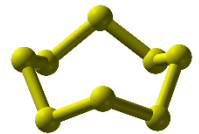


## 9.9. The Like-Dissolves-Like Rule

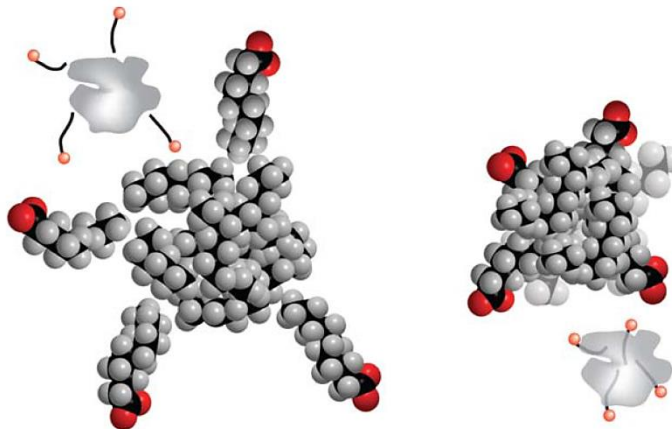
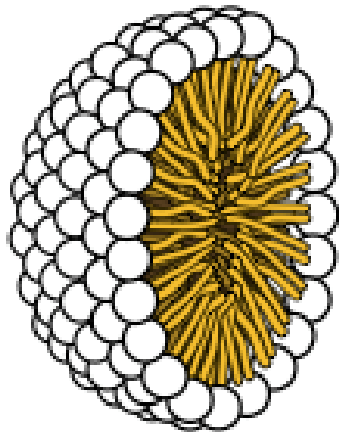
- like-dissolves-like rule
- Hydrophilic vs. hydrophobic
- Soap and surfactant → amphiphilic



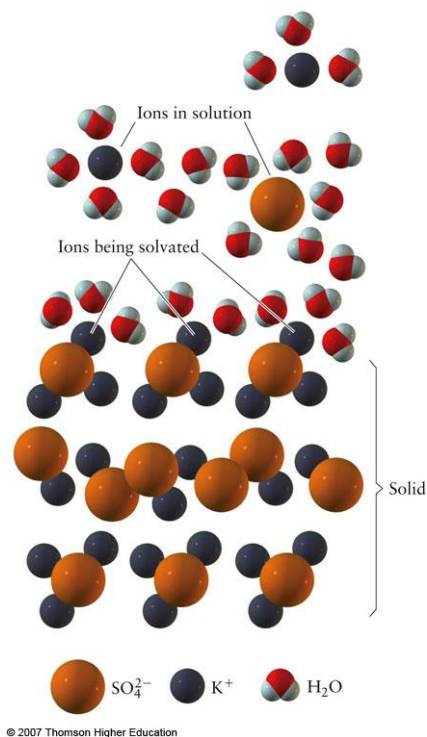
$S_8$



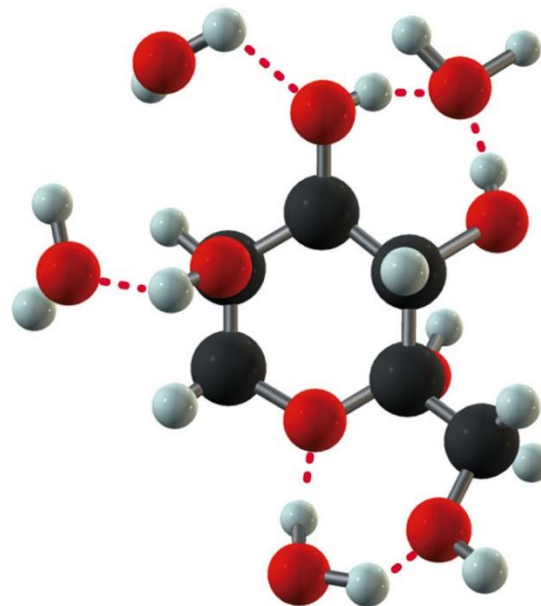
Micelle  
structure



# What kind of molecule can be dissolved in water?



Ions: charge-dipole interaction



H-bonding with water

→ Polar solvent dissolves polar solutes.

→ Non-polar solvent dissolves non-polar solutes.

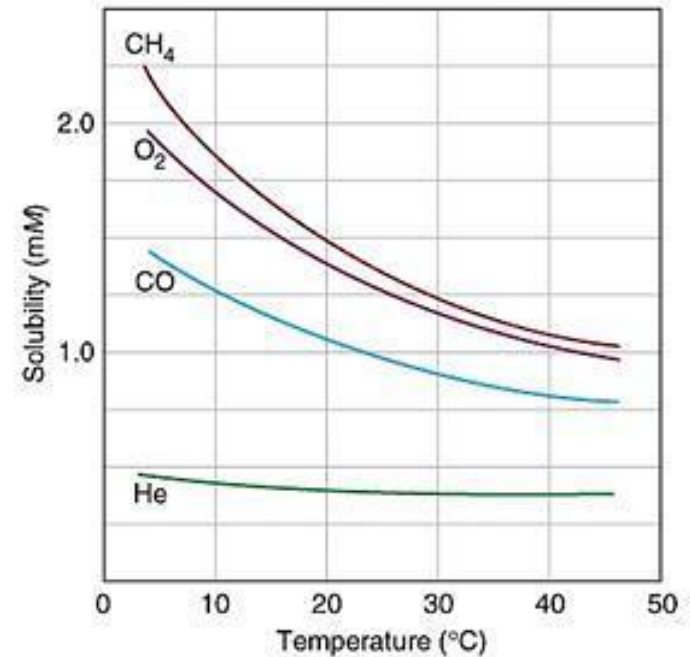
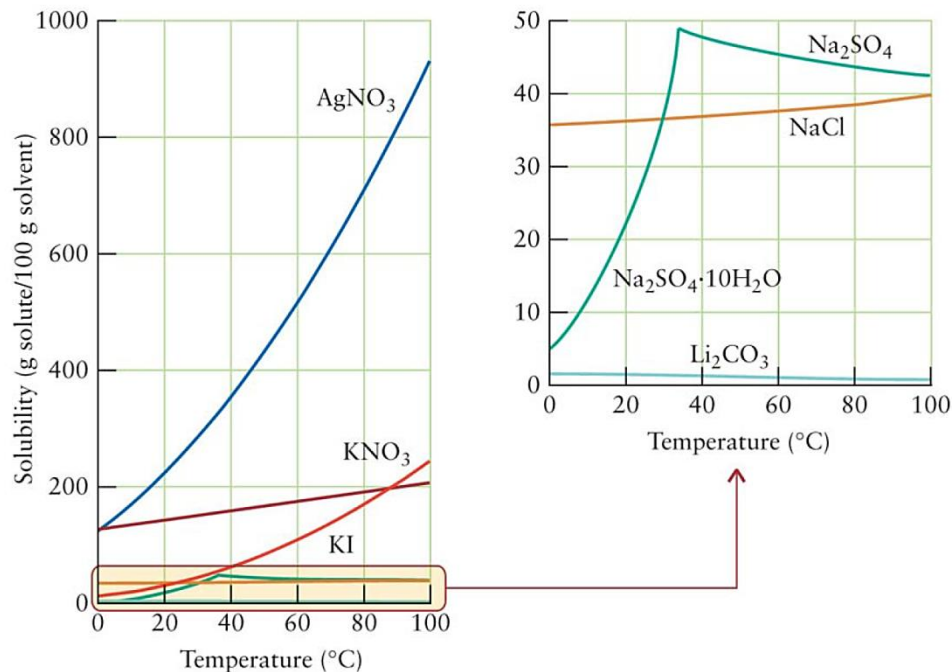
## 9.10. Trend of Solubility

- Dependence of molar solubility on

Solid and liquid solute: solubility usually increases with T

Gaseous solute: usually decreased with T increase

Many exceptions

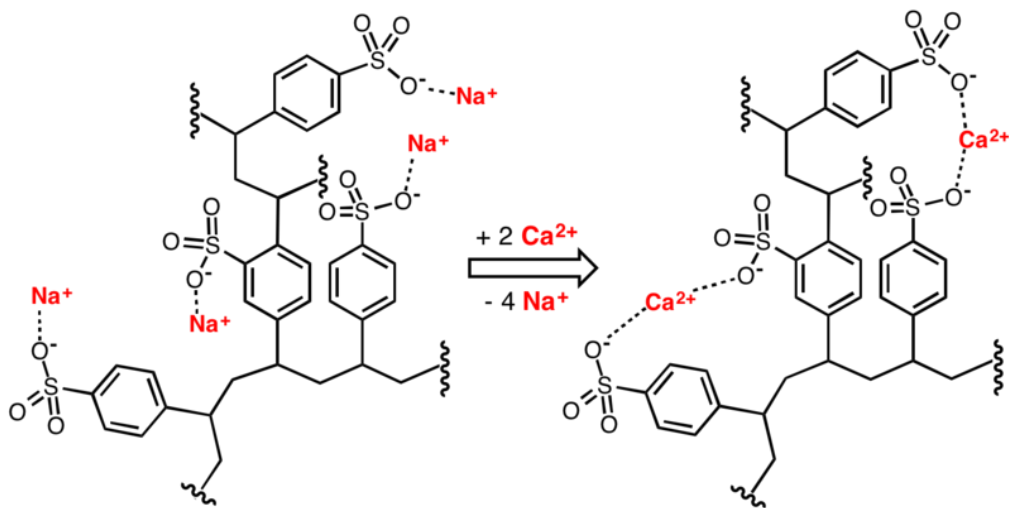
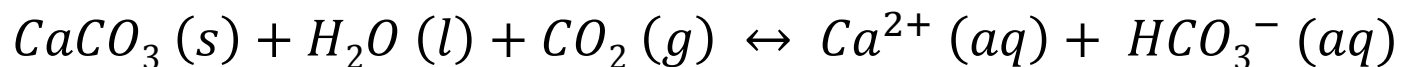


Dependence of solubility on ionic sizes and charges

Ex) (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>), (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>)

(NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>)

Hard and soft water

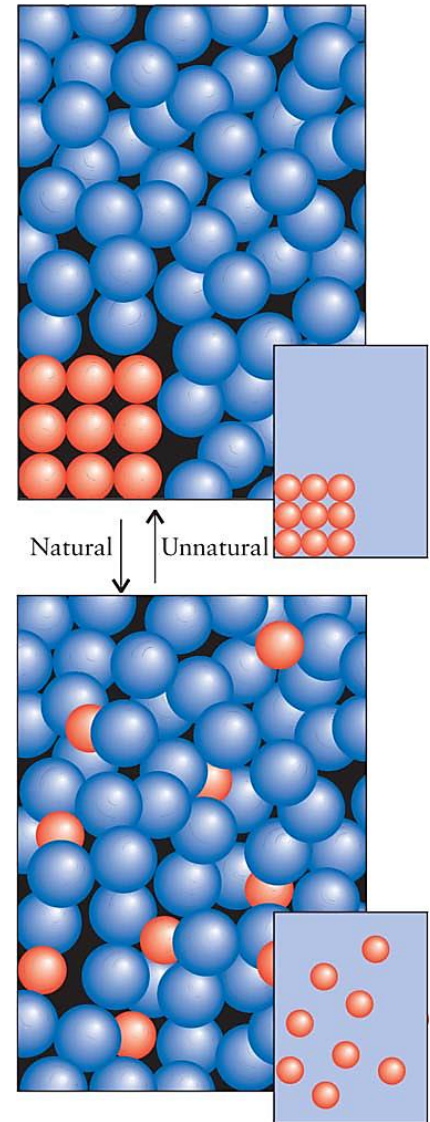


# 9.11. The Gibbs Free Energy of Solution

- Gibbs Free Energy of solution

$$\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol}$$

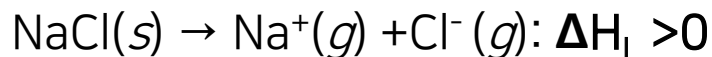
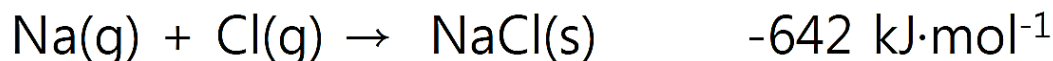
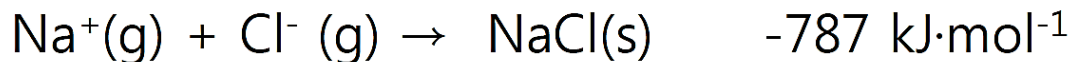
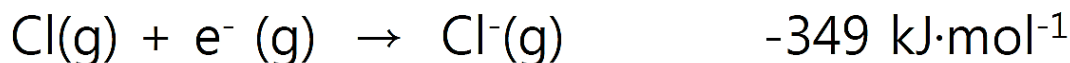
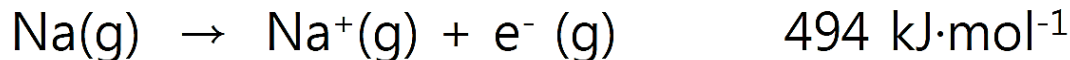
- $\Delta H_{sol} < 0 \rightarrow$  generally soluble
- $\Delta H_{sol} > 0 \rightarrow$  soluble with highly positive  $\Delta S_{sol}$
- For gaseous solutes,  $\Delta S_{sol} < 0$



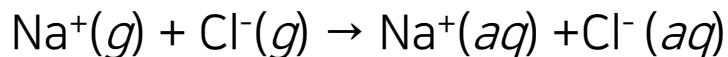
$$\Delta H_{\text{sol}} \text{ Enthalpy of solution} = \Delta H_{\text{L}} + \Delta H_{\text{hydration}}$$

- Interaction of solute-solvent, solute-solute, and solvent-solvent
- Limiting enthalpy of solution: only for **diluted** solution, where only **solute-solvent** but not solute-solute needs to be considered.

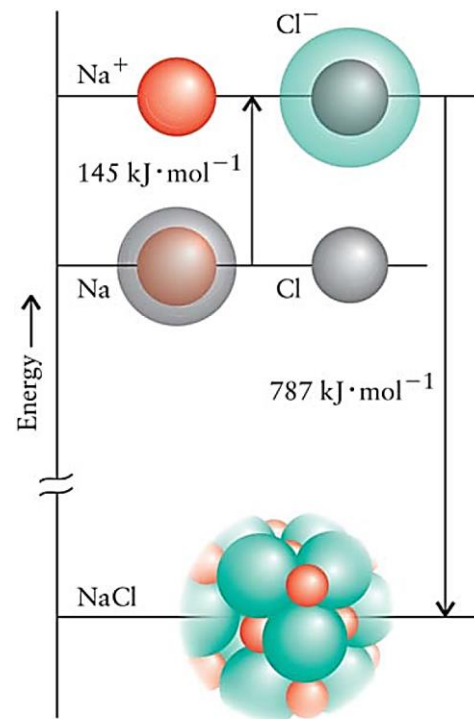
### A. Lattice energy: $\Delta H_{\text{L}}$ (In chapter 2)



### B. Enthalpy of hydration: $\Delta H_{\text{hydration}}$



- Formation of ion-dipole interaction: exothermic:  $\Delta H_{\text{hydration}} < 0$





# Colligative Properties

## 9.12. Molality

- Units of concentration
- Mole fraction – solute mol/total mol (solute+solvent)
- Molality, *b* or *m* = **solute mole/solvent mass (mol/kg)**
- Molality: independent of temperature!

### Example 1

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

### Example 2

Find the molality of sucrose,  $C_{12}H_{22}O_{11}$  in 1.06 M aqueous solution, which is known to have density 1.14 g/ml.



# Physical properties of solutions:

-how do they differ from neat liquids?

Solvent (A) and solute (B): when adding nonvolatile B-solute into pure solvent A,

- Vapor pressure is reduced.
  - Boiling point is elevated.
  - Freezing point is depressed.
- Osmotic pressure

## 9.13. Vapor-Pressure ( $P^{\text{sat}}$ ) Lowering

### - Colligative Properties

: The properties depend on the relative amounts of solvent and solute, and not on their types nor chemical natures

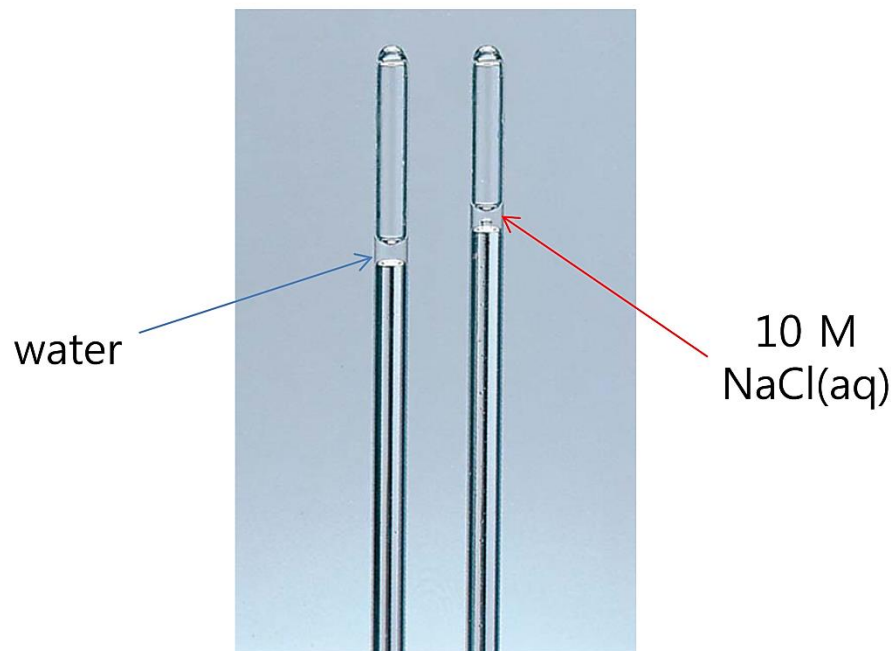
### 1. Vapor pressure lowering

#### Raoult's Law

$$P_{\text{solv}}^{\text{sat}} = x_{\text{solv}} \cdot P_{\text{pure}}^{\text{sat}}$$

$x_{\text{solv}}$ : mole fraction of solvent

\* Corresponds to dilute solutions



## 9.13. Vapor-Pressure ( $P^{\text{sat}}$ ) Lowering

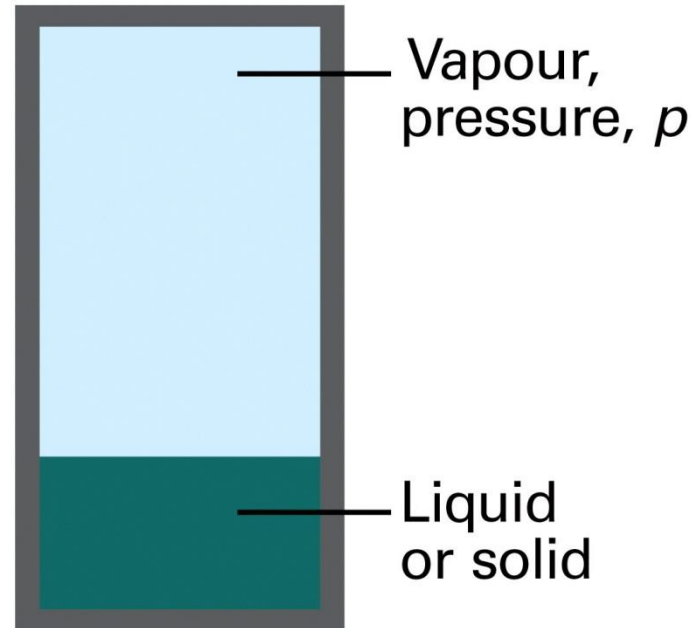
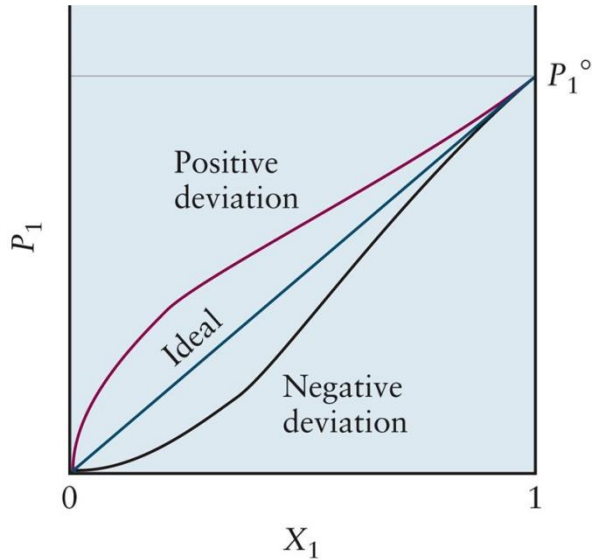


Figure 4-2  
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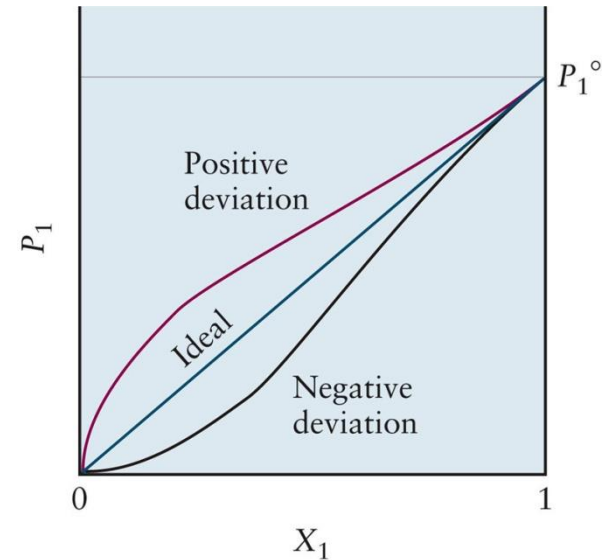
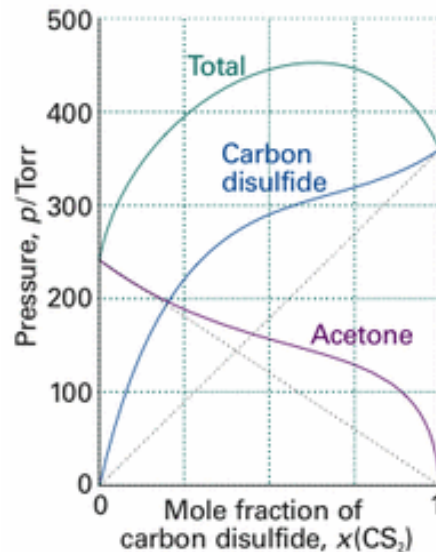
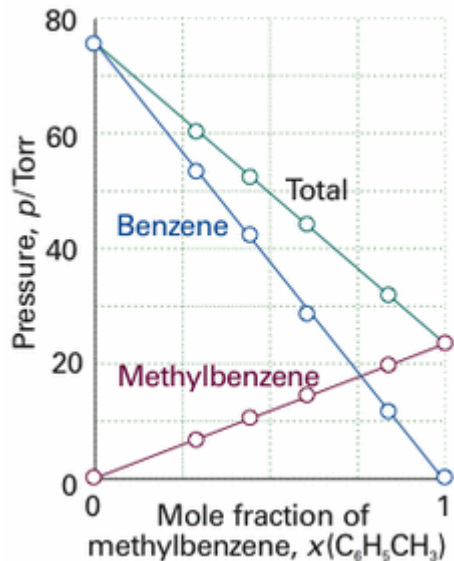
Solutions that obey Raoult's law:  
→ ideal solution

$$G_m(P) = G_m^o + RT \ln \left( \frac{P}{P_0} \right)$$

# Raults Law for volatile A and B:

$$P_A = \frac{n_A}{n_A + n_B} P_A^* = x_A P_A^* \quad P_B = \frac{n_B}{n_A + n_B} P_B^* = x_B P_B^*$$

$$P_{TOT} = x_A P_A^* + x_B P_B^* = x_A P_A^* + (1 - x_A) P_B^*$$



# $T_b$ Elevation and $T_f$ Depression

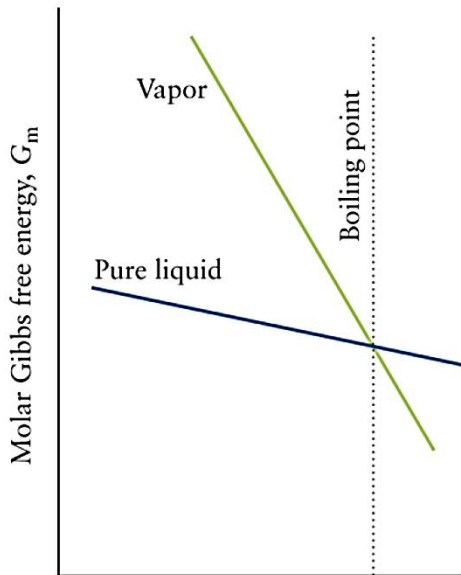
## 2. Boiling point elevation

- Because of the lowering  $P^{\text{sat}}$
- Quantitatively,

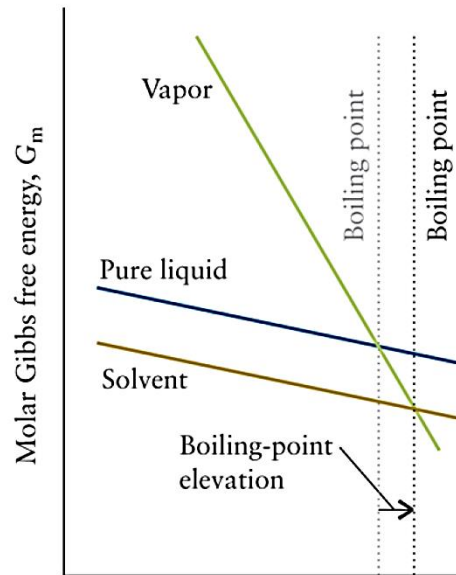
$$\Delta T_b = k_b \cdot b_{\text{solute}}$$

$k_b$ : boiling-point constant

$b_{\text{solute}}$ : molality of solute



(a) Temperature,  $T \longrightarrow$



(b) Temperature,  $T \longrightarrow$

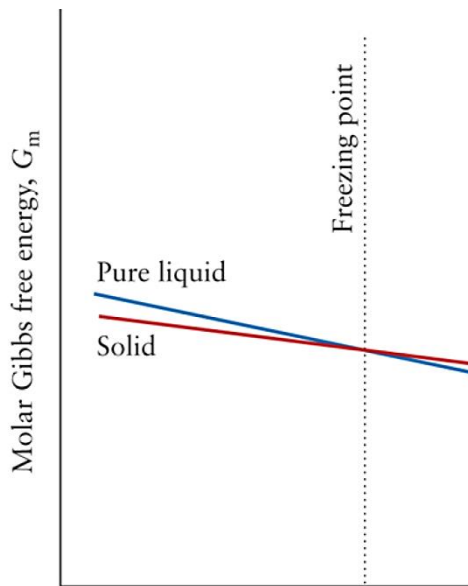
### 3. Freezing point depression

- River vs sea
- Quantitatively,

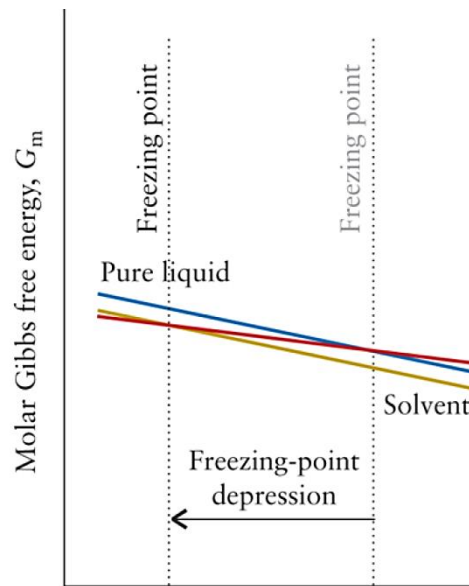
$$\Delta T_f = k_f \cdot b_{\text{solute}}$$

$k_f$ : freezing-point constant

$b_{\text{solute}}$ : molality of solute



(a) Temperature,  $T$



(b) Temperature,  $T$

Solvent	Freezing point (°C)	$k_f$ (K·kg·mol <sup>-1</sup> )	Boiling point (°C)	$k_b$ (K·kg·mol <sup>-1</sup> )
acetone	-95.35	2.40	56.2	1.71
benzene	5.5	5.12	80.1	2.53
camphor	179.8	39.7	204	5.61
carbon tetrachloride	-23	29.8	76.5	4.95
cyclohexane	6.5	20.1	80.7	2.79
naphthalene	80.5	6.94	217.7	5.80
phenol	43	7.27	182	3.04
water	0	1.86	100.0	0.51

## Example

$$\Delta T_f = k_f \cdot b_{solute}$$

The addition of 0.24 g of sulfur to 100 g of the solvent CCl<sub>4</sub> lowers the solvent's T<sub>f</sub> by 0.28 °C. Sulfur is known to exist in molecular form. What is the molar mass and molecular formula of sulfur?

# van't Hoff factor

$$\Delta T_b = i K_b \times \text{molality of solute}$$

$K_b$ ; boiling point constant of the solvent

$$\Delta T_f = -i K_f \times \text{molality of solute}$$

$K_f$ ; freezing point constant of the solvent

$i$ ; van't Hoff factor = # of dissolved species

For a dilute solution ( $< 10^{-3}$  M);  $i(\text{NaCl}) = 2$ ;  $\text{Na}^+ + \text{Cl}^-$

$i(\text{CaCl}_2) = 3$ ;  $\text{Ca}^{2+} + 2 \text{Cl}^-$

HCl in benzene;  $i = 1$ , HCl in water;  $i = 2$

Weak acid HA dissociating 5%,  $i = 0.95 + (0.05 \times 2) = 1.05$

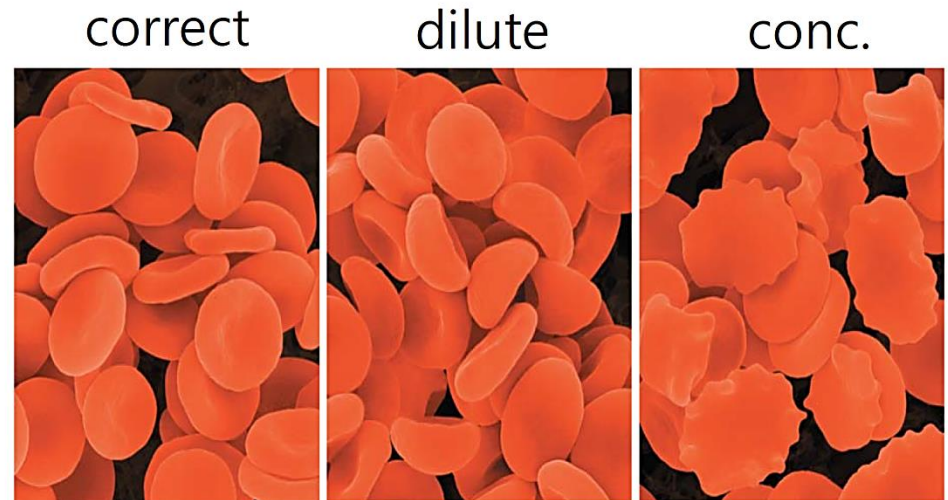
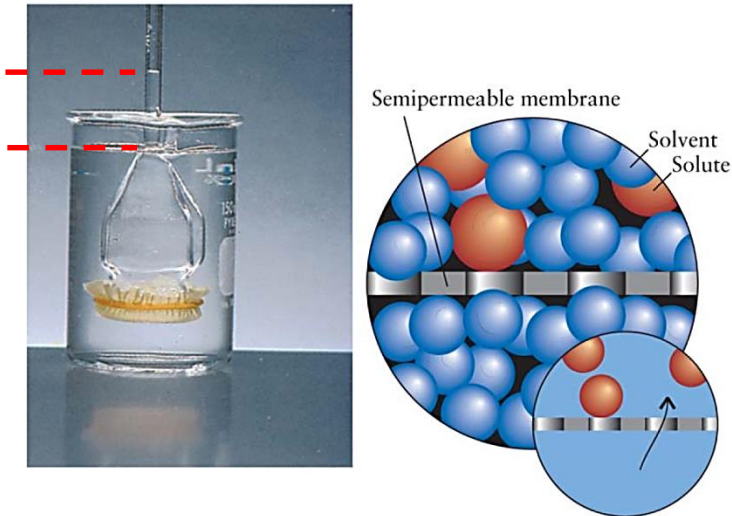


# 9.15. Osmosis

## 4. Osmosis

: the flow of solvent through a membrane into a more concentrated solution (*spontaneous process*)

- Semipermeable membrane: a membrane that permits only certain types of molecules or ions to pass through



Red blood cells

- Osmotic Pressure ( $\Pi$ )

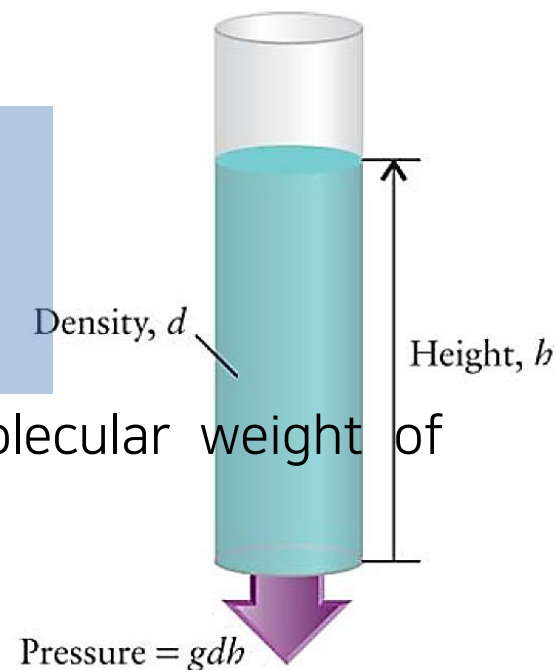
- Quantitatively,

$$\Pi = RT \cdot c_{\text{solute}}$$

$\Pi$ : osmotic pressure

$c_{\text{solute}}$ : **molarity** of solute

- Osmometry: A technique to measure the molecular weight of solute.

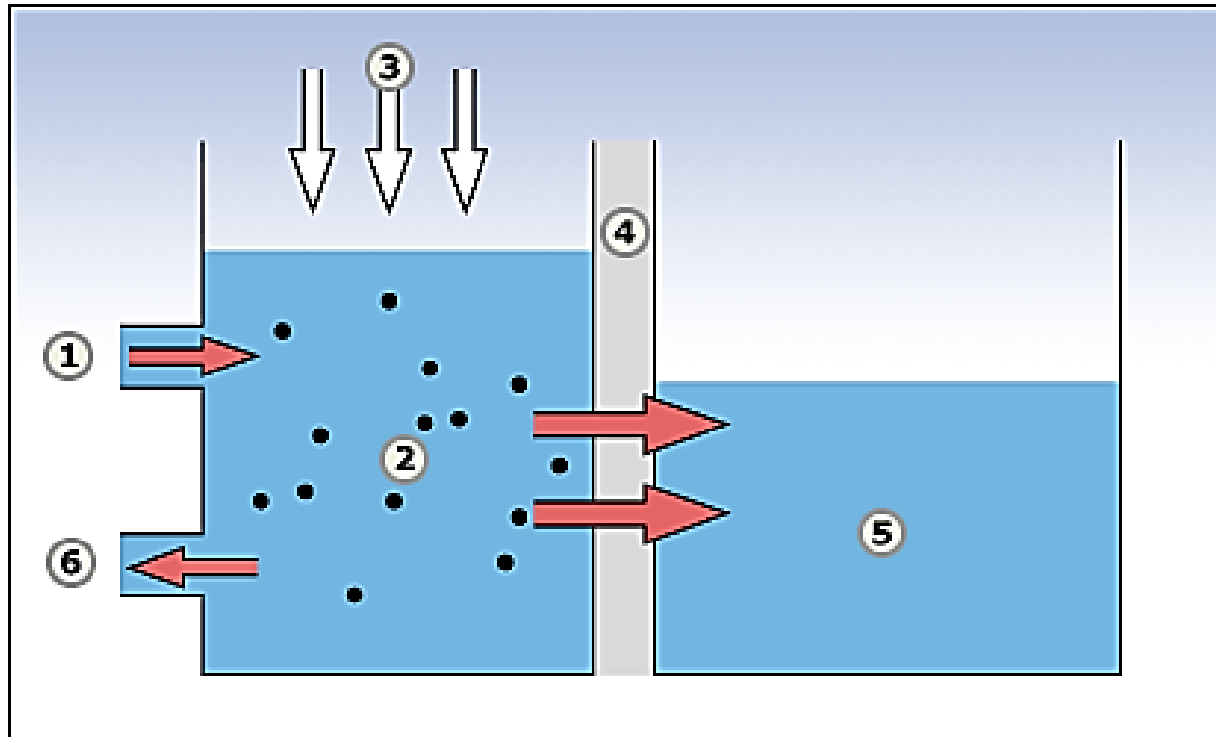


### Example 9.10

The Osmotic Pressure due to 2.20 g of polyethylene dissolved in enough benzene to produce 100 ml of solution was 0.0110 atm at 298 K. Calculate the average molar mass of the polymer, which is a nonelectrolyte.

## Reverse Osmosis

Pressure larger than osmotic power;  
Increase the velocity of solvent leaving solution



## 9.16. Colloids

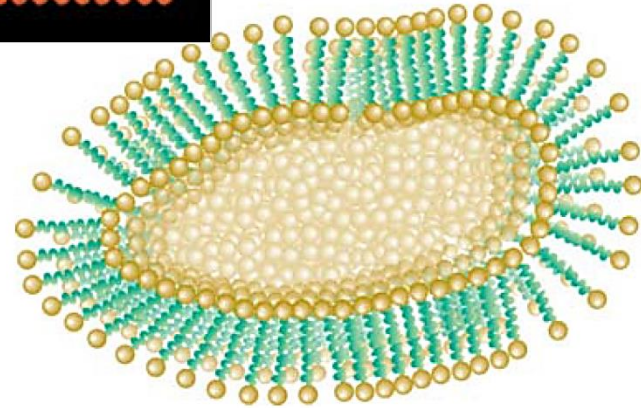
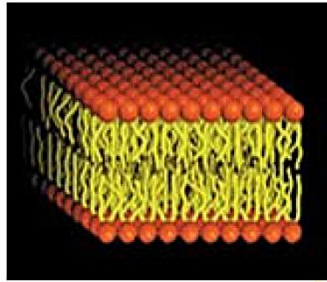
- **colloid**: a dispersion of large particles from 1 nm to 1  $\mu\text{m}$
- Properties between homogeneous solution and heterogeneous mixture

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

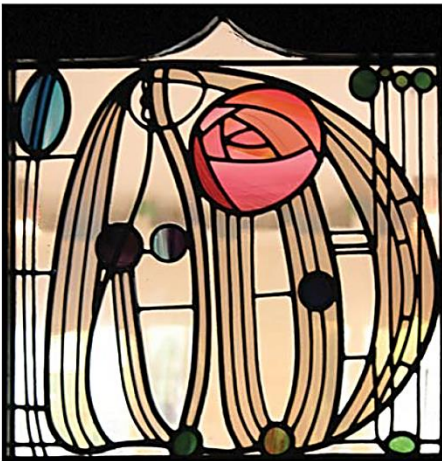
\*Based on R. J. Hunter, *Foundations of Colloid Science*, Vol. 1 (Oxford: Oxford University Press, 1987).



laser beams through misty environments



lipid bilayers forming a 2D colloidal structure



colors of stained glass by colloidal particles



stable dispersion of metallic gold colloids