VI) Factors Affecting Solubility

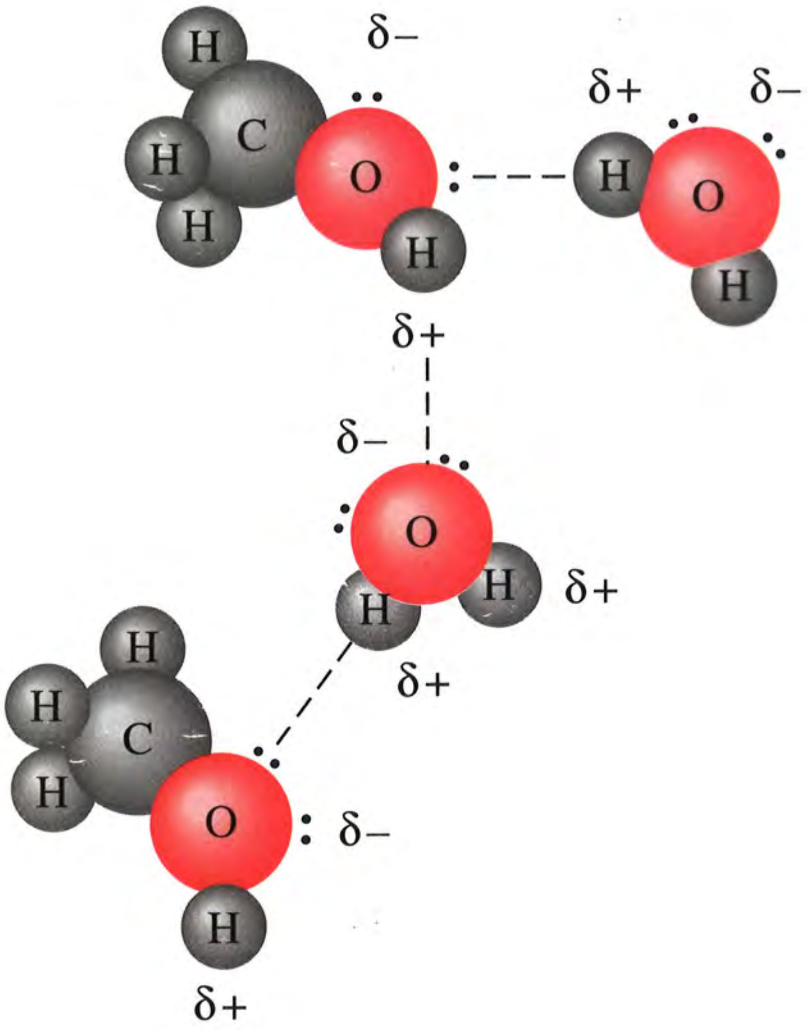
A) Nature of Solute & Solvent

Solute & solvent must possess similar I.A.F.

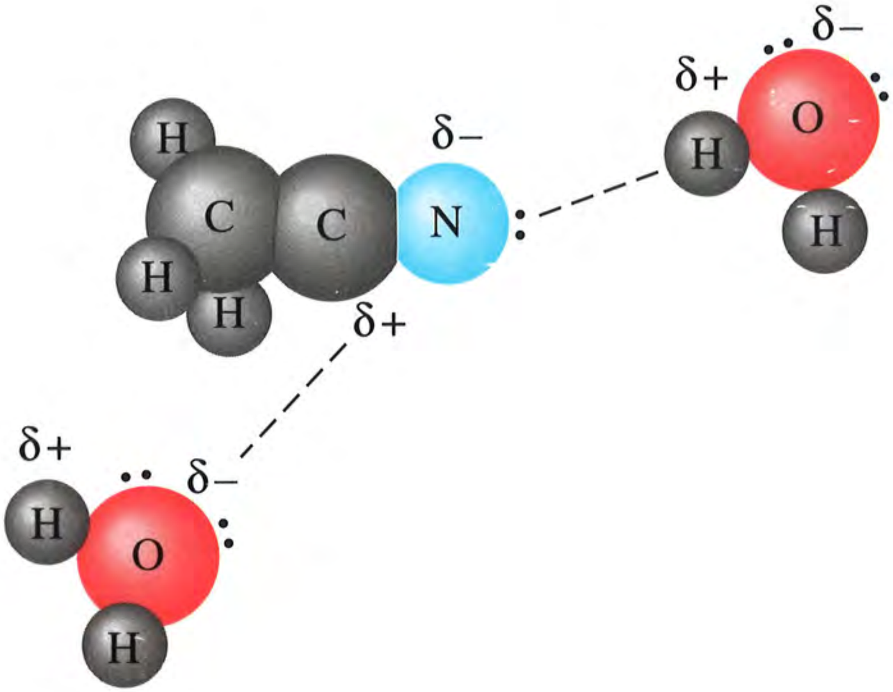
"Like Dissolves Like"

Polar Solvents (H_2O, C_2H_5OH, etc.) dissolve polar & ionic solutes (NH_3, $NaCl$, C_2H_5OH, etc.)

Nonpolar Solvents (CCl_4, C_6H_6, etc.) dissolve nonpolar solutes (grease, fats, oils, hydrocarbons)



(a)



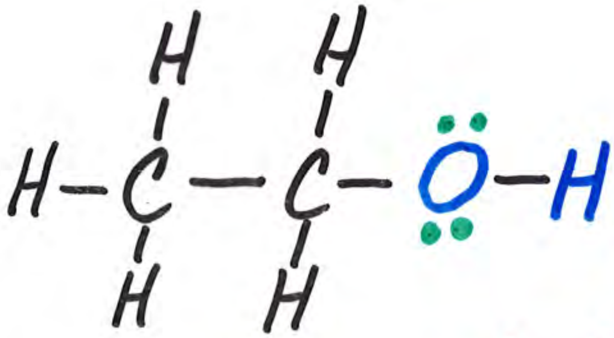
(b)

1) Ex 1: Which is **more** soluble in H_2O; ethanol (C_2H_5OH) or hexane (C_6H_{14}).

H_2O : L.F., D-D, H-bonding

Polar solvent

Ethanol :



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & \ddot{\underset{\cdot\cdot}{O}} & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

L.F., D-D, H-bonding

Polar solute

Hexane : C_6H_{14}

L.F.

Nonpolar solute

2) Ex2: I have a test tube containing a H_2O layer & a hexane (C_6H_{14}) layer. In which layer(s) will I_2 & $CuCl_2$ dissolve?

B) Pressure Effects

Mainly effects solubility of gases

gas + liquid $\rightleftharpoons$ soln.

Dynamic Equil.

What happens if P inc. ?

Le Chatelier's Principle

Apply a "stress" (change in T, P, C) to a system at equil. the system shifts to a new position of equil. to minimize the "stress".

stress : Inc. P

counteract : wants to reduce P

force gas molecules into soln.

- shifts to right

result : Inc. solubility

Inc. P , Inc. solubility

- True for ALL gases

1) Henry's Law

$$\boxed{S_g = k_H P_g}$$

$$\frac{S_2}{S_1} = \frac{P_2}{P_1}$$

c) Temperature Effects

1) Gases

ALL gases dissolve in H_2O w. evolution of heat

$$\text{gas} + H_2O \rightleftharpoons \text{soln.} + \text{heat}$$

Inc. T , Dec. solubility

2) Solids

For most ionic solids:

$$\text{solid} + H_2O + \text{heat} \rightleftharpoons \text{soln.}$$

Inc. T , Inc. solubility

Are exceptions

Fig. 13.15 Solubilities of Several Gases in Water

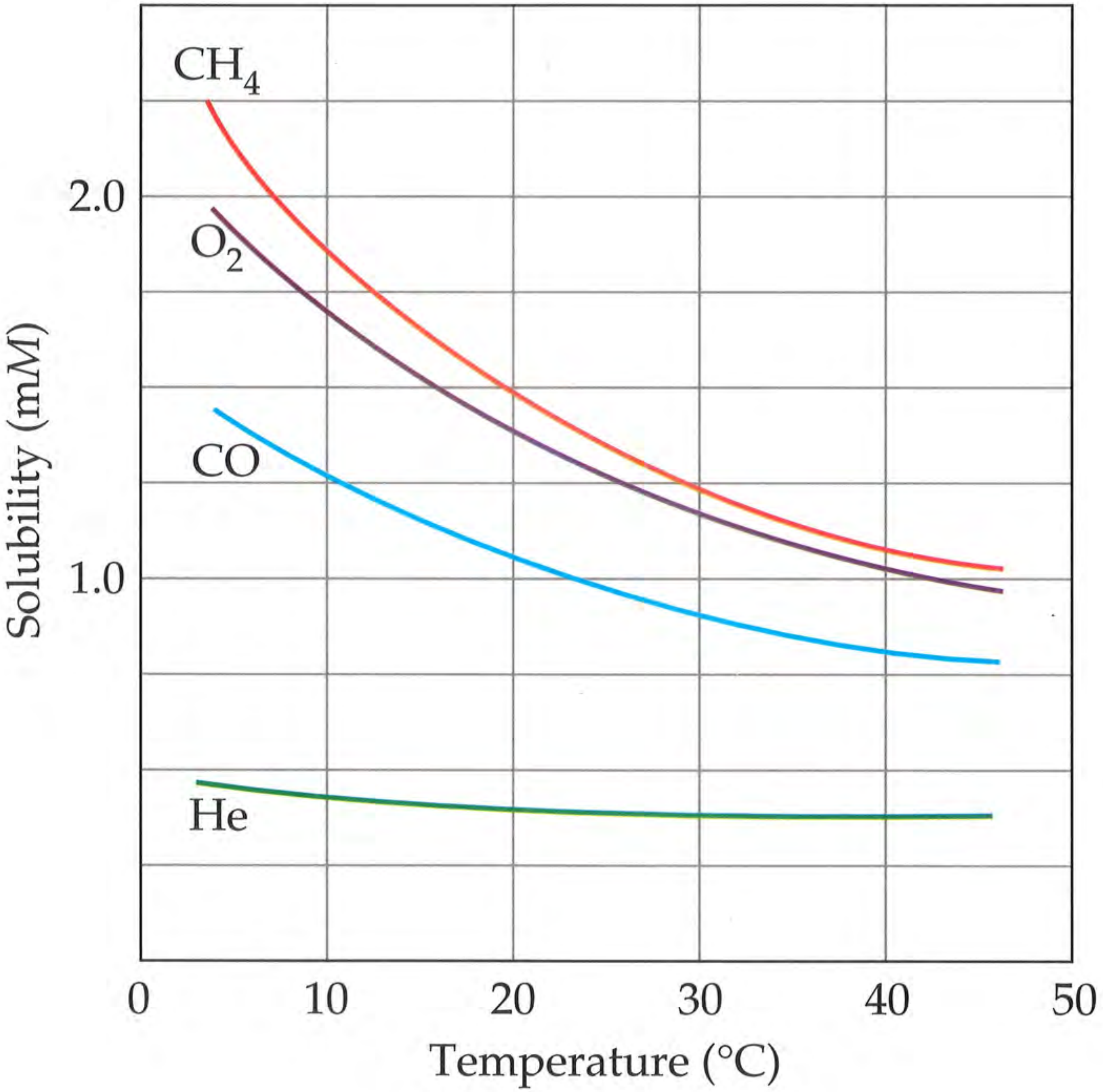


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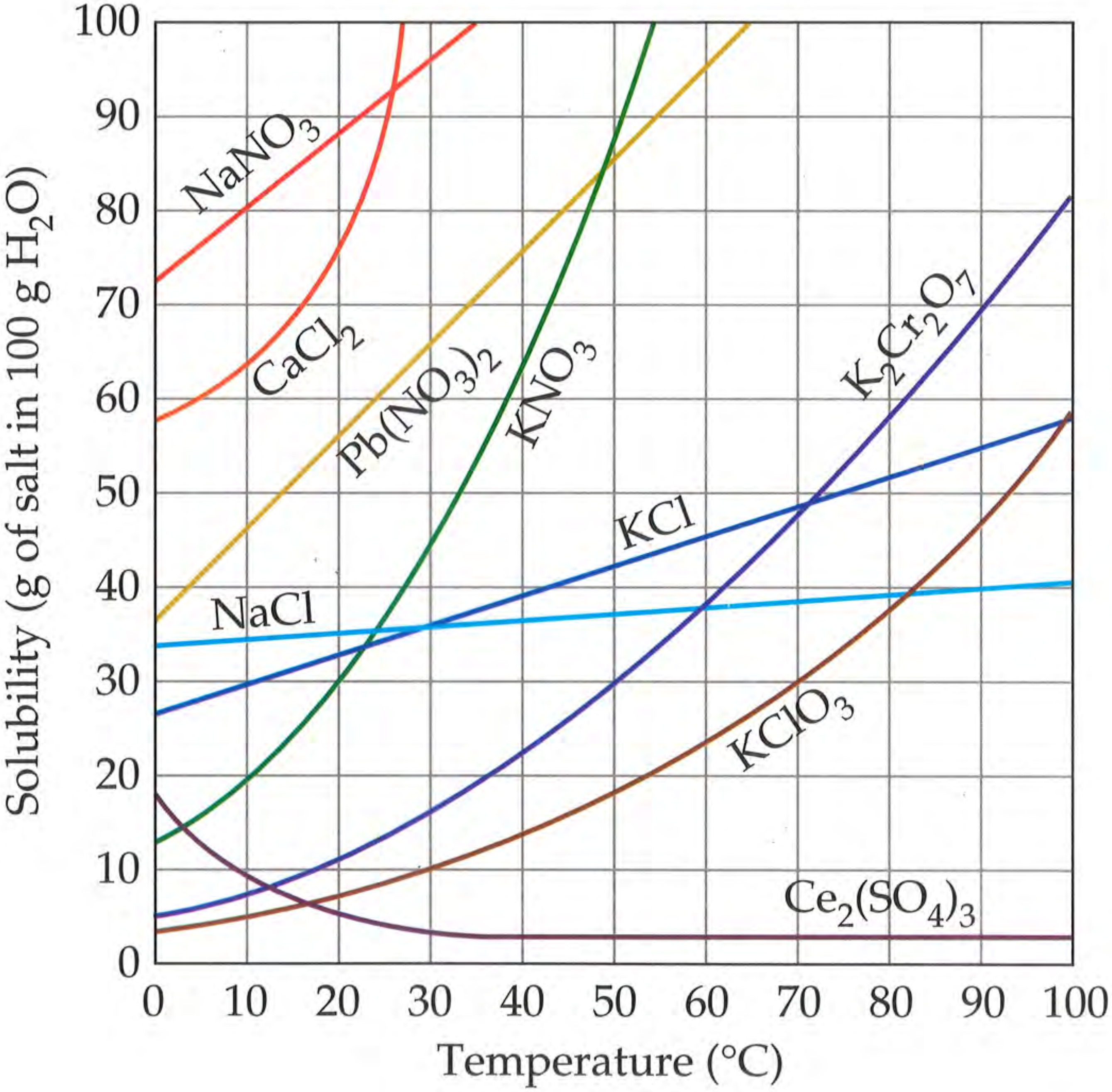
Fig. 13.14 Solubilities of Several Ionic Solids



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VII) Colligative Properties

Prop. of a soln. that depend only on number of solute particles (conc.) & NOT on their identity

A) Vapor Pressure Lowering

1) Nonvolatile solutes

V.P. above soln. due only to solvent

Replace some solvent molecules at surface w. solute molecules

fewer solvent molec.
escape into gas phase
than for pure solvent

$\therefore$ Lower V.P.

greater solute conc. $\Longrightarrow$ greater dec. V.P.

NOT dependent on type of particle

1 M sugar soln. $\equiv$ 0.5 M NaCl soln

a) Raoult's Law

For volatile substance

$$\boxed{P_A = \chi_{A_\ell} P_A^\circ}$$

P_A = V.P. of A above soln

χ_{A_ℓ} = mole fraction of A in liquid phase

P_A° = V.P. of pure A

$$P_{soln} = P_{solvent} + P_{solute}$$

For a soln. of nonvolatile solute

$$P_{soln} = P_{solvent}$$

Ideal soln's obey Raoult's Law

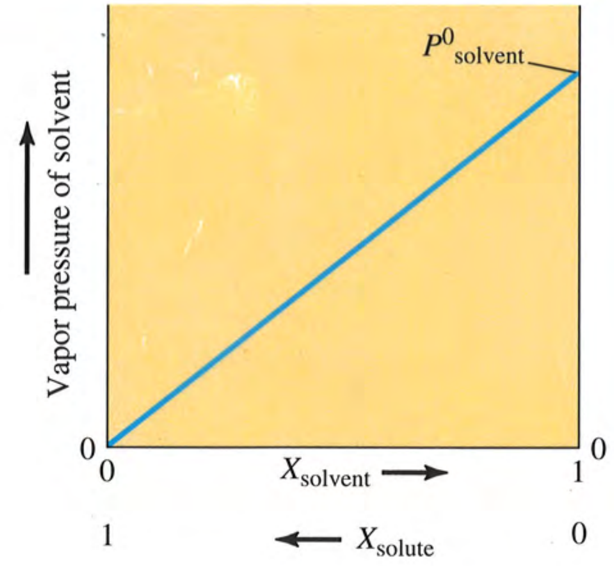
Real soln's ⇒ Ideal soln's

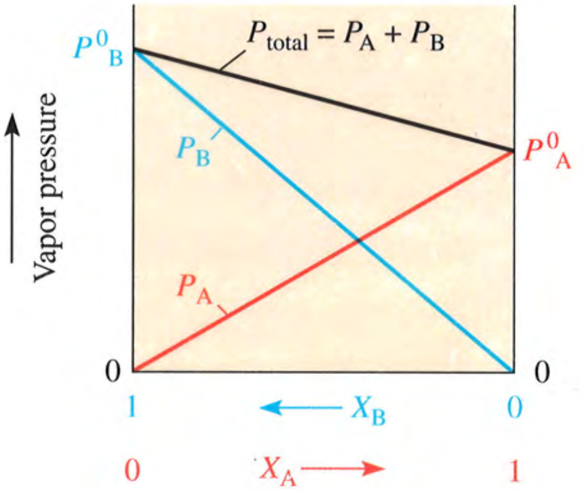
low solute conc.

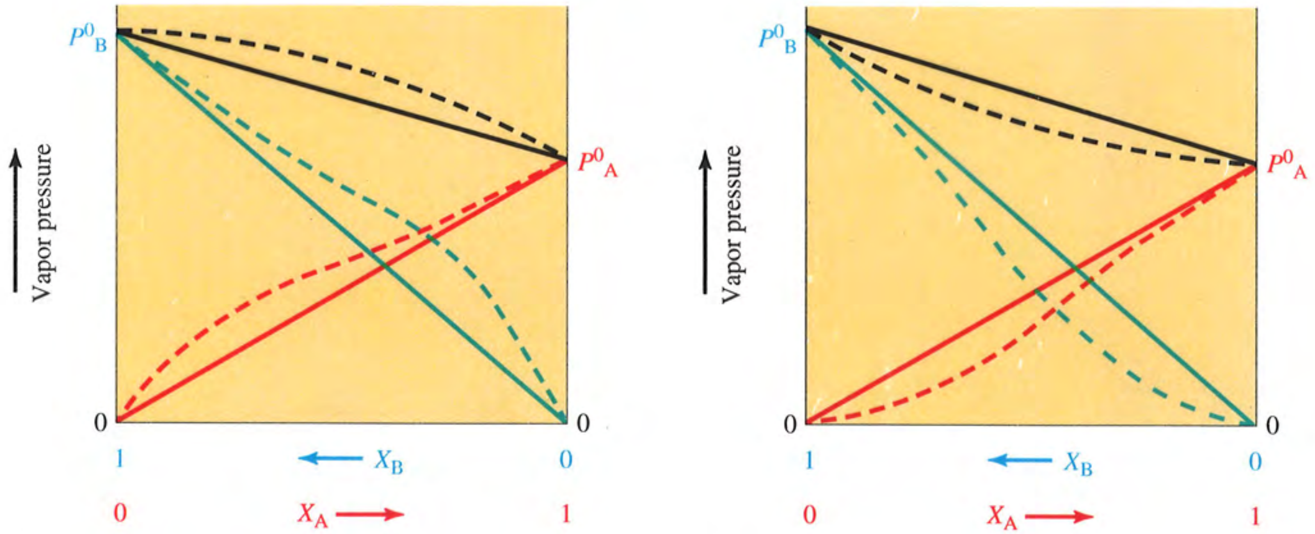
&

similar solute & solvent

Transparency number 98 Text Figures 14.10, 11, 12, pages 513–515







(a) **(b)**

Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis,* 5/e

Saunders College Publishing

b) Expression for V.P. Lowering

$$P_A < P_A^\circ$$

$$\Delta P = P_A^\circ - P_A$$

$$= P_A^\circ - \chi_{A_l} P_A^\circ$$

$$\Delta P = (1 - \chi_{A_l}) P_A^\circ$$

But, for a 2 component soln:

$$\chi_{A_l} + \chi_B = 1$$

$$\therefore \quad \boxed{\Delta P = \chi_B P_A^\circ}$$

V.P. lowering due to solute in soln.

c) Ex: What is the V.P. lowering & V.P. of a soln. containing 8.56g of eugenol ($C_{10}H_{12}O_2$) in 50.0g of ethanol (C_2H_5OH), at 20.0°C.

The V.P. of ethanol at 20.0°C is 44.6 torr.

2) Volatile solutes

Both solute & solvent have appreciable V.P.

Also, suppose A & B form ideal soln.

i.e. both A & B follow Raoult's Law & obey Dalton's Law

$$P_A = \chi_{A_l} P_A^\circ \qquad P_B = \chi_{B_l} P_B^\circ$$

$$P_T = P_A + P_B$$

$$\boxed{P_T = \chi_{A_l} P_A^\circ + \chi_{B_l} P_B^\circ}$$

a) Ex : What is the V.P. of a soln. of 0.250 mole of heptane (C_7H_{16}) + 0.306 mole of octane (C_8H_{18}) at 100°C ?

$P^\circ_{hep} = 791$ torr $\quad P^\circ_{oct} = 352$ torr

B) Boiling Point Elevation

Soln. will not boil at normal b.p. of solvent since V.P. of soln. is not 1 atm at this temp.

Must raise temp. to bring V.P. of soln. to 1 atm.

$$\Delta T_b = K_b\, m_{particles} = K_b\left(i\, m_{stated}\right)$$

K_b ≡ molal b.p.-elevation constant

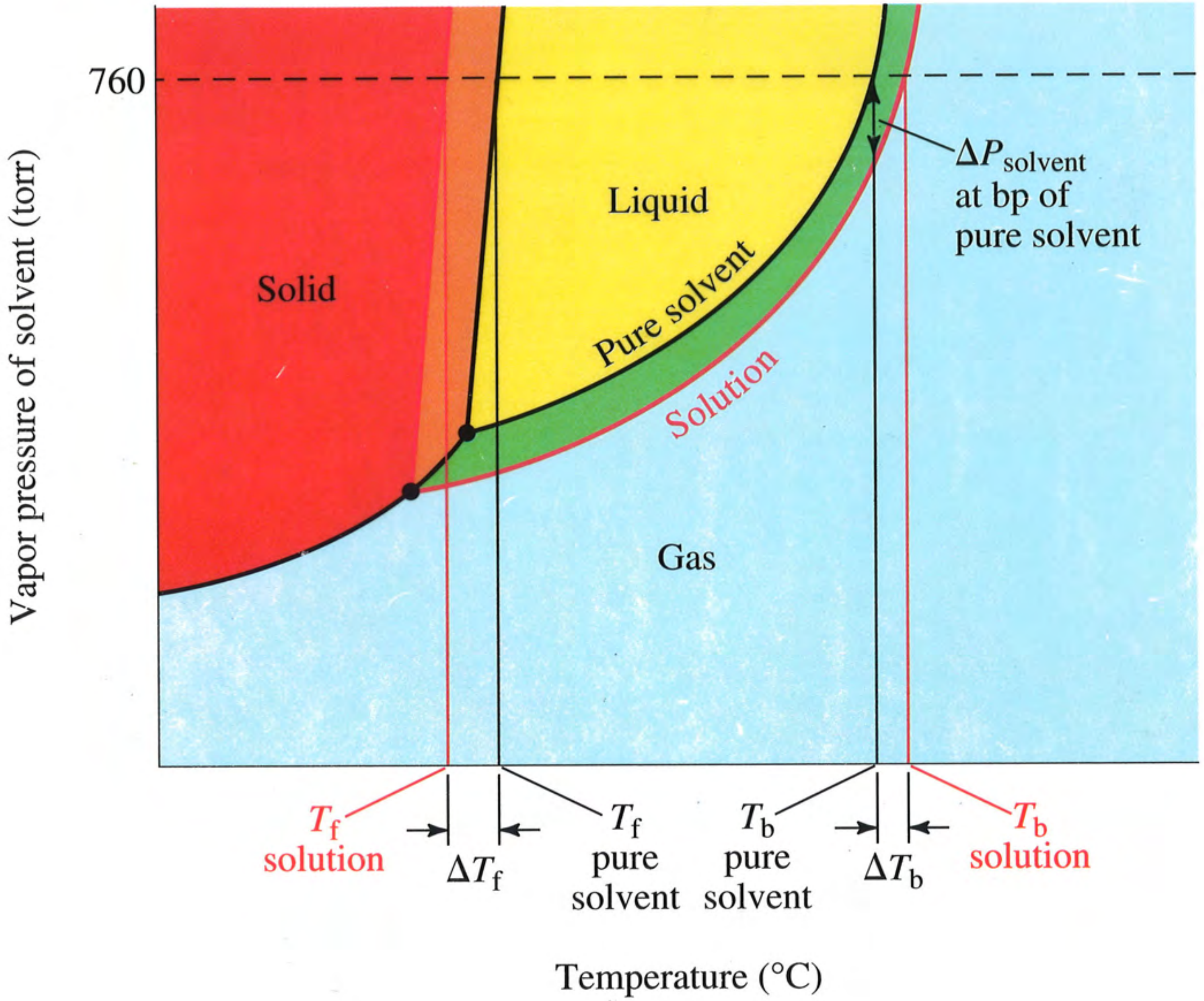
i ≡ # particles in soln.

- integer for ideal behavior

$i = 1$ for nonionizing solutes

i = # ions resulting from f.u.

$m_{particles} = i\, m_{stated}$



Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis,* 5/e

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1) **Ex:** What is the b.p. of a soln. of 35.0g of a nonionizing solute (MW=210 amu) in 450.0g of benzene?

$K_b = 2.61\ °C/m$ n.b.p. = 80.1°C

c) Freezing Point Depression

Solute is not normally soluble in solid solvent.

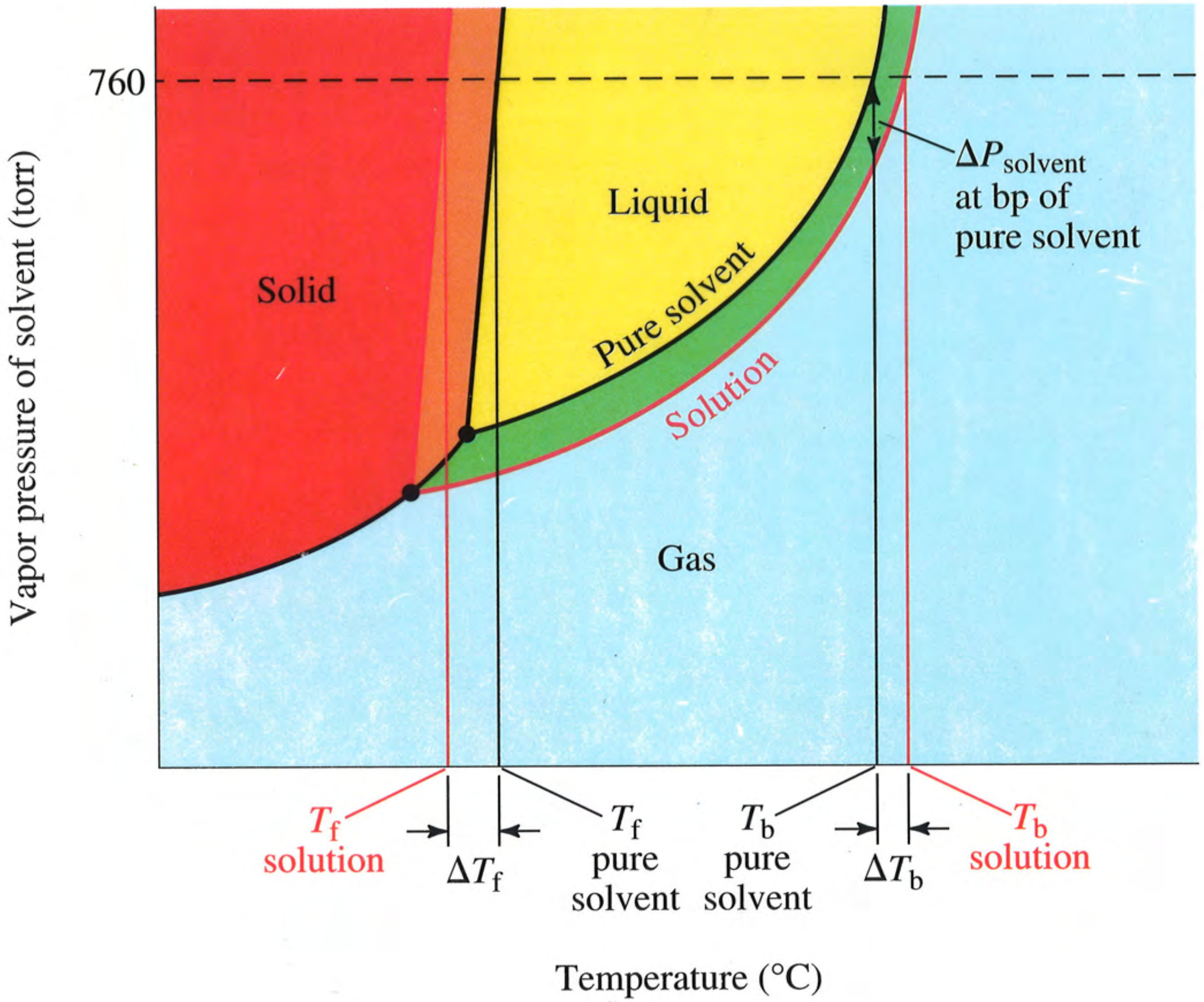
∴ solid in equil. w. soln. is essentially pure solvent

V.P. of solid is unaffected while that of soln. is reduced

$$\text{solid solvent} \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftharpoons}} \text{liquid soln.}$$

Must lower f.p. to reestablish equil.

$$\Delta T_f = K_f m_{part} = K_f(i\, m_{stated})$$


760
Vapor pressure of solvent (torr)
Solid
Liquid
Gas
Pure solvent
Solution
$\Delta P_{\text{solvent}}$ at bp of pure solvent
T_f solution
ΔT_f
T_f pure solvent
T_b pure solvent
ΔT_b
T_b solution
Temperature (°C)

1) Ex: A soln. containing 16.9g of a nonionizing solute in 250.0g H_2O freezes at -0.744°C.

What is the solute's M.W.?

D) Osmotic Pressure

Semipermeable membrane

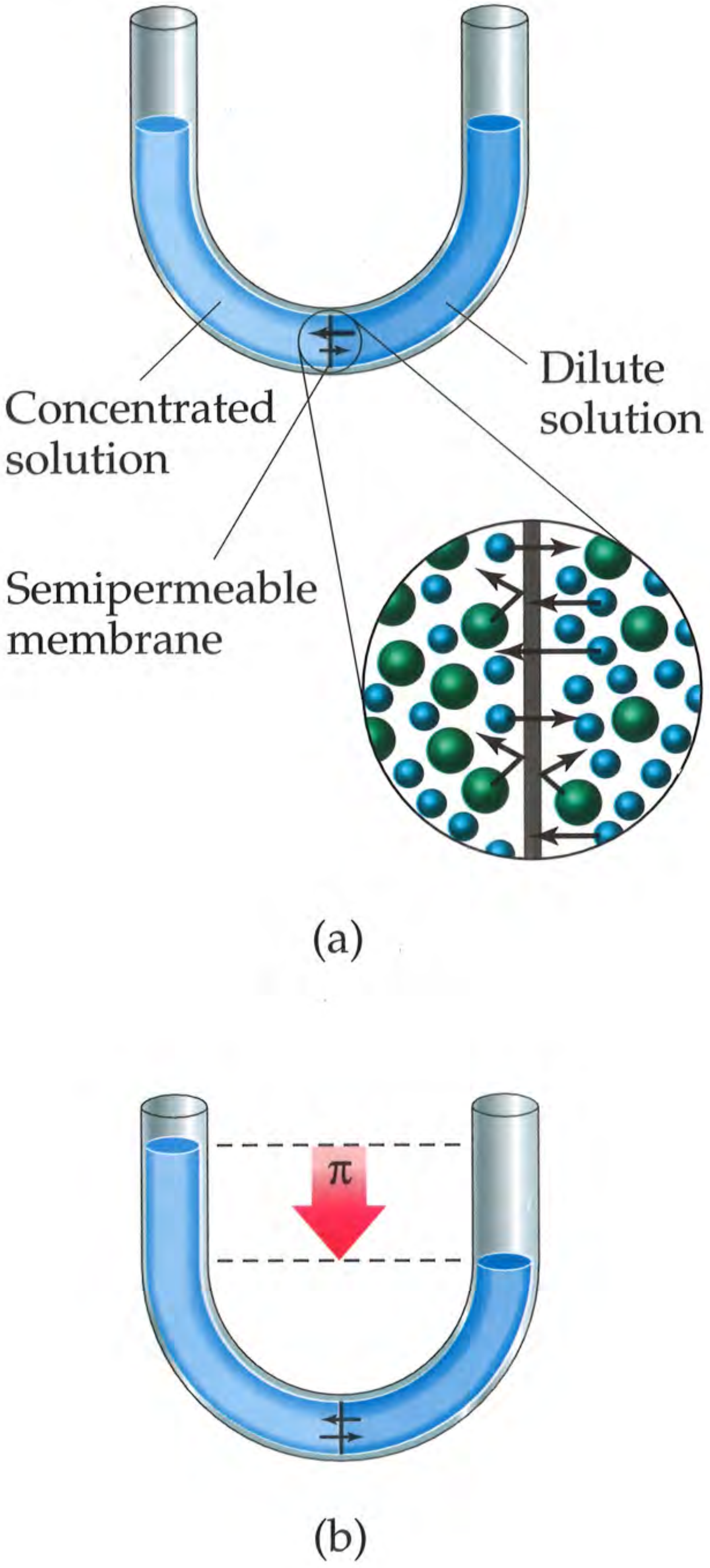
permits passage of some molecules (solvent) but not others (solute)

Osmosis

Passage of solvent through a semipermeable membrane from a region of low solute conc. (high solvent conc.) to a region of high solute conc. (low solvent conc.)

NOTE: net movement of solvent is always toward more conc. soln.

Fig. 13.20 Osmosis



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Osmotic Pressure, Π

Pressure that must be supplied to prevent osmosis

$$\boxed{\Pi = i M R T}$$

or

$$\Pi = M_{\text{particles}} R T$$

Also write as,

$$\boxed{\Pi = \frac{n_{\text{part}}}{V} R T}$$

Used to determine M.W. from very dilute soln.

$$\Pi \gg \Delta T_f > \Delta T_b$$

1) Ex: Calc. the freezing pt. depression & osmotic pressure for a 0.00054 m aqueous soln. (use 25°C to calc π)

$K_f = 1.858\ °C/m$

2) Ex 2: A soln. contains 0.070g of insulin in 10.0 mL of soln. It has an osmotic pressure of 23 torr at 25°C. What is the approx. MW. of insulin?

E) Colligative Prop. of Electrolytes

$$K_2SO_4 \xrightarrow{H_2O} 2\,K^+(aq) + 1\,SO_4^{2-}(aq)$$

a) If Ideal

$i = 3$

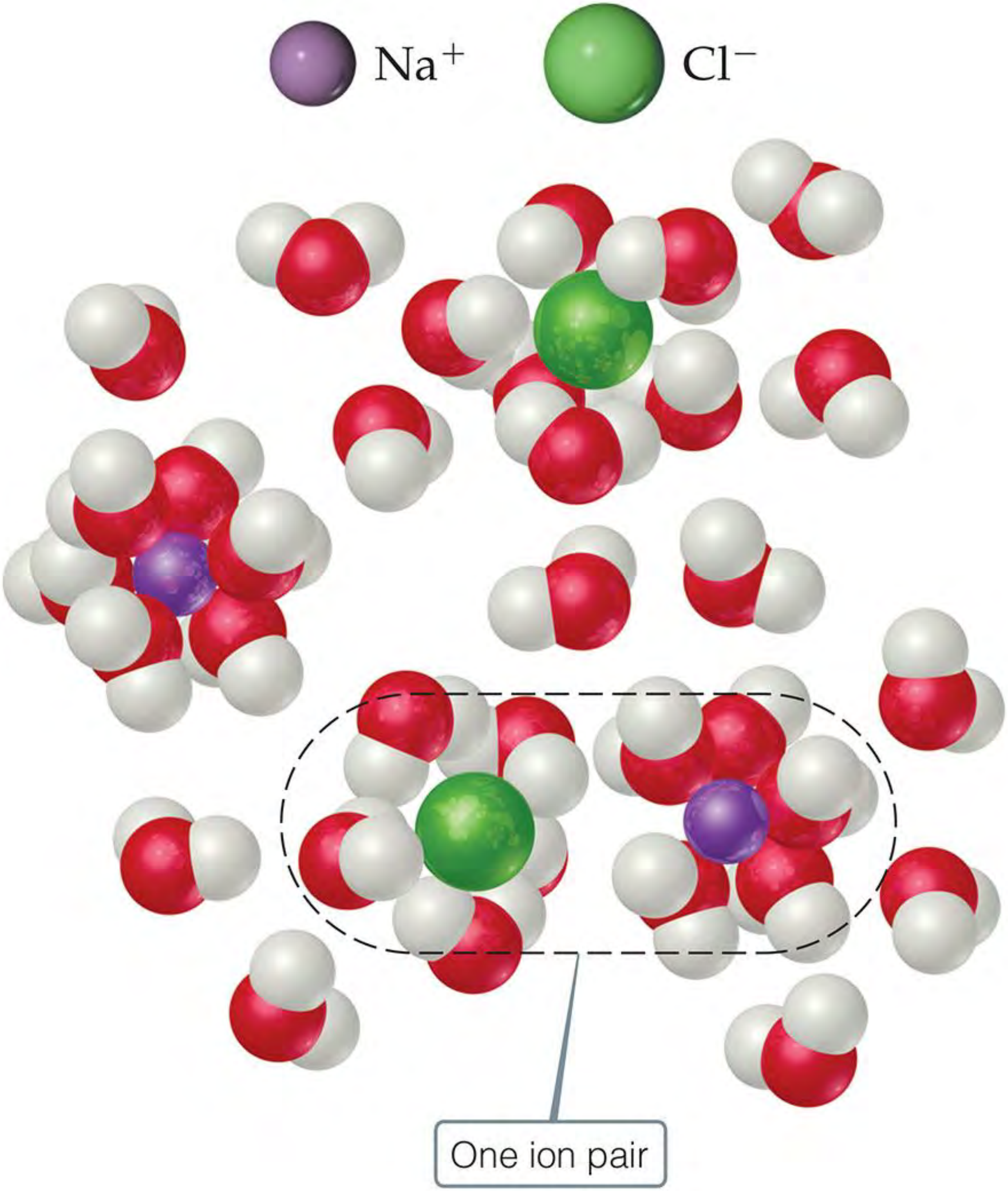
$0.01\ m\ K_2SO_4 \Rightarrow 0.03$ moles of ions per kg H_2O

$$\Delta T_f = i_{ideal} \cdot K_f\, m$$
$$= 3\,(1.858\ ^\circ\mathrm{C}/m)(0.01\ m)$$
$$= 0.0558\ ^\circ\mathrm{C} \quad \text{expected}$$

$$\Delta T_{f_{obs}} = 0.0500^\circ\mathrm{C} \quad \text{observed}$$

Discrepancy due to:

Interionic Attractions


Na^+
Cl^-
One ion pair

b) Non ideal ionic soln.

get ion pairs

- Number of independent particles is reduced

$$i_{obs} = \frac{\Delta T_{f_{obs}}}{K_f \, m}$$

$$= \frac{\text{observed collig. prop}}{\text{calc. prop. (assuming } i = 1)}$$

van't Hoff factor

i_{obs} is diff. for each conc. + approaches # ions per f.u. for very dilute soln.

$$i_{obs} \longrightarrow i_{ideal}$$

c) **Ex** : For a 0.0100 m K_2SO_4 soln. ΔT_f is measured to be 0.0500 °C. What is the van't Hoff factor?

VIII) Colloids

Mixtures in which solute particles are larger than in a soln. but not large enough to settle out.

- colloidal dispersion

Particle size : 10 – 2,000 Å

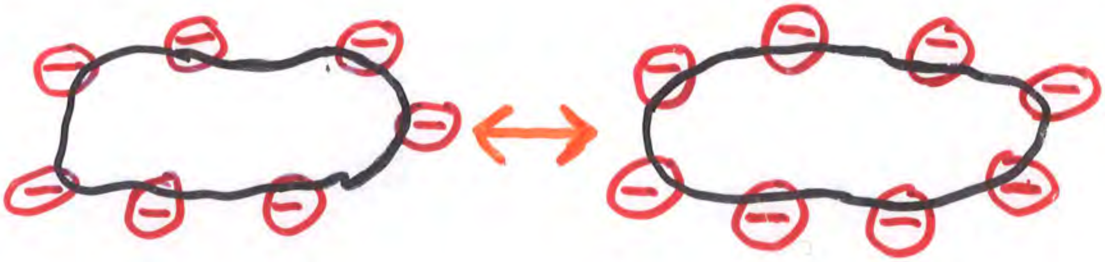
Scatter light – Tyndall Effect

A) Hydrophilic Colloids: "water-loving"

- generally stay in soln.
- have polar groups that interact w. H_2O

B) Hydrophobic Colloids: "water-hating"

- must be stabalized to stay dispersed
- absorb ions on surface
  - causes particles to not aggregate

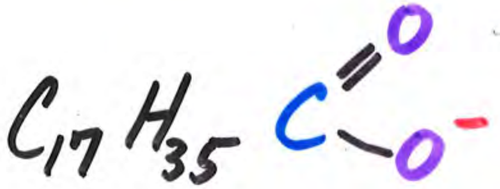


stabilize w. molecules of form,

C) Association Colloids (Micelles)

Micelle: colloid-sized particle formed in water by the association of molecules that have both hydrophilic & hydrophobic ends

Association Colloid: the dispersed phase consists of micelles



$C_{17}H_{35}C(=O)O^-$ stearate ion

$C_{12}H_{25}OSO_3^-$ lauryl sulfate