Chapter 13

Physical Properties of Solutions

Topics

- Types of solutions
- Molecular view of the solution process
- Concentration units
- Factors that affect the solubility
- Vapor pressure of solution
- Colligative properties of solution
- Calculations using colligative properties
- Section 11-7: Colloids-Self study

Solution composition

A ***solution*** **is a homogenous mixture of 2 or more substances**

The *solute* is(are) the substance(s) present in the smaller amount(s)

The *solvent* is the substance present in the larger amount

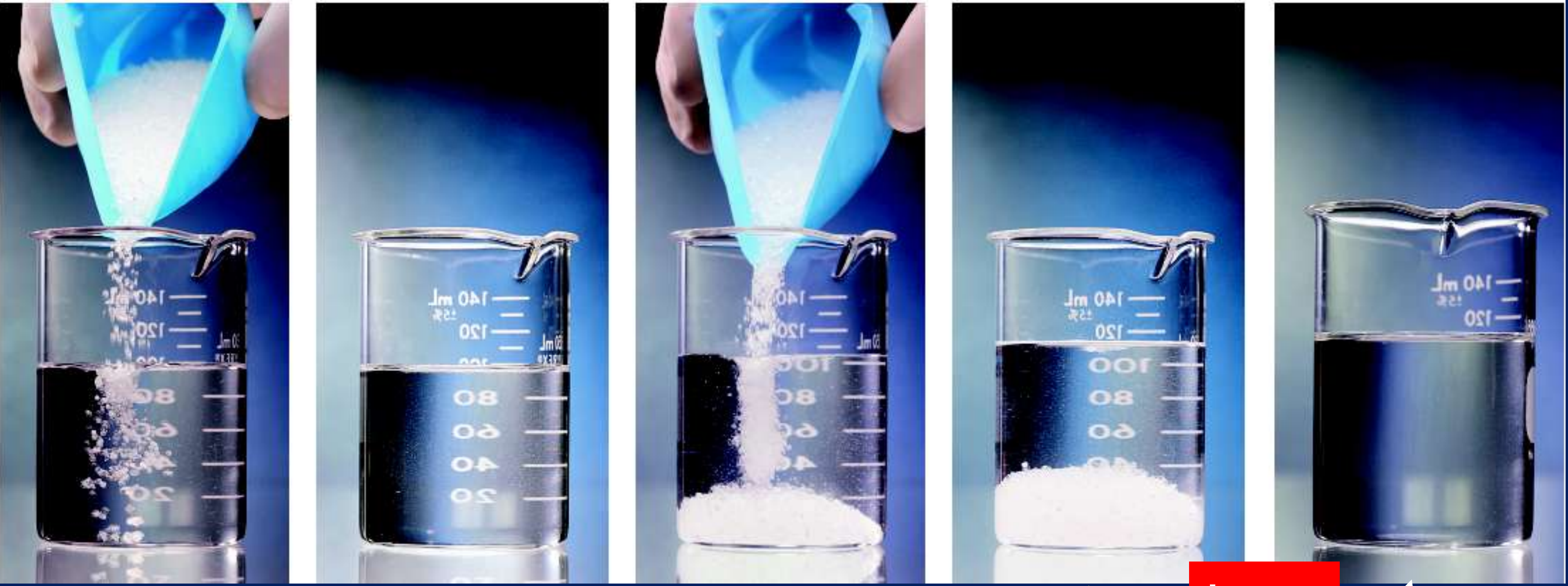
13.1 Types of Solutions

Solution classifications based on amount of solute dissolved relative to the maximum:

- *Saturated* – maximum amount at a given temperature (This amount is termed the *solubility* of the solute.)
- *Unsaturated* – less than the maximum
- *Supersaturated* – more than a saturated solution but is an unstable condition

unsaturated

saturated

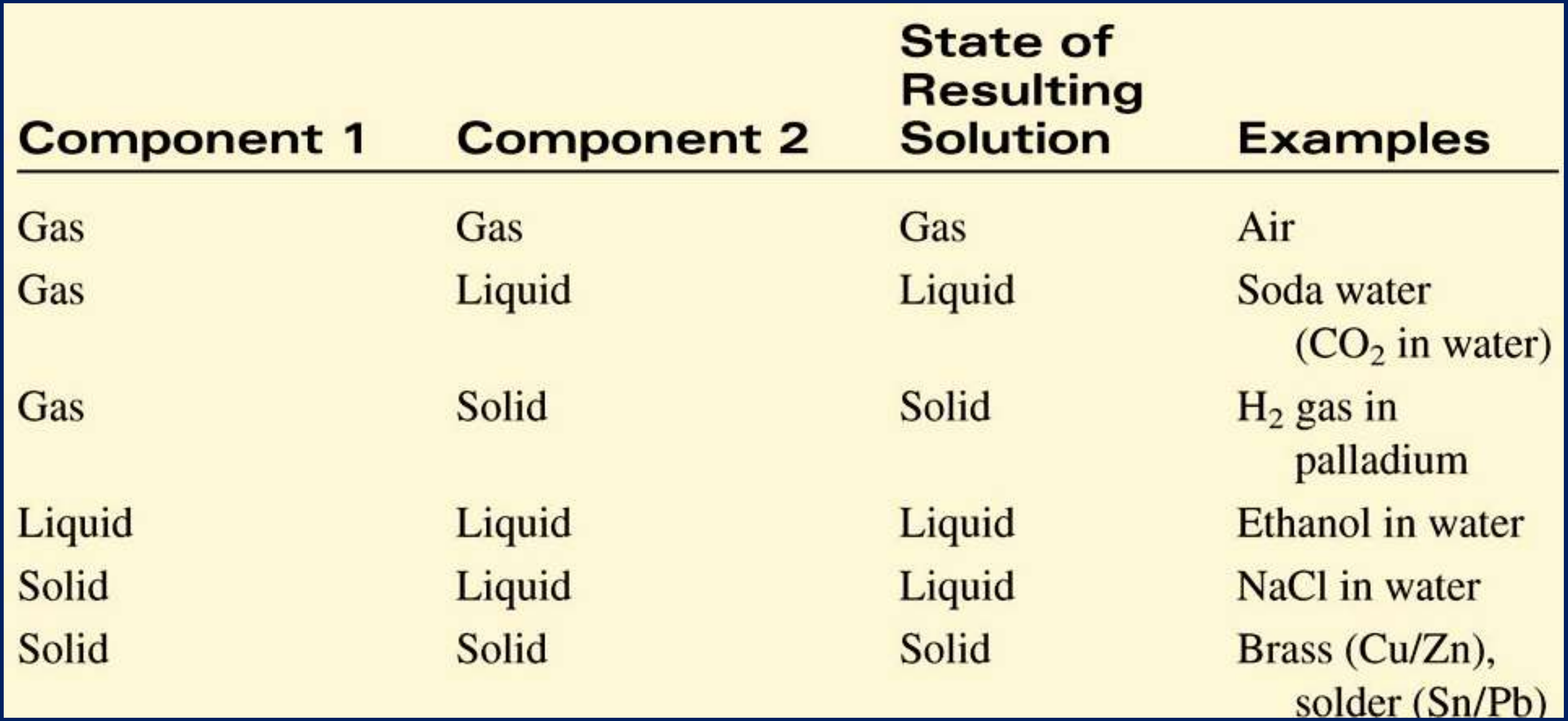


heat

supersaturated

Conversion of a Supersaturated Solution to a Saturated Solution

Various types of solutions based on the type of solute and solvent



Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

Various types of solutions based on the type of solute and solvent

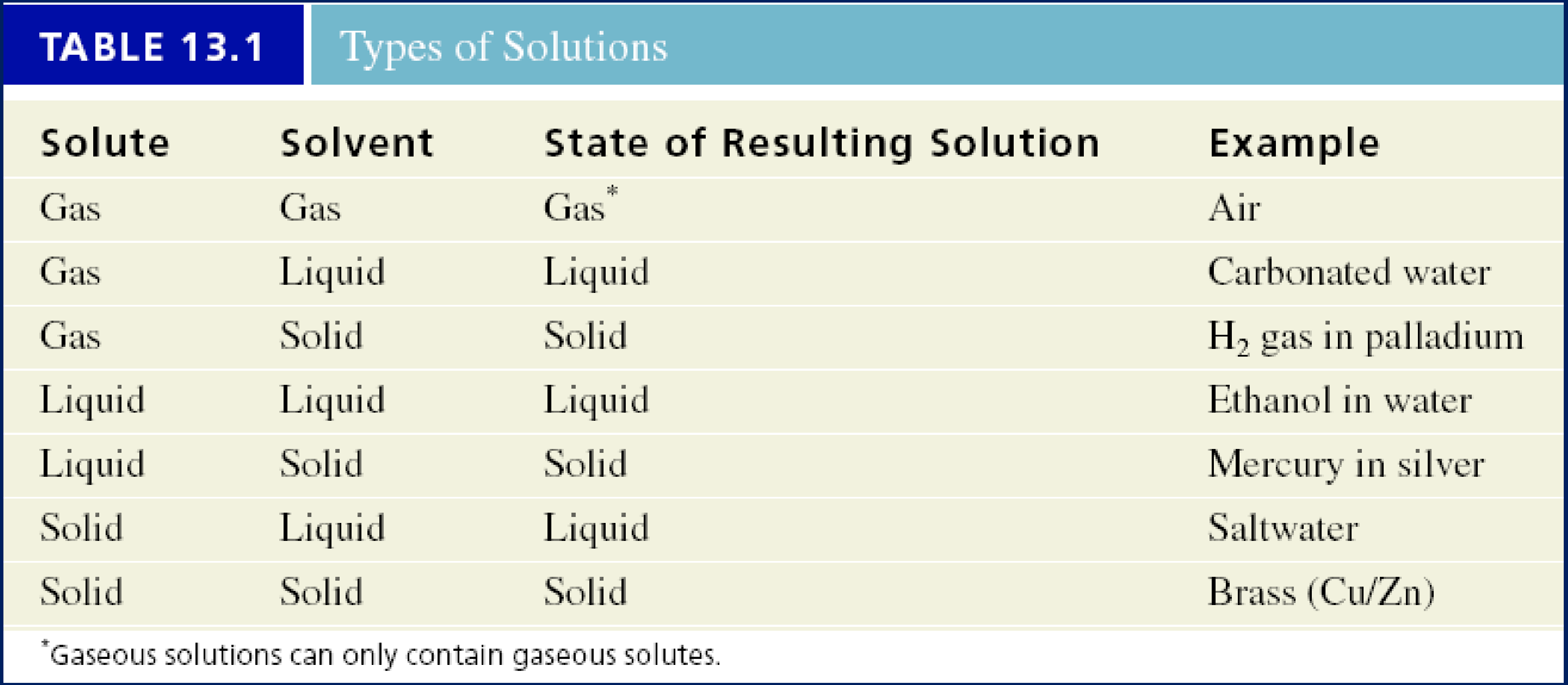


TABLE 13.1 Types of Solutions

Solute	Solvent	State of Resulting Solution	Example
Gas	Gas	Gas*	Air
Gas	Liquid	Liquid	Carbonated water
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Liquid	Solid	Solid	Mercury in silver
Solid	Liquid	Liquid	Saltwater
Solid	Solid	Solid	Brass (Cu/Zn)

*Gaseous solutions can only contain gaseous solutes.

In this chapter we will deal mainly with aqueous solutions

13.2 A Molecular View of the Solution Process

Importance of intermolecular forces

- When solute dissolves in a solvent, solute molecules disperse throughout the solvent
- Solute molecules separate from one another and every solute molecules is surrounded by solvent molecules. This process is known as the solvation

Factors that determine solubility

Intermolecular forces responsible for the solubility:

- Solute-solute interactions
- Solvent-solvent interactions
- Solute-solvent interactions

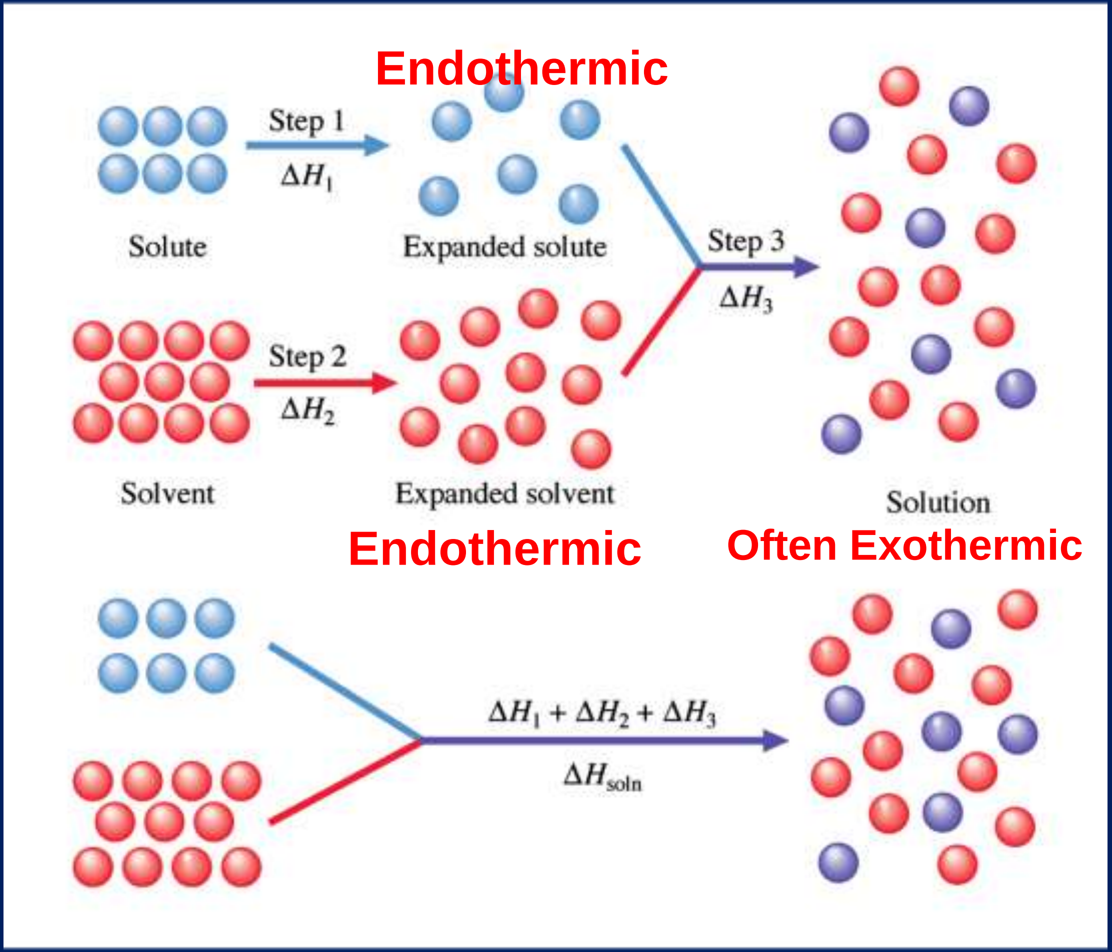
Solution (Solubility) Process

The formation of a liquid solution takes place in 3 steps

1. Separation of solute molecules

2. Separation of solvent molecules

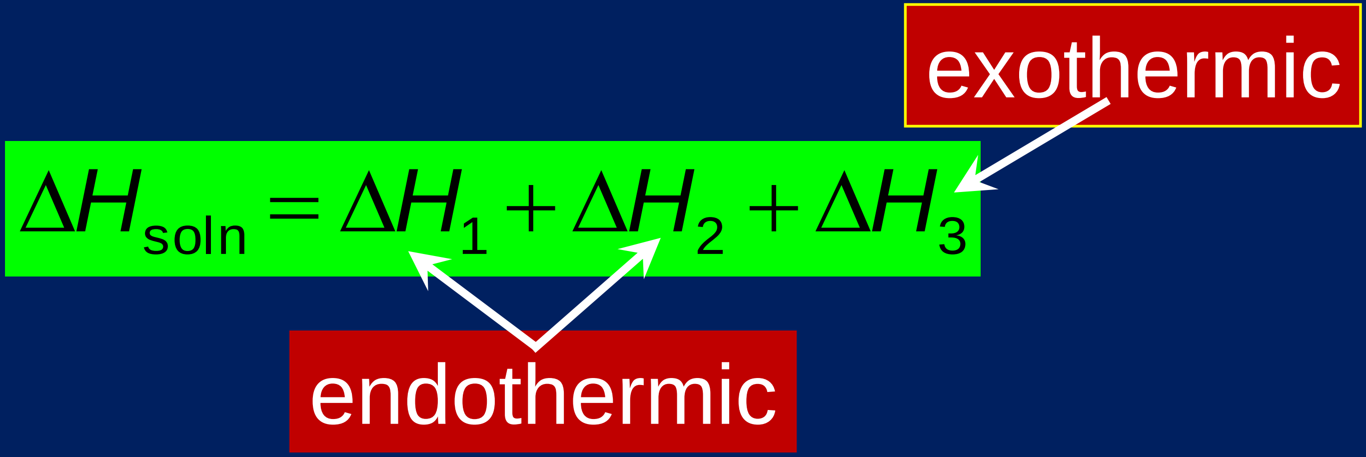
3. Mixing solute and Solvent molecules



$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Energy of Solubility Process

- Steps 1 and 2 require energy to overcome intermolecular forces:
  - endothermic
- Step 3 usually releases energy
  - often exothermic
- enthalpy of solution
  - sum of ΔH values
  - can be – or +
  - $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$



exothermic

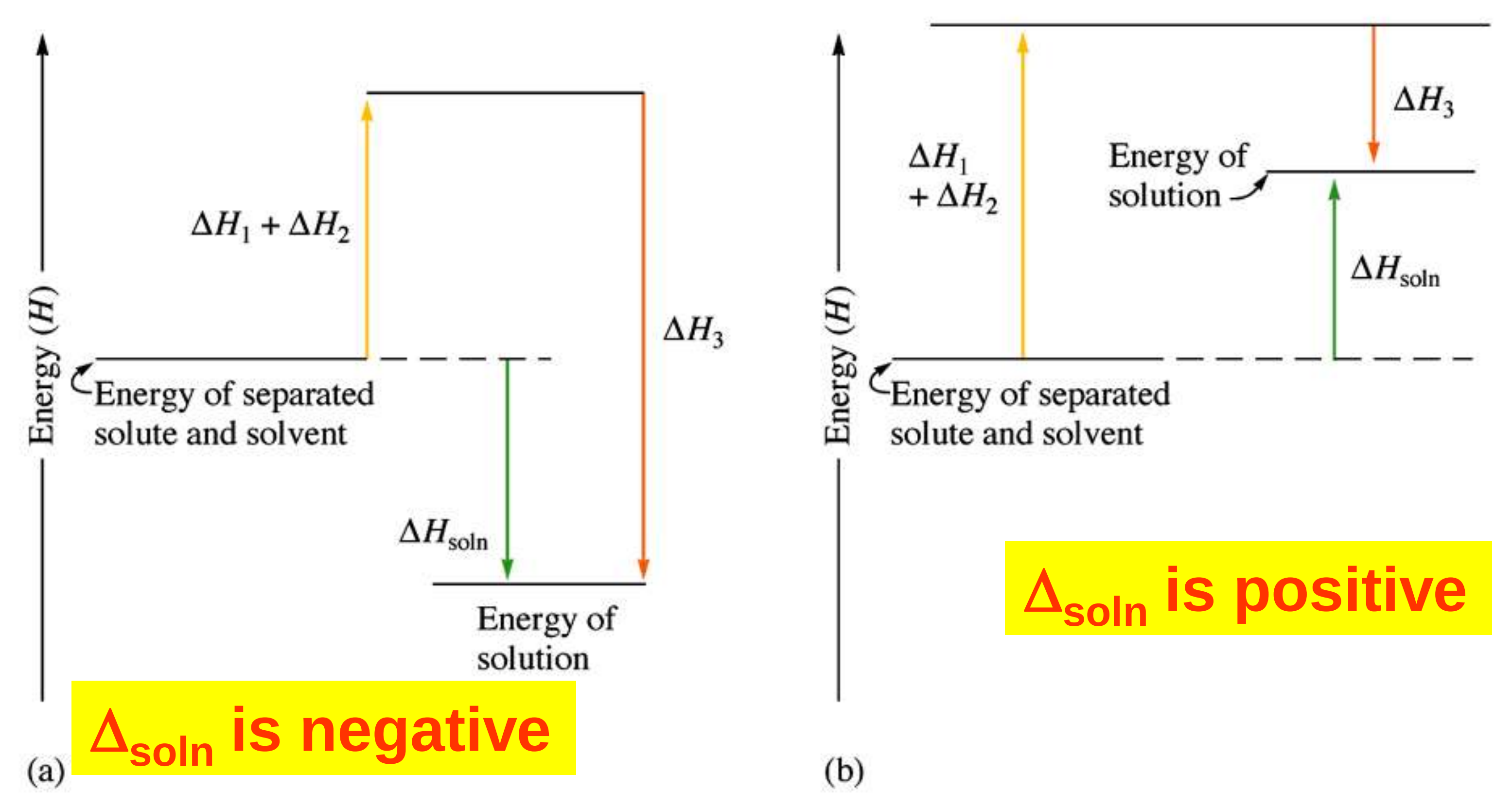
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

endothermic

$$\Delta H_1 + \Delta H_2 < \Delta H_3 \quad \Delta H_{\text{soln}} < 0$$

$$\Delta H_1 + \Delta H_2 > \Delta H_3 \quad \Delta H_{\text{soln}} > 0$$

Energy of Solubility Process



Δ_{soln} is negative

Δ_{soln} is positive

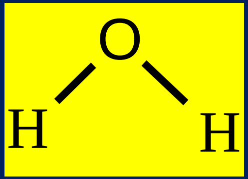
Predicting the solubility of a solute in a given solvent

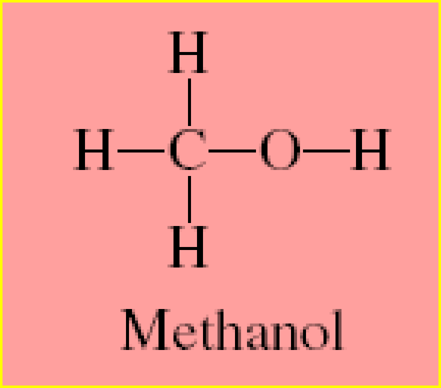
"like dissolves like"

Two substances with similar *intermolecular* forces in type and magnitude are likely to be soluble in each other.

- **Non-polar solutes are soluble in non-polar solvents** CCl_4 in C_6H_6
- **Polar solutes are soluble in polar solvents** C_2H_5OH in H_2O
- **Ionic compounds are more soluble in polar solvents** NaCl in H_2O or NH_3 (*l*)
- **Any explanation for this behavior?**

For example: water and methanol are both polar and dissolve in each other





Methanol

- Two liquids that are soluble in each other in all proportions are termed ***miscible***.

- Ions readily dissolve in polar solvent due to ***solvation*** by the solvent molecules.

oil does not dissolve in water

ΔH_{soln} is largly +Ve

- Oil is nonpolar (London forces)
- Water is polar (H-bonding)
- ΔH_1 will be small for typical molecular size
- *ΔH_2 will be large*
- ΔH_3 will be small since there won't be much interaction between the two
- ΔH_{soln} will be **large and +ve** because energy required by steps 1 and 2 is larger than the amount released by 3

NaCl dissolves in water

ΔH_{soln} is slightly +Ve

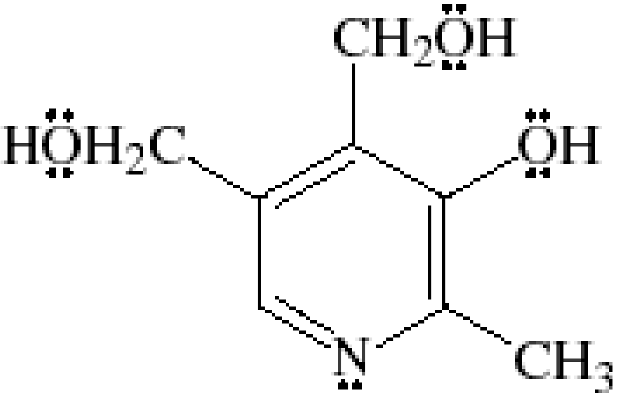
- NaCl is ionic
- water is polar (H-bonding)
- ΔH_1 will be large
- ΔH_2 will be large
- ΔH_3 will be large and –ve because of the ***strong interaction between ions and water***
- **ΔH_{soln} will be close to zero- small but +ve**

Energy and Entropy in solution formation

ΔH_{soln} is small but NaCl is highly soluble, Why?

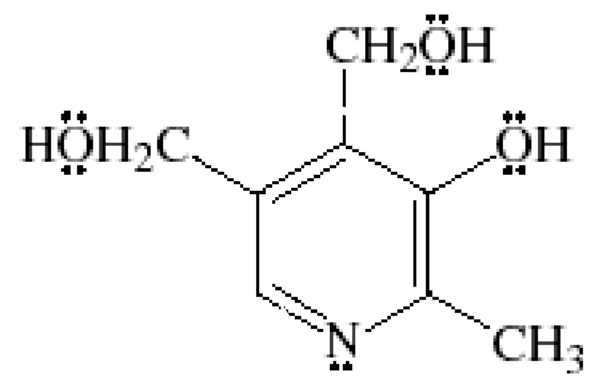
- Entropy is the randomness or disorder. The more order of a system the less entropy for this system.
- There is a tendency for entropy to increase in all natural events
- In the pure state, solute and solvent possess fair degree of order (low entropy)
- When solute and solvent are mixed, the order is disrupted and the entropy will increase. Thus the solution process is accompanied by increase in entropy
- Always the higher entropy is favored
- Consequently, the dissolution takes place even the solution process is endothermic

Predict whether Vitamin B_6 is water soluble or fat soluble.



Vitamin B_6

polar groups



Vitamin B_6

Water soluble due to the presence of polar groups.

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13.3 Concentration Units

The *concentration* of a solution is the amount of solute present in a given quantity of solution or solvent

Percent by Mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{ppm (parts per million)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$\text{ppb (parts per billion)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9$$

Mole Fraction (χ)

$$\chi_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

$$\text{Mole fraction of } A = \chi_A = \frac{n_A}{n_A + n_B}$$

Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{volume of solution (liters)}}$$

Molality (m)

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Example

- 1.00 g C_2H_5OH is added to 100.0 g of water to make 101 mL of solution. Find the molarity, mass %, mole fraction and molality of ethanol. Assume the density of solution was 1.00g/ml

Molarity

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$M = \frac{1.00\ \text{g}\ C_2H_5OH \times \dfrac{1\ \text{mol}}{46.07\ \text{g}}}{101\ \text{mL} \times \dfrac{1\ \text{L}}{1000\ \text{mL}}} = \frac{2.17 \times 10^{-2}\ \text{mol}}{0.101\ \text{L}} = 0.215\ \text{M}$$

Mass Percent

$$\text{Mass\%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

$$\text{Mass\%} = \frac{1.00\text{ g C}_2\text{H}_5\text{OH}}{(1.00\text{ g} + 100.0\text{ g})\text{ solution}} \times 100 = 0.990\ \%$$

$$ppm = \frac{1.00\text{ g C}_2\text{H}_5\text{OH}}{(101.0\text{ g})\text{ solution}} \times 1000000 = 9901$$

Mole Fraction

- ratio of number of moles of a part of solution to total number of moles of solution

$$\chi_A = \frac{n_A}{n_A + n_B}$$

$$\chi_{C_2H_5OH} = \frac{2.17\times10^{-2}\,mol\,C_2H_5OH}{\left(100.0\,g\,H_2O \times \frac{1\,mol}{18.02\,g}\right) + 2.17\times10^{-2}\,mol} = 0.00389$$

Molality

- Number of moles of solute per kg of solvent

$$\mathrm{m} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

$$\mathrm{m} = \frac{2.17\times10^{-2}\,\mathrm{mol}\,\mathrm{C_2H_5OH}}{\left(100.0\,\mathrm{g}\times\dfrac{1\,\mathrm{kg}}{1000\,\mathrm{g}}\right)\text{solution}} = 0.217\,\mathrm{m}$$

Example

An aqueous antifreeze solution is 40% ethylene glycol ($C_2H_6O_2$) by mass. The density of the solution is 1.05 g/cm^3. Calculate the molality, molarity and mole fraction of ethylene glycol

Mass of water (solvent) = 100-40 = 60.0 g

$$Molality = \frac{40.0g\ EG \times \frac{1\mathrm{mol}\ EG}{62.07\,gEG}}{60.0\ g\ H_2O} \times \frac{1000\ g}{kg} = 1.07\ \mathrm{mol/kg}$$

where EG = ethylene glycol ($C_2H_6O_2$)

$$Molarity = \frac{40.0\ g\ EG \times \frac{1mol\ EG}{62.07\ g\ EG}}{100.0\ g\ solution \times \frac{1mL}{1.05g\ solution} \times \frac{1L}{1000mL}} = 6.77 mol / L$$

\# mol EG = 0.644 mol EG

\# mol water = 60.0/18.0 = 3.33 mol

$$\chi_{\mathrm{EG}} = \frac{0.644}{3.33 + 0.644} = 0.162$$

What is the molality of a 5.86 *M* ethanol (C_2H_5OH) solution whose density is 0.927 g/mL?

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \qquad M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

Mass of solute = mass of 5.86 moles ethanol = 270 g ethanol

Mass of solution= mass of 1 L solution=

(1000 mL x 0.927 g/mL) = 927 g of solution

mass of solvent = mass of solution – mass of solute

= 927 g – 270 g = 657 g = 0.657 kg

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92\ m$$

13.4 Factors that affect the Solubility

1. Structure Effects

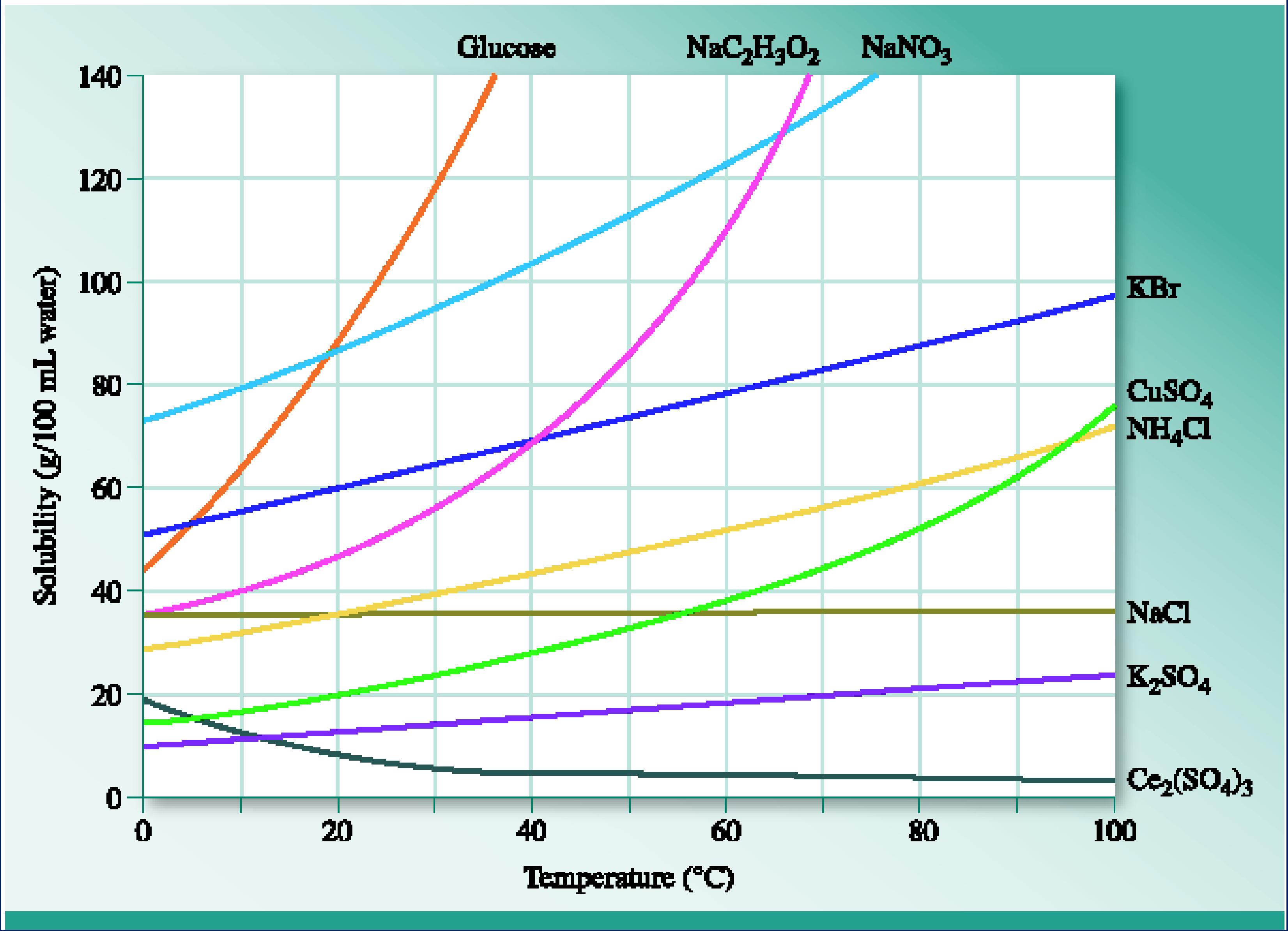
It has been discussed earlier “Like dissolves like”

2. Temperature

- The solubility of **solids** may **increase, decrease or remain** relatively constant with increasing temperature.
  - Temperature effect cannot be predicted; only by experiment

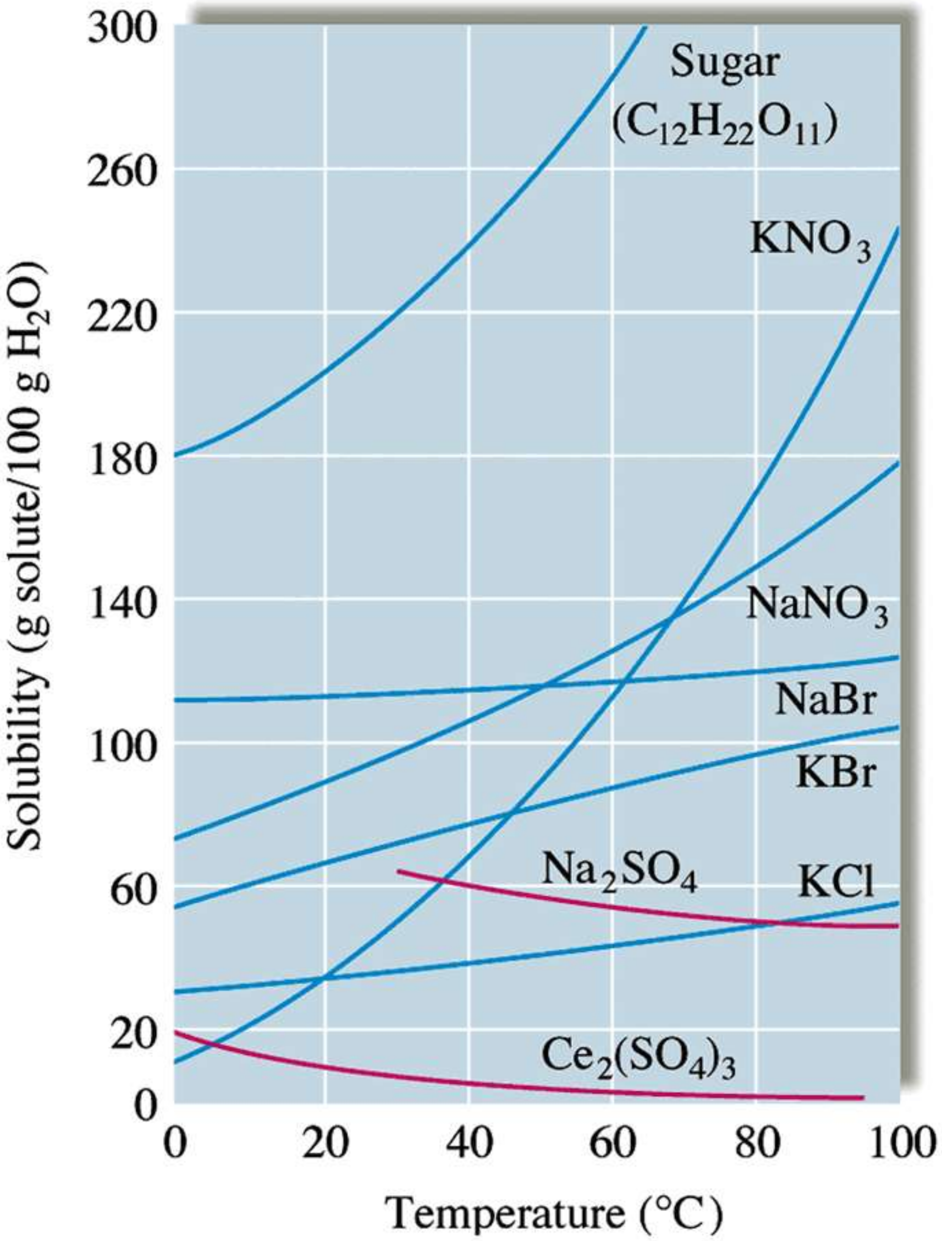
- The solubility of **gases** **decrease** with increasing temperature

Temperature Dependence of the Solubility of Selected Solids



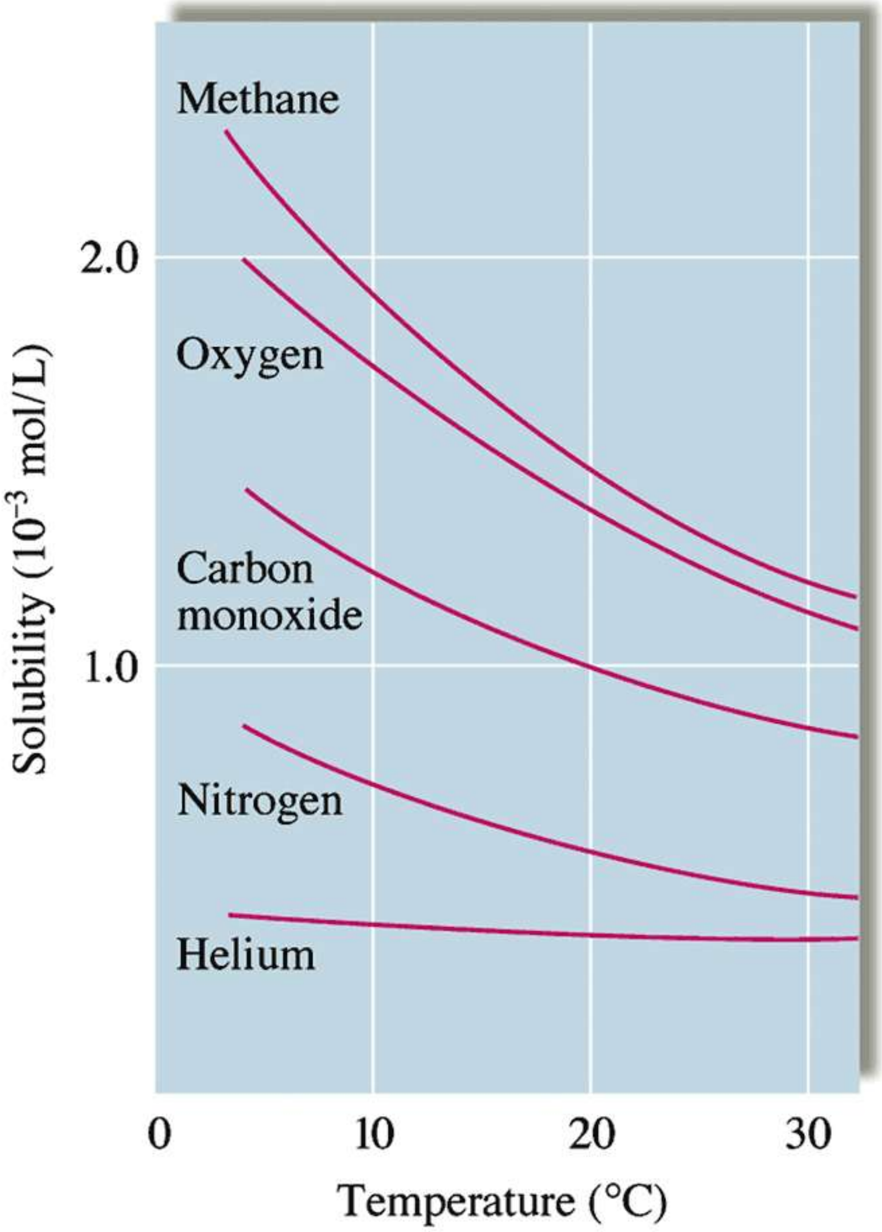
Temperature Dependence of the Solubility of Selected Solids

- dissolving a solid occurs faster at higher T
- but the amount to be dissolved does not change



Temperature effects on solubility of gases

- Solubility of gas in water decreases with T



Solubility and Environment

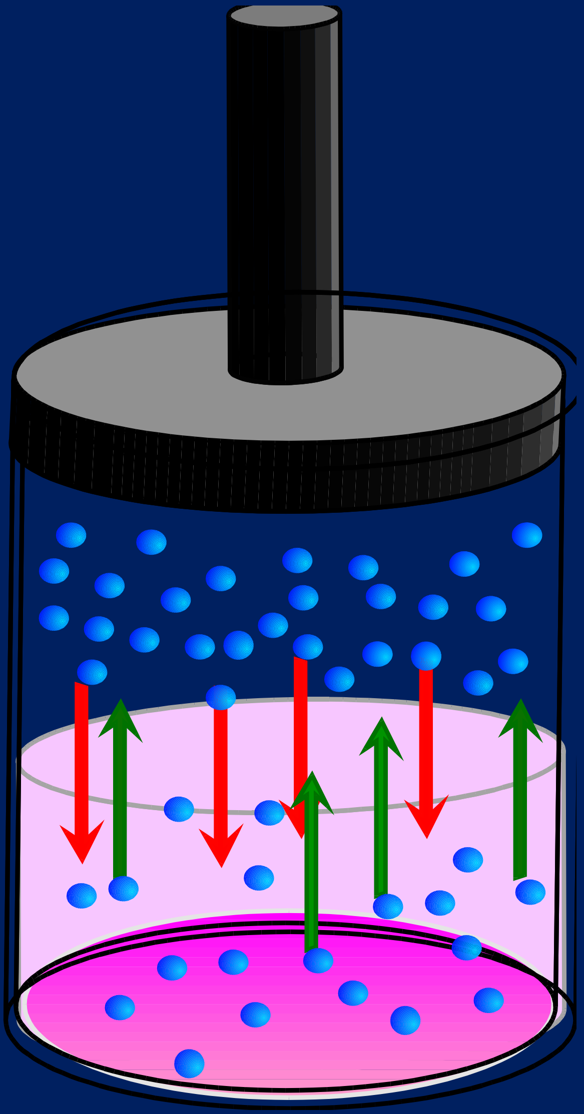
- Thermal pollution
  - Water used as a coolant when pumped again into the source (lakes and rivers) floats on the cold water causing a decrease in solubility of O_2 and consequently affecting the aquatic life.
- CO_2 dissolves in water that contains CO_3^{2-} causing formation of HCO_3^- that is soluble in water.

$$CO_3^{2-}(aq) + CO_2(aq) \rightleftharpoons 2HCO_3^-$$

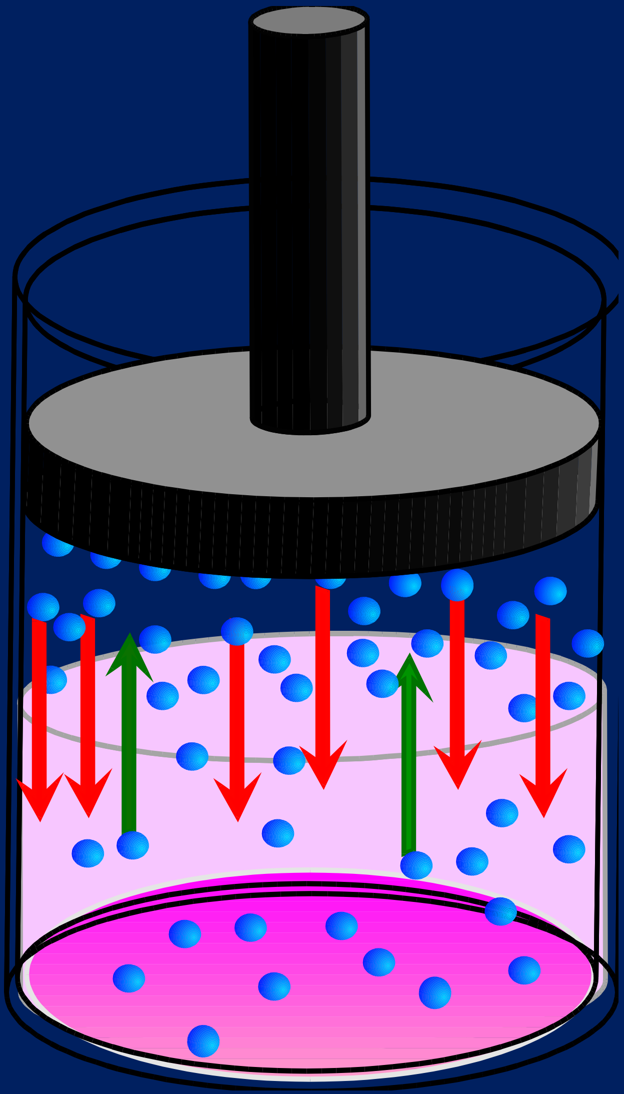
- When temp increases CO_2 will be driven off the water causing precipitation of CO_3^{2-} again forming scales on the wools that blocks the pipes and reduce the heating efficiency

3. Pressure

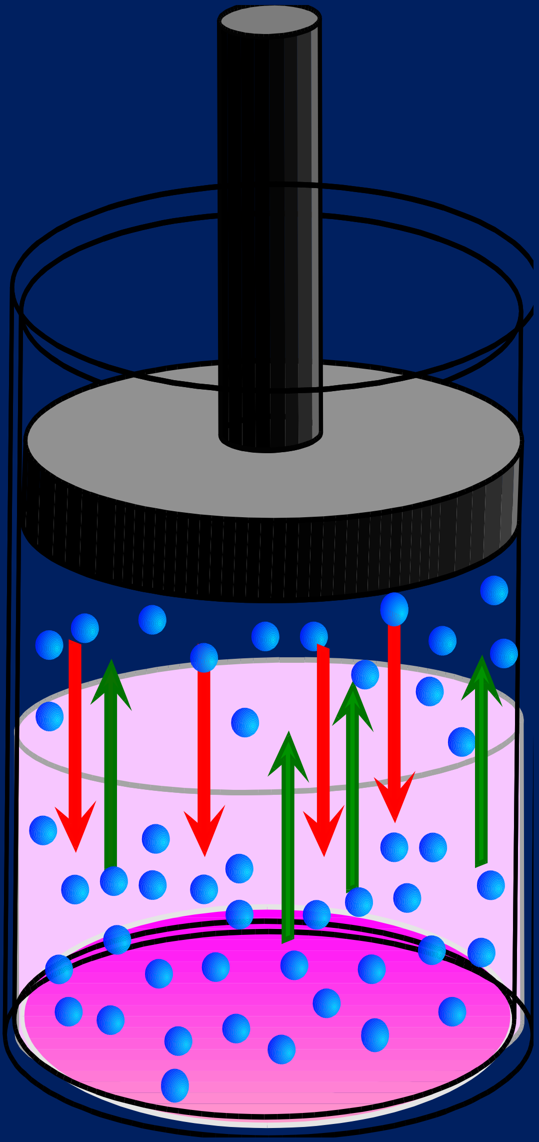
- Changing the pressure doesn’t aeffect the amount of solid or liquid that dissolves; they are incompressible.
- Changing the pressure affects solubility of gases.
- Pressure effects the amount of gas that can dissolve in a liquid.
- The dissolved gas is at equilibrium with the gas above the liquid.



- The gas molecules above the liquid are at equilibrium with the gas molecules dissolved in this solution.
- The equilibrium is dynamic.



- If the pressure is increased the gas molecules dissolve faster.
- The equilibrium is disturbed.



- The system reaches a new equilibrium with more gas dissolved.

Henry's Law

The amount of gas dissolved is directly proportional to the pressure of the gas above solution

- **$C \quad \alpha \quad P \longrightarrow C = kP$**
  - where *c*, is in mol/L, *k* is Henry's law constant with units of mol/L·atm and *P* is in atm.
  - The law is obeyed best by dilute solutions of gases that don't dissociate or react with solvent

$$\frac{C_1}{C_2} = \frac{P_1}{P_2}$$

Calculate the pressure of O_2 necessary to generate an aqueous solution that is 3.4 x 10^{-2} *M* in O_2 at 25°C. The Henry's law constant for O_2 in water at 25°C is 1.3 x10^{-3} mol/L · atm.

$$c = kP$$

$$P = \frac{c}{k} = \frac{3.4\text{x}10^{-2}\,\text{mol}}{\text{L}} \text{ x } \frac{\text{L}\cdot\text{atm}}{1.3\text{x}10^{-3}\,\text{mol}}$$

$$P = 26.2\ \text{atm}$$

$$c = kP$$

$$P = \frac{c}{k} = \frac{3.4\mathrm{x}10^{-2}\,\mathrm{mol}}{\mathrm{L}}\ \mathrm{x}\ \frac{\mathrm{L} \cdot \mathrm{atm}}{1.3\mathrm{x}10^{-3}\,\mathrm{mol}}$$

$$P = 26.2\ \mathrm{atm}$$

Example

soft drink bottled at 25°C contains CO_2 at pressure of 5.0 atm over liquid. Assume that P_{CO_2} atmosphere is 4.0×10^{-4} atm. Find the equilibrium concentration in soda before and after opening. $k = 3.1 \times 10^{-2}$ mol/L.atm at 25°C

- before opening:

$$C_{CO_2} = k \cdot P_{CO_2} \rightarrow C_{CO_2} = 3.1X10^{-2}\,\mathrm{mol/L.atm}(5.0\,\mathrm{atm}) = 0.16\,mol/L$$

- after opening:

$$C_{CO_2} = k_{CO_2}\,xP_{CO_2} = (3.1\mathrm{x}10^{-2}\,\mathrm{mol/L.atm})(4\times10^{-4}\,atm) = 1.2\times10^{-5}\,mol/L$$

13.5 Colligative Properties

Colligative properties are properties that depend only on the number of solute particles (molecules or ions) in solution and not on the nature (identity) of the solute particles.

- **Colligative properties include:**

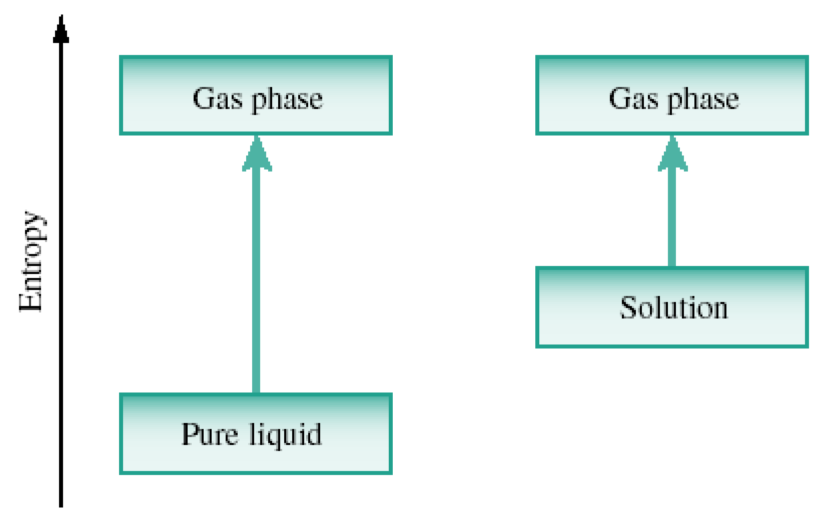
1. **Vapor pressure lowering**
2. **Boiling point elevation**
3. **Freezing point depression**
4. **Osmotic pressure**

- **Each of these properties is a consequence of a decrease in the escaping tendency of solvent molecules brought by the presence of solute particles.**

The vapor pressures of solutions

- A **nonvolatile** solute lowers the vapor pressure of the solvent
- The vapor pressure of the solution is less than that of the pure solvent

- Entropy of pure liquid is much less than that of a gas since the order of molecules in liquids is much more than that in gases.
- Entropy of solution (solvent + nonvolatile solute) is greater than that of pure liquid
- Thus, there is a decreased tendency for solvent molecules in solution to enter the gas phase compared to the tendency for solvent molecules of pure solvent to enter the gaseous phase.
- This results in a lowering of vapor pressure



Vapor pressures of solutions containing nonvolatile solvents were studied by Raoult

Raoult's Law

The presence of a nonvolatile solute lowers the vapor pressure of the solvent.

$$P_{(partial\,pressure\,of\,a\,solvent\,over\,solution)} = P_1 = \chi_{solvent} P^0_{solvent}$$

$\chi_{solvent}$ = Mole fraction of the solvent in the solution = χ_1

$P^0_{solvent}$ = Vapor pressure of the pure solvent = P_1^0

$$P_1 = \chi_1 P_1^0$$

- **This law applies <u>only to an ideal solution</u> where the solute doesn't contribute to the vapor pressure, i.e.,**
- **solute and solvent are alike: solute-solute, solvent-solvent and solute-solvent interactions are very similar).**

In a solution containing only one solute:

$$P_1 = (1 - \chi_2)P_1^0; \quad \chi_2 = \text{mole fraction of the solute}$$

$$P_1 = P_1^o - \chi_2 \times P_1^o$$

$$P_1^o - P_1 = \Delta P = \chi_2 P_1^o$$

$$VPL = \chi_{solute} \times P^o{}_{solvent}$$

Vapor pressure lowering

Thus the decrease in vapor pressure is directly proportional to Solute concentration expressed as mole fraction

Vapor pressure for solutions (non-ideal) of volatile solute and solvent

The vapor pressure of the solution is the sum of the individual partial pressures exerted by the solution components

$$P_A = \chi_A P_A^0 \qquad P_B = \chi_B P_B^0$$

P_A and P_B are the partial pressures over the solution

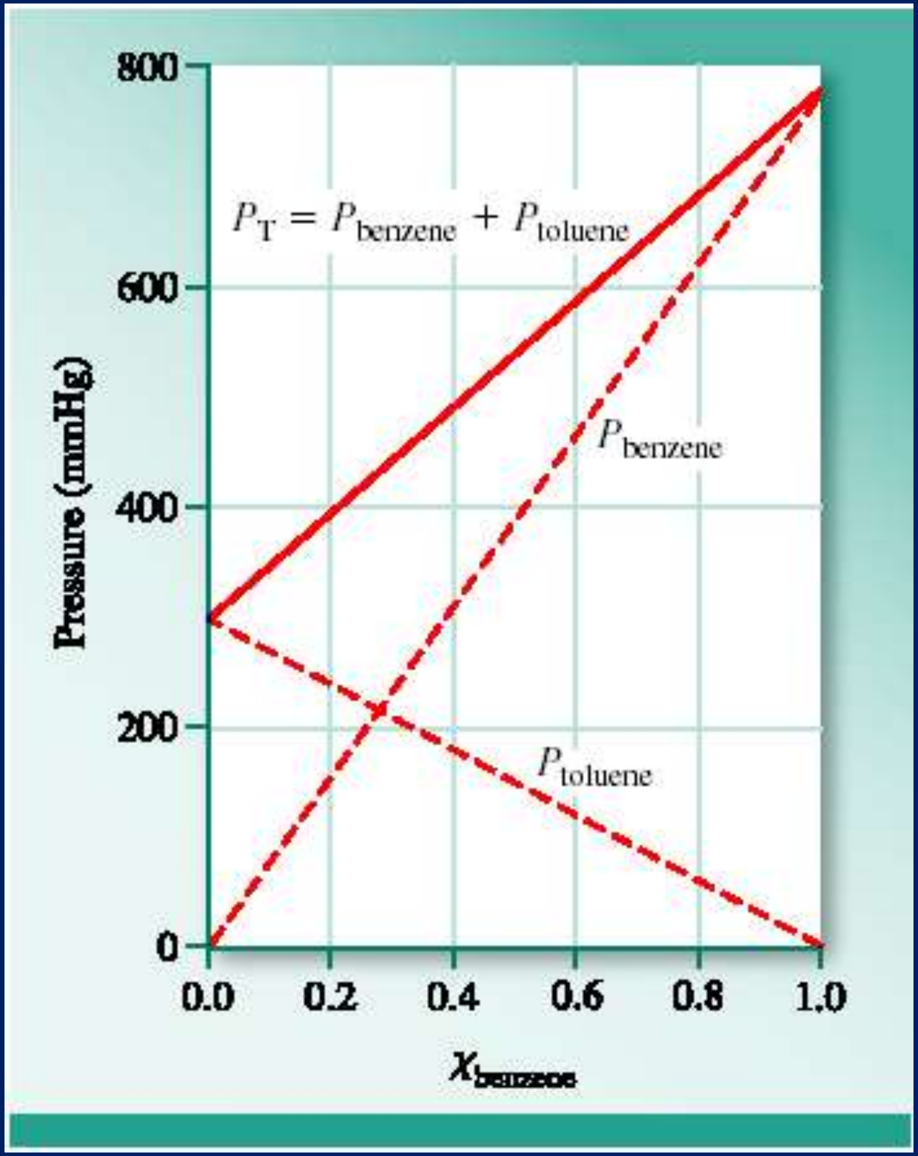
for components A and B

P_A^0 and P_B^0 are the vapor pressures of the pure

Substances A and B. P_T is the solution vapor pressure

$$P_T = \chi_A P_A^0 + \chi_B P_B^0$$

Ideal Solution* of Benzene and Toluene



*Obeys Raoult’s law

Example

Calculate the vapor pressure of a solution made by dissolving 115 g of urea, a nonvolatilesolute, [$(NH_2)_2CO$; molar mass = 60.06 g/mol] in 485 g of water at 25°C.

(At 25°C, $P_{H_2O} = 23.8 \text{ mmHg}$.)

$$P_{H_2O} = \chi_{H_2O} P^0_{H_2O}$$

$$\text{mol}_{H_2O} = 485 \text{ gx} \frac{\text{mol}}{18.02 \text{ g}} = 26.91 \text{ mol}$$

$$\text{mol}_{\text{urea}} = 115 \text{ g x} \frac{\text{mol}}{60.06 \text{ g}} = 1.915 \text{ mol}$$

$$\chi_{H_2O} = \frac{26.91 \text{ mol}}{26.91 \text{ mol} + 1.915 \text{ mol}} = 0.9336$$

$$P_{H_2O} = 0.9392 \text{ x } 23.8 \text{ mmHg} = 22.2 \text{ mmHg}$$

Boiling Point Elevation

- A nonvolatile solute lowers the vapor pressure of the solvent above the solution
- A higher T is required to reach the 1 atm of pressure which defines the boiling point
- A nonvolatile solute elevates the boiling point of the solvent

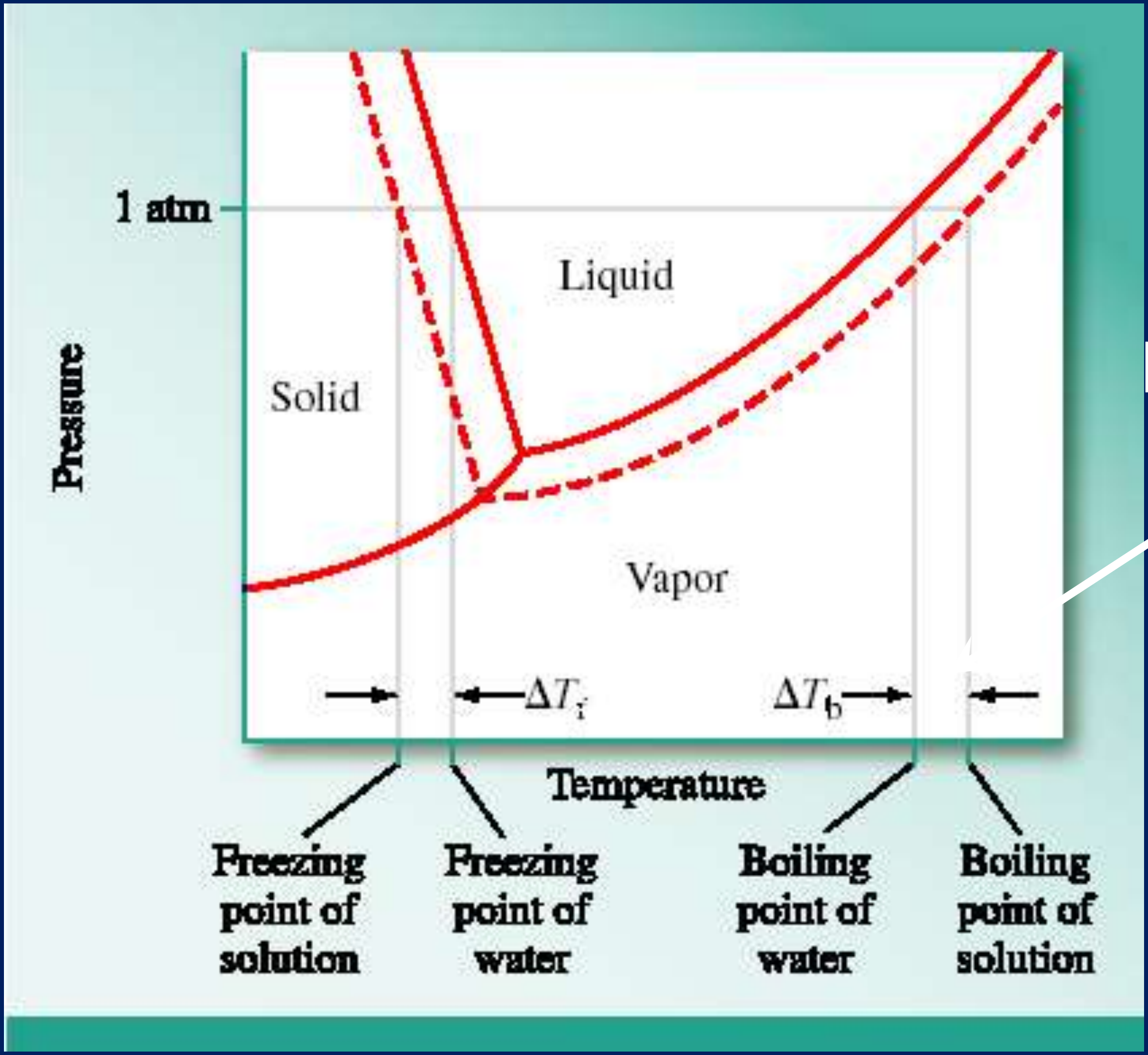
$$\Delta T_b = T_b - T_b^0$$

- The amount of the elevation depends on the molal concentration of the solute

$$\Delta T_b = K_b m$$

K_b is the molal boiling-point elevation constant (ºC/m) .

Effect of Vapor Pressure Lowering



Effect on Boiling Point

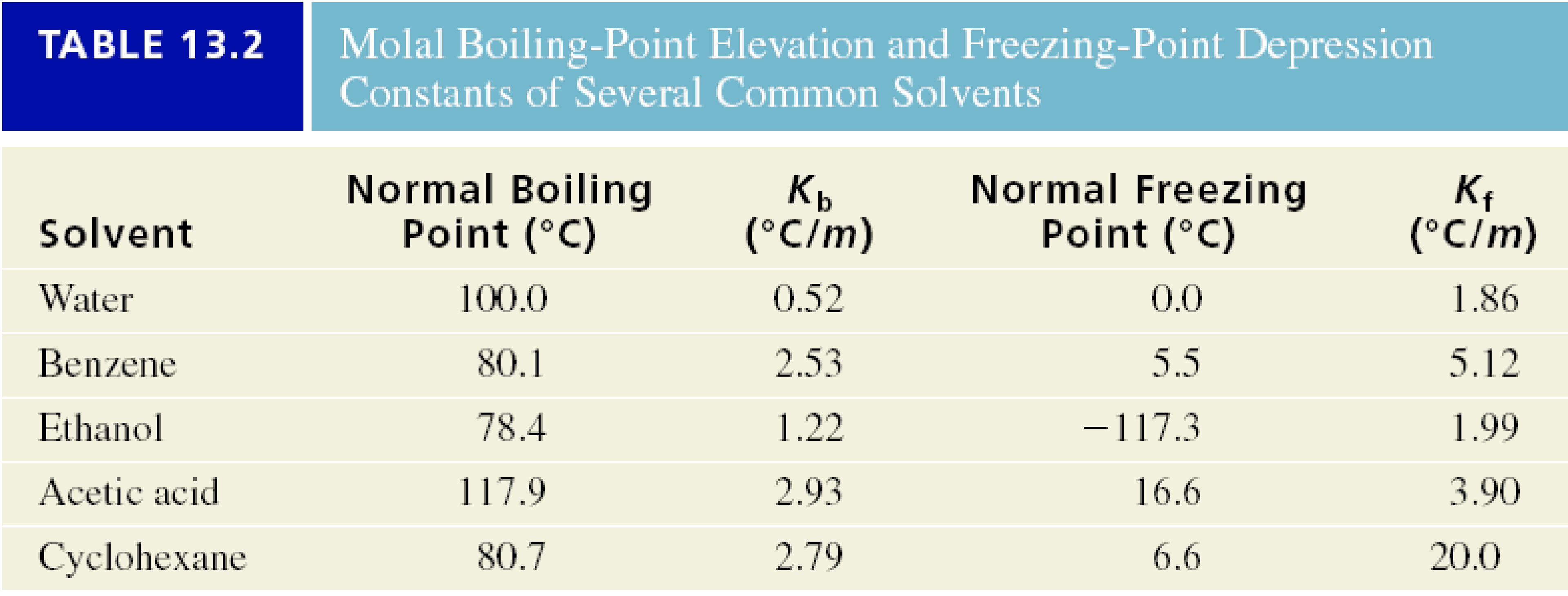


TABLE 13.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Solvents

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water	100.0	0.52	0.0	1.86
Benzene	80.1	2.53	5.5	5.12
Ethanol	78.4	1.22	−117.3	1.99
Acetic acid	117.9	2.93	16.6	3.90
Cyclohexane	80.7	2.79	6.6	20.0

Freezing Point Depression

- Vapor pressure of solid and liquid are equal at freezing point
- nonvolatile solute lowers the vapor pressure so a lower T is needed to decrease the vapor pressure to that of the solid
- a nonvolatile solute depresses the freezing point of the solvent

$$\Delta T_{\mathrm{f}} = T_{\mathrm{f}}^{0} - T_{\mathrm{f}}$$

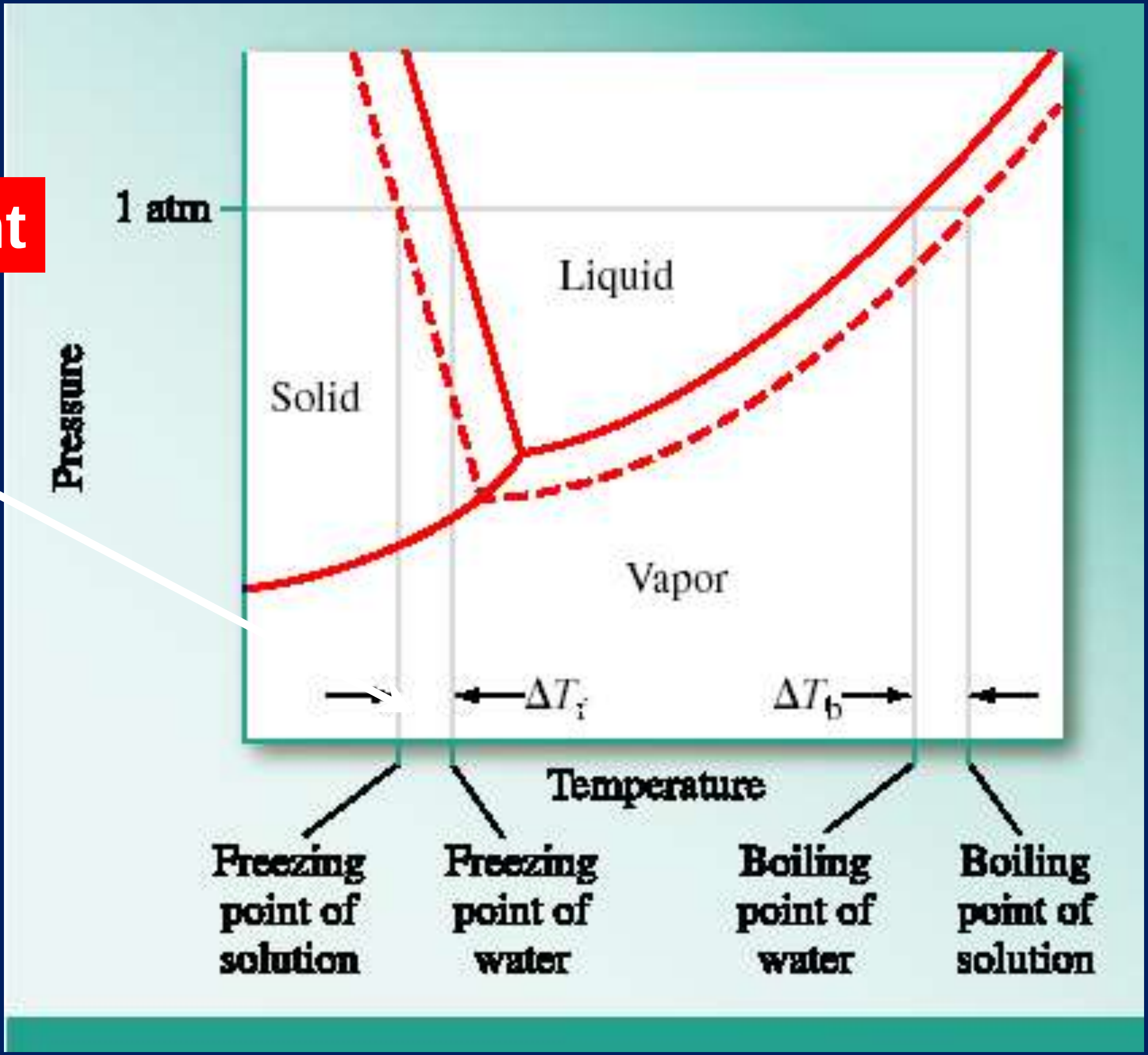
- the amount of the depression depends on the molal concentration of the solute

$$\Delta T_{\mathrm{f}} = K_{\mathrm{f}} m$$

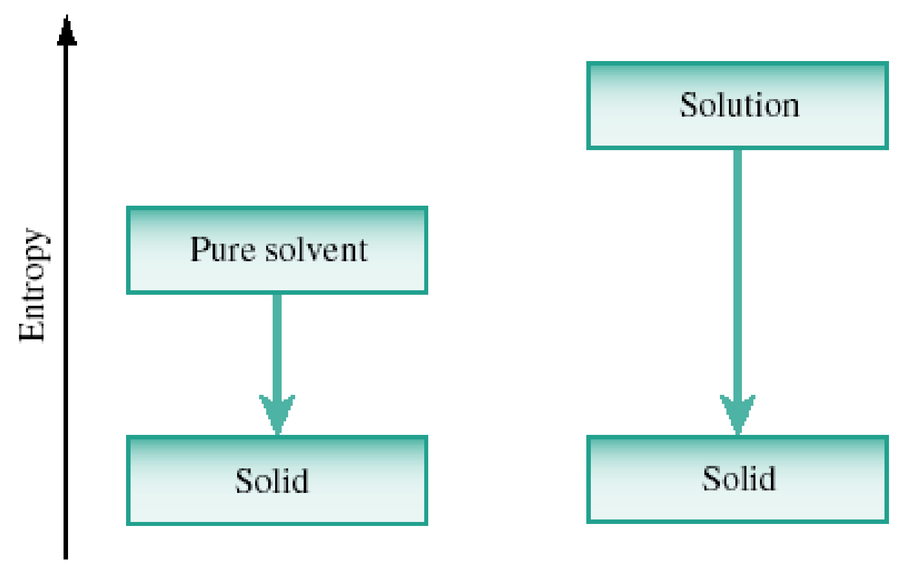
K_f is the molal freezing-point depression constant (°C/m) .

Effect of Vapor Pressure Lowering

Effect on Freezing Point



Entropy and Freezing Point



- Freezing is associated With transition from more disordered liquid state to a more ordered solid state
- The solution has a higher entropy than the solvent
- There is a bigger difference in entropy between the solution and the solid than that between solid and pure solvent
- Bigger difference in entropy means more energy has to be removed to get freezing happens
- Thus a depression in freezing point will occur

Example

Calculate a) the freezing point and b) the boiling point of a solution containing 268 g of ethylene glycol and 1015 g of water. (The molar mass of ethylene glycol ($C_2H_6O_2$) is 62.07 g/mol. K_b and K_f for water are 0.512°C/*m* and 1.86°C/*m*, respectively.)

a) freezing point

$$\text{mol ethylene glycol} = 268\ \text{g x}\ \frac{\text{mol}}{62.07\ \text{g}} = 4.318\ \text{mol}$$

$$m = 4.318\ \text{mol x}\ \frac{1}{1015\ \text{g}}\ \text{x}\ \frac{10^3\ \text{g}}{\text{kg}} = 4.254\ m$$

$$\Delta T_\text{f} = \frac{1.86^\circ\text{C}}{m}\ x\ 4.254\ m = 7.91^\circ\text{C}$$

$$7.91^\circ\text{C} = 0.00^\circ\text{C} - T_\text{f} \quad \Rightarrow \quad T_\text{f} = -7.91^\circ\text{C}$$

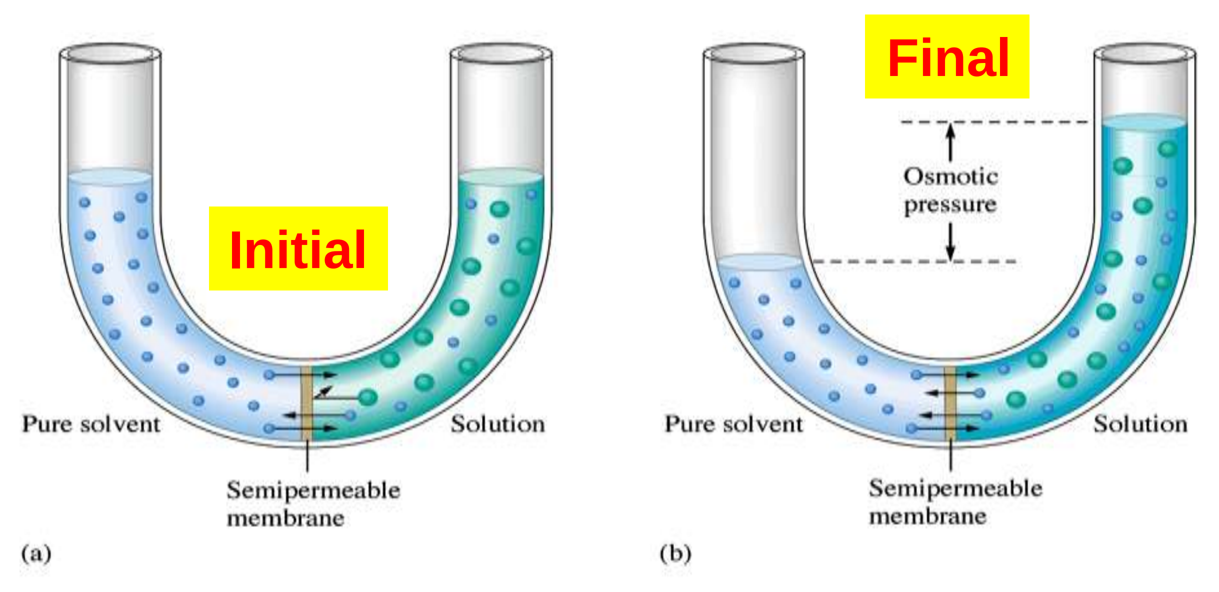
b) boiling point

$$\Delta T_\mathrm{b} = \frac{0.512^\mathrm{o}\mathrm{C}}{m} \;\; x \;\; 4.254 \;\; m = 2.18^\mathrm{o}\mathrm{C}$$

$$2.18^\mathrm{o}\mathrm{C} = T_\mathrm{b} - 100.00^\mathrm{o}\mathrm{C}$$

$$T_\mathrm{b} = 102.18^\mathrm{o}\mathrm{C}$$

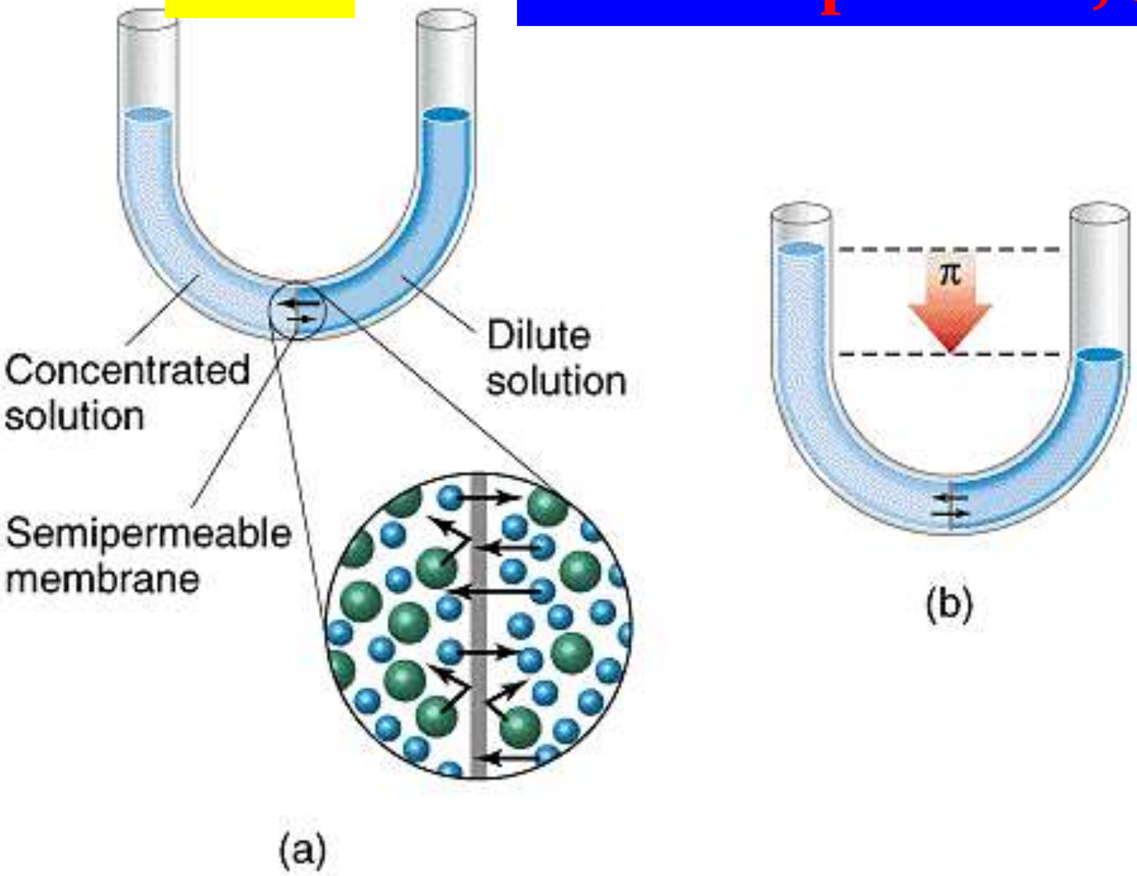
Osmosis



- Osmosis - Selective passage of solvent molecules through a semipermeable membrane
- Semipermeable membrane is a partition with pores that allows small solvent particles to pass through but not bigger solute particles. Thus, it separates a solution and a pure solvent
- when the system has reached equilibrium, the water levels are different
- Because the liquid levels are different, there is a greater *hydrostatic pressure* on the solution than on pure solvent

Osmotic pressure, π

Before



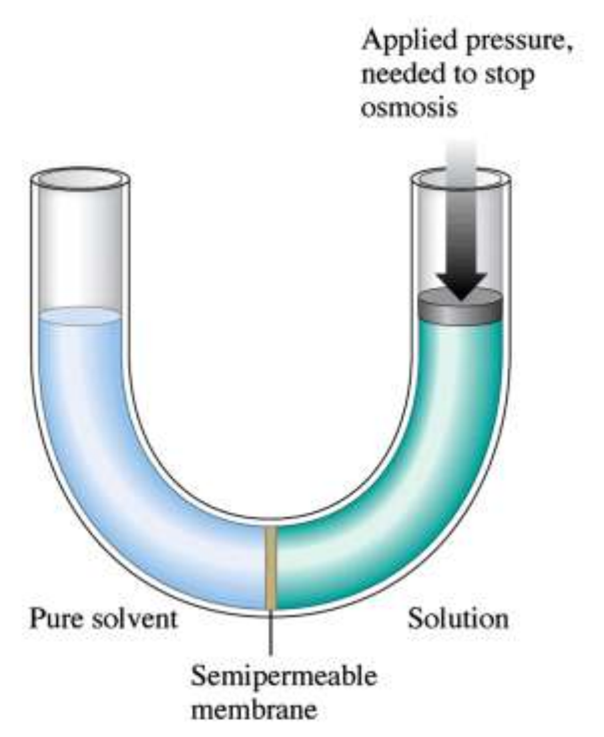
Osmotic pressure of a solution:
The minimum pressure that stops the osmosis

Osmotic pressure, π, and concentration of nonelectrolytes

- π α molarity of soultion, M
- PV = nRT (Ideal gas equation)
- Relation between π and M is the same: $\pi V = nRT$

$$\boxed{\pi = \left(\frac{n}{V}\right)RT = MRT}$$

- Where *R* is 0.08206 L·atm/mol · K and T is in kelvin



Example

- When 1.00x10^{-3} g of a protein is mixed with water to make 1.00 mL of solution, the osmotic pressure is 1.12 torr at 25.0°C. Find the molar mass of this protein.

$$\Pi = M \cdot R \cdot T$$

$$\Pi = 1.12 torr \times \frac{1 atm}{760 torr} = M\left(0.8206\frac{L \cdot atm}{mol \cdot K}\right)(298K)$$

$$M = \frac{6.01\times10^{-5}\ \text{mol protein}}{1\ \text{L solution}}$$

$$1.00\ \text{mL soln} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{6.01\times10^{-5}\ \text{mol}}{1\ \text{L}} = 6.01\times10^{-8}\ \text{mol protein}$$

$$\text{molar mass} = \frac{mass}{moles} = \frac{1.00\times10^{-3}\,g}{6.01\times10^{-8}\,mol} = 1.66\times10^{4}\ g/mol$$

Collegative properties of electrolytes solutions

- Colligative properties are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.
- Since colligative properties only depend on the number of solute particles, ionic compounds (salts) should have a bigger effect.
- When ionic compounds dissolve they dissociate into ions. NaCl dissociates into Na^+ and Cl^- ions
- 1 mole of NaCl makes 2 moles of ions.
- 1mole $Al(NO_3)_3$ makes 4 moles ions.

Electrolyte Solutions and colligative properties

- Dissociation of strong and weak electrolytes affects the number of particles in a solution
- *van't Hoft factor* (*i*) – accounts for the effect of dissociation

$$i = \frac{\text{actual number of particles in solution after dissociation}}{\text{number of formula units initially dissolved in solution}}$$

Modified Equations for Colligative Properties

$$\Delta T_{\mathrm{f}} = iK_{\mathrm{f}}m$$

$$\Delta T_{\mathrm{b}} = iK_{\mathrm{b}}m$$

$$\pi = iRTM$$

Vapor pressure lowering when ionic compounds are dissolved

- When NaCl is dissolved in water, the VPL is twice as much as expected.
- 1 mol NaCl dissociates into 1 mol Na^+ and 1 mol Cl-
- # mols of solute = 2 X # mols NaCl
- Thus, vapor pressure measurement can give information about the nature of the solute
- When Na_2SO_4 is dissolved VPL is <u>3 x expected</u>

The expected value (i) can be determined from the formula of the salt.

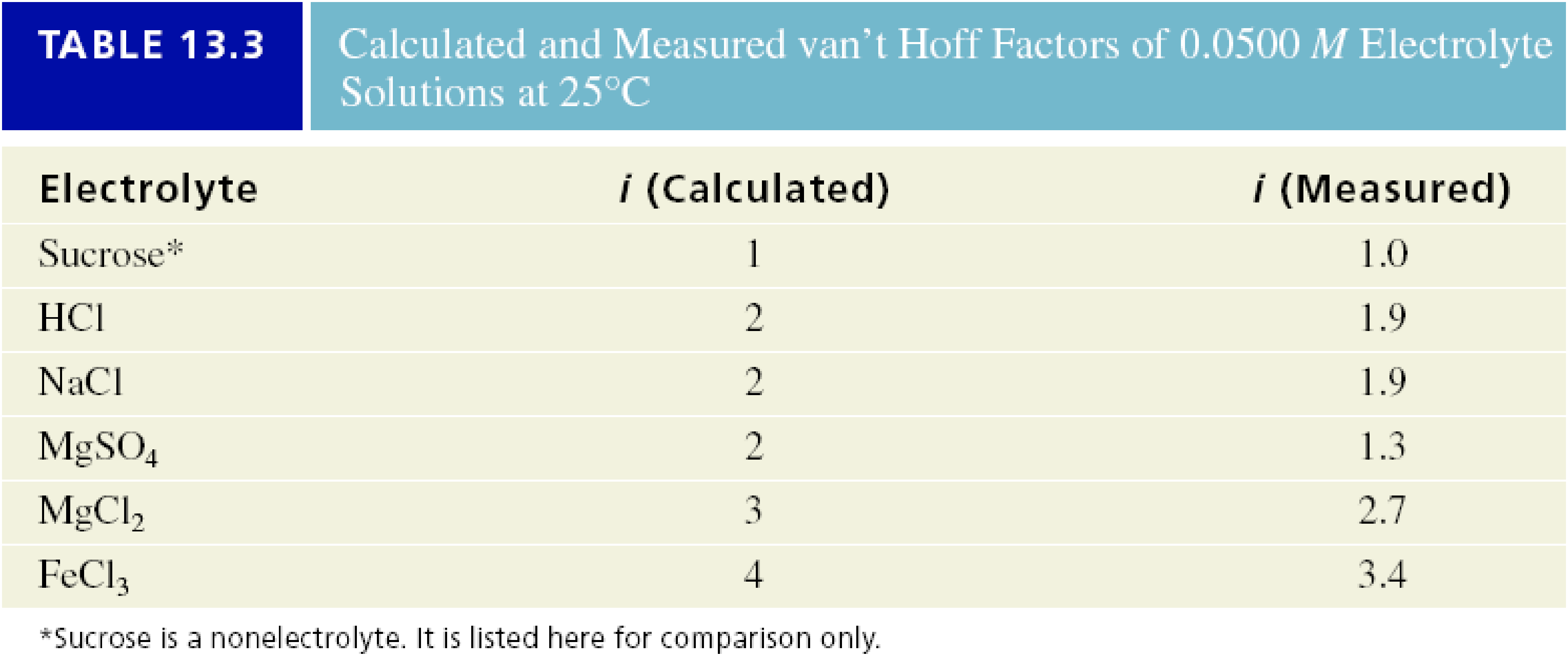


TABLE 13.3 Calculated and Measured van't Hoff Factors of 0.0500 *M* Electrolyte Solutions at 25°C

Electrolyte	*i* (Calculated)	*i* (Measured)
Sucrose*	1	1.0
HCl	2	1.9
NaCl	2	1.9
$MgSO_4$	2	1.3
$MgCl_2$	3	2.7
$FeCl_3$	4	3.4

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

Dissociation Equations and the Determination of *i*

$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ $i = 2$

$AgNO_3(s) \rightarrow Ag^{+}(aq) + NO_3^{-}(aq)$ $i = 2$

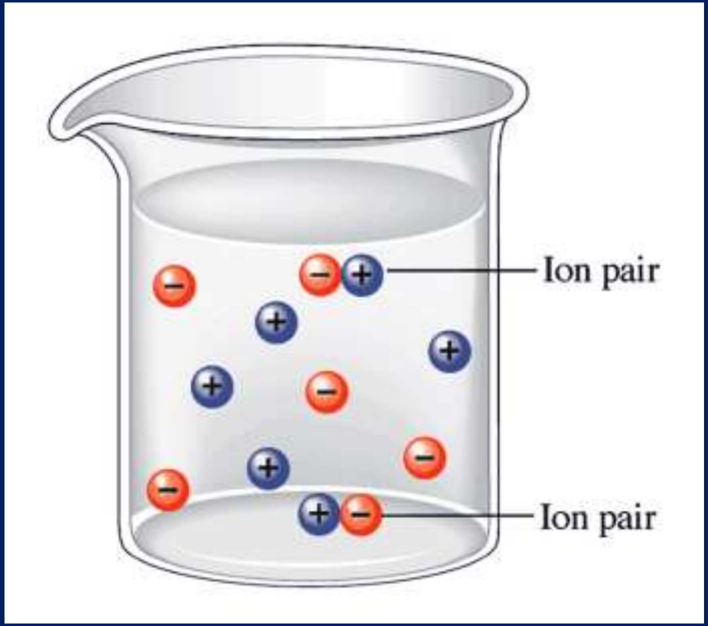
$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2\ Cl^{-}(aq)$ $i = 3$

$Na_2SO_4(s) \rightarrow 2\ Na^{+}(aq) + SO_4^{2-}(aq)$ $i = 3$

$AlCl_3(s) \rightarrow Al^{3+}(aq) + 3\ Cl^{-}(aq)$ $i = 4$

Ion pairing effect

- Observed *i* value is smaller than expected because at any given instant some of the ions in solution will be paired.
- Ion pairing tends to be higher for highly charged ions
- Ion pairing increases with concentration.
- *i* decreases with concentration.



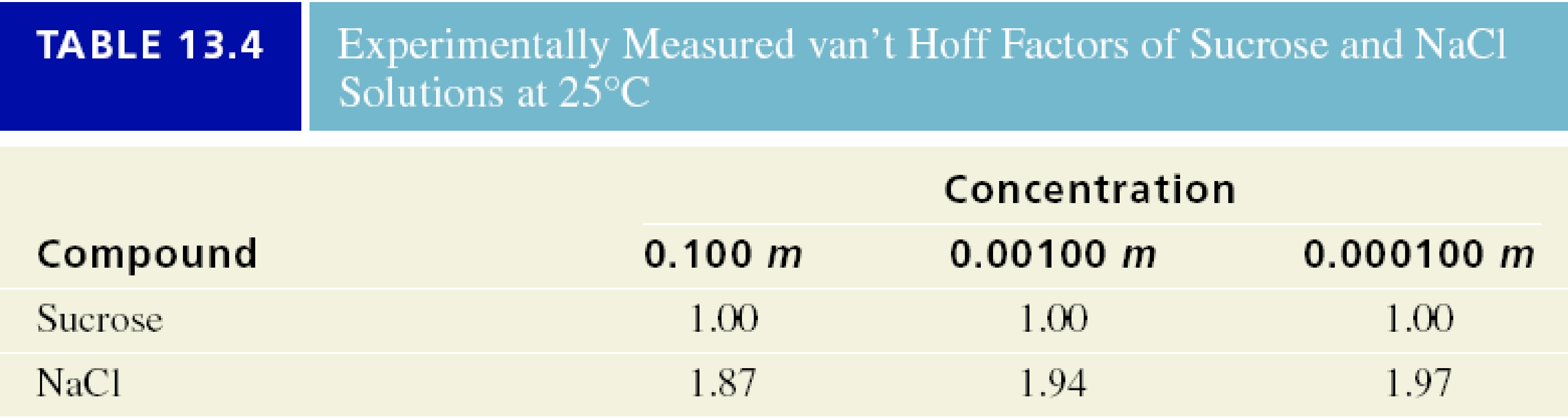


TABLE 13.4 Experimentally Measured van't Hoff Factors of Sucrose and NaCl Solutions at 25°C

	Concentration		
Compound	**0.100 *m***	**0.00100 *m***	**0.000100 *m***
Sucrose	1.00	1.00	1.00
NaCl	1.87	1.94	1.97

The freezing-point depression of a 0.100 *m* $MgSO_4$ solution is 0.225°C. Determine the experimental van't Hoff factor of $MgSO_4$ at this concentration.

$$\Delta T_f = iK_f m$$

$$0.225^\circ\mathrm{C} = i\,\frac{1.86^\circ\mathrm{C}}{m}\ x\ 0.100\ m$$

$$i = 1.21$$

Note, at this concentration the dissociation of $MgSO_4$ is not complete.

Another approach to the same problem:

Ideal freezing point depression

$$\Delta T_f = \frac{1.86^\circ\text{C}}{m} \text{ x } 0.100\ m = 0.186^\circ\text{C}$$

Compare ideal and real freezing point depression

$$i = \frac{0.225^\circ\text{C}}{0.186^\circ\text{C}} = 1.21$$

Example

A solution made by dissolving 25.0 mg of insulin in 5.00 mL of water has an osmotic pressure of 15.5 mmHg at 25°C. Calculate the molar mass of insulin. (Assume that there is no change in volume when the insulin is added to the water and that insulin is a nondissociating solute.)

Calculate the M of the solution

$$\pi = 15.5\ \text{mmHg}\ \text{x}\ \frac{\text{atm}}{760\ \text{mmHg}} = 2.039\text{x}10^{-2}\,\text{atm}$$

$$M = \frac{\pi}{RT} = 2.039\text{x}10^{-2}\,\text{atm}\ \text{x}\ \frac{\text{mol}\cdot\text{K}}{0.08206\ \text{L}\cdot\text{atm}}\ x\ \frac{1}{298\ \text{K}}$$

$$M = 8.338\ \text{x}\ 10^{-4}\,M = \frac{8.338\ \text{x}\ 10^{-4}\,\text{mol}}{\text{L}}$$

Calculate the moles of insulin

$$\text{mol} = \frac{8.340 \times 10^{-4}\,\text{mol}}{\text{L}} \times 5.00\ \text{mL} \times \frac{10^{-3}\,\text{L}}{\text{mL}} = 4.169 \times 10^{-6}\,\text{mol}$$

Molar mass is ratio of grams to moles

$$\mathcal{M} = 25.0\ \text{mg} \times \frac{10^{-3}\,\text{g}}{\text{mg}} \times \frac{1}{4.169 \times 10^{-6}\,\text{mol}}$$

$$\mathcal{M} = \frac{6.00 \times 10^{3}\,\text{g}}{\text{mol}}$$

Example

- Find the vapor pressure at 25°C for solution of 158.0 g of sucrose ($C_{12}H_{22}O_{11}$) in 643.5 mL of water. The density of water at 25°C is 0.9971 g/mL and the partial pressure of water vapor at 25°C is 23.76 torr.

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

$$\chi_{water} = \frac{643.5mL \times \frac{0.9971g}{1mL} \times \frac{1mol}{18.02g}}{\left(643.5mL \times \frac{0.9971g}{1mL} \times \frac{1mol}{18.02g}\right) + \left(158.0g \times \frac{1mol}{342.3g}\right)} = 0.9872$$

$$P_{soln} = (0.9872)(23.76torr) = 23.46torr$$

Example

18.00 g of glucose are added to 150.0 g of water. The boiling point of the solution is 100.34 C. The boiling point constant is 0.51 C*kg/mol.

Find the molar mass of glucose.

$$\Delta T = K_b \cdot m_{solute}$$

$$\Delta T = T_f - T_i = 100.34 - 100.00 = (0.51 \frac{C \cdot kg}{mol}) \cdot m_{solute}$$

$$m_{solute} = \frac{0.34C}{0.51C \cdot kg / mol} = 0.67 \frac{mol}{kg}$$

$$0.67\,\frac{mol}{kg} = \frac{n_{\mathrm{glucose}}}{0.1500\ \mathrm{kg\ water}}$$

$$n_{glucose} = (0.67\,\frac{mol}{kg})(0.1500kg) = 0.10mol$$

$$\text{molar mass} = \frac{mass}{moles} = \frac{18.00g}{0.10mol} = 180g\,/\,mol$$

Example

What mass of $C_2H_6O_2$ (M=62.1 g/mol) needs to be added to 10.0 L H_2O to make a solution that freezes at -23.3°C? density is 1.00 g/mL; boiling point constant is 1.86°C*kg/mol

$$\Delta T = K_f \cdot m_{solute}$$

$$\Delta T = T_f - T_i = -23.3 - 0.0 = (1.86\frac{C \cdot kg}{mol}) \cdot m_{solute}$$

$$m_{solute} = \frac{-23.3^\circ C}{1.86^\circ C \cdot kg/mol} = 12.5\frac{mol}{kg}$$

$$10.0\,\mathrm{L\ H_2O} \times \frac{1000\,\mathrm{mL}}{1\,\mathrm{L}} \times \frac{1\,\mathrm{g}}{1.00\,\mathrm{mL}} \times \frac{1\,\mathrm{kg}}{1000\,\mathrm{g}} = 10.0\,\mathrm{kg}$$

$$10.0\,\mathrm{kg\ H_2O} \times \frac{12.5\,\mathrm{mol\ C_2H_6O_2}}{1\,\mathrm{kg\ H_2O}} \times \frac{62.1\,\mathrm{g\ C_2H_6O_2}}{1\,\mathrm{mol\ C_2H_6O_2}} = 7.76\times10^3\ \mathrm{g\ C_2H_6O_2}$$

What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g.

$\Delta T_f = K_f\, m$ $\qquad$ K_f water = $1.86\ ^0\mathrm{C}/m$

$$\boldsymbol{m} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478\text{ g} \times \frac{1\text{ mol}}{62.01\text{ g}}}{3.202\text{ kg solvent}} = 2.41\ m$$

$$\Delta T_f = K_f\, m = 1.86\ ^0\mathrm{C}/m \times 2.41\ m = 4.48\ ^0\mathrm{C}$$

$$\Delta T_f = T_f^0 - T_f$$

$$T_f = T_f^0 - \Delta T_f = 0.00\ ^0\mathrm{C} - 4.48\ ^0\mathrm{C} = -4.48\ ^0\mathrm{C}$$

Example

- Osmotic pressure for 0.10 M solution of $Fe(NH_2)_2(SO_4)_2$ at 25°C was 10.8 atm. Compare the van't Hoff Factor observed and expected.
- $i_{exp} = 1+2+2=5$

$$\Pi = iMRT$$

$$i_{obs} = \frac{\Pi}{MRT} = \frac{10.8atm}{(0.10mol/L)\left(0.08206\frac{L\cdot atm}{mol\cdot K}\right)(298K)} = 4.4$$

$i_{obs} < i_{exp}$ because of high ion pairing