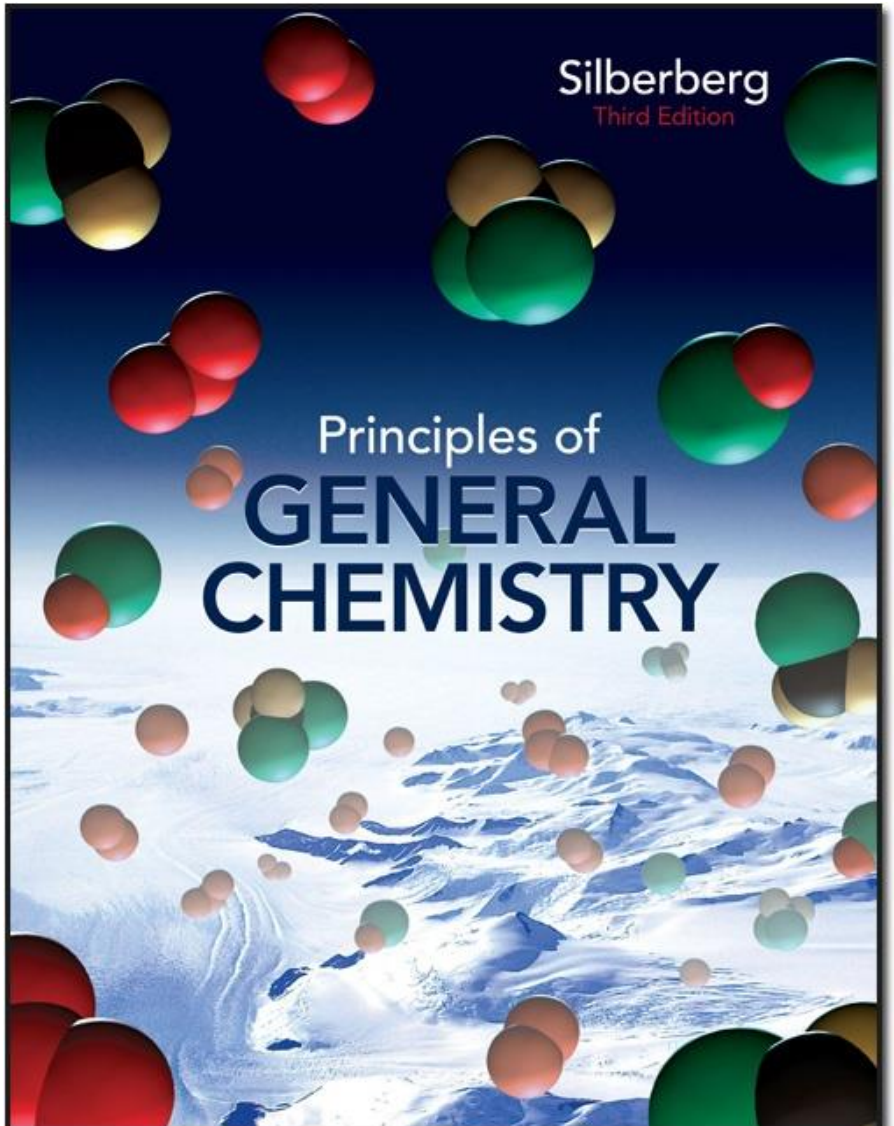


Chapter 13

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 13

The Properties of Solutions

The Properties of Mixtures: Solutions and Colloids

Solutions and Colloids

A ***solution*** is a ***homogeneous*** mixture and exists as a single phase.

The particles in a solution are individual atoms, ions, or small molecules.

A ***colloid*** is a ***heterogeneous*** mixture and exists as two or more phases, which may be visibly distinct.

The particles in a colloid are typically macromolecules or aggregations of small molecules.

Table 13.1 Approximate Composition of a Bacterium

Substance	Mass % of Cell	Number of Types	Number of Molecules
Water	~70	1	$5x10^{10}$
Ions	1	20	?
Sugars*	3	200	$3x10^{8}$
Amino acids*	0.4	100	$5x10^{7}$
Lipids*	2	50	$3x10^{7}$
Nucleotides*	0.4	200	$1x10^{7}$
Other small molecules	0.2	~200	?
Macromolecules (proteins, nucleic acids, polysaccharides).	23	~5000	$6x10^{6}$

*Includes precursors and metabolites.

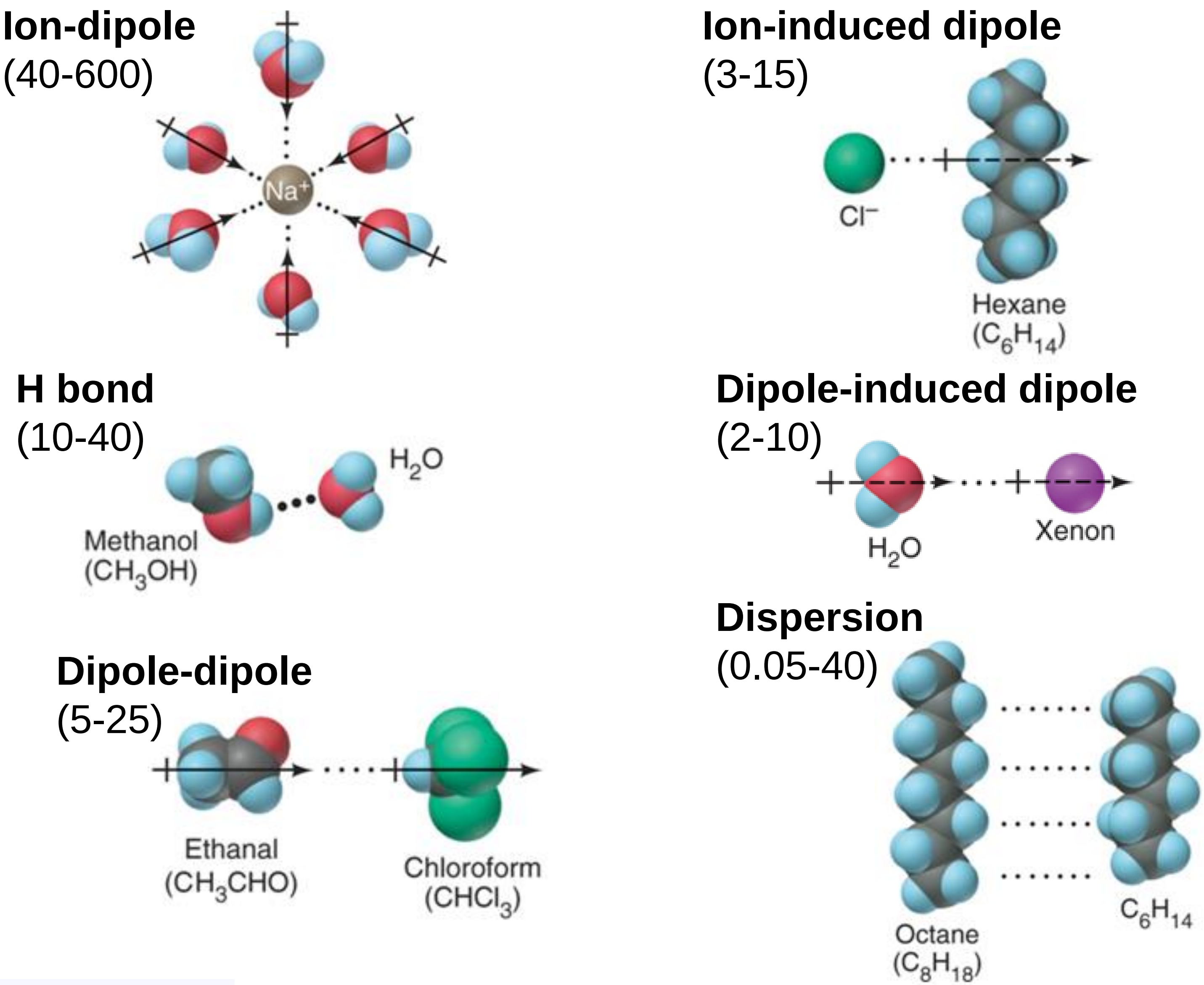
Solutions and Solubility

A ***solute*** dissolves in a ***solvent*** to form a solution.
Usually, the solvent is the most abundant component.

The ***solubility*** (***S***) of a solute is the maximum amount that dissolves in a fixed quantity of solvent at a given temperature.

Substances that exhibit ***similar types of intermolecular force*** dissolve in each other.
This is often expressed by saying "like dissolves in like."

Figure 13.1 Types of intermolecular forces in solutions.

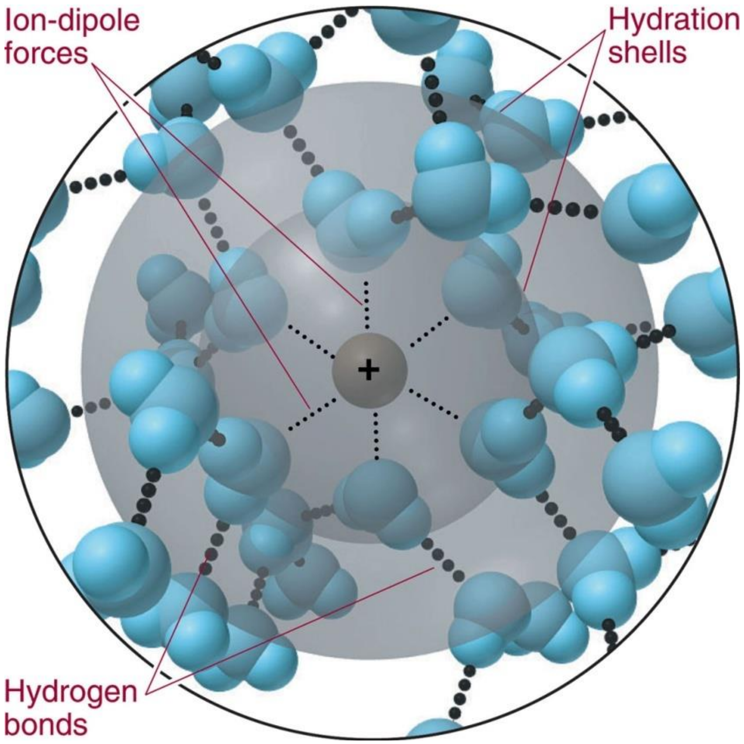


Solutions and Intermolecular Forces

When a solution forms, solute-solute attractions and solvent-solvent attractions are ***replaced*** by solute-solvent attractions.

This can only occur if the forces within the solute and solvent are ***similar*** to the forces that replace them.

Figure 13.2 Hydration shells around an Na^+ ion.

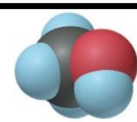
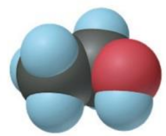
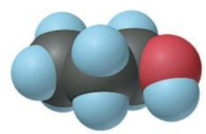
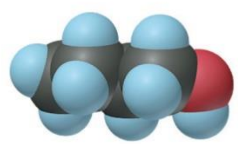
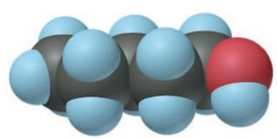
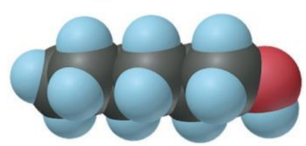


Ion-dipole forces orient water molecules around an ion. In the innermost shell here, six water molecules surround the cation octahedrally.

Dual Polarity and Effects on Solubility

- Alcohols are organic compounds that have ***dual polarity***.
  - The general formula for an alcohol is $CH_3(CH_2)_nOH$.
- The –OH group of an alcohol is ***polar***.
  - It interacts with water through ***H bonds*** and
  - with hexane through weak ***dipole-induced dipole forces***.
- The hydrocarbon portion is ***nonpolar***.
  - It interacts through weak ***dipole-induced dipole forces*** with water
  - and by ***dispersion forces*** with hexane.

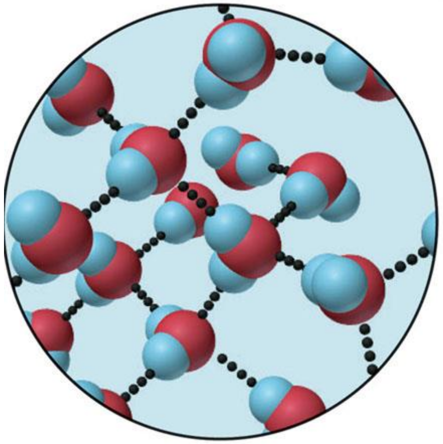
Table 13.2 Solubility* of a Series of Alcohols in Water and in Hexane

Alcohol	Model	Solubility in Water	Solubility in Hexane
CH_3OH (methanol)		∞	1.2
CH_3CH_2OH (ethanol)		∞	∞
$CH_3(CH_2)_2OH$ (propanol)		∞	∞
$(CH_3(CH_2)_3OH$ (1-butanol)		1.1	∞
$(CH_3(CH_2)_4OH$ (1-pentanol)		0.30	∞
$(CH_3(CH_2)_5OH$ (1-hexanol)		0.058	∞

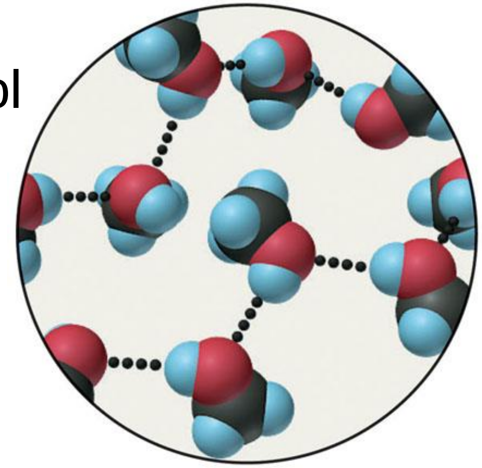
*Expressed in mol alcohol/1000 g solvent at 20°C.

Figure 13.3 Like dissolves like: solubility of methanol in water.

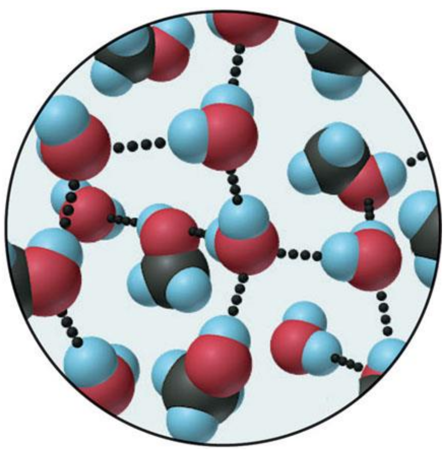
H_2O



Methanol
CH_3OH



Both H_2O and methanol have H bonds between their molecules.



A solution of water and methanol.

Sample Problem 13.1 **Predicting Relative Solubilities**

PROBLEM: Predict which solvent will dissolve more of the given solute.

(a) Sodium chloride in methanol (CH_3OH) or in propanol ($CH_3CH_2CH_2OH$).

(b) Ethylene glycol ($HOCH_2CH_2OH$) in hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or in water.

(c) Diethyl ether ($CH_3CH_2OCH_2CH_3$) in water or in ethanol (CH_3CH_2OH).

PLAN: We examine the formulas of solute and solvent to determine the forces in and between solute and solvent. A solute is more soluble in a solvent whose intermolecular forces are similar to, and therefore can replace, its own.

Sample Problem 13.1

SOLUTION:

(a) **Methanol.** NaCl is ionic, so it dissolves in polar solvents through ion-dipole forces. Both methanol and 1-propanol have a polar –OH group, but the hydrocarbon portion of each alcohol interacts only weakly with the ions and 1-propanol has a longer hydrocarbon portion than methanol.

(b) **Water**. Ethylene glycol molecules have two –OH groups, so they interact with each other through H bonding. H bonds formed with H_2O can replace these H bonds between solute molecules better than the dipole-induced dipole forces that form with hexane.

(c) **Ethanol**. Diethyl ether molecules interact through dipole-dipole and dispersion forces. They can form H bonds to H_2O or to ethanol. However, ethanol can also interact with the ether effectively through dispersion forces because it has a hydrocarbon chain.

Table 13.3 Correlation Between Boiling Point and Solubility in Water

Gas	Solubility (*M*)*	bp (K)
He	4.2×10^{-4}	4.2
Ne	6.6×10^{-4}	27.1
N_2	10.4×10^{-4}	77.4
CO	15.6×10^{-4}	81.6
O_2	21.8×10^{-4}	90.2
NO	32.7×10^{-4}	121.4

* At 273 K and 1 atm

Energy changes in Solution Formation

Step 1: Solute particles separate from each other. This process is ***endothermic***.

Solute (aggregated) + ***heat*** $\longrightarrow$ solute (separated) $\Delta H_{solute} > 0$

Step 2: Solvent particles separate from each other. This process is ***endothermic***.

Solvent (aggregated) + ***heat*** $\longrightarrow$ solvent (separated) $\Delta H_{solvent} > 0$

Step 3: Solute and solvent particles mix and form a solution. This step is ***exothermic***.

Solute (separated) + solvent (separated) $\rightarrow$ solution + ***heat*** $\Delta H_{mix} < 0$

Heat of Solution

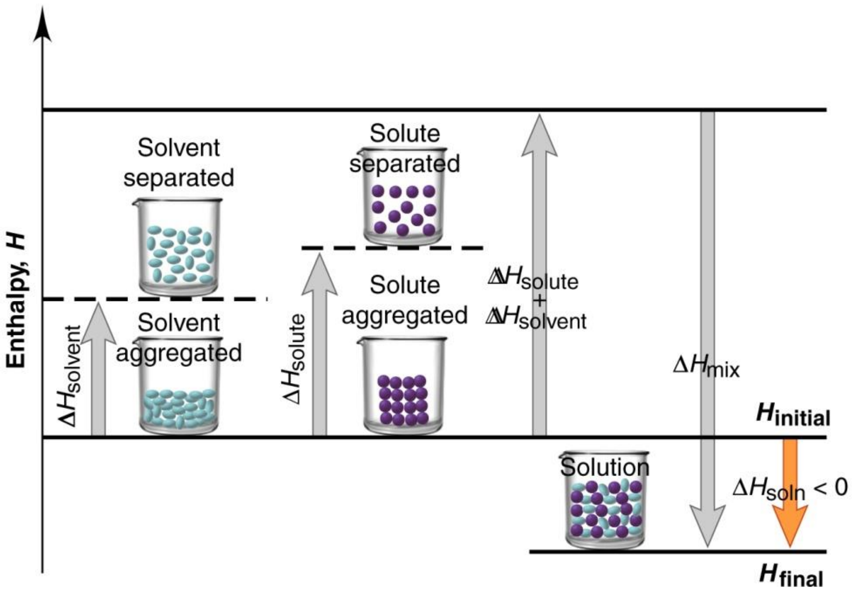
$$\boxed{\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}}$$

The overall solution process may be either exothermic or endothermic.

Exothermic process: $\Delta H_{soln} < 0$ because the sum of the endothermic processes ($\Delta H_{solute} + \Delta H_{solvent}$) is ***smaller*** than the exothermic term (ΔH_{mix}).

Endothermic process: $\Delta H_{soln} > 0$ because the sum of the endothermic processes ($\Delta H_{solute} + \Delta H_{solvent}$) is ***larger*** than the exothermic term (ΔH_{mix}).

Figure 13.4 Enthalpy components of the heat of solution.

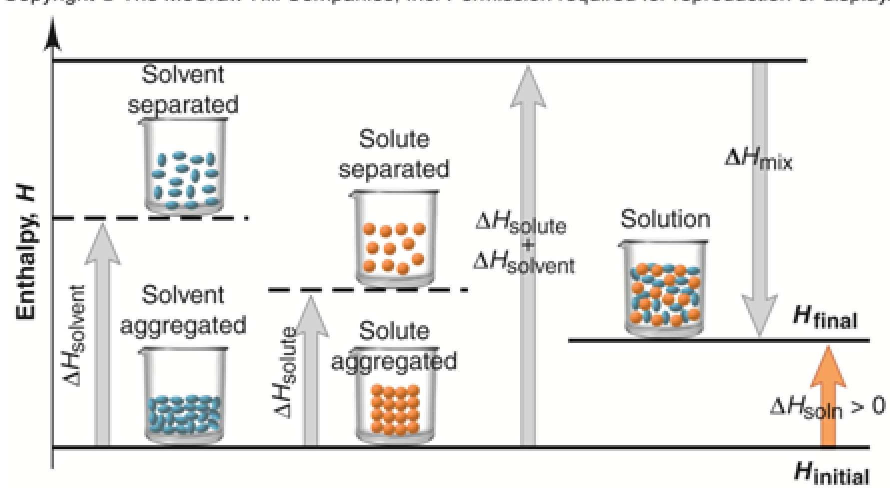


A Exothermic solution process

Exothermic solution process

$\Delta H_{mix} > \Delta H_{solute} + \Delta H_{solvent}$

$\Delta H_{soln} < 0$



B Endothermic solution process

Endothermic solution process

$\Delta H_{mix} < \Delta H_{solute} + \Delta H_{solvent}$

$\Delta H_{soln} > 0$

Solvation and Hydration

Solvation is the process of surrounding a particle with solvent particles. In water, solvation is called ***hydration***.

$$\Delta H_{solvation} = \Delta H_{solvent} + \Delta H_{mix}$$

In water, $\Delta H_{soln} = \Delta H_{solute} + \Delta H_{hydr}$

The hydration of an ion is ***always exothermic*** because ion-dipole forces are very strong.

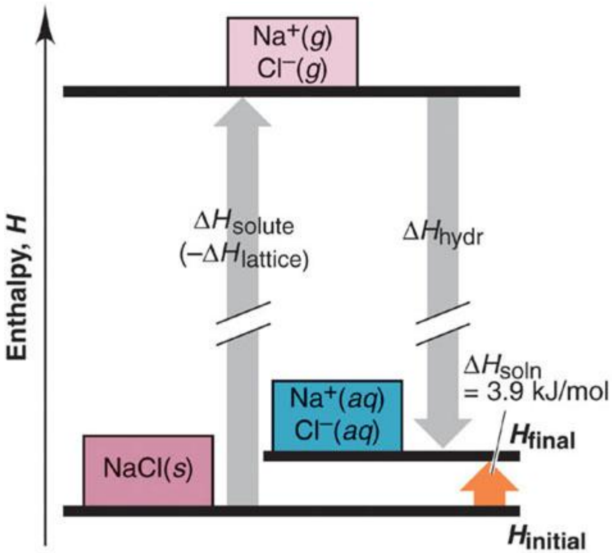
$M^+(g)$ [or $X^-(g)$] $\rightarrow$ $M^+(aq)$ [or $X^-(aq)$] $\Delta H_{\text{hydr of the ion}}$ (always < 0)

charge density

1- 2+ attract H_2O more strongly than +1. $\Delta H_{\text{hydr of the ion}}$ more negative

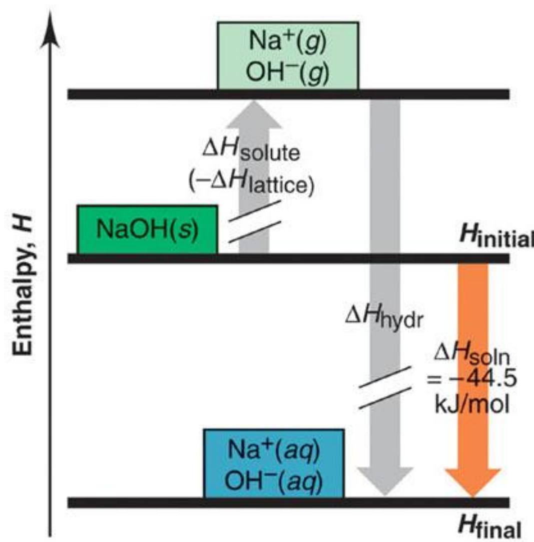
2- small +1 ion attract H_2O more strongly than bigger +1,

Figure 13.5 **Enthalpy diagrams for three ionic compounds dissolving in water.**



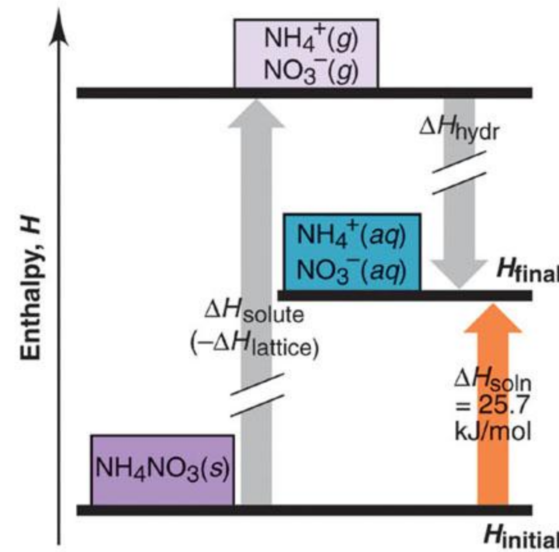
NaCl

endo



NaOH

exo



NH_4NO_3

endo

Solutions and Entropy

The ***entropy*** (***S***) of a system is related to the number of ways a system can disperse its energy and therefore to the ***freedom of motion (particles movements)*** of the particles.

Gases have the highest entropy of the three states of matter. $S_{(g)} > S_{(l)} > S_{(s)}$

$\Delta S_{vap} = S_{(g)} - S_{(l)}$, $\Delta S_{vap} > 0$

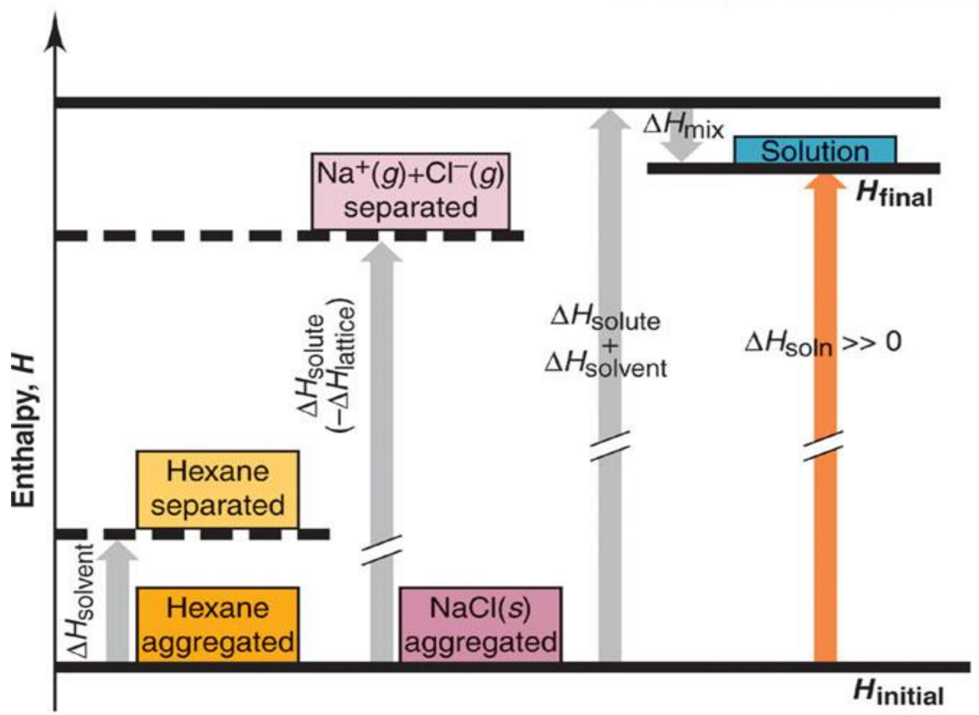
$\Delta S_{fus} = S_{(l)} - S_{(s)}$, $\Delta S_{fus} > 0$

A ***solution*** usually has higher entropy than the pure solute and pure solvent.(more interaction between different molecules)

$S_{soln} > (S_{Solute} + S_{solvent})$ $\Delta S_{sol} > 0$

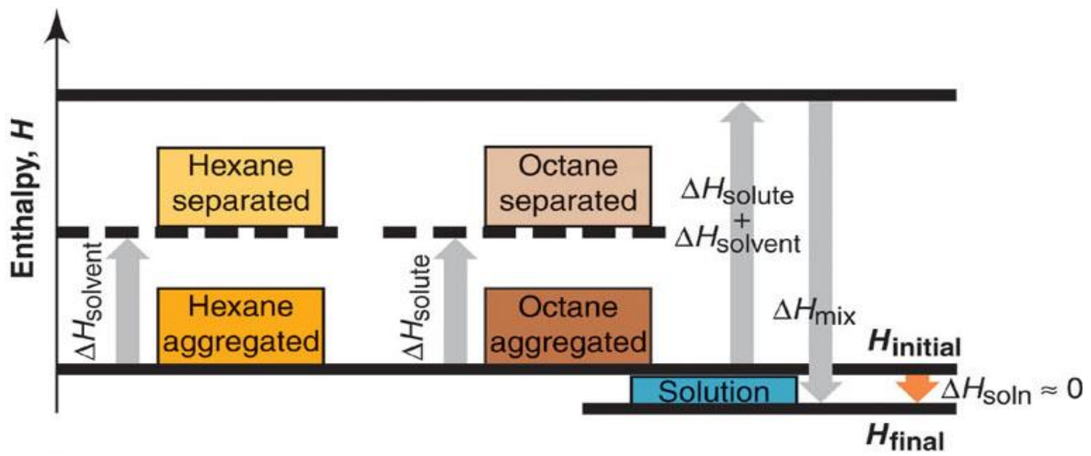
An ***increase in entropy*** is ***favored*** in both physical and chemical processes.

Figure 13.6A Enthalpy diagram for dissolving NaCl in hexane.



For NaCl, ΔH_{mix} is ***much*** smaller than ΔH_{solute}; ΔH_{soln} is so much larger than the entropy increase due to mixing that NaCl does ***not*** dissolve. $\Delta S_{sol} << \Delta H_{sol}$

Figure 13.6B Enthalpy diagram for dissolving octane in hexane.



-For octane, ΔH_{soln} is very small, but the entropy increase due to mixing is large, so octane dissolves. $\Delta S_{sol} >> \Delta H_{sol}$

-For ammonium nitrate NH_4NO_3 in water has $\Delta H_{sol} >> 0$ .But the increase in entropy that occurs when crystal break down and the ion mix with water molecules is greater than the increase in enthalpy $\Delta S_{sol} > \Delta H_{sol}$.

- Relative change of ΔH_{sol} and ΔS_{sol} determine the solution formation.
- If $\Delta H_{sol} > 0$ solute dissolve only if $\Delta S_{sol} > \Delta H_{sol}$

Solubility and Equilibrium

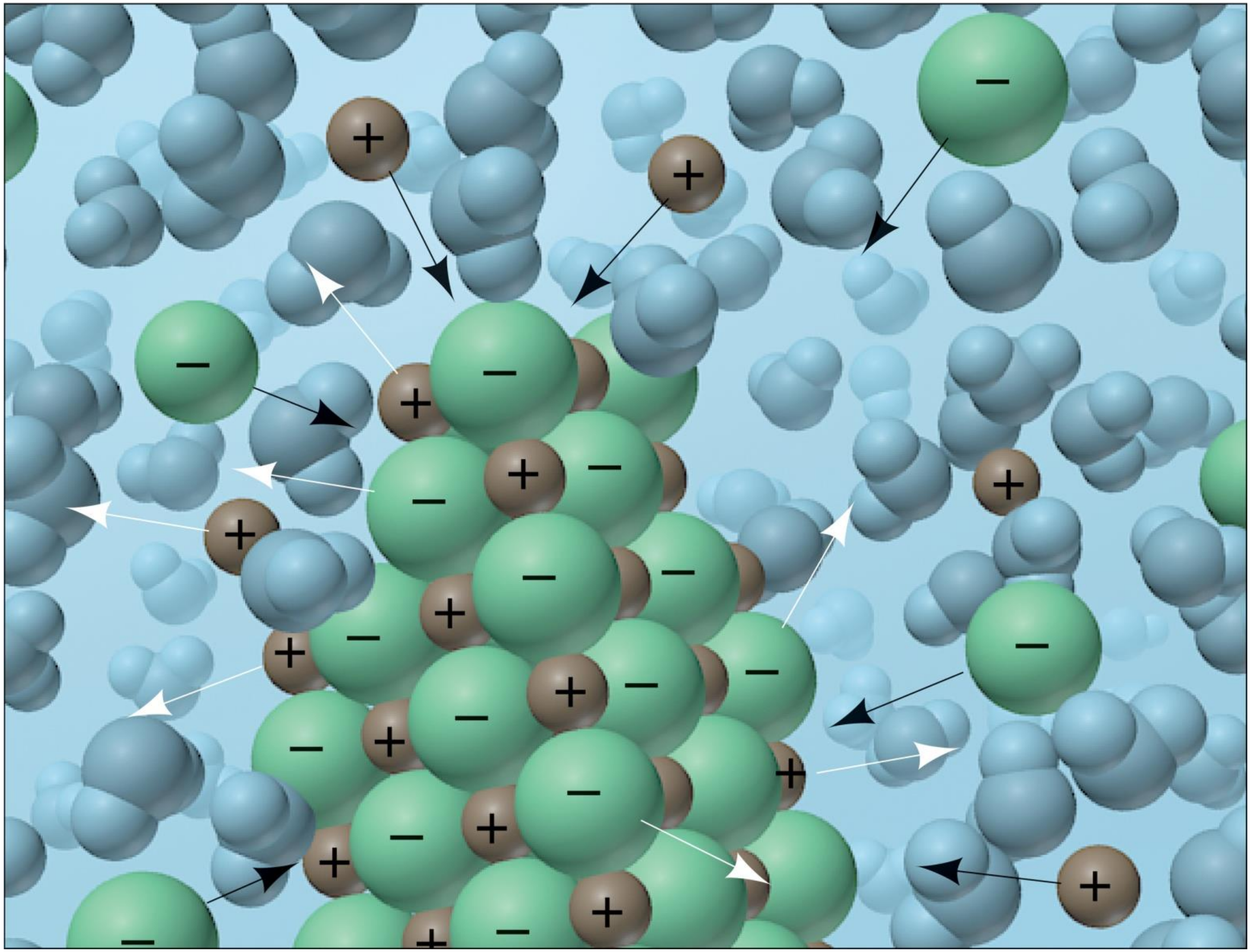
A ***saturated solution*** contains the maximum amount of dissolved solute at a given temperature in the presence of ***undissolved solute***.

Undissolved solute is ***in equilibrium*** with dissolved solute.

Solute (undissolved) ⇌ solute (dissolved)

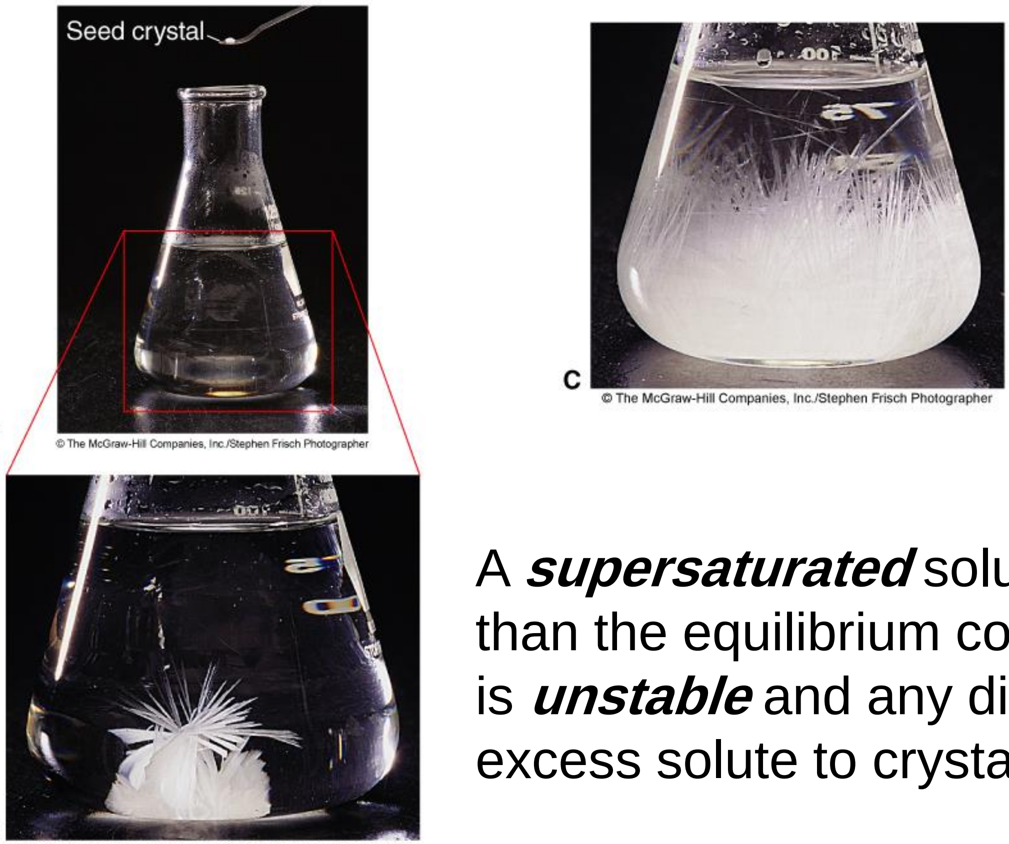
An ***unsaturated solution*** contains less than the equilibrium concentration of dissolved solute. If more solute is added, it will dissolve.

Figure 13. 7 Equilibrium in a saturated solution.



solute (undissolved) $\rightleftarrows$ solute (dissolved)

Figure 13. 8 Sodium acetate crystallizing from a supersaturated solution.



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B © The McGraw-Hill Companies, Inc./Stephen Frisch Photographer

C © The McGraw-Hill Companies, Inc./Stephen Frisch Photographer

A ***supersaturated*** solution contains ***more*** than the equilibrium concentration of solute. It is ***unstable*** and any disturbance will cause excess solute to crystallize immediately.

Factors that affect Solubility

Temperature affects solubility.
Most ***solids*** are ***more*** soluble at higher temperatures.
Gases become ***less*** soluble as temperature increases.

Pressure affects the solubility of gases – they become ***more*** soluble at higher pressure.

Figure 13. 9 Relation between solubility and temperature for several ionic compounds.

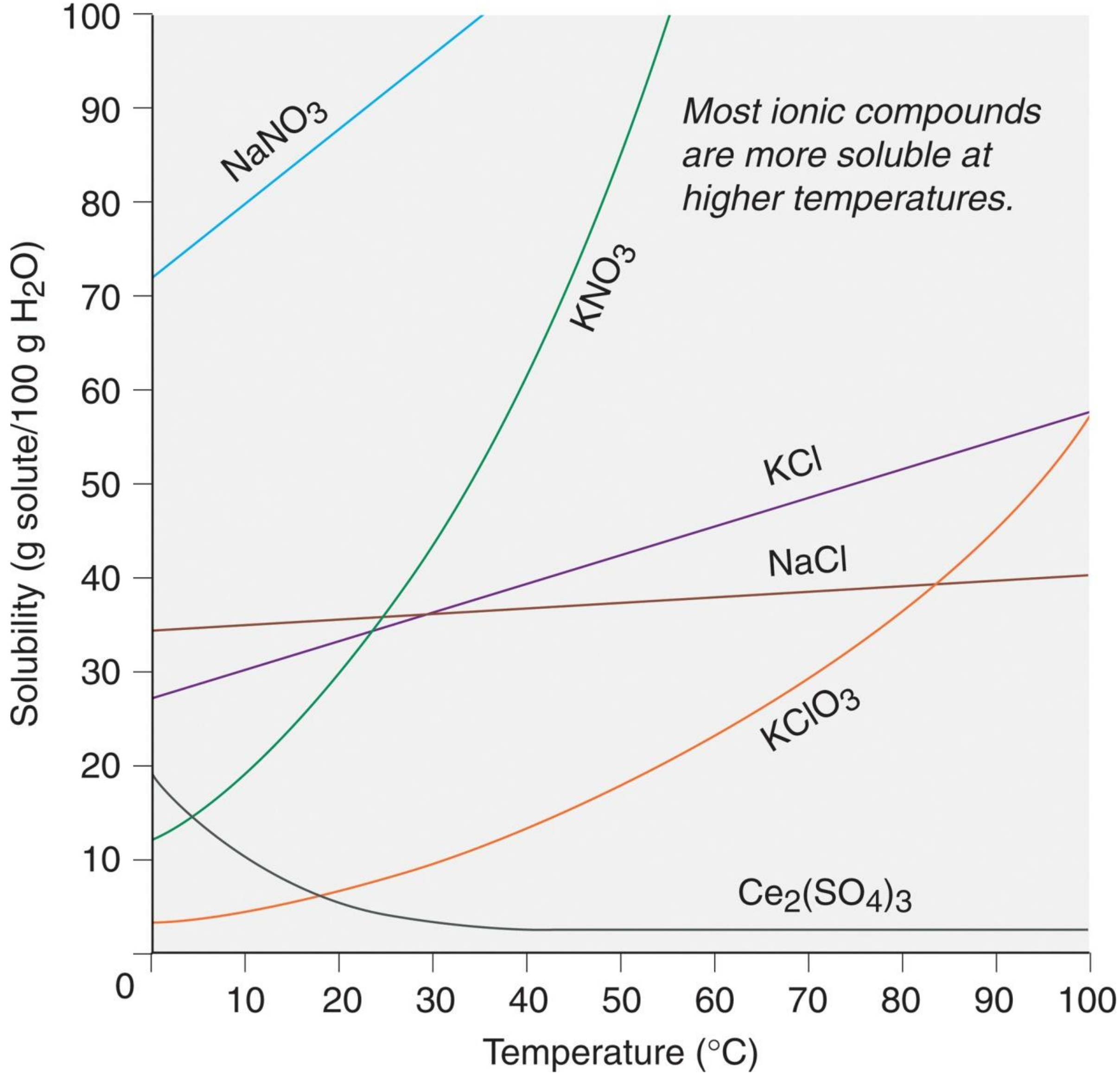
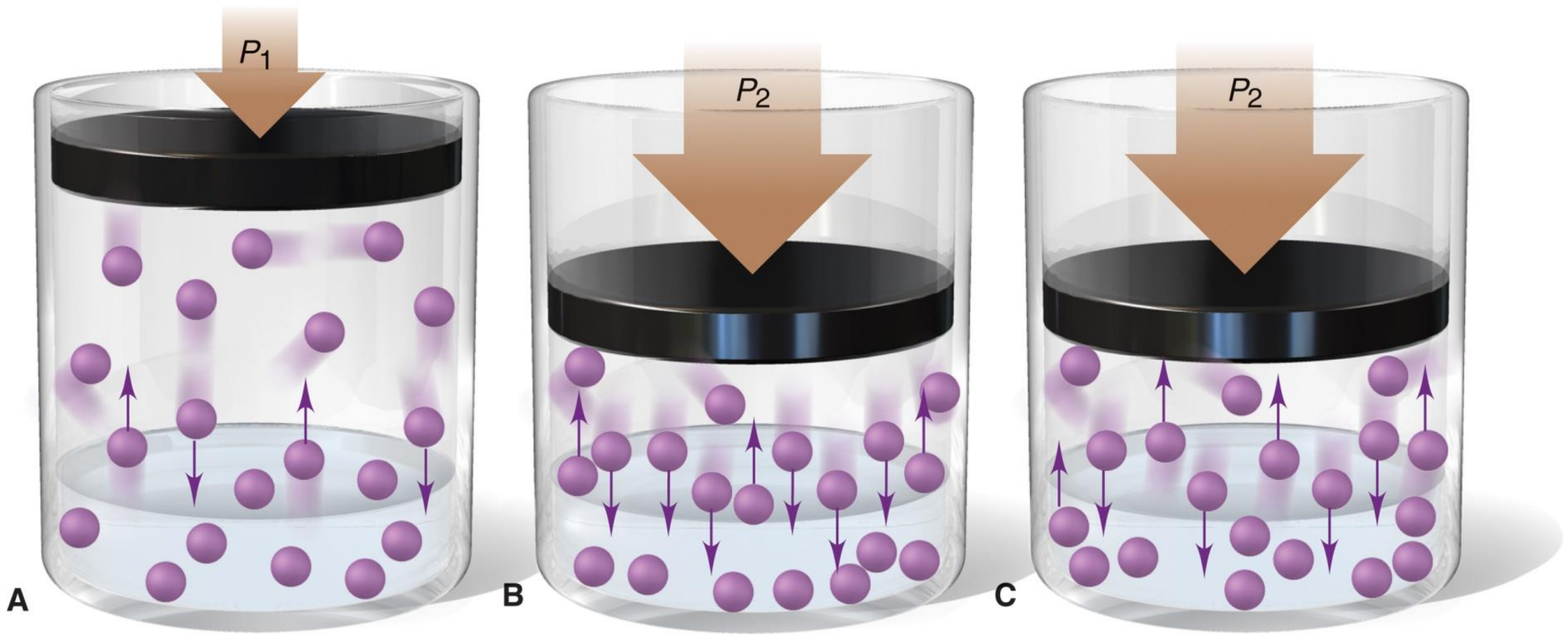


Figure 13.10 The effect of pressure on gas solubility.



As the pressure is increased, more gas particles collide with the liquid surface. More gas particles dissolve until equilibrium is re-established.

Henry's Law

The solubility of a gas (S_{gas}) is ***directly*** proportional to the ***partial pressure*** of the gas (P_{gas}) above the solution.

$$\boxed{S_{gas} = k_H \times P_{gas}}$$

k_H : Henry's law constant, : $mol.L^{-1}.atm^{-1}$

S : $mol.L^{-1}$, P: atm ,

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Sample Problem 13.2 **Using Henry's Law to Calculate Gas Solubility**

PROBLEM: The partial pressure of carbon dioxide gas inside a bottle of cola is 4 atm at 25°C. What is the solubility of CO_2? The Henry's law constant for CO_2 dissolved in water is 3.3 x10^{-2} mol/L·atm at 25°C.

PLAN: We know P for CO_2 (4 atm) and the value of k_H, so we substitute these into the Henry's law equation.

SOLUTION:

$$S_{CO_2} = (3.3 \times 10^{-2}\ \text{mol/L·atm})(4\ \text{atm}) = \boxed{\mathbf{0.1\ mol/L}}$$

Table 13.4 Concentration Definitions

Concentration Term	Ratio
Molarity (M)	$\frac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (m)	$\frac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\frac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\frac{\text{volume of solute}}{\text{volume of solution}}$
Mole fraction (X)	$\frac{\text{amount (mol) of solute}}{\text{amount (mol) of solute + amount (mol) of solvent}}$

Molarity (M) $\dfrac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$

Molarity has two draw back that affect its use in precise work:

1- effect of Temperature : unit volume of hot solution has less solute than cold solution

$\longrightarrow$ Molarity is different.

2- effect of Mixing : some solute solvent interaction are difficult to predict, so volume may not be additive 500 mL+ 500 mL may not 1000mL.

Molality (m) $\dfrac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$

Molality has two advantages

1- masses of component not effect with temperature.

2- mass are additive $\longrightarrow$ no effect for mixing

Sample Problem 13.3 **Calculating Molality**

PROBLEM: What is the molality of a solution prepared by dissolving 32.0 g of $CaCl_2$ in 271 g of water?

PLAN: Molality is defined as moles of solute ($CaCl_2$) divided by kg of solvent (H_2O). We convert the mass of $CaCl_2$ to moles using the molar mass, and then divide by the mass of H_2O, being sure to convert from grams to kilograms.

mass (g) of $CaCl_2$

↓ **divide by $\mathcal{M}$ of (g/mol)**

amount (mol) of $CaCl_2$

↓ **divide by kg of water**

molality (*m*) of $CaCl_2$ solution

Sample Problem 13.3

SOLUTION:

$$32.0\ \text{g CaCl}_2 \times \frac{1\ \text{mol CaCl}_2}{110.98\ \text{g CaCl}_2} = 0.288\ \text{mol CaCl}_2$$

$$\text{molality} = \frac{0.288\ \text{mol CaCl}_2}{271\ \text{g H}_2\text{O} \times \frac{1\ \text{kg}}{10^3\ \text{g}}} \boxed{= \mathbf{1.06}\ m\ \mathbf{CaCl_2}}$$

Sample Problem 13.4 **Expressing Concentrations in Parts by Mass, Parts by Volume, and Mole Fraction**

PROBLEM: **(a)** Find the concentration of calcium (in ppm) in a 3.50-g pill that contains 40.5 mg of Ca.

(b) The label on a 0.750-L bottle of Italian chianti indicates "11.5% alcohol by volume." How many liters of alcohol does the wine contain?

(c) A sample of rubbing alcohol contains 142 g of isopropyl alcohol (C_3H_7OH) and 58.0 g of water. What are the mole fractions of alcohol and water?

PLAN: **(a)** We convert mg to g of Ca^{2+}, find the mass ratio of Ca^{2+} to pill and multiply by 10^6.

(b) We know the volume % of the alcohol and the total volume, so we can find the volume of alcohol.

(c) We convert g of solute and solvent to moles in order to calculate the mole fractions.

Sample Problem 13.4

SOLUTION:

(a)
$$\frac{40.5 \text{ mg } Ca^{2+} \times \dfrac{1 \text{ g}}{10^3 \text{ mg}}}{3.5 \text{ g}} \times 10^6 \quad \boxed{\mathbf{= 1.16x10^4 \text{ ppm } Ca^{2+}}}$$

(b)
$$0.750 \text{ L chianti} \times \frac{11.5 \text{ L alcohol}}{100. \text{ L chianti}} \quad \boxed{\mathbf{= 0.0862 \text{ L alcohol}}}$$

(c)

moles isopropyl alcohol = $142 \text{ g} \times \dfrac{1 \text{ mole}}{60.09 \text{ g}} = 2.36 \text{ mol } C_3H_7OH$

moles water = $58.0 \text{ g} \times \dfrac{1 \text{ mole}}{18.02 \text{ g}} = 3.22 \text{ mol } H_2O$

Sample Problem 13.4

$$X_{C_3H_7OH} = \frac{2.36 \text{ mol } C_2H_8O_2}{2.36 \text{ mol } C_3H_7OH + 3.22 \text{ mol } H_2O} \quad \boxed{= 0.423}$$

$$X_{H_2O} = \frac{3.22 \text{ mol } H_2O}{2.36 \text{ mol } C_3H_7OH + 3.22 \text{ mol } H_2O} \quad \boxed{= 0.577}$$

Interconverting Concentration Terms

- To convert a term based on amount (mol) to one based on mass, you need the ***molar mass***.
- To convert a term based on mass to one based on volume, you need the solution **density**.
- Molality involves quantity of *solvent*, whereas the other concentration terms involve quantity of *solution.*

Sample Problem 13.5 **Interconverting Concentration Terms**

PROBLEM: Hydrogen peroxide is a powerful oxidizing agent used in concentrated solution in rocket fuels and in dilute solution as a hair bleach. An aqueous solution H_2O_2 is 30.0% by mass and has a density of 1.11 g/mL. Calculate its

(a) Molality **(b)** Mole fraction of H_2O_2 **(c)** Molarity

PLAN: **(a)** To find the mass of solvent we assume the % is per 100 g of solution. Take the difference in the mass of the solute and solution for the mass of peroxide.

(b) Convert g of solute and solvent to moles before finding X.

(c) Use the density to find the volume of the solution.

Sample Problem 13.5

SOLUTION:

(a) From mass % to molality:

g of H_2O = 100. g solution - 30.0 g H_2O_2 = 70.0 g H_2O

$$30.0 \text{ g } H_2O_2 \times \frac{1 \text{ mol } H_2O_2}{34.02 \text{ g } H_2O_2} = 0.882 \text{ mol } H_2O_2$$

$$\text{molality} = \frac{0.882 \text{ mol } H_2O_2}{70.0 \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}}} \boxed{= 12.6\ m\ H_2O_2}$$

Sample Problem 13.5

(b) From mass % to mole fraction:

$$70.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 3.88 \text{ mol } H_2O$$

$$X_{H_2O_2} = \frac{0.882 \text{ mol } H_2O_2}{3.88 \text{ mol } H_2O + 0.882 \text{ mol } H_2O_2} \quad \boxed{= 0.185}$$

(c) From mass % and density to molarity:

$$\text{volume (mL) of solution} = 100.0 \text{ g} \times \frac{1 \text{ mL}}{1.11 \text{ g}} = 90.1 \text{ mL}$$

$$\text{molarity} = \frac{\text{mol } H_2O_2}{\text{L soln}} = \frac{0.882 \text{ mol } H_2O_2}{90.1 \text{ mL} \times \frac{1 \text{ L soln}}{10^3 \text{ mL}}} \quad \boxed{= 9.79\ M\ H_2O_2}$$

Colligative Properties of Solutions

Colligative (collective)properties :are properties that depend on the ***number*** of solute particles, not their chemical identity.

-Vapor pressure lowering.

-Boiling point elevation.

-Freezing point depression.

-Osmotic pressure.

Colligative Properties of Solutions

-The number of particles in solution can be predicted from the formula and type of the solute.

Solutes were classified by their ability to conduct the electrical current:

1- ***Electrolyte*** separates into ions when it dissolves in water.

a- Strong electrolytes dissociate completely .

b- Weak electrolytes dissociate very little.

2- ***nonelectrolyte*** does not dissociate to form ions.

Each mole of dissolved compound yields 1 mole of particles in solution.

-Non electrolytes : 1 mol of compound yields I mol of particles in solution. Ex, 0.35 M glucose produce 0.35 mol glucose.

-Strong electrolytes: 1 mol of compound yields the amount of ions in formula. Ex, 0.4 *M* Na_2SO_4 has 0.8 mol of Na^{+1} and 0.4 mol of SO_4^{-2} .

- For week electrolytes, see in Chapter18 and 19.

- In this section we will discuss colligative properties of three types of solute:

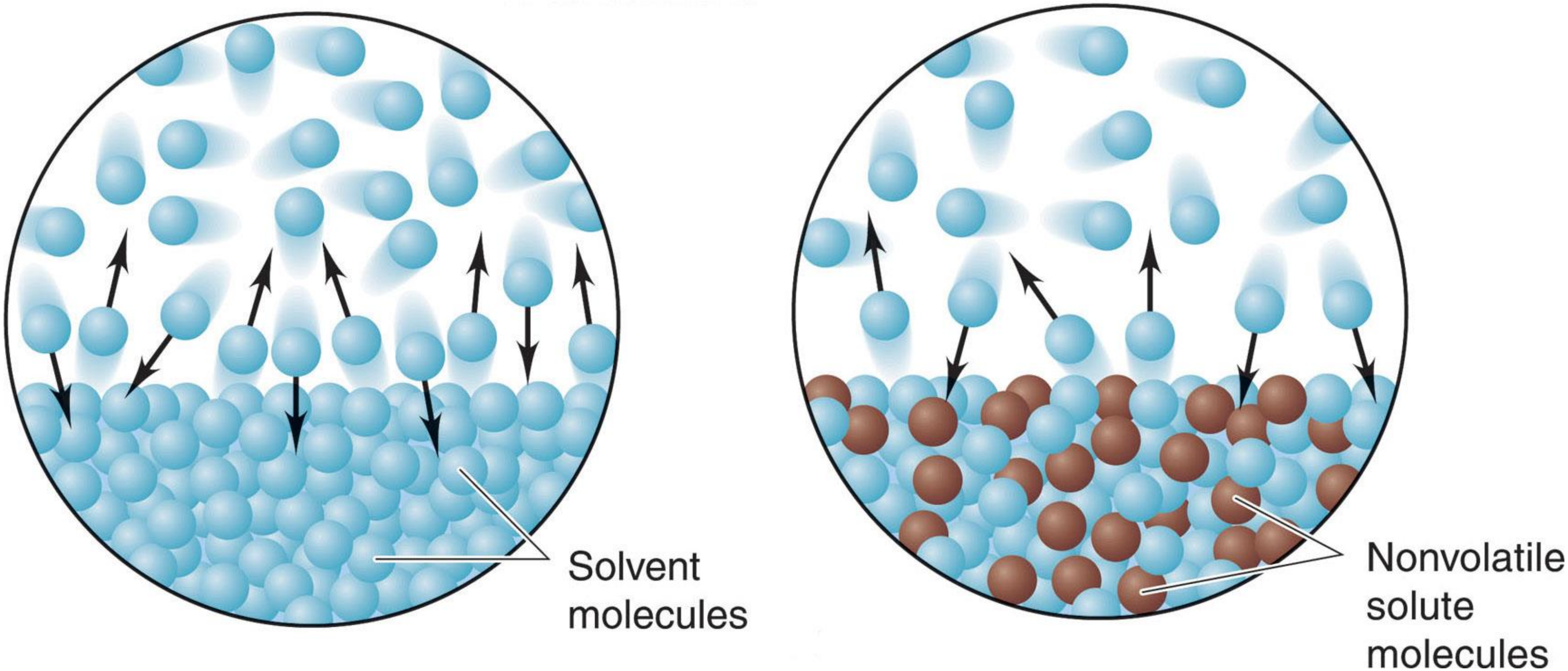
1- nonvolatile-nonelectrolyte.

2- volatile nonelectrolyte.

3- strong electrolyte.

1- Nonvolatile Nonelectrolyte solution

Figure 13.11 Effect of solute on the vapor pressure of solution.



Equilibrium is reached with a given number of particles in the vapor.

Equilibrium is reached with fewer particles in the vapor.

Vapor Pressure Lowering

The vapor pressure of a solution containing a ***nonvolatile nonelectrolyte*** is always ***lower*** than the vapor pressure of the pure solvent. Why? The reason is entropy , the entropy for solution is higher than pure solvent. So, fewer solvent particles need to vaporize to reach same entropy.

-Quantifying vapor pressure lowering

Raoult's law states that the vapor pressure of the solvent above the solution is proportional to the ***mole fraction*** of the solvent present:

$$\boxed{P_{\text{solvent}} = X_{\text{solvent}} * P^{\circ}_{\text{solvent}}}$$

P_{solvent} : vapor pressure of the solvent above solution.

X_{solvent} : mole fraction of solvent , $P^{\circ}_{\text{solvent}}$: Vapor pressure of pure solvent

- Raoult's law work reasonably well for dilute solutions

- How amount of dissolved solute affects ΔP

$$X_{solvent} + X_{solute} = 1$$

$$P_{solvent} = X_{solvent} * P^{\circ}_{solvent} = (1 - X_{solute}) * P^{\circ}_{solvent}$$

$$P_{solvent} = P^{\circ}_{solvent} - X_{solute} P^{\circ}_{solvent}$$

$$P^{\circ}_{solvent} - P_{solvent} = X_{solute} * P^{\circ}_{solvent}$$

$$\boxed{\Delta P_{solvent} = X_{solute} * P^{\circ}_{solvent}}$$

The vapor pressure ***lowering*** is proportional to the mole fraction of the ***solute*** present.

Sample Problem 13.6 **Using Raoult's Law to Find ΔP**

PROBLEM: Find the vapor pressure lowering, ΔP, when 10.0 mL of glycerol ($C_3H_8O_3$) is added to 500. mL of water at 50.°C. At this temperature, the vapor pressure of pure water is 92.5 torr and its density is 0.988 g/mL. The density of glycerol is 1.26 g/mL.

PLAN: We are given the vapor pressure of pure H_2O, so to calculate ΔP we just need the mole fraction of glycerol, $X_{glycerol}$.

volume (mL) of glycerol

↓ **multiply by density**

mass (g) of glycerol

↓ **multiply by $\mathcal{M}$**

amount (mol) of glycerol

↓

mole fraction (X) of glycerol → **multiply by $P°_{glycerol}$** → **vapor pressure lowering**

Sample Problem 13.6

SOLUTION:

$$10.0\ \text{mL}\ C_3H_8O_3 \times \frac{1.26\ \text{g}\ C_3H_8O_3}{1\ \text{mL}\ C_3H_8O_3} \times \frac{1\ \text{mol}\ C_3H_8O_3}{92.09\ \text{g}\ C_3H_8O_3}$$

$$= 0.137\ \text{mol}\ C_3H_8O_3$$

$$500.0\ \text{mL}\ H_2O \times \frac{0.988\ \text{g}\ H_2O}{1\ \text{mL}\ H_2O} \times \frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} = 27.4\ \text{mol}\ H_2O$$

$$X_{glycerol} = \frac{0.137\ \text{mol}\ C_3H_8O_3}{0.137\ \text{mol}\ C_3H_8O_3 + 27.4\ \text{mol}\ H_2O} = 0.00498$$

$$\Delta P = 0.00498 \times 92.5\ \text{torr}\ \boxed{= \mathbf{0.461\ torr}}$$

Boiling Point Elevation

A solution always boils at a ***higher*** temperature than the pure solvent? In boiling $P_{vap} = P_{ex}$, in solution P_{vap} is less than pure solvent, sol its need more a higher temperature to boil.

This colligative property is a result of vapor pressure lowering.

The boiling point elevation is proportional to the ***molality*** of the solution.

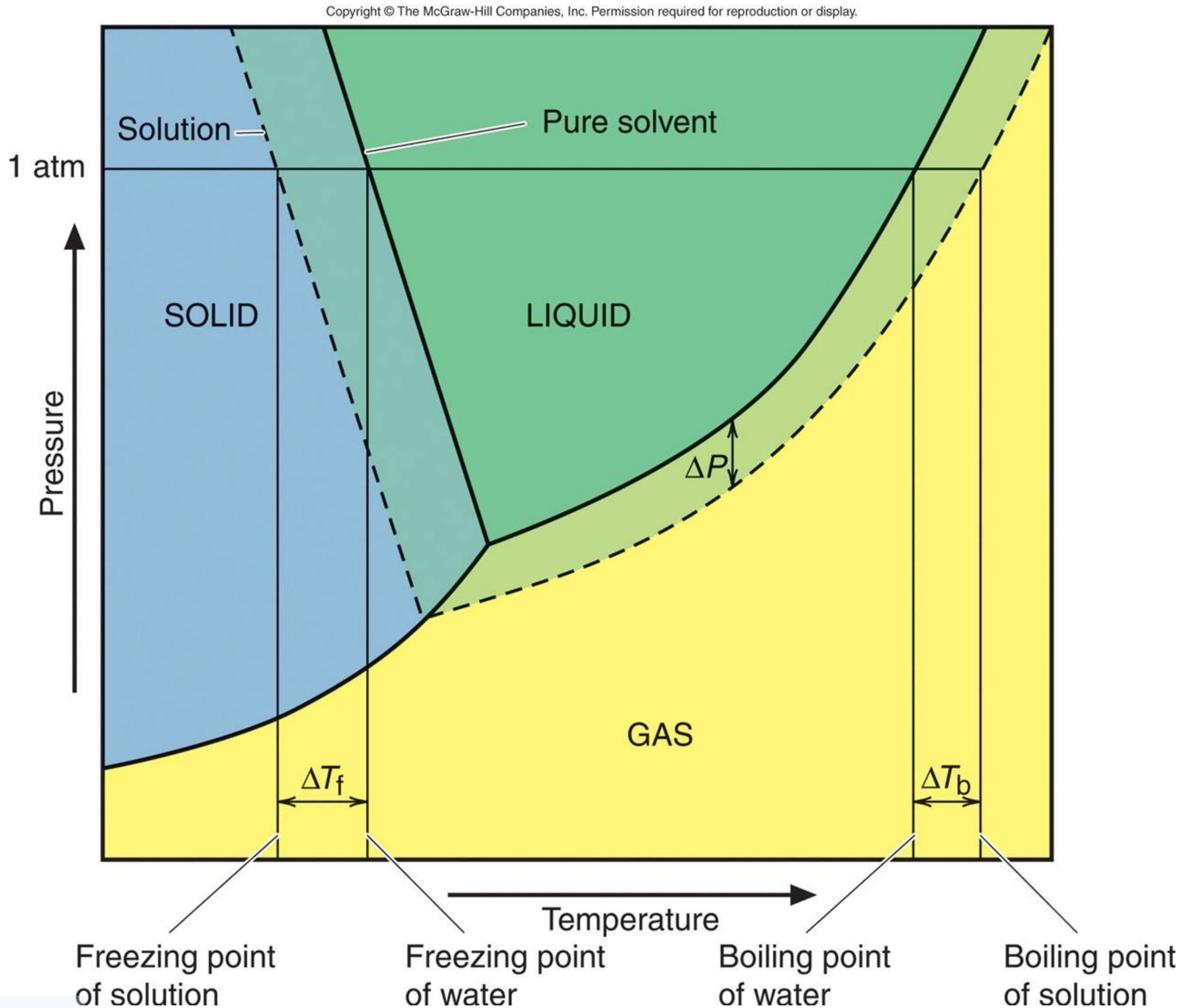
$$\boxed{\Delta T_b = K_b m}$$

K_b is the *molal boiling point elevation constant* for the ***solvent***.

$\Delta T_b = T_{b\,(solution)} - T_{b\,(solvent)}$, $\Delta T_b > 0$.

K_b : $^oC/m$

Figure 13.12 Boiling and freezing points of solvent and solution.



Freezing Point Depression

Freezing point : is the temperature of solution at which its vapor pressure equal that of pure solvent, and that is when solid solvent and liquid solution are in equilibrium.

A solution always freezes at a ***lower*** temperature than the pure solvent?

The freezing point depression is proportional to the ***molality*** of the solution.

$$\boxed{\Delta T_f = K_f m}$$

K_f is the *molal freezing point depression constant* for the ***solvent***.

$\Delta T_f > 0$, $\Delta T_f = T_{f(solvent)} - T_{f(solution)}$.

Table 13.5 Molal Boiling Point Elevation and Freezing Point Depression Constants of Several Solvents

Solvent	Boiling Point (°C)*	K_b (°C/*m*)	Melting Point (°C)	K_f (°C/*m*)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	-111.5	3.83
Carbon tetrachloride	76.5	5.03	-23	30.
Chloroform	61.7	3.63	-63.5	4.70
Diethyl ether	34.5	2.02	-116.2	1.79
Ethanol	78.5	1.22	-117.3	1.99
Water	100.0	0.512	0.0	1.86

*At 1 atm.

Sample Problem 13.7 **Determining Boiling and Freezing Points of a Solution**

PROBLEM: You add 1.00 kg of ethylene glycol ($C_2H_6O_2$) antifreeze to 4450 g of water in your car's radiator. What are the boiling and freezing points of the solution?

PLAN: We need to find the molality of the solution and then calculate the boiling point elevation and freezing point depression.

mass (g) of solute

↓ **divide by $\mathcal{M}$**

amount (mol) of solute

↓ **divide by kg of solvent**

molality (*m*)

↓ $\Delta T_b = K_b m$ ↓ $\Delta T_f = K_f m$

$T_{b(\text{solution})}$ $\xleftarrow{T_b + \Delta T_b}$ ΔT_b ΔT_f $\xrightarrow{T_f - \Delta T_f}$ $T_{f(\text{solution})}$

Sample Problem 13.7

SOLUTION:

$$1.00\text{x}10^3 \text{ g } C_2H_6O_2 \text{ x } \frac{1 \text{ mol } C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2} = 16.1 \text{ mol } C_2H_6O_2$$

$$\text{molality} = \frac{16.1 \text{ mol } C_2H_6O_2}{4.450 \text{ kg } H_2O} = 3.62\ m\ C_2H_6O_2$$

$\Delta T_b = 3.62\ m \text{ x } 0.512°C/m = 1.85°C$

$T_{b(solution)} = 100.00 + 1.85 =$ **101.85°C**

$\Delta T_f = 3.62\ m \text{ x } 1.86°C/m = 6.73°C$

$T_{b(solution)} = 0.00 - 6.73 =$ **-6.73°C**

Osmotic Pressure

Osmosis is the movement of ***solvent*** particles from a region of higher to a region of lower concentration through a semipermeable membrane.

Solvent will always flow ***from*** a ***more dilute*** solution to a more concentrated one.

Osmotic pressure is the pressure that must be applied to prevent the net flow of solvent.

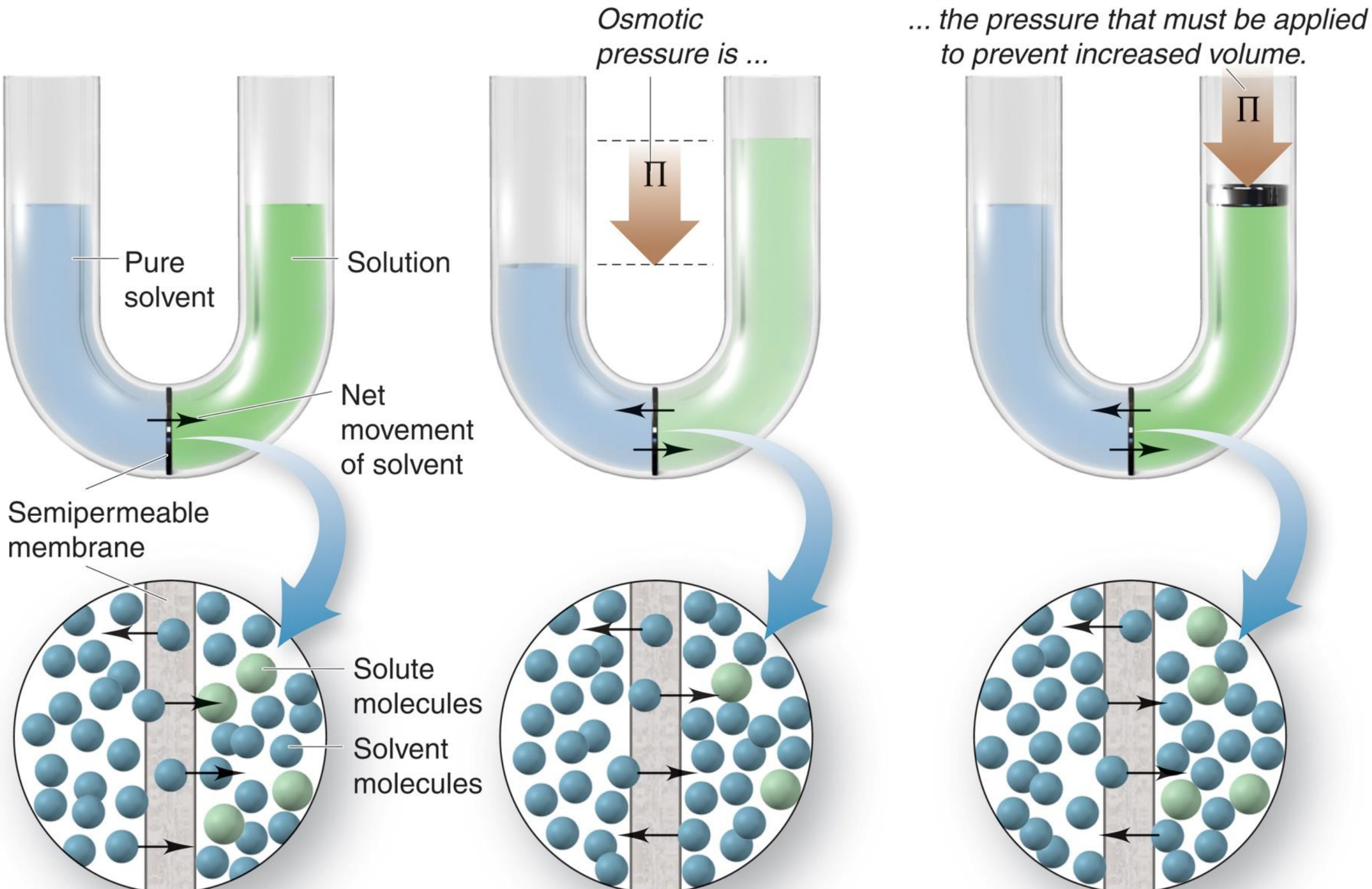
$$\boxed{\Pi = MRT}$$

M = molarity

R = 0.0821 atm·L/mol·K

T = Kelvin temperature

Figure 13.13 The development of osmotic pressure.



A Rate into solution > rate out of solution

B Rate in = rate out due to difference in heights

C Rate in = rate out due to applied (osmotic) pressure

Sample Problem 13.8 **Determining Molar Mass from Osmotic Pressure**

PROBLEM: Biochemists have discovered more than 400 mutant varieties of hemoglobin, the blood protein that carries O_2. A physician dissolves 21.5 mg of one variety in water to make 1.50 mL of solution at 5.0°C. She measures an osmotic pressure of 3.61 torr. What is the molar mass of the protein?

PLAN: We convert Π to atm and T to degrees K and calculate molarity from osmotic pressure. We can then determine the molar mass using the number of moles and the known mass.

Π (atm)

↓ $\Pi = MRT$

M (mol/L)

↓ **convert to mol**

amount (mol) of solute → **divide mass (g) by moles** → **$\mathcal{M}$ (g/mol)**

Sample Problem 13.8

SOLUTION:

$$\mathit{M} = \frac{\Pi}{RT} = \frac{3.61 \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}}}{(0.0821 \text{ L·atm/mol·K})(278.15 \text{ K})} = 2.08 \times 10^{-4}\ \mathit{M}$$

$$\frac{2.08 \times 10^{-4} \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ L}}{10^{3} \text{ mL}} = 3.12\times 10^{-7} \text{ mol}$$

$$21.5 \text{ mg} \times \frac{1 \text{ g}}{10^{3} \text{ mg}} = 0.0215 \text{ g}$$

$$\mathcal{M} = \frac{0.0215 \text{ g}}{3.12\times 10^{-7} \text{ mol}} \quad \boxed{= \mathbf{6.89\times 10^{4} \text{ g/mol}}}$$

Volatile Nonelectrolyte Solutions

For a ***volatile*** nonelectrolyte, the vapor of the solution contains ***both*** solute and solvent.

The presence of each volatile component lowers the vapor pressure of the other, since each one lowers the mole fraction of the other.

$P_{total} = P_{solvent} + P_{solute} = (X_{solvent(solution)} * P^0_{solvent}) + (X_{solute\ (solution)} * P^0_{solute})$

For such a solution, the vapor will have a ***higher*** mole fraction of the ***more volatile component***.

$P = X(\text{in vapour}) * P_{total}$

The vapor has a ***different*** composition than the solution.

-Benzene (C_6H_6) and (C_7H_8) are miscible if $X_{ben} = X_{tol} = 0.5$ at 25 °C. $P^o_{ben} = 95.1$ torr , $P^o_{tol} = 28.4$ torr.

$$P_{ben} = X_{ben} * P^0_{ben} = 0.5 * 95.1 \text{ torr} = 47.6 \text{ torr}$$

$$P_{tol} = X_{tol} * P^0_{tol} = 0.5 * 28.4 \text{ torr} = 14.2 \text{ torr}$$

(Daltons law)

$P_{ben} = y_{benz}$ (vapor)* P_{total} , $$y_{ben} = \frac{47.6 \text{ torr}}{47.6+14.2} = 0.770$$

$$y_{tol} = 0.23$$

mol fraction of the vapor for volatile component is different from their mol fraction in solution.

Strong Electrolyte Solutions

A strong electrolyte dissociates completely to form ions. Each mole of solute gives more than 1 mol of dissolved particles.

The ***formula*** of the compound indicates the expected number of particles in solution.

Each mol of NaCl is expected to give 2 moles of dissolved ions.

The ***van't Hoff factor*** takes into account the dissociation of a strong electrolyte to predict the effect on the solution.

$$i = \frac{\text{measured value for electrolyte solution}}{\text{expected value for nonelectrolyte solution}}$$

Colligative Properties of Electrolyte Solutions

For vapor pressure lowering: $\Delta P = i(X_{\text{solute}} \times P^{o}_{\text{solvent}})$

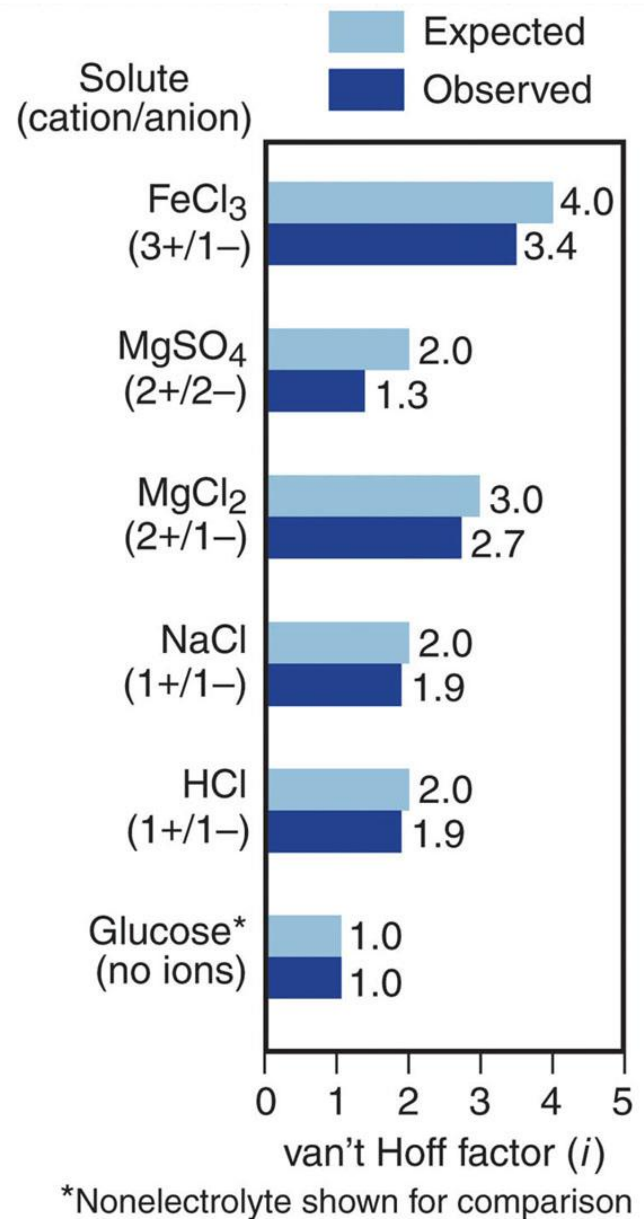
For boiling point elevation: $\Delta T_b = i(K_b m)$

For freezing point depression: $\Delta T_f = i(K_f m)$

For osmotic pressure: $\Pi = i(MRT)$

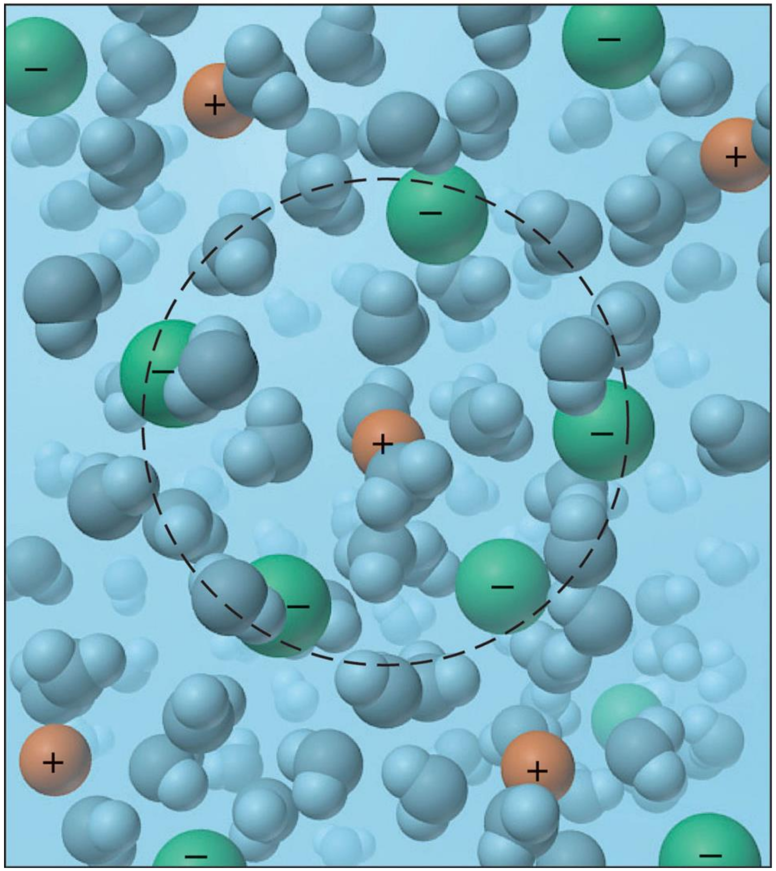
Figure 13.14

Nonideal behavior of strong electrolyte solutions.



Ions in solution may remain clustered near ions of opposite charge, creating an ***ionic atmosphere****. The ions do not act independently, and the effective concentration of dissolved particles is less than expected.*

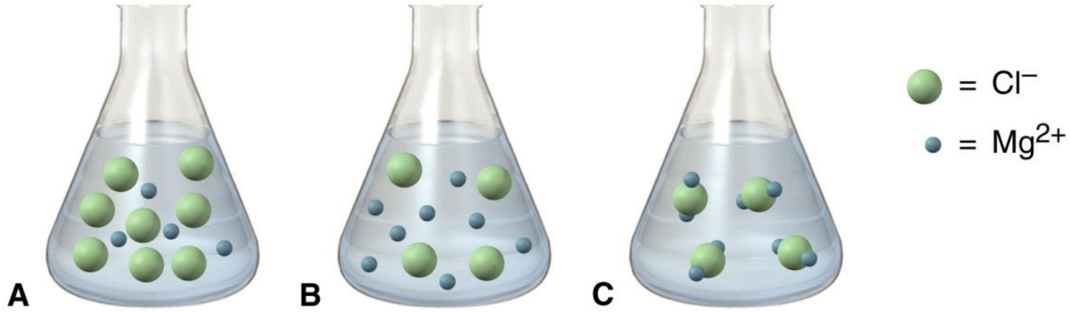
Figure 13.15 An ionic atmosphere model for nonideal behavior of electrolyte solutions.



Ions may remain clustered together in solution, forming an ionic atmosphere. This effect is greater for a more concentrated solution.

Sample Problem 13.9 — Depicting Strong Electrolyte Solutions

PROBLEM: A 0.952-g sample of magnesium chloride dissolves in 100. g of water in a flask.



(a) Which scene depicts the solution best?

(b) What is the amount (mol) represented by each green sphere?

(c) Assuming the solution is ideal, what is its freezing point (at 1 atm)?

Sample Problem 13.9

PLAN: (a) We find the numbers of cations and anions per formula unit from the name and compare it with the three scenes.

(b) We convert the given mass to amount (mol), and use the answer from part (a) to find the moles of chloride ions. We can then determine the number of moles per sphere.

(c) We find the molality (*m*) from the data provided and use it to calculate ΔT_f for the solution.

SOLUTION:

(a) The formula for magnesium chloride is $MgCl_2$. Only **scene A** has 1 Mg^{2+} for every 2 Cl^- ions.

Sample Problem 13.9

(b) The solution contains 0.952 g of $MgCl_2$ in 100. g of water.

$$0.952 \text{ g } MgCl_2 \times \frac{1 \text{ mol } MgCl_2}{95.21 \text{ g } MgCl_2} = 0.0100 \text{ mol } MgCl_2$$

Every 1 mol of $MgCl_2$ forms 1 mol Mg^{2+} and 2 mol Cl^- so there should be 0.0200 mol Cl^- ions. There are 8 green spheres :

$$\frac{0.0200 \text{ mol } Cl^- \text{ ions}}{8 \text{ green spheres}} \boxed{= 2.50\text{x}10^{-3} \text{ mol/sphere}}$$

Sample Problem 13.9

(c) Assuming an ideal solution, $i = 3$ for $MgCl_2$ since there are 3 ions per formula unit.

$$\text{molality} = \frac{0.0100 \text{ mol } MgCl_2}{100.\text{ g} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}} = 0.100\ m\ MgCl_2$$

$$\Delta T_f = i(K_f m) = 3(1.86°C/m \times 0.100\ m) = 0.558°C$$

$$\boxed{T_f = 0.000°C - 0.558°C = \mathbf{-0.558°C}}$$