CHAPTER THIRTEEN

The Properties of Solutions

o Nearly all the gases, liquids, and solids are mixtures- two or more substances physically mixed together but not chemically combined.

o A mixture has two defining characteristics:

  o its composition is variable,

  o and it retains some properties of its components.

o Solutions are the most common type of mixture. A solution is a *homogeneous mixture*, one with no boundaries separating its components; thus, a solution exists as one phase. A *heterogeneous mixture* has two or more phases.

o The essential distinction is that in a solution all the particles are individual atoms, ions, or small molecules.

13.1 TYPES OF SOLUTIONS: INTERMOLECULAR FORCES   AND   SOLUBILITY

o Solution: the solute dissolves in the solvent,

o Usually, the solvent is *the most abundant* component of a given solution.

o In some cases, however, the substances are *miscible*, that is, soluble in each other in any proportion; in such cases, it may not be meaningful to call one the solute and the other the solvent.

o The **solubility** (S) of a solute is the maximum amount that dissolves in a fixed quantity of a particular solvent at a specified temperature, given that excess solute is present.

Example, for NaCl, S = 39.12 g/l00. mL water at 100.ºC, whereas for AgCl, S = 0.0021 g/l00. mL water at 100.°C. Obviously, NaCl is much more soluble in water than AgCl is.

o a **dilute** solution contains much less dissolved solute than a **concentrated** one.

o **like dissolves like**: substances with similar types of *intermolecular forces* dissolve in each other.

Intermolecular Forces in Solution

Intermolecular forces that occur between solute and solvent in solutions:

1 . Ion-dipole forces

➢ The principal force involved in the solubility of ionic compounds in water. When a salt dissolves, each ion on the crystal's surface attracts the oppositely charged end of the water dipole.

➢ Recent evidence shows that water's normal H bonding is disrupted only among molecules in the closest hydration shell.

➢ For monatomic ions, the number of water molecules in the closest shell depends on the ion's size. Four water molecules can fit tetrahedrally around small ions, such as Li^+, while larger ions, such as Na^+ and F^-, have six water molecules surrounding them octahedrally.

Figure 13.2

Figure 13.1

Figure 13.1-cont.
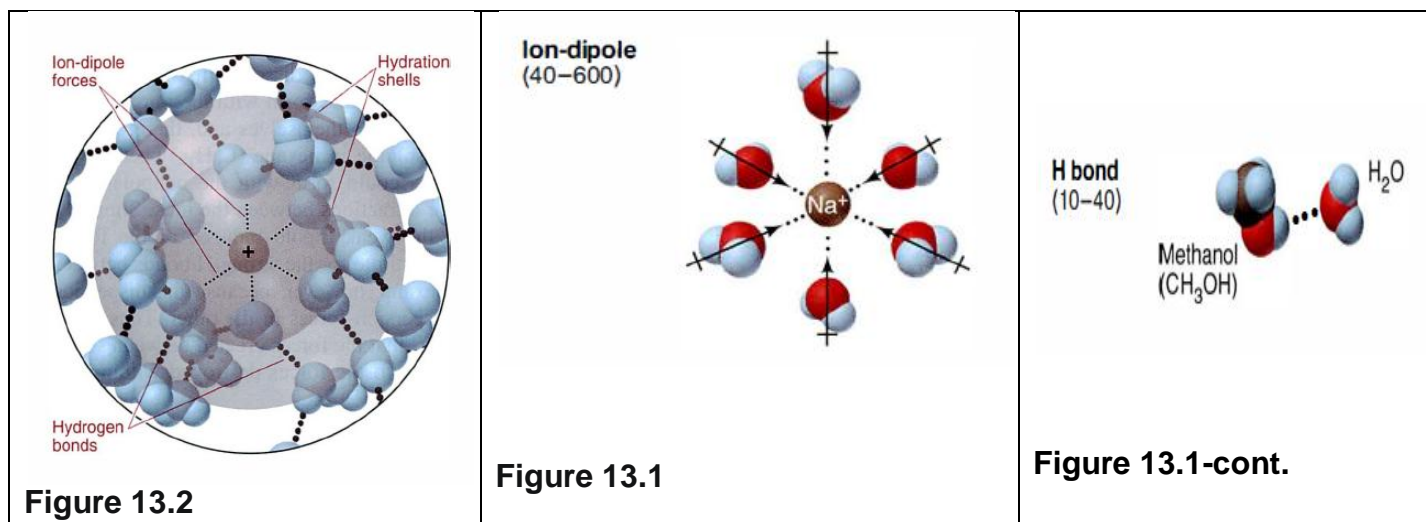
2. Hydrogen bonding

Especially important in aqueous solution, it is a primary factor in the solubility in water-and, thus, cell fluid-of many oxygen- and nitrogen-containing organic and biological compounds, such as alcohols, sugars, amines, and amino acids.

3. Dipole-dipole forces

In the absence of H bonding, account for the solubility of polar organic molecules, such as ethanal (acetaldehyde, CH_3CHO), In polar, nonaqueous solvents like chloroform ($CHCl_3$).

4. Ion-induced dipole forces

➢ Rely on the polarizability of the components, and result when an ion's charge distorts the electron cloud of a nearby nonpolar molecule.

➢ Have essential biological role that initiates the binding of the Fe^{2+} ion in hemoglobin and an O_2 molecule in the bloodstream.

➢ Contribute to the solubility of salts in less polar solvents, such as LiCl in ethanol.

5. Dipole-induced dipole forces

➢ Also based on polarizability, but weaker than the ion-induced dipole forces.

➢ They arise when a polar molecule distorts the electron cloud of a nearby nonpolar molecule.

➢ The solubility in water, limited though it is, of atmospheric O_2, N_2, and the noble gases is due in large part to these forces.

6. Dispersion forces

Contribute to the solubility of all solutes in all solvents, but they are the principal type of intermolecular force in solutions of nonpolar substances, such as petroleum and gasoline.

Figure 13.1-cont.
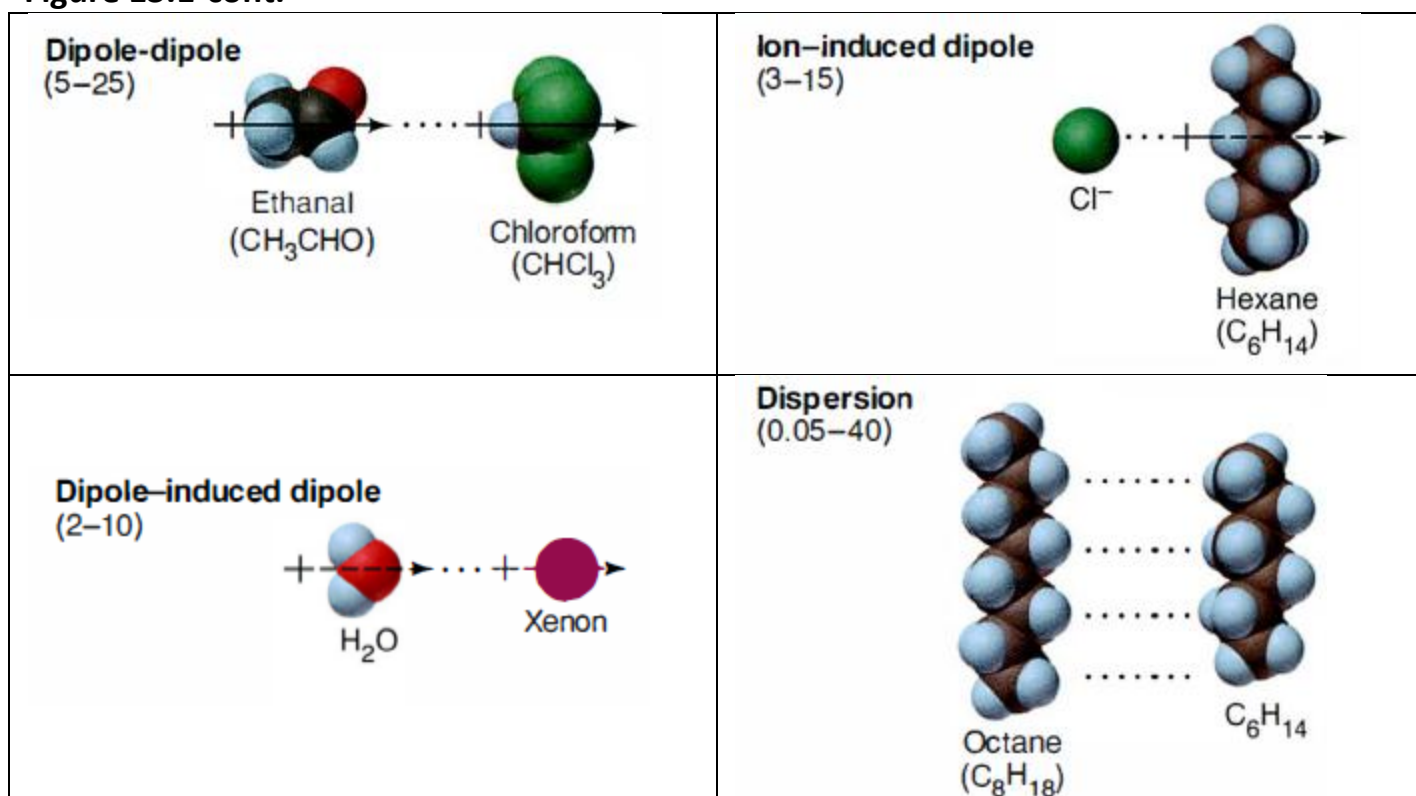
Liquid Solutions and the Role of Molecular Polarity

- o Solutions can be gaseous, liquid, or solid. We focus on liquid solutions because they are by far the most common and important.

- o Water is the most prominent solvent because it is so common and dissolves so many ionic and polar substances. But there are many other liquid solvents, and their polarity ranges from very polar to nonpolar.

Liquid-Liquid and Solid-Liquid Solutions

- o Many salts dissolve in water because the strong ion-dipole attractions that water molecules form with the ions are very similar to the strong attractions between the ions themselves and, therefore, can substitute for them.

- o Oil does not dissolve in water because the weak dipole-induced dipole forces between oil and water molecules cannot substitute for the strong H bonds between water molecules.

o Oil does dissolve in hexane, however, because the dispersion forces in one substitute readily for the dispersion forces in the other.

Example: Solubility of alcohol in water and hexane. The polar hydroxyl (-OH) group of alcohol forms strong H bonds with water. The hydrocarbon portion interacts through dispersion forces with hexane and through dipole-induced dipole forces with water.

Smaller alcohols are more miscible with water, because in the smaller alcohols, the hydroxyl group is a relatively large portion, so the molecules interact more effectively with water molecules through H bonding.

Water solubility decreases for alcohols larger than three carbons, and those with chains longer than six carbons are insoluble in water.

The opposite trend occurs with hexane, where the major solute-solvent and solvent-solvent interactions are dispersion forces.

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

Alcohol	Model	Solubility in Water	Solubility in Hexane
CH_3OH (methanol)		∞	1.2
CH_3CH_2OH (ethanol)		∞	∞
$CH_3(CH_2)_2OH$ (1-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.

SAMPLE PROBLEM 13.1 Predicting Relative Solubilities of Substances

Problem Predict which solvent will dissolve more of the given solute:
(a) Sodium chloride in methanol (CH_3OH) or in 1-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 the solute and each solvent to determine the types of forces that could occur. A solute tends to be more soluble in a solvent whose intermolecular forces are similar to, and therefore can substitute for, its own.
Solution (a) Methanol. NaCl is an ionic solid that dissolves through ion-dipole forces. Both methanol and 1-propanol contain a polar —OH group, but 1-propanol's longer hydrocarbon chain can form only weak forces with the ions, so it is less effective at substituting for the ionic attractions in the solute.
(b) Water. Ethylene glycol molecules have two —OH groups, so the molecules interact with each other through H bonding. They are more soluble in H_2O, whose H bonds can substitute for their own H bonds better than the dispersion forces in hexane can.
(c) Ethanol. Diethyl ether molecules interact with each other through dipole-dipole and dispersion forces and can form H bonds to both H_2O and ethanol. The ether is more soluble in ethanol because that solvent can form H bonds *and* substitute for the ether's dispersion forces. Water, on the other hand, can form H bonds with the ether, but it lacks any hydrocarbon portion, so it forms much weaker dispersion forces with that solute.

FOLLOW-UP PROBLEM 13.1 Which solute is more soluble in the given solvent?
(a) 1-Butanol ($CH_3CH_2CH_2CH_2OH$) or 1,4-butanediol ($HOCH_2CH_2CH_2CH_2OH$) in water
(b) Chloroform ($CHCl_3$) or carbon tetrachloride (CCl_4) in water

Gas-Liquid Solutions

o Gases that are nonpolar, such as N_2, or are nearly so, such as NO, have low boiling points because their intermolecular attractions are weak. Likewise, they are not very soluble in water because solute-solvent forces are weak.

o For nonpolar gases, boiling point generally correlates with solubility in water.

The most important environmental example is the solubility of O_2 in water. At 25°C and 1 atm, the solubility of O_2 is only 3 .2 mL/ l00. mL of water, but aquatic animal life would die without this small amount.

In other cases, the solubility of a gas may seem high because the gas is not only dissolving but also reacting with the solvent or another component. Oxygen seems much more soluble in blood than in water because O_2 molecules are continually bonding with hemoglobin molecules in red blood cells.

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.

Gas Solutions and Solid Solutions

Despite the central place of liquid solutions in chemistry, gaseous solutions and solid solutions also have vital importance and numerous applications.

Gas-Gas Solutions

All gases are infinitely soluble in one another.

Air is the classic example of a gaseous solution, consisting of about 18 gases in widely differing proportions.

Gas-Solid Solutions

When a gas dissolves in a solid, it occupies the spaces between the closely packed particles. Hydrogen gas can be purified by passing an impure sample through a solid metal such as palladium, H_2 molecules are small enough and can form Pd-H covalent bonds.

Solid-Solid Solutions

- o Because solids diffuse so little, their mixtures are usually heterogeneous.
- o Some solid-solid solutions can be formed by melting the solids and then mixing them and allowing them to freeze.

Many alloys, are examples of solid-solid like brass, a mixture of zinc and copper. Waxes are another familiar type of solid-solid solution, a natural wax is a solid of biological origin that is insoluble in water but dissolves in nonpolar solvents.

# 13.2 WHY SUBSTANCES DISSOLVE: UNDERSTANDING THE SOLUTION PROCESS

To see why like dissolves like, let's break down the solution process conceptually into steps and examine them in terms of changes in *enthalpy* and *entropy* of the system.

Heats of Solution and Solution Cycles

For one substance to dissolve in another, three events must occur:

(1) solute particles must separate from each other,

(2) some solvent particles must separate to make room for the solute particles, and

(3) solute and solvent particles must mix together.

Step 1. Solute particles separate from each other, endothermic step:

Solute (aggregated) + heat $\rightarrow$ solute (separated) $\Delta H_{solute} > 0$
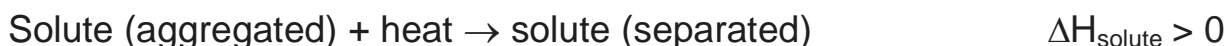
Step 2. Solvent particles separate from each other, endothermic too:

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

Step 3. Solute and solvent particles mix, exothermic step:

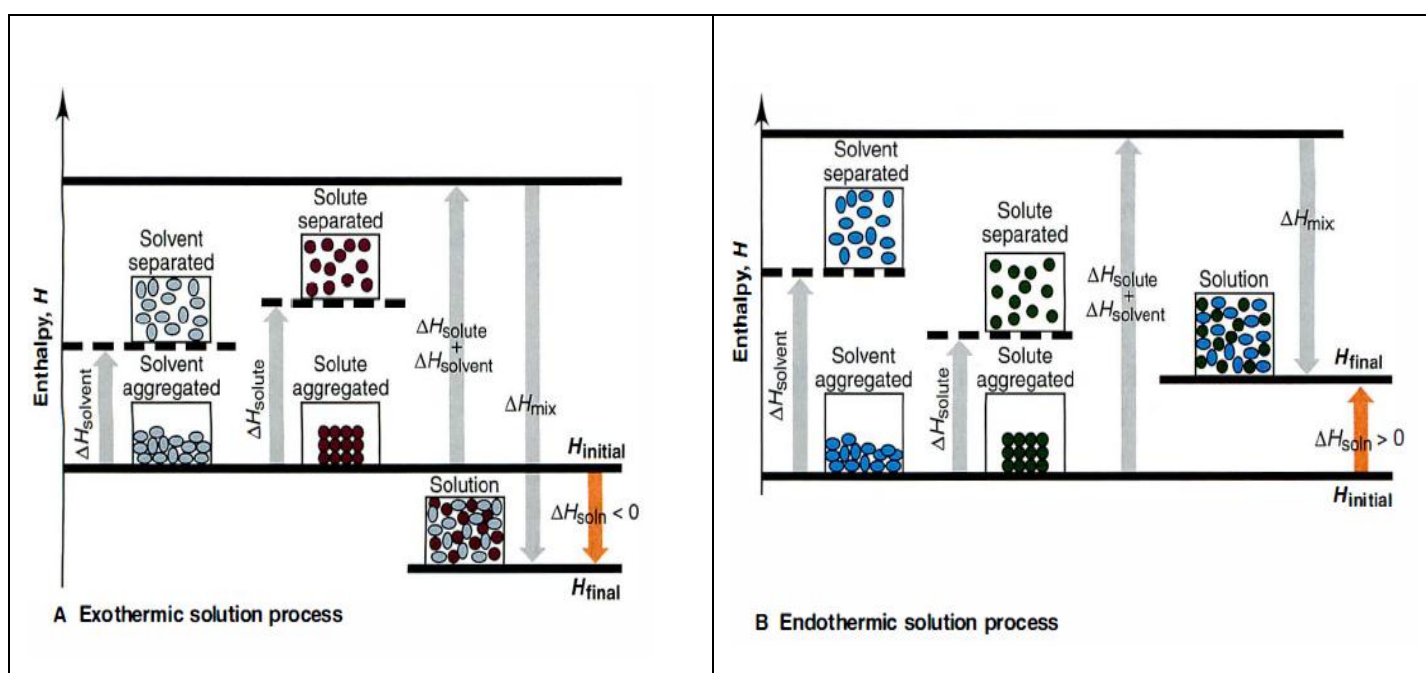Solute (separated) + solvent (separated) $\rightarrow$ solution + heat $\Delta H_{mix} < 0$

Hess's law: $\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$

So depending on the corresponding terms, $\Delta H_{solution}$ can be + or -.

Figure 13.4

A Exothermic solution process   B Endothermic solution process

Heats of Hydration: Ionic Solids in Water

$\Delta H_{solvent}$ and ΔH_{mix} components of the heat of solution are difficult to measure individually. Combined, these terms represent the enthalpy change during solvation, the process of surrounding a solute particle with solvent particles. Solvation in water is called hydration. Thus;

$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{hydr}$$

ΔH_{hydr} of an ion is defined as the enthalpy change for the hydration of 1 mol of separated (gaseous) ions;

$$M^+(g) \text{ [or } X^-(g)] \rightarrow M^+(aq) \text{ [or } X^-(aq)] \qquad \Delta H_{hydr} \text{ of the ion (always } <0)$$
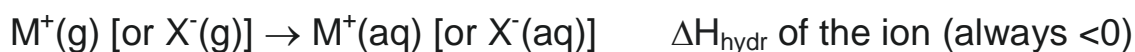
o The heat of hydration is a key factor in dissolving an ionic solid. Breaking H-bonds in water is more than compensated for by forming strong ion-dipole forces, so hydration of an ion is always exothermic.

o In general, the higher the charge density (charge/size) is, the more negative ΔH_{hydr} is.

• A **2+ ion** attracts H_2O molecules more strongly than a **1+ ion** of similar size.

• A **small 1+** ion attracts H_2O molecules more strongly than a **large 1+** ion.

o The energy required to separate an ionic solute (ΔH_{solute}) into gaseous ions is its lattice energy ($\Delta H_{lattice}$), and ΔH_{solute} is highly positive:

$$M^+X^-(s) \rightarrow M^+(g) + X^-(g) \qquad \Delta H_{solute} \text{ (always } >0) = \Delta H_{lattice}$$
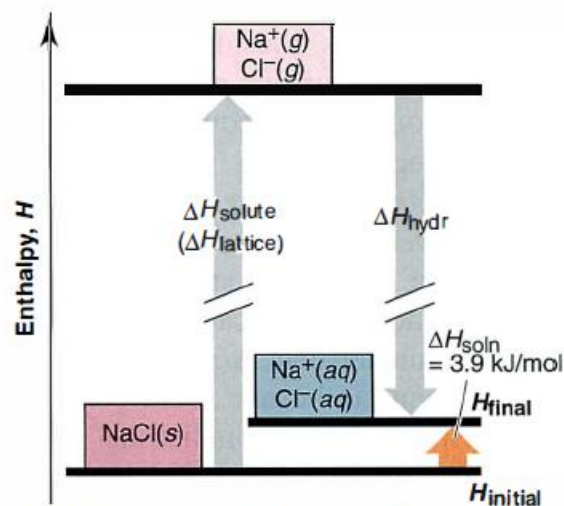
Thus, the heat of solution for ionic compounds in water combines the lattice energy (always positive) and the combined heats of hydration of cation and anion (always negative);

$$\Delta H_{soln} = \Delta H_{lattice} + \Delta H_{hydr \text{ of the ions}}$$

The sizes of the individual terms determine the sign of the heat of solution.

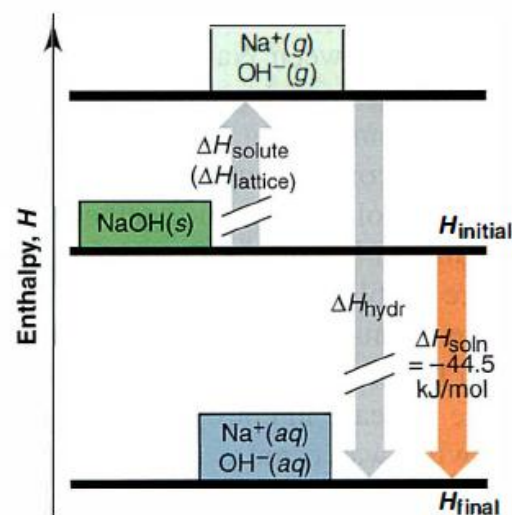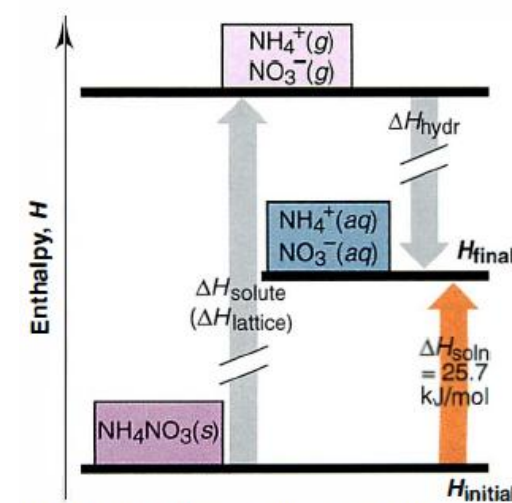|	
Figure 13.5 A *NaCl, has a small positive heat of solution (ΔH_{soln}= 3.9 kJ/mol). Its lattice energy is only slightly greater than the combined ionic heats of hydration, so if you dissolve NaCl in water in a flask, you do not notice any temperature change.*	 **A NaCl.** $\Delta H_{lattice}$ is slightly larger than ΔH_{hydr}: ΔH_{soln} is small and positive.
Figure 13.5 B *If you dissolve NaOH in water, the flask feels hot. The lattice energy for NaOH is much smaller than the combined ionic heats of hydration, so dissolving NaOH is highly exothermic (ΔH_{soln} = - 44.5 kJ/mol).*	 **B NaOH.** ΔH_{hydr} dominates: ΔH_{soln} is large and negative.
Figure 13.5 C If you dissolve NH_4NO_3 in water, the flask feels cold. In this case, the lattice energy is much larger than the combined ionic heats of hydration, so the process is quite endothermic (ΔH_{soln} = 25.7 kJ/mol).	 **C NH_4NO_3.** $\Delta H_{lattice}$ dominates: ΔH_{soln} is large and positive.

The Solution Process and the Change in Entropy

If it takes energy ($\Delta H_{soln} > 0$) for NaCl and NH_4NO_3 to dissolve, why do they?

o   The heat of solution is only one of two factors that determine whether a solution forms.

o   The other factor concerns another thermodynamic property called **entropy** (**S**). Entropy is related to the natural tendency in systems towards disorderness/randomness, which in turn, is closely related to the freedom of motion of the particles and the number of ways they can be arranged.

Based on this; $S_{gas} > S_{liquid} > S_{solid}$

Similarly, *a solution usually has higher entropy than the pure solute and pure solvent,* because there are far more interactions possible when solute and solvent are mixed than when they are pure; thus, $S_{soln} > (S_{solute} + S_{solvent})$, or $\Delta S_{soln} > 0$.

Thus, systems tend toward a state of **lower enthalpy** and **higher entropy**, and the relative magnitudes of ΔH_{soln} and ΔS_{soln} determine whether a solution forms.

Examples:

➢ Sodium chloride does not dissolve in hexane (C_6H_{14}), ΔH_{soln} is highly positive. A solution does not form because the ΔS_{soln} from mixing NaCl and hexane is much smaller than $\Delta H_{lattice}$. (**Fig. 13.6 A**)

➢ Octane (C_8H_{18}) dissolves in hexane, although ΔH_{soln} is around zero. The dissolution occurs because the entropy increases greatly when the pure substances mix. (**Fig. 13.6 B**)

➢ In the case of NaCl and especially NH_4NO_3 dissolving in water, $\Delta H_{soln} > 0$, but the increase in entropy that occurs when the crystal breaks down and the ions mix with water more than compensates for the increase in enthalpy.
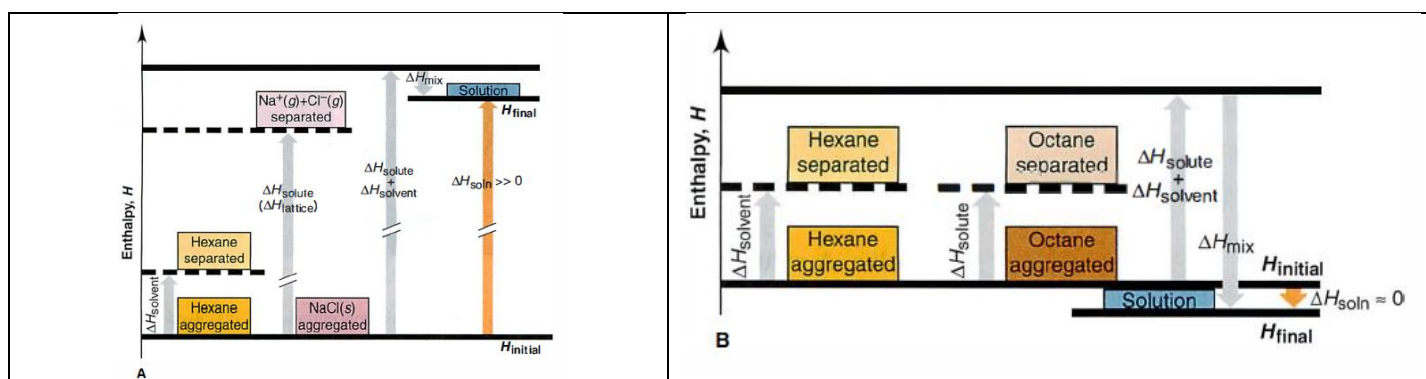
13.3 SOLUBILITY AS AN EQUILIBRIUM PROCESS

When the solubility limit is reached, equilibrium is established. At equilibrium;

Solute (undissolved) ↔ solute (dissolved)
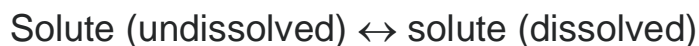
o This solution is called **saturated**; it contains the maximum amount of dissolved solute at a given temperature in the presence of undissolved solute.

o A solution that contains less than this concentration of dissolved solute is called **unsaturated**; add more solute, and more will dissolve until the solution becomes saturated.

Figure 13.7

Equilibrium in a saturated solution. In a saturated solution, equilibrium exists between excess solid solute and dissolved solute. At a particular temperature, the number of solute particles dissolving per unit time equals the number recrystallizing.

o In some cases, we can prepare a solution that contains more than the equilibrium concentration of dissolved solute; **supersaturated**. It is unstable so if you add a "seed" crystal of solute, or just tap the container, the excess solute crystallizes immediately, leaving a saturated solution.

Figure 13.8: Sodium acetate crystallizing from a supersaturated solution. When a seed crystal of sodium acetate is added to a supersaturated solution of the compound (A), solute begins to crystallize out of solution (B) and continues to do so until the remaining solution issaturated (C).
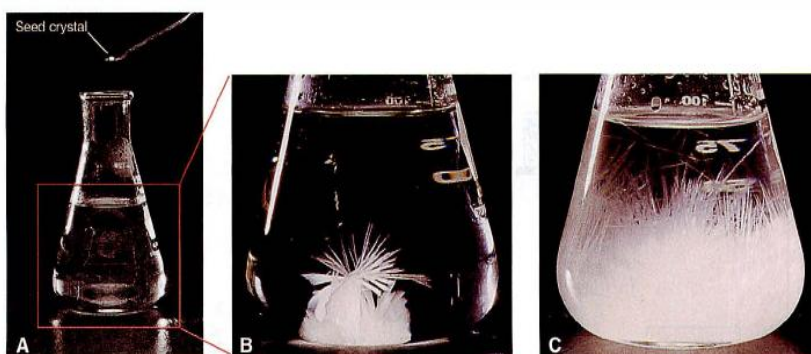
Effect of Temperature on Solubility

Temperature and the Solubility of Solids

- o When a solid dissolves in a liquid, the solute particles must separate, so energy must be added; thus, for a solid, $\Delta H_{solute} > 0$.
- o Most solids are more soluble at higher temperatures.

Figure 13.9 shows the solubility of several ionic compounds in water as a function of temperature. Note that most of the graphed lines curve upward. Cerium sulfate is the only exception shown in the figure, but several other salts, mostly sulfates, behave similarly. Some salts exhibit increasing solubility up to a certain temperature and then decreasing solubility at still higher temperatures. Unfortunately, the effect of temperature on the solubility of a solid solute is difficult to predict.
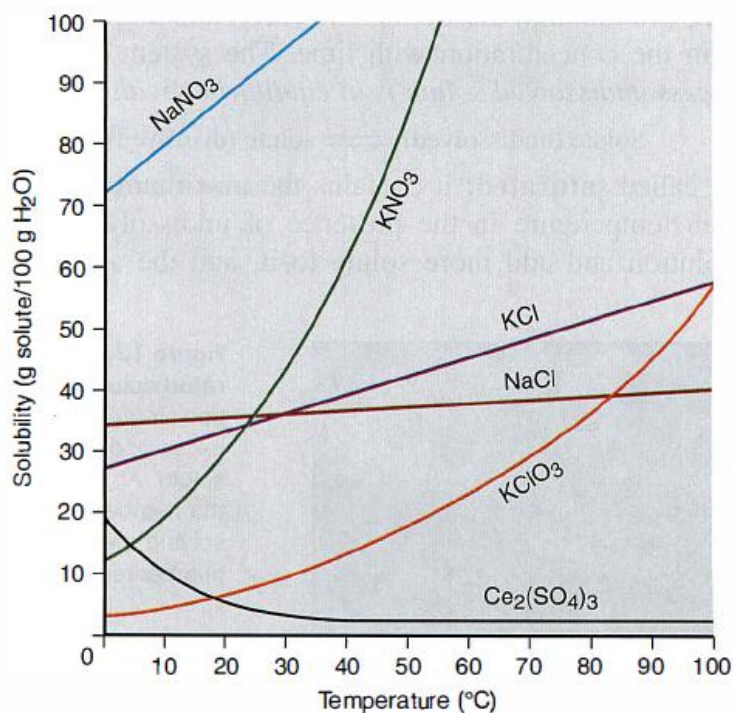
Temperature and Gas Solubility in Water

- o Gas particles are already separated from each other, so $\Delta H_{solute} = 0$. Because the hydration step is exothermic ($\Delta H_{hydr} < 0$), the sum of these two terms must be negative. Thus, for all gases in water, $\Delta H_{soln} < 0$:

$$Solute(g) + water(l) \leftrightarrow saturated\ solution(aq) + heat$$

- o Gas solubility in water decreases with rising temperature, because the average kinetic energy of the particles in solution increases, allowing the gas particles to re-enter the gas phase.
- o This behavior can lead to an environmental problem known as *thermal pollution*. For example, at higher temperature the solubility of O_2 in water decreases and this affects negatively the aquatic life.

Effect of Pressure on Solubility

o Liquids and solids are almost incompressible, so pressure has little effect on their solubility.

o For gases, as the pressure of a gas a bove a solution increases, solubility of the gas increases.

Figure 13.10

The effect of pressure on gas solubility

A: a saturated solution of a gas is in equilibrium at pressure P_1. **B**: if the pressure is increased to P_2, the volume of the gas decreases. The frequency of collisions with the surface increases, and more gas is in solution when equilibrium is re-established.
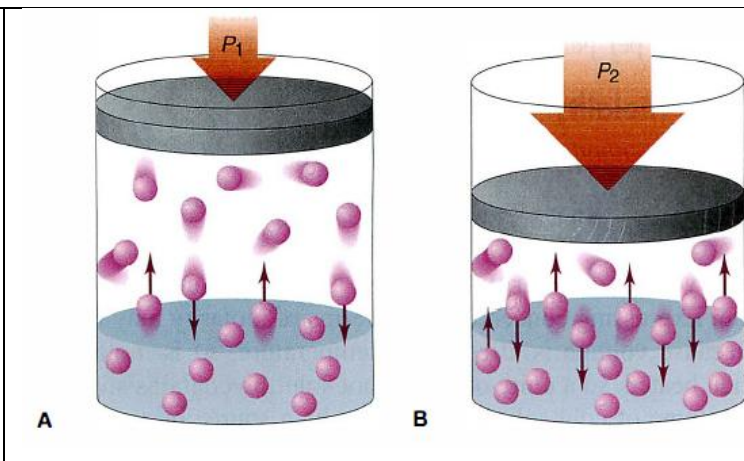
Henry 's law: the solubility of a gas (S_{gas}) is directly proportional to the partial pressure of the gas (P_{gas}) above the solution:

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

where k_H is the Henry's law constant (mol/L.atm) and is specific for a given gas-solvent combination at a given temperature. The unit of S_{gas} is mol/L, and P_{gas} is atm.

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 3.3×10^{-2} mol/L·atm at 25°C.

Plan We know P_{CO_2} (4 atm) and the value of k_H (3.3×10^{-2} mol/L·atm), so we substitute them into Equation 13.3 to find S_{CO_2}.

Solution $S_{CO_2} = k_H \times P_{CO_2} = (3.3 \times 10^{-2}$ mol/L·atm$)(4$ atm$) = $ 0.1 mol/L

Check The units are correct for solubility. We rounded the answer to one significant figure because there is only one in the pressure value.

FOLLOW-UP PROBLEM 13.2 If air contains 78% N_2 by volume, what is the solubility of N_2 in water at 25°C and 1 atm (k_H for N_2 in H_2O at 25°C = 7×10^{-4} mol/L·atm)?

13.4 QUANTITATIVE WAYS OF EXPRESSING CONCENTRATION

o Concentration is most often expressed as the ratio of the quantity of solute to the quantity of solution (e.g. molarity), but sometimes it is the ratio of solute to solvent (e.g. molality).

o Concentration is an intensive property, one that does not depend on the quantity of mixture present: 1.0 L of 0.1 M NaCl has the same concentration as 1.0 mL of 0.1 M NaCl.

Table 13.4 Concentration Definitions	
Concentration Term	**Ratio**
Molarity (M)	$\dfrac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (m)	$\dfrac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\dfrac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\dfrac{\text{volume of solute}}{\text{volume of solution}}$
Mole fraction (X)	$\dfrac{\text{amount (mol) of solute}}{\text{amount (mol) of solute} + \text{amount (mol) of solvent}}$

Molarity and Molality

Molarity (M): the number of moles of solute dissolved in 1 L of solution.

o Expressing concentration in terms of molarity may have drawbacks, because volume is affected by temperature, so is molarity.

o Because of solute-solvent interactions that are difficult to predict, solution volumes may not be additive; that is, adding 500. mL of one solution to 500. mL of another may not give 1000. mL.

Molality (m): the number of moles of solute dissolved in 1000 g (1 kg) of solvent.

o   Mass does not change with temperature, so neither does molality.

o   For the special case of water, 1 L has a mass of 1 kg, so molality and molarity are nearly the same for dilute aqueous solutions.

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 To use Equation 13.5, we convert mass of $CaCl_2$ (32.0 g) to amount (mol) with the molar mass (g/mol) and then divide by the mass of water (271 g), being sure to convert from grams to kilograms.

Solution Converting from grams of solute to moles:

$$\text{Moles of } CaCl_2 = 32.0 \text{ g } CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{110.98 \text{ g } CaCl_2} = 0.288 \text{ mol } CaCl_2$$

Finding molality:

$$\text{Molality} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.288 \text{ mol } CaCl_2}{271 \text{ g} \times \dfrac{1 \text{ kg}}{10^3 \text{ g}}} = 1.06 \text{ } m \text{ } CaCl_2$$

Check The answer seems reasonable: the given numbers of moles of $CaCl_2$ and kilograms of H_2O are about the same, so their ratio is about 1.

FOLLOW-UP PROBLEM 13.3 How many grams of glucose ($C_6H_{12}O_6$) must be dissolved in 563 g of ethanol (C_2H_5OH) to prepare a 2.40×10^{-2} m solution?

Parts of Solute by Parts of Solution

Parts by Mass

The most common of the parts-by-mass terms is **mass percent**, it means the mass of solute dissolved in every 100. parts by mass of solution, or the mass fraction times 100:

$$\text{Mass percent} = \frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}} \times 100$$

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

o   Sometimes mass percent is symbolized as % (w/w), indicating that the percentage is a ratio of weights (more accurately, masses).

o Two very similar terms are **parts per million** (**ppm**) by mass and **parts per billion** (**ppb**) by mass: grams of solute per million or per billion grams of solution. For these quantities, in the equation above you multiply by 10^6 or by 10^9, respectively, instead of by 100.

Parts by Volume

The most common of the parts-by-volume terms is volume percent, the volume of solute in 100. volumes of solution:

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

o A common symbol for volume percent is % (v/v). Commercial rubbing alcohol, for example, is an aqueous solution of isopropyl alcohol that contains 70 volumes of isopropyl alcohol per 100. volumes of solution, and the label indicates this as "70% (v/v)."

o Minor atmospheric components occur in parts per million by volume (ppmv). For example, there are about 0.05 ppmv of the toxic gas carbon monoxide (CO) in clean air.

o A measure of concentration frequently used for aqueous solutions is % (w/v), a ratio of solute weight (actually mass) to solution volume. Thus, a 1.5 % (w/v) NaCI solution contains 1.5 g of NaCI per 100. mL of solution.

Mole Fraction

The mole fraction (X) of a solute is the ratio of number of solute moles to the total number of moles (solute plus solvent), that is, parts by mole. The mole percent is the mole fraction expressed as a percentage:

$$\text{Mole fraction } (X) = \frac{\text{amount (mol) of solute}}{\text{amount (mol) of solute } + \text{ amount (mol) of solvent}}$$
$$\text{Mole percent (mol \%)} = \text{mole fraction} \times 100$$

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 are given the masses of Ca (40.5 mg) and the pill (3.50 g). We convert the mass of Ca from mg to g, find the ratio of mass of Ca to mass of pill, and multiply by 10^6 to obtain ppm. (b) We know the volume % (11.5%, or 11.5 parts by volume of alcohol to 100 parts of chianti) and the total volume (0.750 mL), so we use Equation 13.7 to find the volume of alcohol. (c) We know the mass and formula of each component, so we convert masses to amounts (mol) and apply Equation 13.8 to find the mole fractions.

Solution (a) Finding parts per million by mass of Ca. Combining the steps, we have

$$\text{ppm Ca} = \frac{\text{mass of Ca}}{\text{mass of pill}} \times 10^6 = \frac{40.5 \text{ mg Ca} \times \dfrac{1 \text{ g}}{10^3 \text{ mg}}}{3.50 \text{ g}} \times 10^6 = \boxed{1.16 \times 10^4 \text{ ppm Ca}}$$

(b) Finding volume (L) of alcohol:

$$\text{Volume (L) of alcohol} = 0.750 \text{ L chianti} \times \frac{11.5 \text{ L alcohol}}{100. \text{ L chianti}} = \boxed{0.0862 \text{ L}}$$

(c) Finding mole fractions. Converting from grams to moles:

$$\text{Moles of } C_3H_7OH = 142 \text{ g } C_3H_7OH \times \frac{1 \text{ mol } C_3H_7OH}{60.09 \text{ g } C_3H_7OH} = 2.36 \text{ mol } C_3H_7OH$$

$$\text{Moles of } H_2O = 58.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 3.22 \text{ mol } H_2O$$

Calculating mole fractions:

$$X_{C_3H_7OH} = \frac{\text{moles of } C_3H_7OH}{\text{total moles}} = \frac{2.36 \text{ mol}}{2.36 \text{ mol} + 3.22 \text{ mol}} = \boxed{0.423}$$

$$X_{H_2O} = \frac{\text{moles of } H_2O}{\text{total moles}} = \frac{3.22 \text{ mol}}{2.36 \text{ mol} + 3.22 \text{ mol}} = \boxed{0.577}$$

Check (a) The mass ratio is about 0.04 g/4 g = 10^{-2}, and $10^{-2} \times 10^6 = 10^4$ ppm, so it seems correct. (b) The volume % is a bit more than 10%, so the volume of alcohol should be a bit more than 75 mL (0.075 L). (c) Always check that the *mole fractions add up to 1;* thus, in this case, 0.423 + 0.577 = 1.000.

FOLLOW-UP PROBLEM 13.4 An alcohol solution contains 35.0 g of 1-propanol (C_3H_7OH) and 150. g of ethanol (C_2H_5OH). Calculate the mass percent and the mole fraction of each alcohol.

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 Converting 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 of 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 We know the mass % (30.0) and the density (1.11 g/mL). **(a)** For molality, we need the amount (mol) of solute and the mass (kg) of *solvent*. Assuming 100.0 g of H_2O_2 solution allows us to express the mass % directly as grams of substance. We subtract the grams of H_2O_2 to obtain the grams of solvent. To find molality, we convert grams of H_2O_2 to moles and divide by mass of solvent (converting g to kg). **(b)** To find the mole fraction, we use the number of moles of H_2O_2 [from part (a)] and convert the grams of H_2O to moles. Then we divide the moles of H_2O_2 by the total moles. **(c)** To find molarity, we assume 100.0 g of solution and use the given solution density to find the volume. Then we divide the amount (mol) of H_2O_2 [from part (a)] by *solution volume* (in L).

Solution (a) From mass % to molality. Finding mass of solvent (assuming 100.0 g of solution):

$$\text{Mass (g) of } H_2O = 100.0 \text{ g solution} - 30.0 \text{ g } H_2O_2 = 70.0 \text{ g } H_2O$$

Converting from grams of H_2O_2 to moles:

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

Calculating molality:

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

(b) From mass % to mole fraction:

$$\text{Moles of } H_2O_2 = 0.882 \text{ mol } H_2O_2 \text{ [from part (a)]}$$

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

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

(c) From mass % and density to molarity. Converting from solution mass to volume:

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

Calculating molarity:

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

Check Rounding shows the answers seem reasonable: **(a)** The ratio of ~0.9 mol/0.07 kg is greater than 10. **(b)** ~0.9 mol H_2O_2/(1 mol + 4 mol) ≈ 0.2. **(c)** The ratio of moles to liters (0.9/0.09) is around 10.

FOLLOW-UP PROBLEM 13.5 A sample of commercial concentrated hydrochloric acid is 11.8 *M* HCl and has a density of 1.190 g/mL. Calculate the mass %, molality, and mole fraction of HCl.

13.5 COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties (colligative means "collective") are solution properties that depend on the number of solute particles not their chemical identity.

These include: (i) vapor pressure lowering, (ii) boiling point elevation, (iii) freezing point depression, and (iv) osmotic pressure.

To predict the magnitude of a colligative property, we refer to the solute formula to find the number of particles in solution.

- o Each mole of nonelectrolyte yields 1 mol of particles in the solution. For example, 0.35 M glucose contains 0.35 mol of solute particles per liter.
- o In principle, each mole of strong electrolyte dissociates into the number of moles of ions in the formula unit; 0.4 M Na_2SO_4 contains 0.8 mol of Na^+ ions and 0.4 mol of SO_4^{2-} ions, totally 1.2 mol of particles, per liter.

## Colligative Properties of Nonvolatile Nonelectrolyte Solutions

The simplest case corresponds to the colligative properties of solutes that do not dissociate into ions and have negligible vapor pressure even at the boiling point of the solvent. Such solutes are called nonvolatile nonelectrolytes; sucrose (table sugar) is an example.

Vapor Pressure Lowering

The vapor pressure of a solution of a nonvolatile nonelectrolyte is always lower than the vapor pressure of the pure solvent.

When we add some nonvolatile solute, the number of solvent molecules on the surface is lower, so fewer vaporize per unit time. To maintain equilibrium, fewer gas molecules can enter the liquid, which occurs only if the concentration of gas, that is, the vapor pressure, is lowered (Figure 13.11).

Figure 13.11
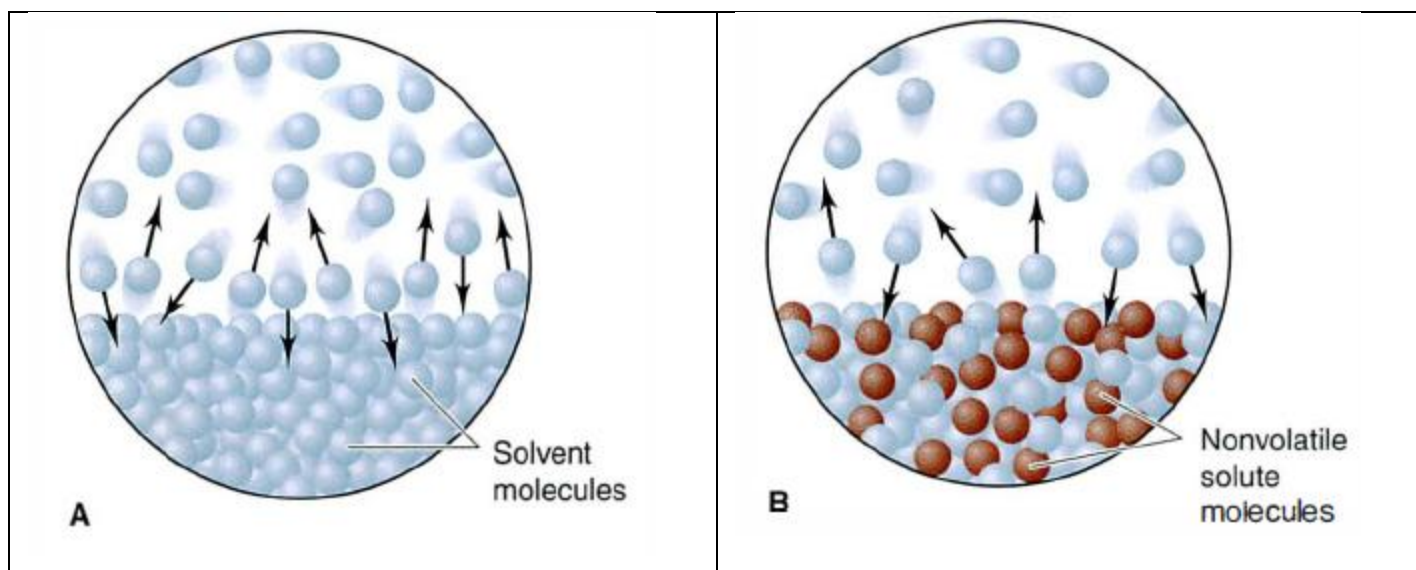
Raoult's law: the vapor pressure of solvent above the solution ($P_{solvent}$) equals the mole fraction of solvent in the solution ($X_{solvent}$) times the vapor pressure of the pure solvent ($P^o_{solvent}$);

$$P_{solvent} = X_{solvent} \times P^o_{solvent}$$

- o In a solution, $X_{solvent}$ is always less than 1 , so $P_{solvent}$ is always less than $P^o_{solvent}$.
- o An ideal solution is one that follows Raoult's law at any concentration. However, Raoult's law gives a good approximation of the behavior of dilute solutions only, and it becomes exact at infinite dilution.

How does the amount of solute affect the magnitude of the vapor pressure lowering, ΔP?

$$X_{solvent} + X_{solute} = 1 \; ; \text{thus, } X_{solvent} = I - X_{solute}$$
$$P_{solvent} = X_{solvent} \cdot P^o_{solvent} = (1 - X_{solute}) \cdot P^o_{solvent}$$
$$P_{solvent} = P^o_{solvent} - (X_{solute} \cdot P^o_{solvent})$$
$$P^o_{solvent} - P_{solvent} = \Delta P = X_{solute} \cdot P^o_{solvent}$$

Thus, the magnitude of ΔP equals the mole fraction of solute times the vapor pressure of the pure solvent.

SAMPLE PROBLEM 13.6 Using Raoult's Law to Find Vapor Pressure Lowering

Problem Calculate 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 To calculate ΔP, we use Equation 13.10. We are given the vapor pressure of pure water ($P^{\circ}_{H_2O}$ = 92.5 torr), so we just need the mole fraction of glycerol, $X_{glycerol}$. We convert the given volume of glycerol (10.0 mL) to mass using the given density (1.26 g/L), find the molar mass from the formula, and convert mass (g) to amount (mol). The same procedure gives amount of H_2O. From these, we find $X_{glycerol}$ and ΔP.

Solution Calculating the amount (mol) of glycerol and of water:

$$\text{Moles of glycerol} = 10.0 \text{ mL glycerol} \times \frac{1.26 \text{ g glycerol}}{1 \text{ mL glycerol}} \times \frac{1 \text{ mol glycerol}}{92.09 \text{ g glycerol}}$$

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

$$\text{Moles of } H_2O = 500. \text{ mL } H_2O \times \frac{0.988 \text{ g } H_2O}{1 \text{ mL } H_2O} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 27.4 \text{ mol } H_2O$$

Calculating the mole fraction of glycerol:

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

Finding the vapor pressure lowering:

$$\Delta P = X_{glycerol} \times P^{\circ}_{H_2O} = 0.00498 \times 92.5 \text{ torr} = 0.461 \text{ torr}$$

Check The amount of each component seems correct: for glycerol, $\sim$10 mL $\times$ 1.25 g/mL $\div$ 100 g/mol = 0.125 mol; for H_2O, $\sim$500 mL $\times$ 1 g/mL $\div$ 20 g/mol = 25 mol. The small ΔP is reasonable because the mole fraction of solute is small.

Comment The calculation assumes that glycerol is nonvolatile. At 1 atm, glycerol boils at 290.0°C, so the vapor pressure of glycerol at 50°C is so low it can be neglected.

FOLLOW-UP PROBLEM 13.6 Calculate the vapor pressure lowering of a solution of 2.00 g of aspirin ($\mathcal{M}$ = 180.15 g/mol) in 50.0 g of methanol (CH_3OH) at 21.2°C. Pure methanol has a vapor pressure of 101 torr at this temperature.
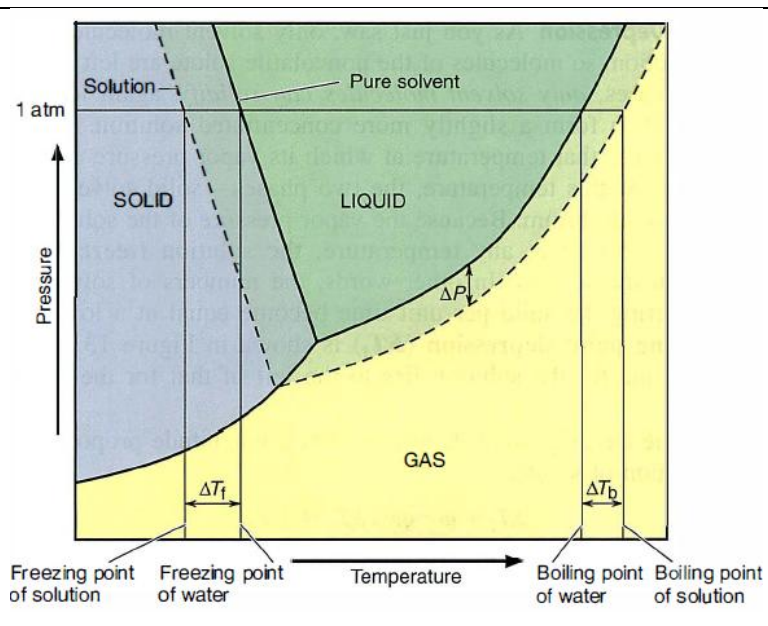
Boiling Point Elevation

A solution boils at a higher temperature than the pure solvent. Why?

The boiling temperature, T_b, of a liquid is the temperature at which its vapor pressure equals the external pressure. The vapor pressure of a solution is lower than the external pressure at the solvent's boiling point because the vapor pressure of a solution is lower than that of the pure solvent at any temperature. Therefore, the solution does not yet boil. A higher temperature is needed to raise the solution's vapor pressure to equal the external pressure.

Figure 13.12

Phase diagrams of solvent and solution. Phase diagrams of an aqueous solution (dashed lines) and of pure water (solid lines) show that, by lowering the vapor pressure (ΔP), a dissolved solute elevates the boiling point (ΔT_b) and depresses the freezing point (ΔT_f).

The magnitude of the boiling point elevation is proportional to the concentration of solute particles:

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m$$

where m is the solution molality, K_b is the molal boiling point elevation constant (°C/m), and ΔT_b is the boiling point elevation.

We typically speak of ΔT_b as a positive value, so we subtract the lower temperature from the higher; $\Delta T_b = T_b$(solution) - T_b(solvent)

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.

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Freezing Point Depression

In many cases, only solvent molecules can solidify, again leaving solute molecules behind to form a slightly more concentrated solution.

As can be seen from Fig. 13.12 above, the solution freezes at a lower temperature than the solvent.

The freezing point depression, ΔT_f, has a magnitude proportional to the molal concentration of solute:

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m$$

where K_f is the molal freezing point depression constant, in °C/m (see Table 13.5). Also ΔT_f is considered a positive value, so: $\Delta T_f = T_f(\text{solvent}) - T_f(\text{solution})$

You have encountered practical applications of freezing point depression if you have added antifreeze-a solution of ethylene glycol in water-to your car's radiator or have seen airplane de-icers used before takeoff. Also, roads are "salted" with NaCl and $CaCl_2$ in winter to lower the freezing point of water, causing road ice to melt.

SAMPLE PROBLEM 13.7 Determining the Boiling Point Elevation and Freezing Point Depression of a Solution

Problem You add 1.00 kg of ethylene glycol ($C_2H_6O_2$) antifreeze to your car radiator, which contains 4450 g of water. What are the boiling and freezing points of the solution?
Plan To find the boiling and freezing points of the solution, we first find the molality by converting the given mass of solute (1.00 kg) to amount (mol) and dividing by mass of solvent (4450 g). Then we calculate ΔT_b and ΔT_f from Equations 13.11 and 13.12 (using constants from Table 13.5). We add ΔT_b to the solvent boiling point and subtract ΔT_f from the solvent freezing point. The roadmap shows the steps.
Solution Calculating the molality:

$$\text{Moles of } C_2H_6O_2 = 1.00 \text{ kg } C_2H_6O_2 \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2} = 16.1 \text{ mol } C_2H_6O_2$$

$$\text{Molality} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{16.1 \text{ mol } C_2H_6O_2}{4450 \text{ g } H_2O \times \frac{1 \text{ kg}}{10^3 \text{ g}}} = 3.62 \; m \; C_2H_6O_2$$

Finding the boiling point elevation and $T_{b(solution)}$, with $K_b = 0.512°C/m$:

$$\Delta T_b = \frac{0.512°C}{m} \times 3.62 \; m = 1.85°C$$

$$T_{b(solution)} = T_{b(solvent)} + \Delta T_b = 100.00°C + 1.85°C = \boxed{101.85°C}$$

Finding the freezing point depression and $T_{f(solution)}$, with $K_f = 1.86°C/m$:

$$\Delta T_f = \frac{1.86°C}{m} \times 3.62 \; m = 6.73°C$$

$$T_{f(solution)} = T_{f(solvent)} - \Delta T_f = 0.00°C - 6.73°C = \boxed{-6.73°C}$$

Check The changes in boiling and freezing points should be in the same proportion as the constants used. That is, $\Delta T_b/\Delta T_f$ should equal K_b/K_f: $1.85/6.73 = 0.275 = 0.512/1.86$. **Comment** These answers are only approximate because the concentration far exceeds that of a *dilute* solution, for which Raoult's law is most useful.

FOLLOW-UP PROBLEM 13.7 What is the minimum concentration (molality) of ethylene glycol solution that will protect the car's cooling system from freezing at 0.00°F? (Assume the solution is ideal.)

Osmotic Pressure

When two solutions of different concentrations are separated by a semipermeable membrane, one that allows solvent, but not solute, molecules to pass through. This process is called *osmosis*.

Organisms have semipermeable membranes that regulate internal cellular concentrations by osmosis. Our kidneys maintain fluid volume osmotically by controlling Na^+ concentration.

Consider a simple apparatus in which a semipermeable membrane lies at the curve of a U tube and separates an aqueous sugar solution from pure water. The membrane allows water molecules to pass in either direction, but not the larger sugar molecules (Figure 13.13A).

This net flow of water into the solution increases the volume of the solution and thus decreases its concentration.

Figure 13.13
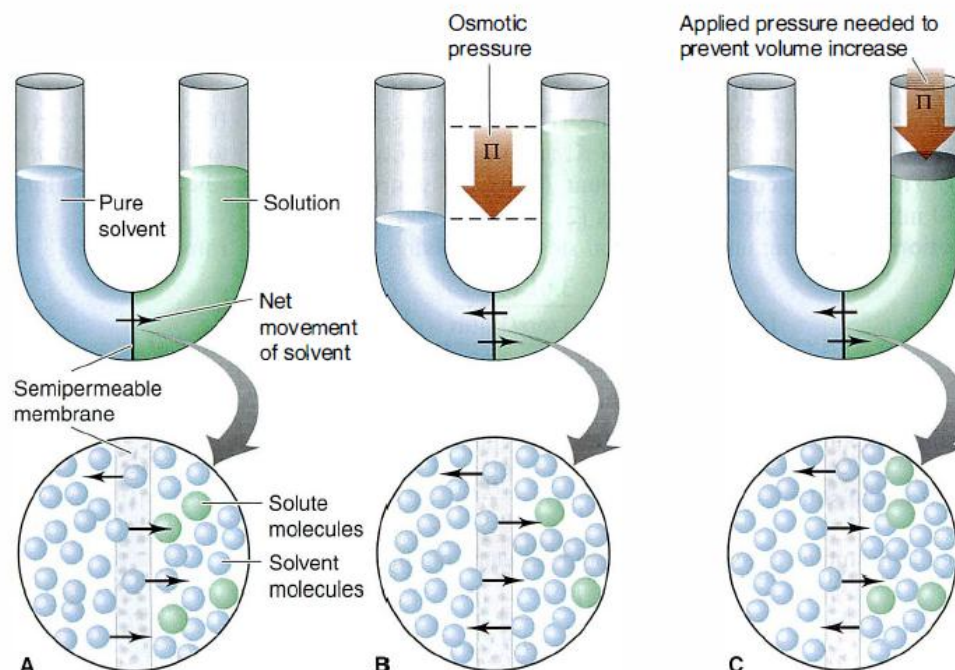
As the height of the solution rises and that of the solvent falls, the resulting pressure difference pushes some water molecules from the solution back through the membrane. At equilibrium, water is pushed out of the solution at the same rate it enters (Figure 13.13B).

The pressure difference at equilibrium is the osmotic pressure (π), which is defined as the applied pressure required to prevent the net movement of water from solvent to solution (Figure 13.13C).

The osmotic pressure is proportional to the number of solute particles in a given volume of solution, that is, to the molarity (M):

$$\Pi = \frac{n_{solute}}{V_{soln}} RT = MRT$$

R is the ideal gs constant, T is the absolute temperature. The similarity of the equation to the ideal gas law (P = nRT IV) is not surprising, because both relate the pressure of a system to its concentration and temperature.

Using Colligative Properties to Find Solute Molar Mass

Of the four colligative properties, osmotic pressure creates the largest changes and can therefore be used to get the most precise measurements for molar mass. Biological chemists estimate molar masses as great as 10^5 g/mol by measuring osmotic pressure. Because only a tiny fraction of a mole of a macromolecular solute dissolves, it would create too small a change in the other colligative properties.

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 oxygen throughout the body. A physician studying a variety associated with a fatal disease first finds its molar mass ($\mathcal{M}$). She dissolves 21.5 mg of the protein in water at 5.0°C to make 1.50 mL of solution and measures an osmotic pressure of 3.61 torr. What is the molar mass of this variety of hemoglobin?

Plan We know the osmotic pressure (Π = 3.61 torr), R, and T (5.0°C). We convert Π from torr to atm, and T from °C to K, and then use Equation 13.13 to solve for molarity (M). Then we calculate the amount (mol) of hemoglobin from the known volume (1.50 mL) and use the known mass (21.5 mg) to find $\mathcal{M}$.

Solution Combining unit conversion steps and solving for molarity from Equation 13.13:

$$M = \frac{\Pi}{RT} = \frac{\dfrac{3.61 \text{ torr}}{760 \text{ torr/1 atm}}}{\left(0.0821 \dfrac{\text{atm·L}}{\text{mol·K}}\right)(273.15 \text{ K} + 5.0)} = 2.08\times10^{-4} \, M$$

Finding amount (mol) of solute (after changing mL to L):

$$\text{Moles of solute} = M \times V = \frac{2.08\times10^{-4}\,\text{mol}}{1 \text{ L soln}} \times 0.00150 \text{ L soln} = 3.12\times10^{-7}\,\text{mol}$$

Calculating molar mass of hemoglobin (after changing mg to g):

$$\mathcal{M} = \frac{0.0215 \text{ g}}{3.12\times10^{-7}\,\text{mol}} = 6.89\times10^4 \text{ g/mol}$$

Check The answers seem reasonable: The small osmotic pressure implies a very low molarity. Hemoglobin is a protein, a biological macromolecule, so we expect a small number of moles [($\sim2\times10^{-4}$ mol/L) (1.5×10^{-3} L) = 3×10^{-7} mol] and a high molar mass ($\sim21\times10^{-3}$ g/3×10^{-7} mol = 7×10^4 g/mol).

FOLLOW-UP PROBLEM 13.8 A 0.30 M solution of sucrose that is at 37°C has approximately the same osmotic pressure as blood does. What is the osmotic pressure of blood?

Colligative Properties of Volatile Nonelectrolyte Solutions

What is the effect on vapor pressure when the solute is volatile, that is, when the vapor consists of solute and solvent molecules?

From Raoult's law;

$$P_{solvent} = X_{solvent} \cdot P^o_{solvent} \quad \text{and} \quad P_{solute} = X_{solute} \cdot P^o_{solute}$$

According to Dalton's law of partial pressures, the total vapor pressure is the sum of the partial vapor pressures:

$$P_{total} = P_{solvent} + P_{solute} = (X_{solvent} \cdot P^o_{solvent}) + (X_{solute} \cdot P^o_{solute})$$

Just as a nonvolatile solute lowers the vapor pressure of the solvent by making the mole fraction of the solvent less than 1 , the presence of each volatile component lowers the vapor pressure of the other by making each mole fraction less than 1.

Let's examine this effect in a solution that contains equal amounts (mol) of benzene (C_6H_6) and toluene (C_7H_8): $X_{ben} = X_{tol} = 0.500$. At 25°C, the vapor pressure of pure benzene (P^o_{ben}) is 95.1 torr and that of pure toluene (P^o_{tol}) is 28.4 torr; note that benzene is more volatile than toluene.

We find the partial pressures from Raoult's law:

$$P_{ben} = X_{ben} \cdot P^o_{ben} = 0.500 \times 95.1 = 47.6 \text{ torr}$$
$$P_{tol} = X_{tol} \cdot P^o_{tol} = 0.500 \times 28.4 = 14.2 \text{ torr}$$

Does the composition of the vapor differ from that of the solution?

$$X_{ben} = \frac{P_{ben}}{P_{total}} = \frac{47.6 \text{ torr}}{47.6 \text{ torr} + 14.2 \text{ torr}} = 0.770$$

$$X_{tol} = \frac{P_{tol}}{P_{total}} = \frac{14.2 \text{ torr}}{47.6 \text{ torr} + 14.2 \text{ torr}} = 0.230$$

The vapor composition is very different from the solution composition. The essential point to notice is that *the vapor has a higher mole fraction of the more volatile solution component.* The 50:50 ratio of benzene:toluene in the liquid created a 77:23 ratio of benzene:toluene in the vapor.

Condense this vapor into a separate container, and that new solution would have this 77:23 composition, and the new vapor above it would be enriched still further in benzene. In the process of *fractional distillation*, this phenomenon is used to separate a mixture of volatile components.

Colligative Properties of Strong Electrolyte Solutions

When we consider colligative properties of strong electrolyte solutions, the solute formula tells us the number of particles. Thus, we include a multiplying factor (the van 't Hoff factor) in the equations for the colligative properties of electrolyte solutions.

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

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

If strong electrolyte solutions behaved ideally, the factor i would be the amount (mol) of particles in solution divided by the amount (mol) of dissolved solute; that is, i would be 2 for $NaCl$, 3 for $Mg(NO_3)_2$, and so forth.

Careful experiment shows, however, that most strong electrolyte solutions are not ideal. For example, comparing the boiling point elevation for 0.050 m NaCl solution with that for 0.050 m glucose solution gives a factor i of 1 .9, not 2.0:

$$i = \frac{\Delta T_b \text{ of } 0.050 \, m \text{ NaCl}}{\Delta T_b \text{ of } 0.050 \, m \text{ glucose}} = \frac{0.049°C}{0.026°C} = 1.9$$

This deviation implies that the ions are not behaving as independent particles. The fact that the deviation is greater with divalent and trivalent ions is a strong indication that the ionic charge is somehow involved (Figure 13.14).

Figure 13.14

Nonideal behavior of strong electrolyte solutions. The van't Hoff factors (i) for various ionic solutes in dilute (0.05 m) aqueous solution show that the observed value (dark blue) is always lower than the expected value (light blue). This deviation is due to ionic interactions that, in effect, reduce the number of free ions in solution. The deviation is greatest for multivalent ions.
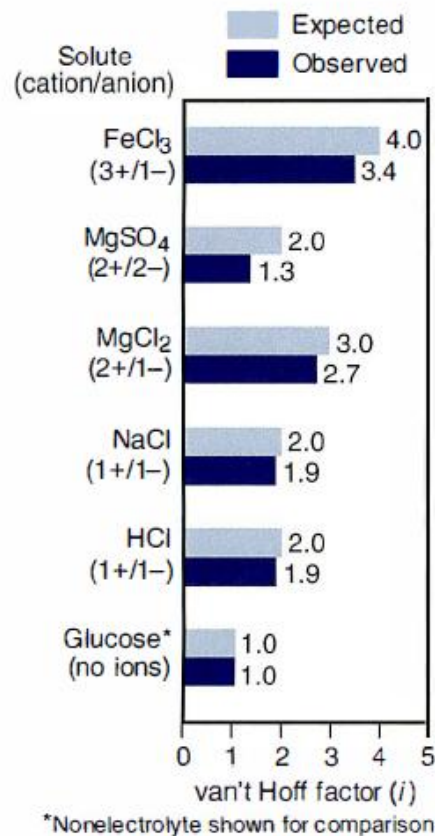

Figure 13.15 shows each ion sunounded by an *ionic atmosphere* of net opposite charge. Through these electrostatic associations, each type of ion behaves as if it were "tied up," so its concentration seems lower than it actually is.

Figure 13.15

An ionic atmosphere model for non ideal behavior of electrolyte solutions. Hydrated anions cluster near cations, and vice versa, to form ionic atmospheres of net opposite charge. Because the ions do not act independently, their concentrations are effectively less than expected. Such interactions cause deviations from ideal behavior.
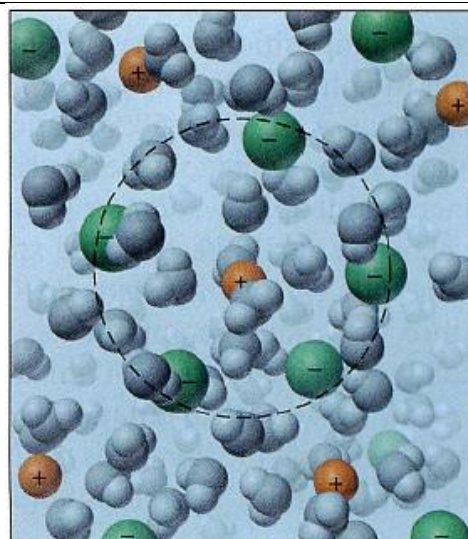
SAMPLE PROBLEM 13.9   Depicting a Solution to Find Its Colligative Properties

Problem A 0.952-g sample of magnesium chloride is dissolved in 100. g of water.
(a) Which scene depicts the solution best?
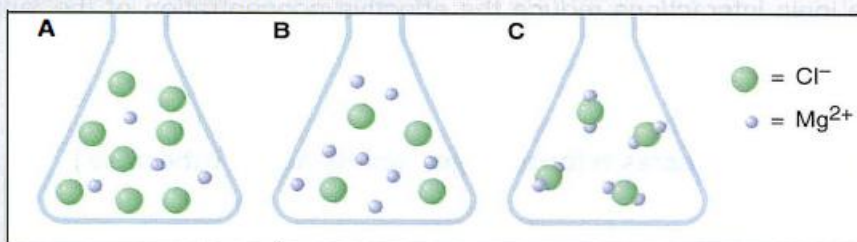
(b) What is the amount (mol) represented by each green sphere?
(c) Assuming the solution is ideal, what is its freezing point (at 1 atm)?

Plan (a) From the name, we recognize an ionic compound, so we determine the formula to find the numbers of cations and anions per formula unit and compare this result with the three scenes: there is 1 magnesium ion for every 2 chloride ions. (b) From the given mass of solute, we find the amount (mol); from part (a), there are twice as many moles of chloride ions (green spheres). Dividing by the total number of green spheres gives the moles/sphere. (c) From the moles of solute and the given mass (kg) of water, we find the molality (m). We use K_f for water from Table 13.5 and multiply by m to get ΔT_f, and then subtract that from 0.000°C to get the solution freezing point.

Solution (a) The formula is $MgCl_2$; only scene A has 1 Mg^{2+} for every 2 Cl^-.

(b) $\qquad$ Moles of $MgCl_2$ = $\dfrac{0.952 \text{ g } MgCl_2}{95.21 \text{ g/mol } MgCl_2}$ = 0.0100 mol $MgCl_2$

Therefore, $\qquad$ Moles of Cl^- = 0.0100 mol $MgCl_2 \times \dfrac{2 \text{ } Cl^-}{1 \text{ } MgCl_2}$ = 0.0200 mol Cl^-

$\qquad\qquad$ Moles/sphere = $\dfrac{0.0200 \text{ mol } Cl^-}{8 \text{ spheres}}$ = 2.50×10^{-3} mol/sphere

(c) $\qquad$ Molality (m) = $\dfrac{\text{mol of solute}}{\text{kg of solvent}}$ = $\dfrac{0.0100 \text{ mol } MgCl_2}{100. \text{ g} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}}$ = 0.100 m $MgCl_2$

Assuming an ideal solution, the van't Hoff factor, i, is 3 for $MgCl_2$ because there are 3 ions per formula unit, so we have

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

And $\qquad\qquad\qquad T_f = 0.000°C - 0.558°C =$ $-0.558°C$

Check Let's quickly check part (c): We have 0.01 mol dissolved in 0.1 kg, which gives 0.1 m. Then, rounding K_f, we have about $3(2°C/m \times 0.1 \text{ } m) = 0.6°C$.

FOLLOW-UP PROBLEM 13.9 The $MgCl_2$ solution in the sample problem has a density of 1.006 g/mL at 20.0°C. (a) What is the osmotic pressure of the solution? (b) A U-tube fitted with a semipermeable membrane is filled with this $MgCl_2$ solution in the left arm and a glucose solution of equal concentration in the right arm. After time, which scene depicts the U-tube best?