14 Solutions

(What happens when you mix solids, liquids and gases together)

Introduction. As we have meandered through the various states of matter, we have evolved from a kinetic molecular model in which particles of various energies bounced off of each other in elastic collisions to the notion that those particles are in fact atoms, molecules and ions, which are made of fundamental charged particles that feel intermolecular attraction to one another. These intermolecular attractions resulted in the formation of condensed phases, either liquids or solids. All sorts of physical properties can be reasoned from an evaluation of the intermolecular forces that these particles exhibit. These intermolecular interactions thus explain the non-ideality of gases.

Impure thoughts about solutions. In this chapter we move a step closer to reality with yet another complication. Gases, liquids and solids don't have to be pure. Now you were able to deal with this notion of mixtures in examining gases by applying Dalton's law of partial pressures. Of course things were simplified in the case of gases because we still operated with the kinetic molecular model that assumed there were no attractive forces between the different particles. A molecule of gas A behaved the same as a molecule of gas B so you could just add up their partial pressures.

Things are not so simple in condensed phase, and in particular, in liquids. As you learned in Chapter 4, it is possible to pour solids into liquids and they will dissolve—will become soluble. In that chapter we ignored the question of why compounds dissolved. Now, here in Chapter 14 we ask it. We ask questions like: how fast can dissolution occur? or What effect do temperature or pressure have on dissolution?

Chapter 14 Part 2: Colligative Properties: In the second half of the chapter we will ask questions about the properties of solutions in which compounds are dissolved. Anyone who has dumped a bucket of salt onto a frozen porch, knows that something important and actually useful is happening. The collection of properties that we assign to the dissolution process are called colligative properties and include boiling point elevation and freezing point depression and osmotic pressure among others.

Definition Time: Now as we begin this chapter, a few terms need to be defined.

- Solutions are composed of a solvent and solutes. The solvent is typically a liquid, is in greatest abundance in the mixture. It is the medium into which one or more solutes are dissolved.

- The term solute is more general and refers to either gas, liquid or solids that are dissolved in the solvent. There is one solvent and, potentially, multiple solvents.

- A homogeneous solution is one in which a single phase is apparent. In other words, the solute has dissolved completely in the solvent.

- A heterogeneous solution is one in which separate phases are observed. For example, when we have achieved a saturated salt solution, a heterogeneous mixture is formed with the liquid phase containing water and dissolved salt ions, and a precipitate of crystalline salt lying on the bottom of the container.

The dissolution process. To understand the process by which a solute dissolved, it is necessary to distinguish two physical processes that determine whether dissolution occurs—(1) a change in the energy of the solution associated with the breaking and reformation of solvent and solute intramolecular and intermolecular attractive forces and (2) a change in the entropy of the solution, the process by which a system becomes more or less disordered. These concepts, energy and entropy, will be the detailed subject of the next chapter on thermodynamics, and I'm actually sorry I had to being them up. But for now, let's accept on faith that:

- When a solution decreases in energy (gives off heat in an exothermic process), dissolution is favored. In other words, if you add a solute to a solvent and things gets hotter to the touch, the likelihood that dissolution will occur increases.
- When a solution becomes more disordered (entropy increases), the likelihood that dissolution will occur increases.

Combining entropy (disorder) and enthalpy (heat energy) terms:

As we will see in the next chapter, there are four possible combinations of these possibilities when we mix two things together. If we can quantify the entropy and energy, we can know precisely whether dissolution is favored.

For the time being we can use some common sense in qualitatively determining whether something can dissolve.

Dissolution Case I: Dissolving solids in water.

Close your eyes and imagine dumping some salt into water. As the salt enters the water, it is a nice, stable crystalline form. The water, as well, has established some nice hydrogen bonding action. Given this, why would the salt and the water want to form a partnership in which the salt crystal breaks apart into ions and the water molecules break hydrogen bonds to accommodate the Na^+ and Cl^- ions?

Of course the answer is that the overall process, a heat of solution, ΔH_{soln}, must be favorable in that energy is released. The picture shown below identifies all the different steps in this dissolution process. As we will see in Chapter 15, when all is said and done, if the ΔH_{soln} is negative, the dissolution is energetically favored. We will also learn, though, that even when ΔH_{soln}, it is possible for dissolution to occur because of positive entropy effects.

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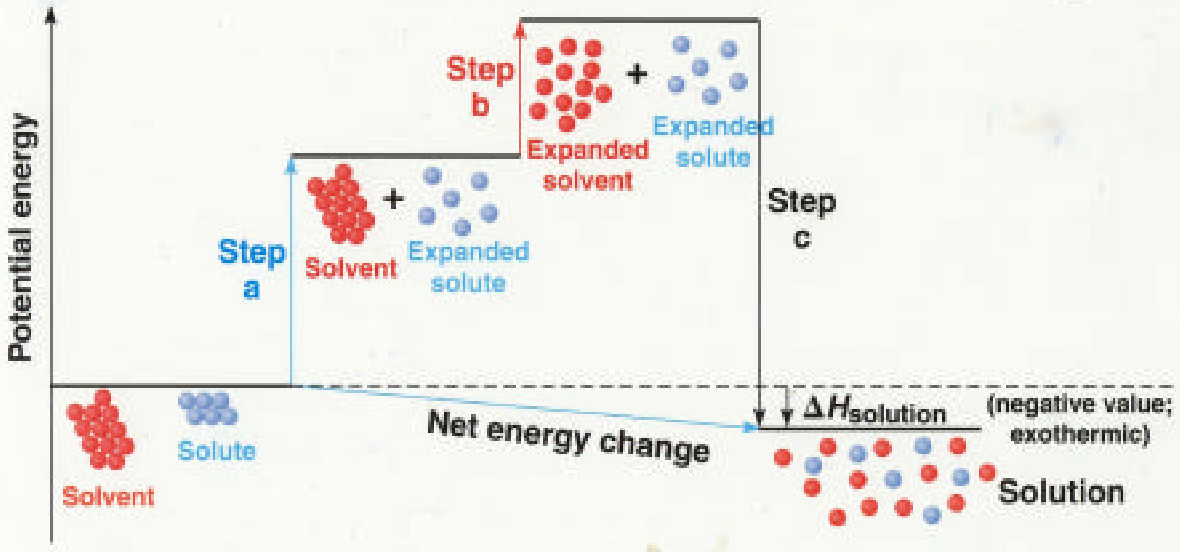
Figure 14.1



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Dissolution of Ionic Solids. So what are the specific steps in the figure? First, there is the process of reversing the formation of a crystal lattice. Na^+ likes being around Cl^-, so the crystal lattice energy is favorable.

$$Na^+ + Cl^- \rightarrow NaCl + \text{energy}$$

This crystal lattice energy has to be overcome or the salt will sink to the bottom of the container as an insoluble solid. What can inspire this separation? The solvation process, which in the case of water, is called the hydration process. Water molecules are polar in nature and have positive and negative regions of electron density. The hydration energy describes just how much the electron rich region of the water will be attracted to the Na^+ and how much the electron poor region of the water will be attracted to the Cl^-.

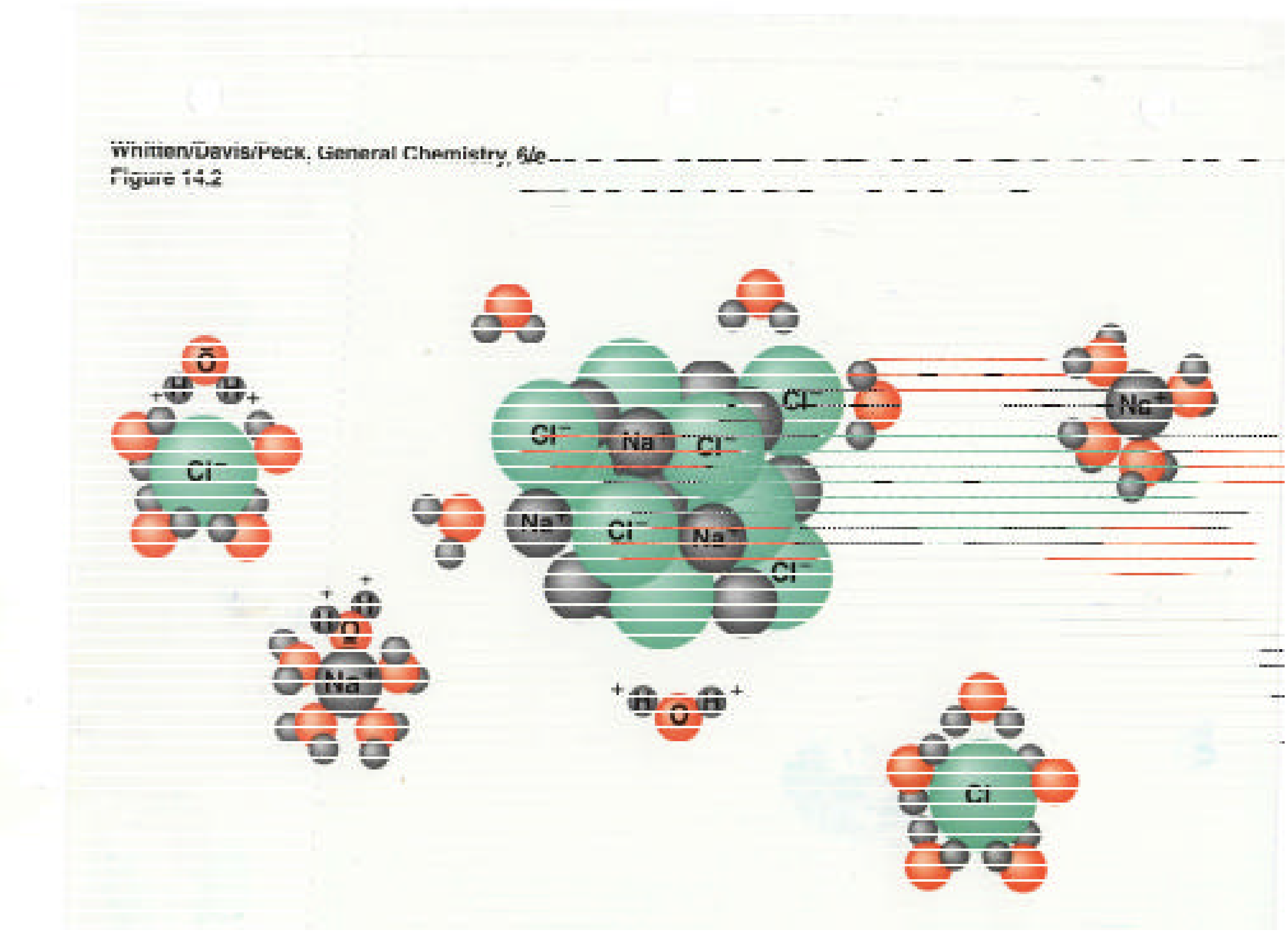
$$Na^+ + xH2O \rightarrow Na(H2O)_x^+ + \text{energy}$$

$$Cl^- + yH2O \text{ ----) } Cl\,(H2O)_y^- + \text{energy}$$

So we have two competing processes, crystal lattice energy and hydration energy. These are what define $\Delta H_{soln.}$

$$\Delta H_{soln} = (\text{heat of solvation} - \text{crystal lattice energy})$$

Presented in the attached figure is an attractive visual of a salt crystal undergoing the dissolution process. Note carefully the orientation of the waters around the Na^+ and the Cl^- so that strong dipole interactions and hydrogen bonding can occur. It is these new intermolecular interactions that are favored, even over those for the pure water or salt crystal.



Why “like dissolves like” made sense. Now you can see how the notion of “like dissolves like” was created. The polar water molecules have electron rich and poor regions that are attracted Coulombically to other electron rich and poor species (like cations and anions). Hence the solvation process is highly favored and dissolution occurs.

So why don’t all salts dissolve? Obviously not all salts will dissolve in water. If they did we wouldn’t have to have solubility rules. In fact, most salts are sparingly soluble or not soluble at all. This means that the crystal lattice energy is more favored than the hydration energy. An in-depth discussion of this awaits something like upper division inorganic chemistry, but there are certain trends.

Trends for whether salts dissolve (recalling the most famous of all solubility rules.)

- Salts of singly charged species are more likely to dissolve because the crystal lattice energy is comparable to the hydration energy. This means that the increase in system disorder (increased entropy) will play the major role in the spontaneity of dissolution. For example, as I will show you in class, dissolving something like NH_4NO_3 in solution happens, even though the reaction is exothermic because of increased entropy. Not only is the salt dissolved, but ammonium ion will form ammonia gas and leave the container, creating even more disorder.

- In contrast, salts of multiply charges species, like Al_2O_3 (Al^{+++} and O^{-2}) have very high crystal lattice energies and thus are less likely to dissolve.

Case 2: Dissolving liquids and gases in solution. Although we don't think of it as much, the dissolution of liquid and gaseous solutes in a solvent should also be considered. In the case of liquids, we use the term miscible to describe the fact that two liquids form a homogeneous mixture. Water and ethanol are miscible. Water and oil are not.

The process of mixing liquids or gases with a solvent is not generally as complicated as the mixing of solids with a solvent; this is because the crystal lattice energy need not be considered, but there is still a consideration of the relative strength of the intermolecular forces that hold a liquid together and whether those can be overcome by the solvation process.

The important rule for whether liquids dissolve: Like dissolves like. In general, a comparison of intermolecular forces will give a good indication of whether solubility will occur. The more alike the solvent and solute, the more likely dissolution will occur. Thus polar liquids that exhibit hydrogen bonding will be more likely to dissolve in water than non-polar liquids that exhibit only London forces.

Like dissolves like for gases in liquids. Polar gases will also dissolve to a greater extent in water than non polar gases. For example, HCl and other hydrogen halides are gases and dissolve readily in water to give us some of our favorite strong acids. The reason dissolution is favored is clear and is shown in the next figure. The H^+ from the HCl is strongly solvated by the electron rich oxygen region of a water molecule. The process is so favored that HCl is considered to be a strong electrolyte and hence a strong acid. Every proton dissociates and dissolves into water.

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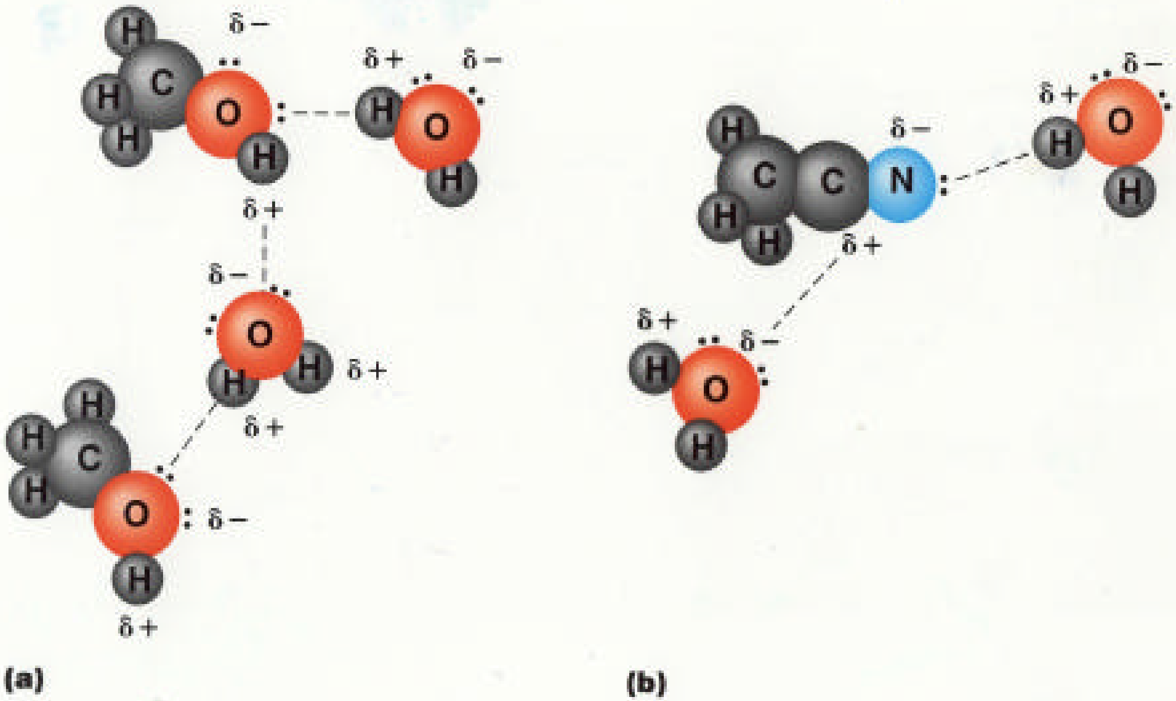
Figure 14.3



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What about non-polar gases in water? It is possible for non-polar gases to dissolve in water. For example O_2 dissolves in water, which is a good thing for fish. One of the things that favors the dissolution of nonpolar gases (basically violating the “like versus like” adage, is that gases don’t have strong intermolecular forces. This while hydration energy must fight crystal lattice energy or other intermolecular forces in solids and liquids in order for dissolution to happen, there is little intermolecular attraction to be overcome in gases and the formation of simple London forces between gas and liquid is possible.

Temperature and pressure effects on solubility. This section is presented in Davis without a good introduction to LeChatlier's Principle (which comes in Chapter 17.) So I will keep what you need to know brief.

As you are aware, solubility can depend upon temperature. You have all experienced the fact that if you want to make a solution really salty, you heat it up to dissolve more salt. This is true because for NaCl and most salts, the ΔH_{soln} is endothermic, though only slightly so, and it is entropy that is responsible for the salt dissolving. As we will see, when a process is endothermic, adding heat places a stress on the system that causes a shift in equilibrium to form more products, in this case, salt ions. Shown below is a graph that shows that most salts exhibit this phenomenon.

Why fish die when water temperature goes up. Not all salts have endothermic ΔH_{soln} and it leads to the one exception shown in the graph. Na_2SO_4 has an exothermic ΔH_{soln} and will actually start to precipitate out of solution as the temperature is raised. A more important example of this is the dissolution of O_2 in water. O_2 dissolves in water with an exothermic ΔH_{soln}. Consequently as the temperature of water rises, oxygen solubility decreases, obviously not a great thing for sea life—red tide, which results from increasingly anaerobic conditions in water, is an example of this.

Pressurechanges and solutions: Henry’s Law. Pressure effects are not as important in determining solubility in solutions. As you learned at the beginning of Chapter 13, one of the ways in which condensed matter is defined is that it is not very compressible. Thus when we put the squeeze on a solution (increase the pressure), we aren’t really doing much to the system in terms of a stress. So pressure doesn’t effect the solubility of solids and liquid solutes in a liquid solvent.

Pressure does effect the solubility of a gas in a solution. Obviously if you can increase the concentration of a gas above the surface of a liquid, you increase the solubility of the gas in the liquid. This common sense notion is Henry's Law, which states that as the pressure of a gas above a solution surface increases, the concentration of the gas in the solution increases.

$$P_{gas} = kC_{gas}$$

I personally always thought this was so obvious, that I wondered why this guy got a whole law named after him.

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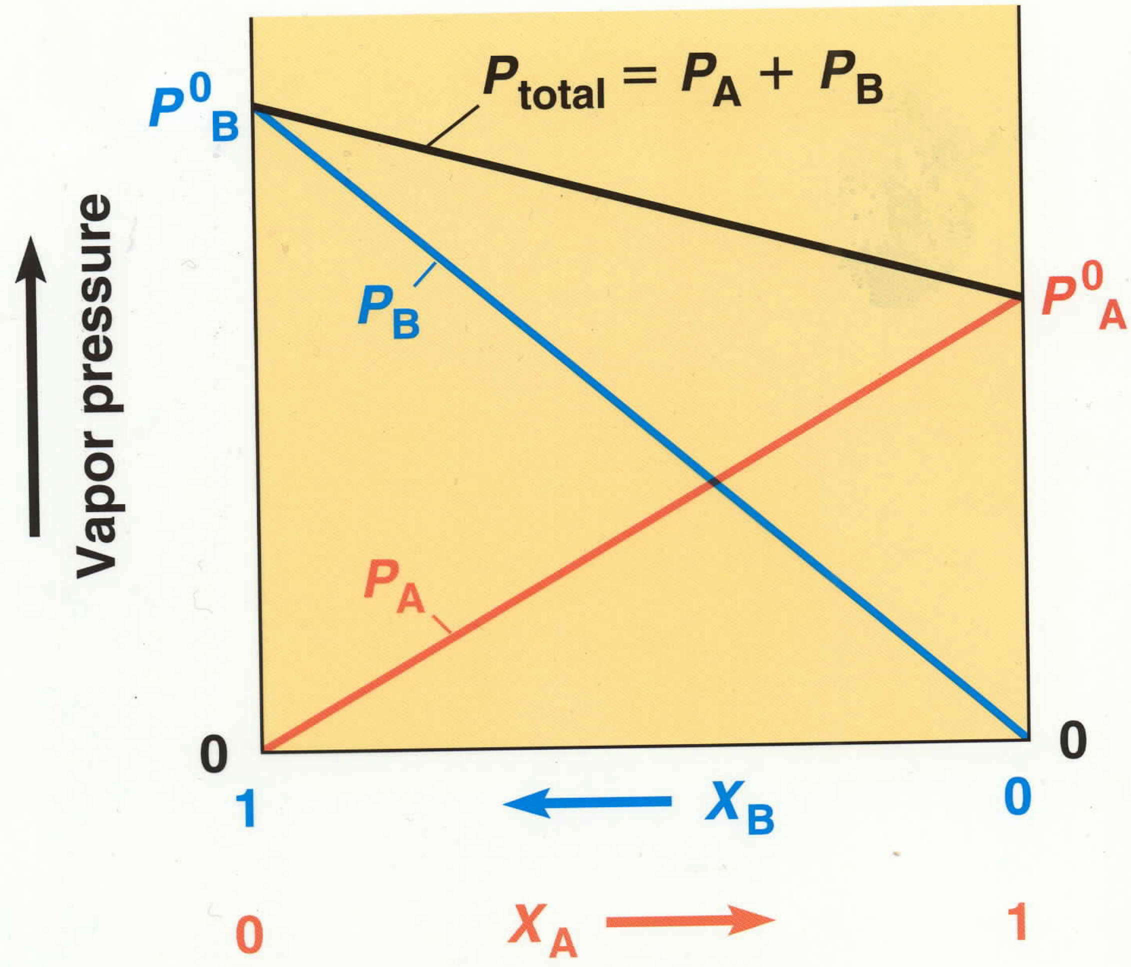
Figure 14.10



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Part 2 of Chapter 14: Properties of Solutions.

Time Out for New Kinds of Solution Concentration. Since we are talking about solutions, it is important to remember that when you dissolve something in a solvent, it is a good idea to quantitative how much stuff was dissolved. We have learned to use concentration defined as molarity, mole fraction and % by mass or volume. Now I introduce the molal. (Note the letter l replacing the letter r.) Molality is defined below:

m = Molality = moles solute/kilograms of solvent

compared to

M = Molarity = moles of solute/ liters of solution

We simply use kilograms of solvent instead of liters of solvent. We introduce molality here because in the study of colligative properties we use it in calculations.

Colligative Properties. Remember kinetic molecular theory and how it depended only on the number of particles and not what the particles were? Well kinetic theory has found a pen pal, colligative properties.

Colligative properties: Properties of solutions that depend on the number of solute particles (whether molecules or ions) and not the kind of particles.

Thus 1000 particles of Na^+ will ideally have the same effect as 1000 O_2 gas molecules in a solution when we are looking at a colligative property. And what are the big four of colligative properties?

- Vapor pressure lowering
- Boiling point elevation
- Freezing point depression
- Osmotic pressure.

Non-ideality means colligative properties are only kind of true.

Now before we look at the details of these four properties, understand that you are being told about an ideal case. In fact, when you add a Na^+ to solution it behaves very differently from an O_2 in terms of intermolecular interactions. This leads to non-ideal conditions in which the simple proportional relationship involving colligative properties falls apart (in the same way that the simple proportional relationship involving the ideal gas law fall apart when non-ideal behavior ruins the kinetic molecular model.)

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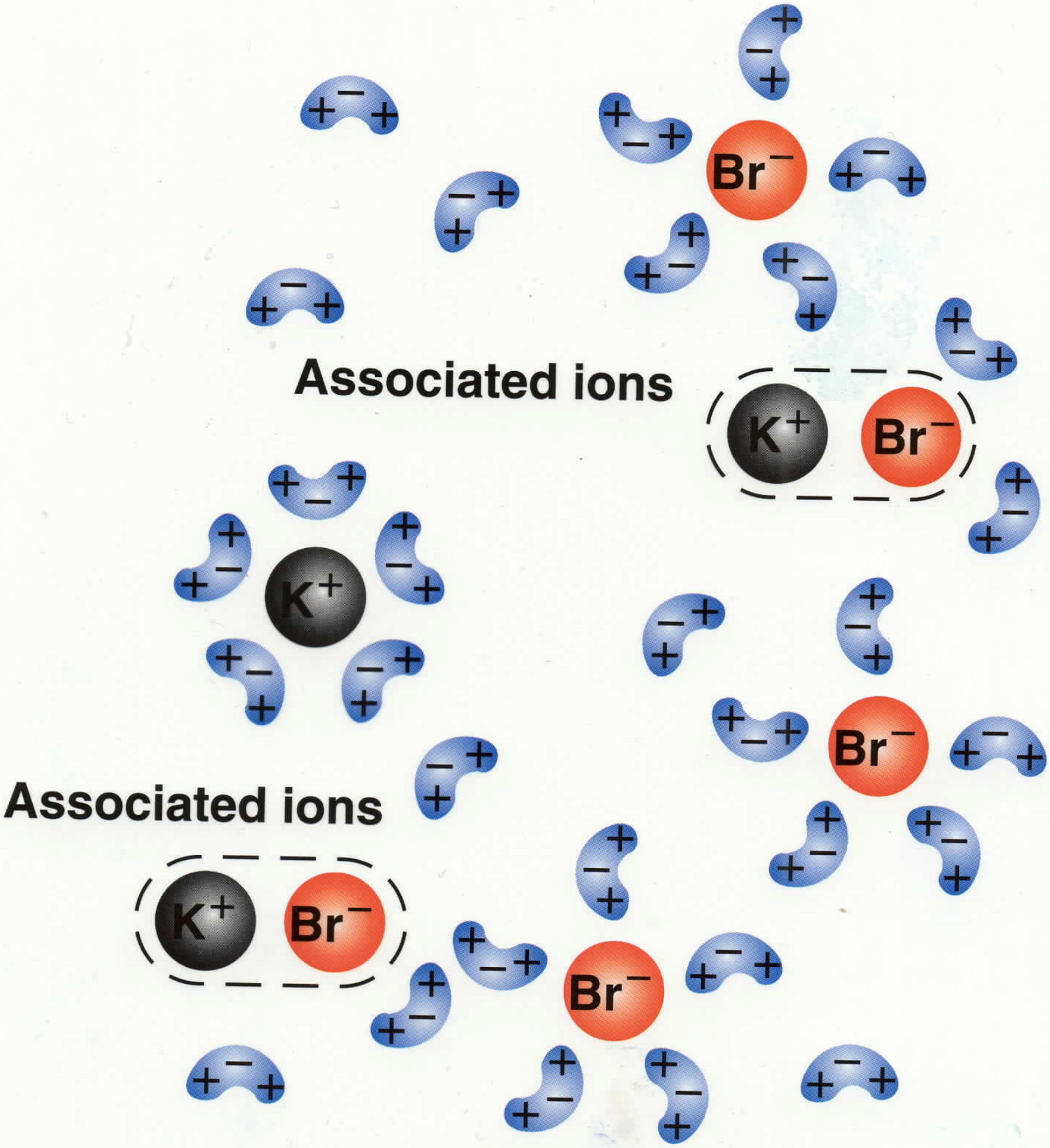
Figure 14.15



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Colligative Property 1: Lowering the vapor pressure. When you add a solute to a solvent, the vapor pressure of the solvent decreases. Practically speaking, this means that if you add some salt to a bowl of water, it will take longer to evaporate. What are the reasons?

Reason 1:

- The obvious one is that the non-volatile solute takes up the space that would have been occupied by the solvent, thus less room at the surface for solvent to evaporate is available.

Reason 2:

- The more important (but harder to understand) reason is that one of the big things favoring evaporation is the increasing disorder that comes when a liquid becomes a gas. A pure liquid is already relatively well order, so there is a big increase in entropy pushing the evaporation process. In contrast, a solution containing a solute is already less ordered. Thus the entropy push that promotes evaporation isn’t as great (there isn’t as much disorder to be gained), so evaporation isn’t as favored.

Time out for the general form of a colligative property law:

Because vapor pressure lowering is a colligative property, the law that describes it has to involve a simple proportional relationship. (By the way, this is an advantage of all colligative property laws, they all look like this

$$A = K\ B.$$

Of course, they all look alike so you can get confused, so maybe it is a disadvantage.)

Raoult's Law: Anyway, the law describing vapor pressure lowering is Raoult's law:

$$P_{solvent} = X_{solvent}\, P^{o}_{solvent}$$

where $P_{solvent}$ is the reduced vapor pressure of the solvent, $P^{o}_{solvent}$ is the vapor pressure of the pure solvent and $X_{solvent}$ is the mole fraction of the solvent. The equations shows very simply that as the fraction of the solvent decreases, the vapor pressure decreases proportionally.

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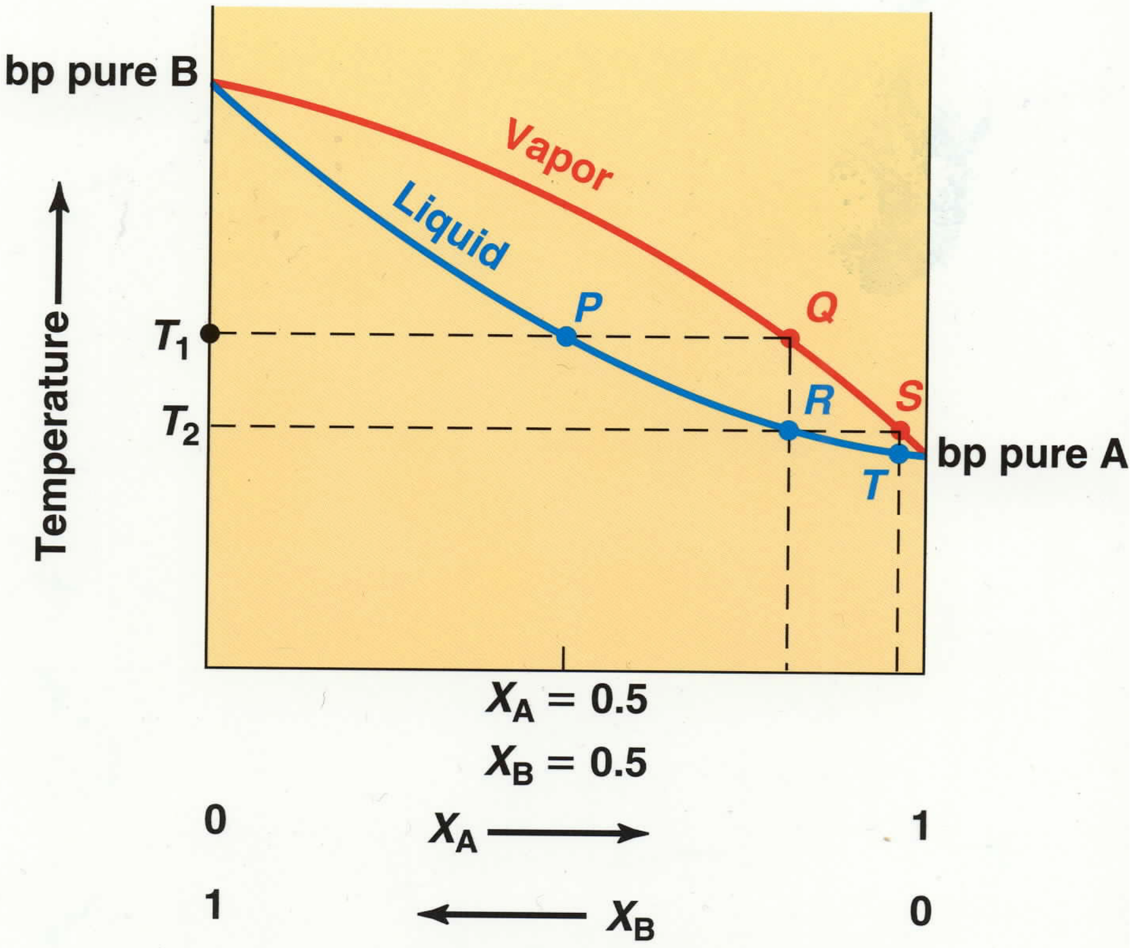
Figure 14.12



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Colligative property 2: Boiling Point Elevation. (Here is your one chance to use molality, so pay attention.) For arguments similar to those made for vapor pressure lowering, the temperature necessary to boil a solution increases with amount of solute. More energy is necessary to promote the formation of gas bubbles in the solution (to cause the vapor pressure of the gas bubbles in the solvent to equal atmospheric pressure.) Thus the temperature of the system needs to be raised.

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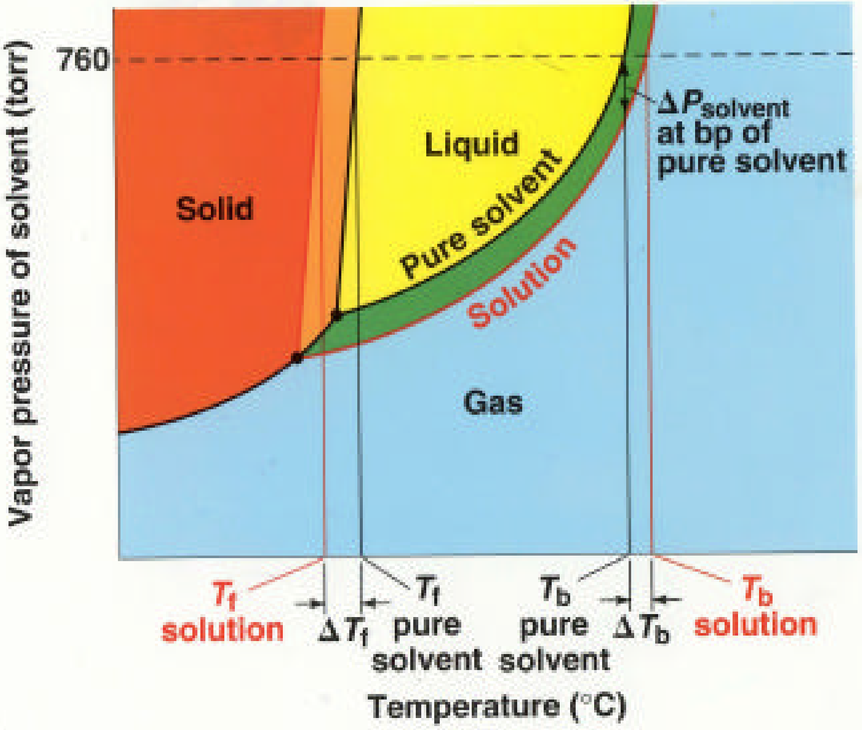
Figure 14.14



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Boiling point elevation equation: Again, this being a colligative property, a simply equation involving solute concentration describes the phenomenon.

$$\Delta T_b = K_b m$$

Where ΔT_b is the increase in temperature above the boiling point, K_b is a solvent dependent constant that determines the magnitude of the BP elevation, and m is the molality of the solution. As the concentration increases, the ΔT_b increases. In general, the magnitude of K_b is not great. This means that you should not expect to see a huge increase in ΔT_b for a solvent just because you throw a little solute in.

Sample calculation:

What is the increase in boiling point that occurs for a 1.25 m sugar solution. From the table above, K_b is 0.512^{o}C/m for water.

$$\Delta T_b = (0.512)(1.25) = 0.64^oC.$$

Thus the boiling point of water increases to just 100.64^{o}C. This isn't a big change, and when you consider that 1.25m is a pretty significant concentration, this is about the limit of what you can expect for BP elevation.

Colligative property 3: Freezing point depression. The process by which a liquid becomes a solid requires that an increased ordering of the solvent into a crystalline structure occur. This ordering occurs as the solvent molecules slow down at decreasing temperature. The addition of a solute complicates the ordering process, creating an impediment to the freezing process. To compensate, the temperature must be depressed below the freezing point of a pure liquid. Again the equation describing this phenomenon looks like that for the other colligative properties:

$$\Delta T_f = K_f m$$

The table above includes K_f values for common solvents and again we can get an idea of the magnitude of the depression.

Sample freezing point calculation:

What is the freezing point depression when we add 1.25m sugar to water?

$$\Delta T_f = (1.86)(1.25) = 2.23^oC.$$

Thus the freezing point of water has dropped a couple of degrees.

The famous real-life colligative property experience: pouring rock salt on ice. Of course those of you from the north know that big example of this—rock salt everywhere in the winter. By pouring salt onto frozen roads, the necessary temperature for creating a frozen salt water solution is reduced by a few degrees, causing the ice to melt.

A second famous real-life colligative property experience: anti-freeze. This notion of boiling point elevation and freezing point depression is also of value to the automobile you drive. It is important to have a radiator for the purpose of carrying excess heat away from an engine. However is water is used as the solvent, the temperature range before bad things happen (your radiator freezes up or the water evaporates blowing the radiator pressure cap is 0 ^{o}C to 100^{o}C. As you know, by adding an appropriate solute, we can significantly extend this 100 ^{o}C range. Salt obviously doesn't cut it, giving us a degree or two in either direction. So don't add it to your radiator. However the extension of BP and FP range when two miscible solvents are added together can be much higher. The theory behind this is well beyond this course, but the general concepts are the same. But a nice piece of trivia to have with you is that in appropriate ratio of water to ethylene glycol to water, the temperature range expands by about 100 ^{o}C!!

Time Out for Turning Colligative Properties into Stoichiometry Problems. You may have noticed that everytime a difficult concept is introduced, it is made harder by asking you to tack on some of the stuff you learned about stoichiometry back in Chapter 2. For example, when you were learning PV=nRT for the ideal gas law, n/V turned out to be molarity. But molarity is (g/MW)/liters. So back in Chapter 12 you were asked to find the MW of gases by giving you a bunch of other information that you stuck into the ideal gas law.

Well it is happening again. Notice that both the freezing point depression and the boiling point elevation equations have molality in them. But molality is (g/MW)/kg solvent. This means you can stick in a bunch of numbers to either the freezing point depression or boiling point elevation equation and get a MW. You get the chance to do this in your homework.

One final thought on freezing point depression. This concept will rear its ugly head to your great disadvantage if you take organic lab. In organic lab you will supposedly be making pure compounds. If the compounds aren’t pure because you did a lousy job in the synthesis, then the mixture you have made will have a reduced melting point and you will be graded down accordingly. Another example of colligative properties in action.

Colligative property 4: Osmotic pressure. One final colligative property, quite unlike the other three we have seen. In life, we tend toward more disorder. Put a drop of food coloring in solution and it tends to disperse rather than to become more concentrated. Place two solution of different concentration next to each other and the solutions will tend to a uniform concentration.

As a special case of this, it is possible to place a semi-permeable membrane between two solutions, one in which the solvent is free to pass in either direction, but the solute cannot. The solvent want to move in the direction of the more concentrated solute. If it does, there is a swelling or increase in volume of the region with more solute molecules. This process continues until a back pressure from the sheer weight of the solution counters the flow due to concentration differences. The picture below gives a sense of what this pressure is that must be exerted to counter the disproportionate flow through the membrane.

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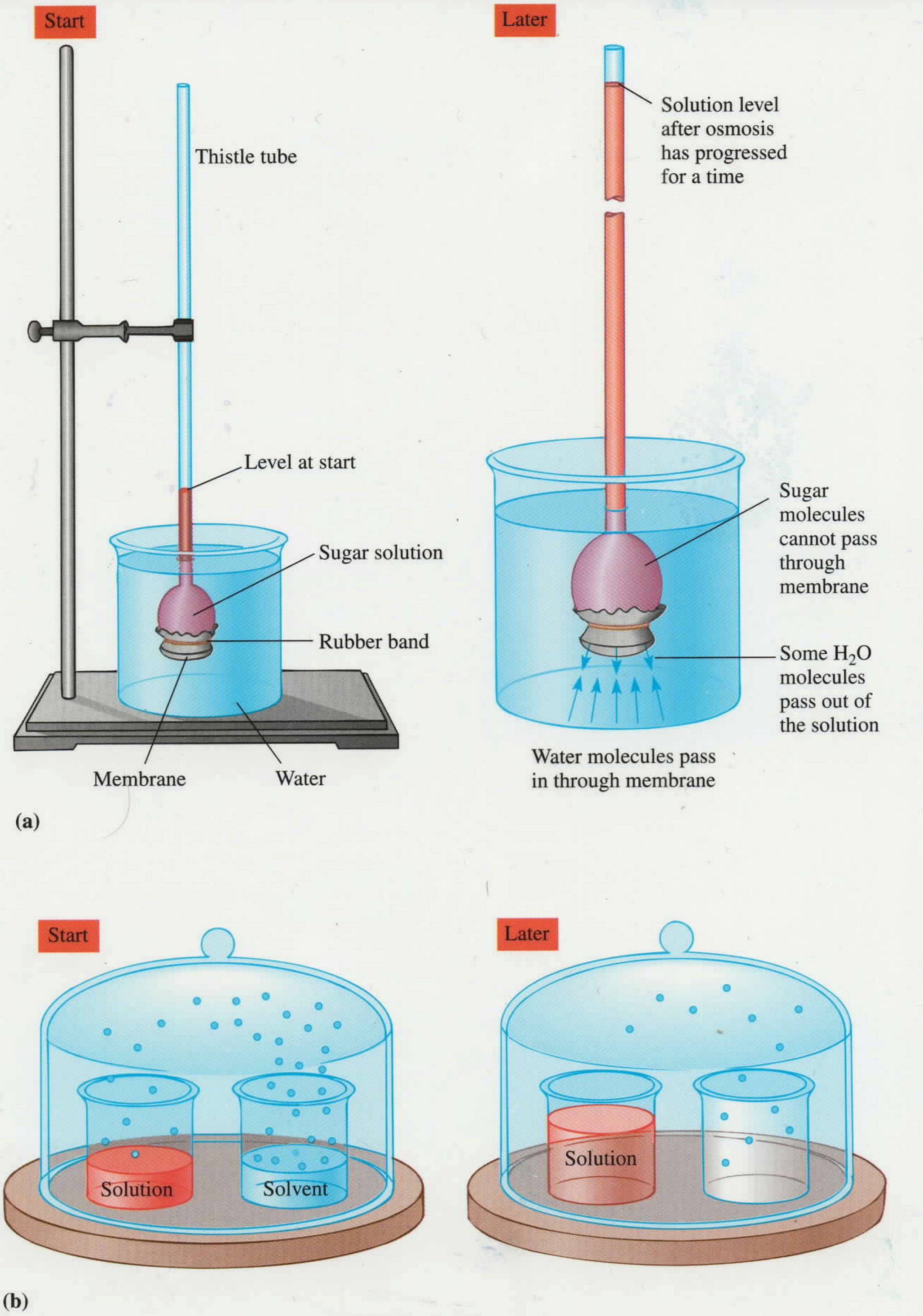

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The Osmotic Pressure Equation: There is actually a very simple equation to describe the parameters involved. In some ways it is not surprising that in the same way the ideal gas law depends upon the kinetic theory which doesn't consider the kind of particle in developing PV=nRT, osmotic pressure, a colligative property that is independent of the type of solute, has a very similar equation

$$\Pi = MRT$$

where Π is the osmotic pressure, M is the molarity and R and T are the same as for the ideal gas law.

Sample Problem. Calculate the osmotic pressure of a 1.17 M solution of sugar water.

$$\Pi = (1.17)().0821)(298) = 28.6 \text{ atm.}$$

Wow. In contrast with our first three colligative properties for which relatively small changes in the physical system were measured, a huge change in pressure was observed for a simple sugar solution.

Important biology thought on osmotic pressure: It is not our purpose to delve deeply into osmotic pressure here, we leave it for the physicists and the biologists. But it is important to note that biological systems make great use of osmotic pressure differences to alter the physiological concentrations of cells. Even small deviations from expected concentrations of solute can wreak havoc of cell structure. In fact, the process of ripping open cell membranes (lysing) is readily accomplished using the principles of osmotic pressure.