The properties of the various phases that we've discussed up to this point are properties of pure substances. However, most chemicals we deal with exist as part of mixtures, whether it is the air we breath, which is primarily a mixture of nitrogen and oxygen, the coffee we drink in the morning, the afternoon, the evening and late into the night, or the tungsten carbide alloy from which razor blades are made. We are going to talk primarily in this chapter about the physical properties of solutions, but let's begin by talking briefly about three types of mixtures in liquids - suspensions, colloids and solutions. They are distinguished in three ways - the size of the particles mixed in the liquid, the effect of the mixture on the physical properties of the liquid, and the ease of the separation of the two constituents from each other.

The easiest distinction between the three types of mixtures is the size of the particles that are suspended in the liquid. The two extremes are suspensions and solutions. In a suspension, the particle is very large compared to the size of the molecules that make up the liquid. Often the particles in a suspension are large enough that individual particles can be seen without any magnification. Because we can see the particles, you typically can't see through a suspension. Because the size of the particles in a suspension is large, it is usually easy to remove the suspended material from the liquid. This can be done by filtering the liquid or often by waiting for gravity to pull the particles to the bottom of the liquid. Often we aid the settling of the particles in a suspension by using a device called a centrifuge. A centrifuge is a device that by spinning rapidly, generates a centrifugal force which can be many times the force of gravity. Under this kind of force, particles in a suspension will settle more rapidly. Another result of the large size of the particles in a suspension is that they tend to have little or no effect
on the physical properties of the liquid. This is because in a suspension you tend to have regions that are pure liquid, and regions which are pure solid, and very few regions in which the liquid and the solid are in contact. Since it is the region in which the two substances are in contact that causes any changes in the properties of the liquid, the solid particle will have very little effect on the properties of the liquid.

The opposite extreme in the size of particles in a mixture is a solution. In a solution, the particles suspended, or solutes, are individual molecules, atoms or ions, spread randomly throughout the solvent. Each molecule is completely surrounded by solvent molecules. Because the contact between the solute and the solvent is so intimate, the attractive forces between them are strong, and the solute and solvent do not spontaneously separate.

In addition, because each molecule of the solute is in contact with several solvent molecules, there are lots and lots of opportunities for the solute and solvent molecules to interact, so solutions often have physical properties which are very different from the pure solvent. Another property of solutions that is a result of this even distribution of molecular sized particles is that solutions are always clear, i.e., you can easily see through them. Note that by saying that solutions are clear, I am not saying that they are colorless, merely that they are transparent.

The third type of mixture is intermediate between the first two, and is called a colloid. In a colloid, the suspended particles are large compared to molecules, but small compared to the particles in a suspension. The most common form of colloid that you are probably already familiar with is called a sol, which is a colloid in which solid particles are suspended in a liquid. Examples of sols are Jell-O and paint. Another common form of colloid is called an
emulsion, in which small droplets of one liquid are suspended in another. Examples of emulsions are mayonnaise and bearnaise sauce.

We can distinguish a colloid from a suspension because the particles are small enough that they don't spontaneously settle, and won't even settle if we centrifuge the mixture. On the other hand the particles are large enough that the physical properties of the solvent are typically not changed by the presence of the colloid. Colloids are often clear, just as solutions are. However, it is possible to experimentally distinguish a clear colloid from a solution by the way a laser beam passes through the liquid. In a true solution, the laser beam will be nearly invisible, while in a colloid, the laser beam will be easy to see. This is because the particles in the colloid are big enough for the light to bounce off of, a process called scattering. The scattering of laser light from colloidal particles is called the Tyndall Effect.

You need to be comfortable with these definitions, because in lab this semester, you will be dealing with mixtures continually. Part of the objective of the labs will be learning how to separate these mixtures. This means that you will be learning how to separate the components in a solution, typically by turning them into suspensions, i.e., by making a precipitate of one of the components. You can see that if the idea is to separate the components, formation of colloids is undesirable, since it is difficult to separate the colloids from the liquid in which they are suspended.

As I said earlier, the main focus of this chapter is on the physical properties of solutions. It turns out that all of these properties depend on the concentrations of the solutes in these solutions. Unfortunately, the equations that we use to describe the way that these properties depend on concentration use several different units to describe concentration. In addition, the
units that may be used to describe a concentration of a particular solution may even be different from these. For these reasons, I'd like to go over the various **units we use to describe concentration** and **how to convert between these various units**.

We've already worked with one concentration unit, **Molarity**, which is defined as **moles of solute divided by the number of liters of the solution**, i.e.,

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

If we have a 0.350 L aqueous solution of Ca(NO₃)₂ containing 5.00 x 10⁻² moles of calcium nitrate, the molarity is 5.00 x 10⁻² mol / 0.350 L = 0.143 M.

Notice that the molarity is defined in terms of a ratio, the number of moles of solute over the number of liters of solution. In fact, **all concentration units are ratios**, so all we have to do to define the various concentration units is specify what goes in the numerator and what goes in the denominator. The most important units of concentration, in addition to molarity, are mole fraction, weight percent, and molality. Let's go through them one by one.

The **mole fraction**, which we introduced in the context of mixtures of gases, is the ratio of the number of moles of one component of the solution to the total number of moles in the solution. The mole fraction is symbolized by X, so if we call our solute A and our solvent B, then we have

$$X_A = \frac{\text{number of moles of A}}{\text{total number of moles}} = \frac{n_A}{n_A + n_B + \ldots}$$
This definition implies that all the mole fractions for a solution add up to one. For example, if we have a sample which is 1.00 mol of methanol in 19.0 moles of ethanol, the mole fraction of methanol is

$$X_{\text{MeOH}} = \frac{1.00}{1.00 + 19.0} = 0.0500.$$ 

We could calculate the mole fraction of the ethanol two different ways. First, we could use our formula and get

$$X_{\text{EtOH}} = \frac{19.0}{1.00 + 19.0} = 0.950.$$ 

Second we could recognize that since our mixture is made of only ethanol and methanol, 

$$X_{\text{MeOH}} + X_{\text{EtOH}} = 1,$$

and therefore

$$X_{\text{EtOH}} = 1 - X_{\text{MeOH}} = 1.000 - 0.0500 = 0.950.$$

The weight fraction is the ratio of the weight (or mass) of one substance to the total weight (or mass) of the solution, i.e.,

$$w_A = \frac{\text{grams of } A}{\text{total grams of solution}}.$$ 

This is used less commonly than the weight percent, which is the weight fraction times 100%,

$$\text{weight } \% \text{ of } A = \frac{\text{grams of } A}{\text{total grams of solution}} \times 100\%.$$ 

The most common way that weight percent is referred to is with words, i.e., I have a 4 weight percent solution of sugar in water. We also use the symbol % w/w to indicate weight percent.
As an example suppose we have a 75g sample containing 6.0 g NaCl. Then the weight percent of NaCl is 6.0 g/75g x 100% = 8.0 weight percent NaCl, also symbolized as 8.0% w/w.

Finally, the **molality** of a solution is defined as the **number of moles of solute divided by the number of kilograms of solvent**, i.e.,

\[
m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}
\]

Since molarity and molality have similar names it is important not to confuse them. To clarify the difference let's compare the way we would prepare a 1.00 M solution of iodine in carbon tetrachloride with the way we would prepare a 1.00 m solution of iodine in carbon tetrachloride.

To prepare the 1.00 M solution, we would place 1.00 mole of iodine in a volumetric flask, and add exactly enough carbon tetrachloride to bring the volume up to exactly 1.00 L of solution. In contrast, to make a 1.00 m solution, we would add our 1.00 mole of iodine to 1.00 Kg of carbon tetrachloride. However, carbon tetrachloride is a very dense liquid, so the 1 kg of solvent has a volume of only 0.630 L. Let's approximate the molarity of this one molal solution. Remember that molarity is moles of solute/liter of solution. Since the volume of the solution will be approximately the volume of the solvent, we can use 0.630 L as the approximate volume of our solution. This means that the approximate molarity of our 1.00 m solution will be 1.00 mol/0.630 L = 1.59 M. Note that when the density of the solution is substantially different from one gram/mL, the molality will be significantly different from the molarity.

Now we need to talk about **converting between the various concentration units**. It's pretty easy to convert between mole fraction, weight percent, and molality. All you need are the definitions of the units, and the molecular masses of the components.
There's a nice simple way of thinking about these conversions. The first step in a conversion is to use the definition to take apart the unit you are starting out with. To see this lets take our 0.0500 mole fraction solution of methanol in ethanol and convert the concentration into weight % and molality. We'll start by remembering that mole fraction is moles of methanol over total moles, so a mole fraction of 0.0500 means that we have 0.0500 moles of methanol over 1.00 total moles of solution. Let's convert to weight % first. To calculate weight percent, we'll want grams of methanol over total grams. To get this we need to determine the number of grams of methanol from the moles of methanol, and the total mass of the solution from the moles of methanol and the total number of moles of the solution. This process is greatly simplified by using the following table. This table, which can be used for conversions between mole fraction, weight percent, and molality, has grams and moles as its column headings, and solute, solvent, and total as its row headings.

<table>
<thead>
<tr>
<th>Grams</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>solute</td>
<td>A</td>
</tr>
<tr>
<td>solvent</td>
<td>B</td>
</tr>
<tr>
<td>Total</td>
<td>C</td>
</tr>
</tbody>
</table>

The ratio we start with will always give us two of these pieces of information, and we will use these to figure out the ones we need to know for our conversion. Let’s use the table for our two conversions.

The information we begin with is mole fractions, the number of moles of methanol divided by the total number of moles. Since our mole fraction is 0.0500, this means that we have 0.0500 moles of methanol for every mole of solution. We fill this into our table.
<table>
<thead>
<tr>
<th></th>
<th>Grams</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>.802</td>
<td>.0500</td>
</tr>
<tr>
<td>Ethanol</td>
<td>28.567</td>
<td>.950</td>
</tr>
<tr>
<td>Total</td>
<td>29.4</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Weight percent is the weight of methanol over the total weight x 100%, so we need to determine total mass and mass of methanol. [Circle these] To determine grams of methanol we just multiply the number of moles by the molecular weight. To determine total mass we first have to determine grams of ethanol, and for this we need moles of ethanol, which we get by subtracting moles of methanol from the total, to get 0.95 moles. Now we multiply this by the molecular weight of ethanol to get the number of grams of ethanol and add the two masses to get the total mass. Now we have all the information we need to determine the weight percent, which is 0.802 g/29.4 g x 100% = 2.73% methanol w/w.

Let's use this same table to determine the molality of our solution. Remember that molality is the moles of solute divided by kilograms of solvent. We've already calculated both of these quantities, so our molality is just given by 0.05 moles of methanol divided by 0.0286 kg of ethanol, our solvent, so the $m_{\text{methanol}} = 0.05 \text{ mol}/0.0286 \text{ kg} = 1.74 \text{ mol/kg}$. So you see by constructing a table of this sort, we can easily convert between weight percent, molality and mole fraction.

**Conversion from molarity** to any of our other concentration units involves an additional step, using the density of the solution to convert from volume of solution to total mass of the solution. Let's suppose we have a 4.03 M solution of ethylene glycol, $C_2H_4(OH)_2$, in water, and want to know its molality. Molarity is moles of solute / L of solution, and we need to
know moles of solute/ kg of solvent. To figure out the mass of the solvent we need to know the mass of the solution. \textbf{To convert from the volume of the solution to the mass of the solution we use the density}, which in this case is 1.045 g/ml. Let’s use this to fill in our table.

<table>
<thead>
<tr>
<th>Grams</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>250.1</td>
</tr>
<tr>
<td>Water</td>
<td>795</td>
</tr>
<tr>
<td>Total</td>
<td>1045</td>
</tr>
</tbody>
</table>

The first thing we need is the number of grams of solution, which we get using the volume and the density,

\[ m_{\text{soln}} = 1.00 \text{ L sol’n} \times 1000 \text{ mL/L} \times 1.045 \text{ g/mL} = 1045 \text{ g solution}. \]

To get grams of water, we need to subtract grams of ethylene glycol from the total weight. We have 4.03 moles EG \( \times 62.07 \text{ g/mol} = 250.1 \text{ g} \). Therefore the mass of the water is 1045 g-250.1 g = 795 g, and our molality is 4.03 mol/0.795 kg = 5.07 m. Notice that for this calculation we didn't need to know anything about moles of water or total moles, so we left these items blank.

Now that we’ve defined these various measures of concentration, and the ways that we convert between them, I’d like to turn to solutions and their properties. I’d like to begin by defining some of the terms that are commonly used in talking about solutions. As we said on Tuesday, a solution is a mixture in which the mixing occurs at the level of molecules or atoms. In the solution, the component with the largest mole fraction is called the solvent, while the smaller component is called the solute. In a 1.00 M solution of sugar in water, the sugar crystals break up into single molecules, which are surrounded by water molecules. This process of surrounding molecules of the solute by solvent molecules is called solvation. For the specific
case where the solvent is water, and the solute is surrounded by water molecules, the process is called **hydration**.

**Not all substances dissolve to the same extent.** For example, sodium chloride, common table salt, can dissolve to an almost indefinite degree in water. In contrast, AgCl, silver chloride, dissolves sparingly. The maximum amount that will dissolve in a liter of water at 10°C is $8.9 \times 10^{-4}$ g. In order to quantify this we define the solubility of a substance. The **solubility** is the amount of substance that will dissolve to form a saturated solution in a fixed amount of solute.

This means that we need to define a saturated solution. When the maximum amount of a substance has dissolved and an equilibrium has been established between the solid and the solution, we say that we have a **saturated solution**. If a solution contains less than the saturation amount of a solute we say that it is **unsaturated**. So for example, if we make a solution of 22 g of nickel sulfate in 100 mL of water at 0°C, this is an unsaturated solution, since a saturated solution at 0°C contains 29.3 g. Sometimes it is possible to make a solution that temporarily contains more solute than the saturation amount. We call such a solution **supersaturated**.

So for example, if the most NiSO$_4$ I can dissolve in 125 mL of water at 0°C is 36.63 g, then the solubility of NiSO$_4$ at 0°C is 36.63 g/125 mL. The most common ways that solubilities are reported are in g/100 mL, g/L, and moles/L. So in our first example, the solubility in g/100 mL is calculated by

\[
\frac{36.63 \text{ g}}{125 \text{ mL}} = x \frac{\text{g}}{100 \text{ mL}}
\]
and solving for $x$ yields a solubility of $29.3 \text{ g/100 mL}$. The solubility of a substance depends on the identity of the solvent, the identity of the solute, the pressure and the temperature. We will describe the exact way in which these dependences occur later in the lecture.

How do we find out the solubility of a substance? Let's say that we're measuring the solubility of our nickel sulfate. We can start by adding 5 g to our 100 ml of water. We stir a bit and the 5 g dissolves completely. This process of dissolution means that molecules of the solute have left the surface of the solid and have become solvated. This happens until all five grams are gone. \textbf{HOW CAN WE TELL IT'S DISSOLVED?} [Phase Boundary Disappears] Now we add another 5 g and stir and it dissolves. If we keep on doing this we find that after we've added 30 g to our 100 ml of water, a small amount of the nickel sulfate stays undissolved no matter how much we stir or how hard we shake. The fact that a small amount of nickel sulfate is left undissolved tells us that the solubility is a bit less than $30 \text{ g/100 mL}$. To determine it exactly, we’d filter out the remaining solid, carefully dry it, and mass it, and subtract this mass of solid from the total we placed in the liquid.

It's important to realize that when we've reached the limit of our solubility the system is not static. Molecules of the solute are constantly leaving the surface of the solid, and at the same time, molecules of the solute are constantly leaving the solution and reattaching themselves to the solid. At the point where the maximum solubility is achieved, the rate at which solute molecules go into solution is the same as the rate at which solute molecules back to the solid. \textbf{WHAT DO WE CALL IT WHEN TWO OPPOSING PROCESSES OCCUR AT THE SAME RATE?} [Dynamic equilibrium.]

\textbf{What determines the solubility of two substances?} Why is table salt so soluble, while silver chloride is almost completely insoluble? Let's start by asking \textbf{why a solution forms}. Let's
start with the simplest possible case, a solution of two ideal gases, He and Ne. If we start out with a container with He on one side and Ne on the other side, and remove the barrier between the two the two gases will begin to diffuse. After a time, the two gases will be completely mixed and we will have a solution of the two gases.

Now remember that an ideal gas has no intermolecular forces, so the solution hasn't formed because of attractive forces. The only change that has occurred is that before the solution was made all of the helium was in one bulb, and all of the neon is in the other bulb, while afterwards the helium and neon atoms are randomly distributed between the two bulbs. In other words, after the solution has formed, the disorder of our gases has increased. **The driving force, the main cause for the formation of solutions is this drive toward randomness.** This drive toward randomness is the primary driving force for the formation of all solutions, whether they involve gases, liquids, solids or any combination.

However, when we start turning to mixtures of liquids and solids, or liquids and liquids, we find, as noted above, that not all of them form solutions with equal ease. For example, if we take water and rubbing alcohol and mix them, we find that they form a solution no matter what proportions we mix. For another example, if I take two oily substances like olive oil and gasoline they will also make a solution. Liquids that form solutions when they are combined are said to be **miscible.** Now if, in contrast, we mix olive oil and vinegar (which is mostly water), we find that they will not form a solution. Liquids that do not form solutions when mixed are said to be **immiscible.**

It turns out that **it is the nature of the intermolecular forces in the solvent and solute that determines which substances readily form solutions and which do not.** You have all
almost certainly heard the expression “like dissolves like.” What this means exactly is that liquids with similar types of intermolecular forces will form solutions, whereas liquids whose interactions are dominated by different types of intermolecular forces will not. For example, liquids in which the dominant forces are dipole forces or hydrogen bonding forces will form solutions with each other. Liquids in which the dominant forces are van der Waals forces will form solutions with each other. However, dipole liquids and van der Waals liquids will rarely make solutions with each other.

Let's see how this applies to the cases we have already mentioned. What is the strongest type of intermolecular force in water? The formula of rubbing alcohol is CH₃CH₂CH₂OH. What is the strongest type of intermolecular force in rubbing alcohol? So we see that in this case the intermolecular forces are the same kind, and a solution forms. Olive Oil and gasoline are both a class of molecules called hydrocarbons, made entirely of hydrogen and carbon. What kind of intermolecular forces will they have? Now if we mix olive oil and water, we're mixing one substance which is hydrogen bonding with another substance in which the strongest forces are van der Waals forces. Since the forces are different, they don't make a solution.

But why is this? Why do liquids with different types of polarity, or different types of forces, not make solutions? To see why let's consider a solution of methanol in water. We start out with each methanol molecule surrounded only by other methanol molecules, and each water molecule surrounded by other water molecules. When the solution is formed, each methanol molecule is surrounded by water molecules. In order to surround our methanol molecule with water molecules, or, in other words, hydrate it, we have to pull two water molecules apart, and
squeeze our methanol molecule in between. Since water molecules are held together by hydrogen bonds, it takes a fair amount of energy to separate them. However, a fair amount of energy is also gained when the water surrounds the methanol, because both molecules are polar. So you see, when a polar molecule dissolves in water, the energy it takes to separate the water molecules is close to the energy gained when the molecule is surrounded by water, so energy effects don't overcome the drive to greater disorder, and the solution forms. We call the energy change which occurs when a solution is formed the enthalpy of solution, \( \Delta H_{\text{sol}} \). Since the energy change is not large, it means that little heat is absorbed or released when this solution is made, so we could also say that \( \Delta H_{\text{solution}} \) is small for this case. So we can conclude that when \( \Delta H_{\text{solution}} \) is small or negative a solution will form.

In contrast consider what happens if we try to make a solution between octane and water. Octane is an extremely nonpolar molecule. When we separate water molecules, and try to insert an octane molecule, it still takes as much energy to separate the water molecules as before. Now, however, because the forces between the nonpolar octane molecules and the polar water molecules are much weaker, the energy gained from hydrating the octane is much less than the energy it takes to separate the water molecules. In other words, in order for this solution to form, a substantial amount of heat must be absorbed, \( \Delta H_{\text{solution}} > 0 \) and large. Thus when we try to make a solution between polar and nonpolar liquids, energy effects overcome the tendency toward disorder, and the solution won't form.

Now consider a solution between two nonpolar liquids, for example, hexane and octane. To make the solution we have to insert the octane between hexane molecules. Separating the
hexane molecules takes relatively little energy, because the hexanes are nonpolar, exert weak intermolecular forces, and are easy to separate. When we insert the octane, we get only a small amount of energy out, but since it only took a small amount of energy to separate the hexanes, the energies balance, $\Delta H_{\text{solution}}$ is once again small and the drive toward randomness causes the solution to form.

To summarize, the drive toward randomness in the universe is what causes solutions to form. If polar liquids are mixed with polar liquids, or nonpolar liquids are mixed with nonpolar liquids, the effect of the energy of solvation is more or less neutral, and solutions form. If polar and nonpolar liquids are mixed, the effect of the energy it takes to make a solution overcomes the drive toward randomness, and the solution does not form. This is the basis for the folk saying “oil and water don't mix.”

We can extend this discussion to solutions between solids and liquids. For molecular (or covalent) solids, we find that the behavior is identical to what we found with mixtures of solutions of liquids. If our molecular solid is nonpolar, like napthalene (mothballs), or wax, it will dissolve in nonpolar solvents. If it is polar, like sugar, or like deoxyribose, the sugar that is one of the building blocks of DNA, it will dissolve in polar solvents. In contrast, polar solids won't dissolve in nonpolar solvents, and nonpolar solids won't dissolve in polar liquids.

Ionic solids like nickel (II) sulfate or sodium chloride, are a little more complicated, because they will not always dissolve even in polar solvents. In order to understand this, we need to consider the energy it takes to separate the ions in the solid, which is called the lattice energy and which is large. Because it is large, ionic solids never dissolve in nonpolar solvents. It is so
large for some of these ionic compounds, that even aqueous solutions, solutions in water, won't form. This is because even though the energy of hydration is large for ionic solids, it may not be large enough to overcome the lattice energy. In order to understand solutions of ionic solids, however, we need to learn about a new type of intermolecular force. In chapter 11, we discussed the various types of intermolecular forces that are important in the gas phase and in pure liquids. These included dipole-dipole forces, hydrogen bonding, dipole-induced dipole forces and induced dipole - induced dipole forces, commonly called London or van der Waals forces. In solutions of ionic solids, though, we have a new kind of force to deal with because of the presence of charged particles. The strongest of these forces is the ion-ion force, called a Coulomb force. This is the force we have to overcome when we separate the atoms in an ionic solid. The second strongest force is an ion-dipole force. This is the kind of force we have when an ion like Na⁺ or Cl⁻ is next to a water molecule. It is weaker than the ion-ion force. This might make it seem like hydration can never make up for the energy lost when two ions are pulled apart. However, in an aqueous solution, each ion will be surrounded by six water molecules. So the balance in energy isn't between one ionic bond, and one ion-dipole bond, but between one ionic bond and 12 ion-water bonds. Sometimes the energy released from the hydration equals the energy necessary to break the ionic bond. However, sometimes it doesn't.

The only way we can tell if a solution will form is to look up the enthalpy of solvation of the solute in the solvent. If the energy of solvation is negative or reasonably close to zero the salt will dissolve easily. If it is large, only a tiny amount of the salt will dissolve. If we examine a typical table of heats of solution, such as the one on page 566 of the General Chemistry text by Kotz and Purcell, we find that the salts listed which dissolve easily have $\Delta H_{\text{solution}}$ between $+6 \text{ kJ}$
mol\(^{-1}\) and -51 kJ mol\(^{-1}\). In contrast a molecule like silver chloride has an enthalpy of solution of +65 kJ/mol, and dissolves only sparingly.

We can estimate \(\Delta H_{sol}\) two ways. Remember that I said that there are two factors in determining \(\Delta H_{sol}\). The first is the energy necessary to break the ionic bond. This is known as the lattice energy. The second is the energy that is released when the ions are hydrated. This is called the hydration energy. If we can find values of these two energies, then

\[
\Delta H_{sol} = \text{lattice energy} + \text{hydration energy}.
\]

For example, for LiF, an ionic compound which is used to make infrared transmissive windows, the lattice energy is 1032 kJ/mol, and the hydration energy is -1005 kJ/mol. Therefore

\[
\Delta H_{sol} = \text{lattice energy} + \text{hydration energy} = 1032 \text{ kJ/mol} - 1005 \text{ kJ/mol} = 27 \text{ kJ/mol}.
\]

The problem with this method is that both the lattice energy and the hydration energy are difficult to measure, and are available only for a few compounds. However, an alternative is to use the heats of formation of the ionic compound in solid and aqueous forms, since we can write the process of solution as the reaction

\[
\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq).
\]

Therefore, since \(\Delta H_{rxn} = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})\),

\[
\Delta H_{sol}(\text{NaCl}) = \Delta H_f(\text{Na}^+(aq) + \text{Cl}^-(aq)) - \Delta H_f(\text{NaCl}(s)).
\]

For example in the table of thermodynamic quantities on page A-8 of Chang, we find that \(\Delta H_f(\text{NaCl}(s)) = -411.0 \text{ kJ/mol}\), \(\Delta H_f(\text{Cl}^-(aq)) = -167.2 \text{ kJ/mol}\) and \(\Delta H_f(\text{Na}^+(aq)) = -239.66 \text{ kJ/mol}\). Therefore,
\[ \Delta H_{\text{sol}}(\text{NaCl}) = \Delta H_f(\text{Na}^+(aq) + \Delta H_{\text{Cl}^-(aq)}) - \Delta H_f(\text{NaCl}(s)) = -239.66 \text{ kJ/mol} + (-167.2 \text{ kJ/mol}) - (-411.0) \text{ kJ/mol} = 4.14 \text{ kJ/mol}. \]

**WILL NaCl BE SLIGHTLY SOLUBLE IN WATER OR BE READILY SOLUBLE?**

It is useful to ask how external factors such as pressure and temperature affect solubility. In general, it is found that for solutions of liquids in liquids or for solutions of solids in liquids, there is almost no effect of pressure on the solubility unless the pressures are hundreds of atmospheres. However, pressure can have a significant effect on the solubility of gases in liquids. Suppose we have a closed container which contains both a gas, and a solution of the gas and a liquid. Then the solubility of the gas is related to the pressure of the gas in the container by

\[ m = kp, \]

where \( p \) is the pressure of the gas, \( m \) is its molality, and \( k \) is a constant. This law for the solubility is called Henry’s law. If the container encloses a mixture of gases, then Henry's law becomes \( m_A = k_A p_A \), where \( m_A \) is the molality of substance \( A \), \( k_A \) is the Henry's Law constant for the substance, and \( p_A \) is its partial pressure. It is important to realize that each substance has a different Henry’s Law constant.

Let's do a quick example. What is the molal concentration of \( \text{CO}_2 \) in water at sea level at \( 25^\circ \text{C} \)? The partial pressure of atmospheric \( \text{CO}_2 \) at sea level at \( 25^\circ\text{C} \) is 0.24 torr and the Henry's Law constant for \( \text{CO}_2 \) in water at \( 25^\circ\text{C} \) is \( 4.4 \times 10^{-5} \) molal/torr. For the answer we just plug the appropriate values into Henry’s Law and get

\[ m_A = k_A p_A = 0.24 \text{ torr} \times 4.4 \times 10^{-5} \text{ molal/torr} = 1.1 \times 10^{-5} \text{ molal}. \]
Solubilities depend strongly on the temperature of the liquid. For example, the solubility of AgCl at 10°C is $8.9 \times 10^{-4}$ g/100 ml, while at 35°C it is $8.5 \times 10^{-2}$ g/100 ml, 100 times greater. We will deal quantitatively with the dependence of the solubility on temperature when we deal with equilibria in chapter 14, but now we will learn a qualitative treatment. The key concept we will need for this qualitative treatment is called **LeChatelier’s Principle**.

LeChatelier’s principle says “**When a stress is applied to a system in equilibrium, the system responds in a way that reduces the stress.**” So to take our case directly in hand, if we stress the system by raising the temperature, i.e. by adding heat, the system will respond in a way that reduces the heat. We know that endothermic processes can be written as

$$\text{reactant} + \text{heat} \rightarrow \text{product}.$$  

If we increase the temperature of a system in which some process is occurring, Le Chatelier’s principle tells us that the system will respond in a way that absorbs heat. Notice that for an endothermic process, as the system goes from reactant to product, heat is absorbed. Therefore in order to absorb heat, the reaction must move toward products and therefore, **for an endothermic process, raising the temperature increases the amount of products.**

Now consider the solubility of AgCl. We know that $\Delta H_{\text{sol}}$ of AgCl = 65 kJ/mol. What happens to the solubility when we raise the temperature? We can write the reaction as

$$\text{AgCl(s)} + 65 \text{ kJ/mol} \rightarrow \text{AgCl(aq)}$$

So we see that dissolving of AgCl is an endothermic process. **What does LeChatelier's principle tell us will happen when we increase the temperature? [More AgCl will dissolve.]**
Now consider an exothermic process. This can be written as
\[ \text{reactant} \rightarrow \text{product} + \text{heat}. \]

Le Chatelier's principle tells us that if we raise the temperature of the system, the system will respond in a way that absorbs heat. **What has to happen for this exothermic system to absorb heat?** [System makes more reactants from products.] Therefore **raising the temperature of an exothermic reaction increases the amount of reactant.**

Let's look at the solubility of RbF which has \( \Delta H_{\text{sol}} = -16 \text{ kJ/mol} \). We can write the reaction as
\[ \text{RbF}(s) \rightarrow \text{RbF}(aq) + 16 \text{ kJ/mol}. \]

**What will happen if we increase the temperature?** [Solubility of RbF decreases] We can use similar arguments to show that for any substance, if \( \Delta H_{\text{sol}} \) is positive, **that increasing the temperature increases the solubility**, while if \( \Delta H_{\text{sol}} \) is negative, **increasing the temperature decreases the solubility**. So we see that the effect of temperature on solubility is as follows. If forming a solution is an endothermic process, then increasing the temperature increases the solubility, while decreasing the temperature decreases the solubility. If forming the solution is an exothermic process, then increasing the temperature decreases the solubility, while decreasing the temperature increases the solubility.

Up to now we've been talking about solutions themselves, and about the factors that allow solutions to form, or, like the temperature of the system, that affect the amount of a solute which will dissolve in a solvent. At this point I'd like to turn to a discussion of the way in which the physical properties of solutions differ from those of pure liquids. These include changes in
vapor pressure, changes in freezing and boiling points, and a new phenomenon called osmosis. We are interested in these phenomena not just for their own sake, but also because they provide a means for calculating the molecular weights of substances in solution.

Let’s look at changes in vapor pressure, and begin with the simplest case, a nonvolatile solvent dissolved in a liquid solvent. By nonvolatile, we mean a solute with very low (<< 1 torr) vapor pressure at room temperature. At this point we'll add the additional simplification of considering only nonionic solids, also called nonelectrolytes. An example of a nonelectrolyte solute would be sugar, which dissolves without dissociating to ions. For this case, nonvolatile nonelectrolyte solutes, the vapor pressure of the solvent is related to mole fraction by

$$p_{solvent} = X_{solvent} p^\circ_{solvent},$$

where $X_{solvent}$ is the mole fraction of the solvent in the solution, and $p^\circ_{solvent}$ is the vapor pressure of the pure solvent. This equation is called **Raoult's law**.

Here's an example. Pure ethylene bromide has a vapor pressure of 173 torr at 85°C. What is the vapor pressure of a solution containing 0.300 moles of iodine and 0.800 moles of ethylene bromide at 85°C? According to Raoult's law, $p_{EB} = X_{EB} p^\circ_{EB}$. So we need to find the mole fraction of ethylene bromide. What's the definition of mole fraction? [moles of compound / total moles]. So $X_{EB} = 0.800 / (0.300 + 0.800) = 0.727$ and the vapor pressure of ethylene bromide will equal $0.727 \times 173 \text{ torr} = 126 \text{ torr}$.

Raoult's law essentially says that if you add a nonvolatile solute to a liquid the vapor pressure of the liquid diminishes. The more solute you add, the more the vapor pressure diminishes. Why is this so? Remember that the vapor pressure is the result of a dynamic
equilibrium between evaporation and condensation at the surface of a liquid. In other words, the vapor pressure is the pressure that results when evaporation from a liquid and condensation of its vapor occur at the same rate. Now suppose we have an equilibrium like this, and we add some solute to our liquid. Some portion of the surface area now consists of solute molecules. CAN ANYONE TELL ME WHAT THE EFFECT OF SURFACE AREA IS ON THE RATE OF EVAPORATION? Since the solute is taking up part of the surface area, the surface area of the liquid must be lower, and since the surface area is lower, the rate of evaporation must be lower. If the rate of evaporation is lower, the vapor pressure must be lower, too.

We can use **Raoult's law to calculate the molar mass of a solute** when we have a solution containing only one solute. Let’s do an example of this. A solution containing 18.26 g of an unknown nonelectrolyte in 33.25 g of ethyl bromide, C₂H₅Br, has a vapor pressure of 336.0 torr. Pure ethyl bromide has a vapor pressure of 400.0 torr. What is the molar mass of the unknown? According to Raoult's Law, \( p_{\text{ethyl bromide}} = X_{\text{ethyl bromide}} p^\circ_{\text{ethyl bromide}} \). Therefore \( X_{\text{ethyl bromide}} = \frac{p_{\text{ethyl bromide}}}{p^\circ_{\text{ethyl bromide}}} \). So in this case, \( X_{\text{ethyl bromide}} = \frac{336.0 \text{ torr}}{400.0 \text{ torr}} = 0.8400 \).

\[ X_{\text{ethyl bromide}} = \frac{n_{\text{ethyl bromide}}}{n_{\text{ethyl bromide}} + n_{\text{unknown}}}. \]

We already know the mole fraction of ethyl bromide, and since we know the mass of ethyl bromide and its formula we can solve for the number of moles of the unknown. **WHAT IS THE NUMBER OF MOLES OF THE UNKNOWN?** [5.924 x 10⁻²] Now since we know the number of moles of the unknown and the number of grams we can solve for the molar mass. **WHAT IS THE MOLAR MASS?** [347.2 g/mol]

We can use **Raoult's law to treat solutions where both the components are volatile liquids** (i.e. both have detectable vapor pressures). In this case **Raoult's law tells us the partial**
pressure of each component, and the total pressure is the sum of the two partial pressures. In other words if we have two liquids A and B, then

\[ p_A = X_A p_A^o, \text{ and } p_B = X_B p_B^o. \]

The total vapor pressure over the solutions is the sum of the partial pressure of the two liquids,

\[ p_T = p_A + p_B. \]

For example, suppose we have a solution of benzene and toluene in which the mole fraction of benzene is 0.33 and the mole fraction of toluene is 0.67. The vapor pressure of pure toluene is 22 torr, while the vapor pressure of pure benzene is 75 torr. The partial pressure of benzene is given by Raoult's law, \( p_{\text{benzene}} = 0.33 \times 75 \text{ torr} = 25 \text{ torr} \), while the vapor pressure of Toluene is \( p_{\text{toluene}} = 0.67 \times 22 \text{ torr} = 15 \text{ torr} \). The total pressure is the sum of the two partial pressures, \( p_T = p_{\text{benzene}} + p_{\text{toluene}} = 40 \text{ torr} \).

Not all solutions follow Raoult's law. Often if we measure the vapor pressure of a liquid in solution we find that it is higher or lower than Raoult's law predicts. If the solution follows Raoult's law it is called an ideal solution, and if it fails to follow Raoult's law it is called a non-ideal solution. We say that a solution that has higher vapor pressures than Raoult's law predicts shows a positive deviation from ideality. A solution that shows a lower vapor pressure than an ideal solution is said to exhibit a negative deviation from ideality. An ideal solution is also one which has \( \Delta H_{\text{solution}} = 0 \), while a solution with a positive deviation would have \( \Delta H_{\text{solution}} > 0 \), and a solution with a negative deviation would have \( \Delta H_{\text{solution}} < 0 \). This should tell us the reason for non-ideal behavior. If the solution is ideal, that means that the
solute molecules are held in solution no more tightly than they are held in the pure liquid. The same has to be true for the solvent. This in turn implies that the energy holding the solute in the solvent is the same as the energy holding the solute in its pure liquid.

For a solution with a positive deviation from ideality, the solvent and solute are held more loosely in the solution than they are in their pure liquids, and therefore the energies holding them in place must be less. For a negative deviation from ideality, the solute and solvent have to be held in place more tightly, and therefore the energies holding them in place must be higher.

Notice that because for a solution containing only one solute and the solvent, the mole fractions of solute and solvent have to total 1, i.e., $X_{\text{solute}} + X_{\text{solvent}} = 1$, we can rewrite Raoult's law as $p_{\text{solvent}} = (1 - X_{\text{solute}}) p_{\text{solvent}}^\circ$. This equation tells us that as we increase the mole fraction of the solute, the vapor pressure of the solvent decreases. Notice, however, that this equation refers only to the mole fraction of the solute and not its identity. This means that for ideal solutions, the vapor pressure of the solvent depends only on the concentration of the solute and not on the identity of the solute. We call a property of a solution which depends only on the concentration of a solute and not on its identity a colligative property.

The fact that the concentration of solutes affects the vapor pressure of the solvent leads us to another colligative property, boiling point elevation. This comes about because the normal boiling point is the temperature at which the vapor pressure is equal to the atmospheric pressure. Now suppose we have a sample of pure water at 373.15K. What is its vapor pressure? [1 atm] Now suppose we add some sugar to it. What will happen to its vapor pressure. [Drops] Since its vapor pressure is now lower than atmospheric pressure it will stop boiling. To
get it to boil again, we need to raise its vapor pressure. What can we do to raise its vapor pressure? [Raise temperature] If we raise the temperature enough, the vapor pressure will reach an atmosphere again, and the water will boil again. So we see that adding a solute to a liquid increases its boiling point. This phenomenon is called boiling point elevation.

The amount by which the boiling point will be elevated is given by the equation

$$\Delta T_{bp} = K_{bp} m_{solute}.$$  

In this equation $\Delta T_{bp}$ refers to the change in boiling point of the solvent, $K_{bp}$ is a constant called the molal boiling point elevation constant, or the ebullioscopic constant, which has units of $^\circ$C/m, and m is the concentration of the solute in units of molality. It is important to understand that $K_{bp}$ is a characteristic of the solvent and does not depend on the identity of the solute. For example, $K_{bp}$ for water is $0.51 ^\circ$C/m, while for acetic acid it is $2.93 ^\circ$C/m.

As an example consider the following problem. Suppose you were making tea, and accidentally added 10 g of sugar, $C_{12}H_{18}O_9$, to a pot containing 0.650 L of water. The density of water is 1.00 g/ml. At what temperature would the sugar water boil? Our equation says that $\Delta T_b = K_b m$. We know that $K_b$ for water is $0.51 ^\circ$C/m, so to find $\Delta T_b$ we need only find the molality of the solution. The molecular weight of sugar is 306.2 g/mol, so our 10 g of sugar is $3.26 \times 10^{-2}$ mol. The 650 ml of water weighs 650 ml x 1.00g/ml = 650 g or 0.650 kg, so the molality of the solution is $m = 3.26 \times 10^{-2}$ mol/0.650 kg = 0.0502 m. Therefore $\Delta T_b = 0.0502 \times 0.51 = 0.026 ^\circ$C. Since adding the sugar elevates the temperature by this much, our new boiling point is 100.03$^\circ$C.

Just as boiling points are changed by the presence of a solute, freezing points of liquids are changed as well. In this case we have to bring the liquid to a lower temperature in order to
get it to freeze. This phenomenon is called **freezing point depression**. The amount that the freezing point changes is given by the equation

\[ \Delta T_f = K_f m_{\text{solute}}. \]

In this equation, \( \Delta T_f \) is the amount that the freezing point decreases, \( K_f \) is a constant called the molal freezing point depression constant, and \( m \) is the molality of the solute. In analogy to \( K_b \), \( K_f \) is a property of the solvent alone, and is independent of the identity of the solute. For water, \( K_f \) is 1.86 °C/m.

One application of boiling point elevation and freezing point depression is that you can use them to determine molecular masses. To see how this is done, let's do an example with freezing points. When 1.00 g of sulfur is dissolved in 20 g of naphthalene, the resulting solution freezes at a temperature 1.28°C lower than pure naphthalene does. \( K_f \) for naphthalene is 6.8°C/m. What is the molecular weight of sulfur? [The equation for change in freezing point is \( \Delta T_f = K_f m \). For this problem this becomes \( \Delta T_f = K_f n_{\text{solute}} / k_{\text{gsolvent}} \). If we remember that \( n_{\text{solute}} = m_{\text{solute}} / \text{MW}_{\text{solute}} \) this becomes \( \Delta T_f = K_f m_{\text{solute}} / (\text{MW}_{\text{solute}} * k_{\text{gsolvent}}) \) or \( \text{MW}_{\text{solute}} = K_f m_{\text{solute}} / (\Delta T_f * k_{\text{gsolvent}}) \). Plugging in our values gives \( \text{MW} = 6.8 * 1.00 / (1.28 * .02) = 266 \text{ g/mol} \). Since sulfur atoms weigh 32 g/mol, this tells us that pure sulfur has a molecular formula of \( S_8 \).]

There is one more colligative property I'd like to mention called **osmosis**, which has great biological significance. Suppose you have a pure solvent and a solution separated only by a special kind of membrane called a **semipermeable membrane**. A semipermeable membrane is one that allows solvent molecules to pass through it but not solute molecules. Experiments show that some of the solvent will pass from the pure solvent side into the solution side. If we put a
tube on the solution side, we find that for a given concentration of solution, the flow of solvent into the solution will cause the liquid to rise to a characteristic height. The pressure exerted by the liquid in the tube is called the osmotic pressure. The osmotic pressure is related to the concentration of the solute in the solution by

$$\pi = MRT,$$

where \(\pi\) is the osmotic pressure, \(M\) is the molarity of the solution, \(R\) is the ideal gas constant, and \(T\) is the temperature in Kelvin. For example if we have a 1.00 molar sugar solution at 298K, the osmotic pressure is \(\pi = 1.00 \times 0.08206 \times 298 = 24\) atm! Osmotic pressure is responsible for, among other things, the ability of trees to send water hundreds of feet to their highest leaves.

When we first started talking about colligative properties, we specified that for simplicity the solutes had to be nonelectrolytes. This is because it turns out that colligative properties depend on the concentration of particles in solution. If we dissolve something like sugar, which does not dissociate, 1 mole of sugar results in a mole of particles in solution. However if we dissolve 1 mole of NaCl, an electrolyte, we get two moles of particles in solution, a mole of Na\(^+\) and a mole of Cl\(^-\). How many moles of particles would result if we dissolved 1 mol of Mg(NO\(_3\))\(_2\)?[3]. Let’s see how we include this in colligative properties with an example. How many moles of NaCl would we have to add to 1.00 kg of water to depress its freezing point by 2.00\(^\circ\)C? Our freezing point equation is \(\Delta T_f = Kfm_{\text{particles}}\) or \(\Delta T_f = Kn_{\text{particles}}/\text{kg solvent}\). If we solve for the number of moles of particles we get \(n_{\text{particles}} = 1.00 \text{ kg} \times 2.00\Delta C/(1.86\text{\(^\circ\)}C/\text{m}) = 1.08\) mol particles. To find the number of moles of NaCl we use 1.08 mol particles x 1 mol NaCl/2 mol particles = 0.540 mol NaCl. If we had used sugar to depress the freezing point by this much,
we would have had to use 1.08 mol. **How many mol would we have to use to depress the freezing point by this much if our solute was CaCl$_2$?** So you see that it takes less moles of an electrolyte to achieve the same freezing point depression as it does a nonelectrolyte. This is why salts are usually used to melt ice in winter.