Lecture Notes 3: Solubility, Solutions, and mixing

Up to now we have been dealing with pure compounds. Now we are going to begin to look at mixtures. The next two sets of notes will address mixtures. This first one is one mixing, solutions, and solubility. The next will be on the effect of mixing on phase transitions.

A few terms to define before we begin

**Solution**: A homogeneous mixture of two (or more) substances
Solvent: The majority substance
Solute: The minority substance

For example, if you put sugar into water you make a sugar water solution. The water is the solvent. The sugar is the solute. This is to be contrasted with putting sand into water. Then you have solid sand sitting at the bottom of your water- a heterogeneous system.

Let's answer a very important question about mixing: what happens to the entropy? First ,I'll just tell you that when you mix two things up, the entropy increases. (there are rare cases when this is not true, but this is only because of strong interactions between the molecules).

What is an example of this? The mixing of two ideal gases.
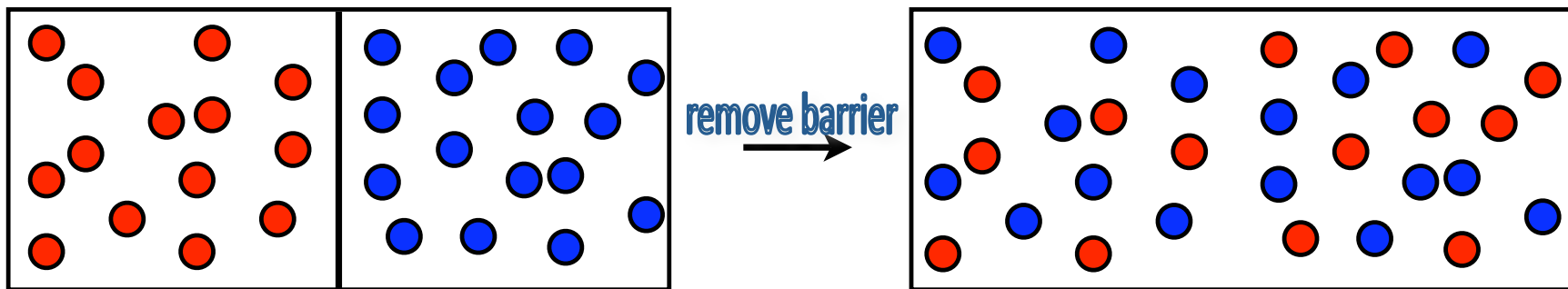
This process is spontaneous (it will actually happen). As such, we know that the change in free energy is negative (remember that a negative change in free energy (ΔG) for a process is the requirement for spontaneity). Things that actually occur lower the free energy.
Why does the free energy decrease? Is it due to the enthalpy (energy) or the entropy or both?

Since these are ideal gases we know it cannot be the enthalpy since there are no intermolecular forces (remember the ideal gas approximation is that there are no intermolecular forces at all). So we know that $\Delta H = 0$. Therefore since $\Delta G < 0$, and $\Delta G = \Delta H - T\Delta S$, we know that $\Delta S > 0$. That is, mixing increases the entropy!

What about systems in which there are intermolecular forces? These are the ones we are generally interested in.

Then ΔH is heavily dependent on the identity of the solute and the solvent.

For example, for NaCl dissolving in water $\Delta H > 0$
while N_2 gas dissolving in water $\Delta H < 0$

To look at ΔH we have to think about what is happening when we make a solution.

The differences in energy result from differences (or changes) in the intermolecular forces (IMF). If you can't remember your IMF review them!

Let's look at how the IMF are changed during the formation of the solution.

There are two key parts to the changes in the forces. The largest changes are for the solute. Before mixing, the solute molecules only interact with other solute molecules. In the solution, the solute molecules only interact with solvent molecules. Thus the changes result from the loss of the solute-solute interaction and the gain of the solute-solvent interactions (it should be noted that along with these changes there is a small loss of solvent-solvent interactions).

The process described above can be expressed mathematically as the following:

$$\Delta H_{solution} = \Delta H_{lattice-energy} + \Delta H_{solvation}$$

The first term is the change in enthalpy on forming the solution. The other two terms are the change broken down into the two changes in details above: the loss of solute-solute interaction and the gain in solute-solvent interactions. The first term is noted here as the Lattice Energy. This is what we typically associate with the energy of forming an ionic solid from separated ions. This is the energy **required** to pull the solute apart. The second term is the enthalpy of solvation. This is the energy **released** when the solute interacts with the solvent.

VERY IMPORTANT NOTE. It is critical that you keep track of the sign of these two enthalpy changes. Often the lattice-energy is negative number. However, here you need to use it as a positive. It is the energy input to overcome the solute/solute interactions. Thus you need it as a positive number. Energy in. Positive change.

Likewise, the enthalpy of solvation should be negative. It is energy out. Negative change. Also, this term often assumes that the solvent is water. In these cases it is noted as the enthalpy of hydration. If you see the enthalpy of hydration, it is referring to the enthalpy of solvation (where the solvent is specified to be water).

This is a great example of why understanding the actual process is so important. People choose different notation. People choose different sign conventions. You have to know what they mean. Breaking up the solute/solute interactions will always cost energy. Creating the solute/solvent interactions will always release energy.

Now the question remains--which is bigger?

IN NEARLY ALL CASES the "lattice-energy" term is larger than the solvation term.

This means that generally the enthalpy of solution is positive.

So how do we figure out what might dissolve and what won't?   Again we can look at the free energy

$$\Delta G = \Delta H - T\Delta S$$

We have established that generally for forming solutions $\Delta H_{solution} > 0$ and $\Delta S_{solution} > 0$.
Thus, the entropy contribution helps to lower the free energy, but the enthalpy is raising it.
If the change in free energy is going to be negative we need

$$|T\Delta S_{solution}| > \Delta H_{solution}$$

There are two ways we can think about this.

The first is to raise the temperature. This will lead to the entropy term dominating the process.

The second is to make sure the enthalpy term is very small.

How can we do this? We need to make sure that the changes in the intermolecular forces in going from the unmixed solute and solvent to the solution are minimal.

With this we happen upon the general idea of understanding what substances will dissolve (mix).

You may have heard the phrase "Like dissolves like"

This means that similar things dissolve in similar things.

What do we mean by similar? Similar intermolecular forces. Similar intermolecular forces between solute and solvent means there isn't much change in energy upon making the solution. This is what we mean by minimizing $\Delta H_{solution}$.

Polar things dissolve polar (ionic) things.
Non-polar things dissolve non-polar things.

When is similar not similar enough?
We can get a good idea looking at ionic compounds and water.

Water is polar. It isn't ionic. So already we know the IMF are not exactly the same. However, dipole-ion forces are substantial, even though they are likely not as large as ion-ion forces. When will this difference be too much? When the ion-ion forces are really large.

If you remember from studying ionic bonding, the forces between the ions depends on the charge and the separation between the ions. These two ideas can be combined into one: charge density. This is how compact the charge is. When the ion is small and has a large charge (Mg^{2+}) it has a very large charge density. When it is large and has a low charge (I^-) is has low charge density. The larger the charge density of the two ions the stronger the forces holding together the solute and the less likely they are to dissolve. So for example while NaCl is very soluble in water, MgO is not. Neither ionic compound is soluble in hexane (a non-polar solvent).

There is a second complication with large charge density ions. Remember the entropy term we said was almost always positive for mixing. One of the reasons for the "almost" is high charge density ions. When they dissolve into solution they interact very strongly with the water molecules. This strong interaction that leads to the water to essentially cling to the ion, reduces the entropy of the water. Before it was wandering all over. Now it is stuck to the ion. As such, the entropy of solution for high charge density ions is negative! Now we have a situation were enthalpy is very large (that is bad for making a solution since it is a large positive contribution to $\Delta G_{solution}$) and the entropy is negative (that is also bad). Neither thermodynamic quantity favors mixing (large positive $\Delta H_{solution}$ and negative $\Delta S_{solution}$). Thus, these compounds are extremely insoluble.
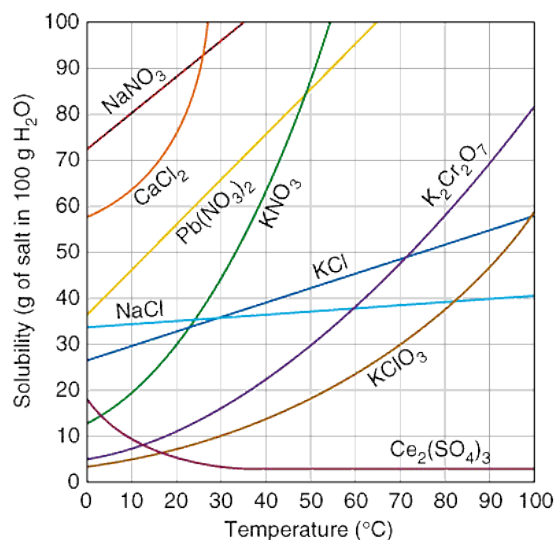
Back to temperature. As we showed before, increasing the temperature will increase the solubility of most substances. That can be seen in the plot on the left. Nearly all the compounds show an increase in solubility with increasing temperature.

The exception is $Ce_2(SO_4)_3$ (that isn't the only exception. It is just the only one on the graph). What is up with this compound? This one and similar compounds have a $\Delta H_{solution} < 0$. That is, forming the solution is exothermic. In these cases the solubility decreases with increasing temperature.

Making a solution of two liquids:

If two liquids mix in any proportions we call them miscible.

If they don't, we term the liquids immiscible.

The picture at the left shows to immiscible liquids.
These are liquids with very different IMF

A classic example is oil (long hydrocarbon chain, non-polar) and water (polar, H-bonding).

Again, we can invoke the general solubility rule that "like dissolves like". In the case of two liquids, we can say "like is miscible with like".

When you are deciding what molecules are alike, look at the intermolecular forces not just the atom.

For example:
CH_3OH (methanol) is an alcohol that is miscible with water. Both are polar and both have H-bonds.   However, you might think that methanol is more like CH_4 (methane) since is only different due to the missing oxygen atom. However methane has totally different IMF from methanol. It is non-polar and has very weak dispersion forces. As such it is a gas at standard temperature and pressure (25 C and 1 atm).

Mixing gases into liquids

When gases dissolve into liquids, we have a slightly different situation. In this scenario, we don't have to overcome any intermolecular forces in pulling the solute molecules away from each other, which means there is zero lattice energy. The solute molecules are in the gas phase and already apart. Therefore,

$$\Delta H_{solution} = \Delta H_{solvation} \text{ since } \Delta H_{lattice-energy} = 0.$$

Since the $\Delta H_{solvation}$ term is negative, we find that $\Delta H_{solution} < 0$ when mixing gases into liquids. Since this process is exothermic, it is helping to reduce the free energy upon forming the solution. This is important since the entropy is sure to be decreasing. The solute was a gas, the highest entropy phase, so even though we are making a mixture the entropy will be going down.

As such, while gases are soluble in liquids, they aren't that soluble.

We can quantify this using Henry's Law. Henry's Law states that the mole fraction of gas dissolved in the liquid (similar to concentration) is directly proportional to the gas pressure over the liquid.

$$P_{gas} = KX_{gas}$$

The constant K depends on the IMF between the solute and the solvent and thus it depends on both what the gas is and what the liquid is. The mole fraction is defined as n_{gas}/n_{total}.
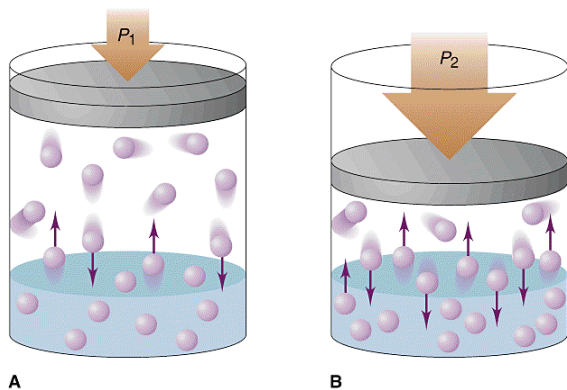
This is straight-forward to figure out. Double the pressure. Double the mole fraction.

A   B

This seems a bit random, but in fact Henry's Law crops up in every day life.   Have you ever wondered how they get all the CO_2 into carbonated beverages? They apply a big pressure of CO_2 above the liquid and the CO_2 dissolves. When the pressure goes away (the pssst when you open the can), the amount dissolved gas decreases and bubbles appear.

Also, if you are a scuba diver you know you do not surface from great depths too quickly. This is because when your body is at higher pressure, N_2 dissolves into your blood. Should you come up to the surface too quickly, the pressure drops and, just like the soda can, bubbles form. N_2 bubbles in your brain are very bad for your health.

Finally, Henry's law is important for fish (and marine life in general).   Fish, if you didn't know, manage to get O_2 out of the water to live. As the earth's atmosphere has a partial pressure of oxygen of around 0.18 atm, there is always some O_2 dissolved in water (rivers, lakes, oceans, the glass of water you are drinking,…) However, remember that the enthalpy of solution for gases is negative. This means that the solubility of the gases will drop when the temperature increases. Thus rising ocean temperatures, mean less O_2, means tough times for marine life.

Note: this is a very easy (if a bit boring) experiment to do at home. Put a pan of water on the stove and heat it up. What happens? Way before the solution begins to boil, little bubbles form on the bottom of the pan. Why? This is the dissolved air coming out of the water. As you raise the temperature, the solubility of dissolved gases drops and the gas comes out.(note: they tend to form in the same place as the surface tension of water makes the bubble formation slow. So the bubbles will form at little defects or scratches in the bottom of your pan).