5.6: Back to Phase Changes

Let us now return to the situation with solids, liquids, and gases. How do we think about entropy in these systems? Doesn't a substance become more ordered as we move it from gas to liquid to solid? Clearly the entropy of a solid is lower than that of a liquid, and the entropy of a liquid is lower than that of a gas. We can calculate (or simply look up) how entropies change for materials as they go from gas to liquid to solid. As we have predicted, they decrease. How can a change occur when the entropy of the system decreases (such as ice freezing)? Are we forced to conclude that things we know to happen are impossible according to the second law of thermodynamics? Of course not!

The second law of thermodynamics tells us that for every change that occurs, the entropy of the universe must increase. The problem with this is that we are all well aware of changes where the entropy apparently decreases. How can we resolve this seeming paradox? The answer lies in the fact that for any system the entropy may indeed decrease; water freezing is an example of this phenomenon. For the universe as a whole however (or more easily defined, the system and its surroundings) total entropy must increase. For example, when water freezes, the water molecules form stable interactions (hydrogen bonding interactions). As we have seen previously, the formation of stabilizing interactions means that the potential energy of the system has decreased. Because energy is conserved, this energy must be released to the surroundings as thermal (kinetic) energy. That is, the freezing of water is an exothermic process.

Now we can see the solution to our thermodynamic problem. The reason that the freezing of water does not violate the second law is that even though the system (ice) becomes more ordered and has lower entropy, the energy that is released to the surroundings makes those molecules move faster, which leads to an increase in the entropy of the surroundings. At the freezing point of ice the increase in entropy in the surroundings is greater than the decrease in entropy of the ice! When we consider both system and surroundings, the change in entropy (ΔS) is positive. The second law is preserved (yet again), but to understand why we must actively embrace systems thinking.