4.7: Looking Back and Ahead

A fascinating result of the last model is the connection of the thermodynamic state function entropy to notions of probability. The second law of thermodynamics is really nothing more than an expression of the probability of certain configurations occurring in multiparticle systems. In most of the examples you worked out in discussion/lab and in the homework, the number of particles was fairly small. In these small-number-of-particle examples, you could actually calculate probabilities of different configurations of a system. You found that the configurations that were not the most probable still had values that were significant. The system would actually find itself in these less probable configurations some of the time. When we focus on real *macroscopic* samples of matter, the number of particles gets to be the order of Avogadro's number. Now the probability of a system not being in the most probable configuration is vanishingly small. It is because we always deal with systems in everyday experience that have 10^{20} or more particles, that we can make absolute statements like, "heat always flows from a hotter object to a cooler object." It is not that some fundamental law of physics would be violated (conservation of energy, for example) if we sometimes ran across an interaction in which energy was transferred from the cooler to the warmer system as heat. It is just that the probability of this happening is so small, it would never be observed, even if we waited and watched for the entire age of the universe. The probability is just that small!

We also got a taste of what it is like to do some simple thermodynamics. You should have a much better feel now for some of the thermodynamic variables you run across in your chemistry and biology courses. For example, the idea of negative enthalpies of such-and-such should not be so mysterious now. A negative enthalpy change for a reaction (or other interaction/change) means what? Simply that in a constant pressure process, the combination of change of internal energy and PV work is such that heat energy was transferred out of the system, since in such a process, $\Delta H = Q$. The fundamental ideas expressed in the 1st and 2nd laws of thermodynamics are the basis for understanding much of the bio-chemistry that underlies all of the bio-sciences.

An interesting question arises with regard to living systems. Aren't living systems highly ordered systems? Living systems seem to evolve in a direction that contradicts the second law of thermodynamics. They are low entropy, not high entropy configurations. The resolution of this paradox is straight forward. First, it is crucial to remember what the 2nd law actually says. It refers to the change in the ***total*** entropy of all systems that are involved in an interaction (which includes the environment). It says nothing about how a particular system is constrained. It is perfectly OK for some systems to be in low entropy configurations, if there are other systems that increase in entropy and are in high entropy configurations. If we look at living processes what do we find? The low entropy part always interacts with other parts whose entropy increases. For example, a lot of thermal energy is transferred to the environment by living systems.

We can ask, "Can this process go on forever?" The answer is no. As heat energy enters the environment, its entropy continually increases. Simultaneously, sources of low-entropy energy (the sun, for example) are gradually "used up." The energy that was initially in the lower-entropy sun ends up in the higher-entropy environment. This is the one-way fate of our universe. Why? Simply because the probability of ending up in the configuration with the highest number of microstates is so close to unity, that we might as well accept it as a certainty. Too bad other things in life aren't as certain!

In Part 2 of the course, we will continue to use a conservation or before and after approach for two different kinds of phenomena. We will apply our fundamental energy-interaction model to various fluid phenomena, but formulated in such a way to make it useful for this purpose. It turns out that electric circuits behave in many respects the same way as fluids, such as blood flowing around in a human's circulatory system. Yet, all of these phenomena, which seem so different, can be understood using the basic ideas and concepts we have now become fairly familiar with. We use a very similar approach to introduce the basic question Isaac Newton addressed some 300 years ago. Namely, what is the relationship of force to change in motion of an object? It turns out, we can actually make a lot of headway using an approach, *conservation of momentum*, that is very similar to energy conservation. But then, we "have to bite the bullet" and look at the details of the interaction. We want to be able to make sense of the time evolution of physical systems, as well as just knowing their final states. We have to understand what is meant by the simple statement of Newton's 2nd Law and how to use these ideas to relate some common motions to the forces acting on the objects.