

IX. ENTROPY

9-1 STATES AND SYSTEMS

We learned in Chapter 4 that Nature prescribes a specific energy distribution given by the Boltzmann equation:

$$p(\epsilon_o) = A e^{-\frac{\epsilon_o}{kT}}$$

where $p(\epsilon_o)$ is the probability that a particle will have an energy ϵ_o . We called Nature's energy preference the second law of thermodynamics. There is, however, a tremendously powerful way to think about the second law that follows from the Boltzmann equation and that is the topic of this chapter. Before proceeding however we need to be specific with our terminology, which up until now has been a little fuzzy. Among the terms that demand great specificity are *state* and *system*.

We know that energy is conserved and so if we are observing a lone particle that interacts with nothing else, its energy must be fixed. It can neither gain nor lose energy. The state of this lone particle—its past and subsequent behavior—is determined by its energy. We say that the particle is in an energy state and often use the Greek letter psi, ψ , with a subscript to denote this energy state. For example, ψ_ϵ signifies the energy state of a particle that possesses energy ϵ .

Lone particles are not particularly interesting. We generally want to understand systems containing many particles. For the moment, we will confine ourselves to the study of isolated systems of particles. By isolated we mean that there is some boundary (real or imagined) around the system, and contained inside are some number of particles that cannot change. In addition, energy can neither enter or leave the system. Simply, neither mass nor energy can cross the boundary. We can approximate an isolated system in a laboratory using well insulated flasks or other containers. The universe as a whole is thought to be an isolated system, as its mass-energy does not appear to change with time. Hence anything that is true for an isolated system is true for the universe.

Just as we characterize the states of a particle by its energy, we characterize the states of a system by its energy. In analogy to particle states we use Ψ_E to represent the state of a system with total energy of E.

Consider an isolated system containing a mole of interacting particles. The total energy of the system we will call E_{sys} , so the system is in a state designated as $\Psi_{E_{\text{sys}}}$ that does not change with time. However, the particles in the system are colliding and constantly changing their state. We can designate the state of one of these particles as $\psi_{1\varepsilon}$, where the 1 indicates this is the state of particle 1 with an energy ε . Recall there are a mole of particles in this system and therefore we know that the particle energies must sum to the system energy, i.e.,

$$E_{\text{sys}} = \sum_i \varepsilon_i$$

where the sum runs over all of the particles in the system, from 1 to Avogadro's number.

There are an infinite number of ways to distribute the system's energy among its particles so as to satisfy equation 1. And it should not come as a surprise that Nature picks the Boltzmann distribution. But why? What is it about this distribution that makes it so attractive to Nature?

9-2 A TWO STATE SYSTEM

Let's imagine that we have an isolated system containing a very large number, N , of particles. Each of these particles can be in one of two states **A** or **B** with energies ε_A or ε_B , where $\varepsilon_A < \varepsilon_B$. Clearly the energy of the system is given by,

$$E_{\text{sys}} = N_A \varepsilon_A + N_B \varepsilon_B = N(p_A \varepsilon_A + p_B \varepsilon_B)$$

where N_A and N_B are the number of particles in state **A** and state **B** and p_A and p_B are the probabilities of being in state **A** and **B** as given by Boltzmann's equation.

The system's minimum energy occurs when all particles are in state **A**, which requires $p_A = 1$ and $p_B = 0$. Energy can only be added to the system—its temperature increased—by increasing the number of particles in state **B** and hence increasing p_B , which necessarily requires a decreasing the number of particles in state **A** and hence a decrease in p_A .

As we have done before (you should verify that you can derive this equation), we can use Boltzmann's equation to show that,

$$\frac{p_B}{p_A} = e^{-\frac{(\varepsilon_B - \varepsilon_A)}{kT}} \quad (1)$$

Only when $T = 0$ is $p_B = 0$ and as the temperature increases p_B increases. At very high temperatures the ratio p_B to p_A approaches 1. To summarize: at $T = 0$ all the particles are in state **A**, as the temperature increases more particles are found in state **B**. At very high temperature, the numbers of particles in state **A** and state **B** are nearly equal. Apparently, no matter how hot the system becomes, there will never be more particles in state **B** than in **A**.

This may seem counterintuitive, so let's look at it from another vantage point. At $T = 0$, we are absolutely certain that every particle is in state **A**. We call such systems ordered. A person who keeps their bedroom orderly is one who knows where everything is. On the other hand, at elevated temperatures, we are less certain in what state a particle will be found. The system is becoming less ordered. At nearly infinite temperatures, we will be maximally uncertain as to a particle's state. Such a system is said to be disordered. (Note that a system where p_B is greater than p_A would be more ordered than the case where $p_B = p_A$.) A system where the particles are equally distributed between all possible states is maximally disordered.

We can define a quantity that measures the extent of disorder. We call this quantity entropy, S , and it can be found through the equation,

$$S(T) = -k \sum_i p_i \ln(p_i)$$

where the sum is taken over all the states of the system, p_i is the probability of being in state i and k is the Boltzmann constant. Note that entropy is a function of temperature. As an example, let's calculate the entropy of our two-state system at 0 K and as T goes to infinity.

$$S(0) = -k \sum_i p_i \ln(p_i) = 1 \ln(1) + 0 \ln(0) = 0$$

and

$$\lim_{T \rightarrow \infty} S(T) = -k \sum_i p_i \ln(p_i) = -k \left(\frac{1}{2} \ln\left(\frac{1}{2}\right) + \frac{1}{2} \ln\left(\frac{1}{2}\right) \right) = k \ln(2)$$

It is not too difficult to show that $S(T)$ reaches its maximum value when all p_i are equal. I leave it to interested readers to do so.

Entropy provides a measure of disorder, a system where $S = 0$ is totally ordered and

the entropy increases in value as system becomes more disordered. The Boltzmann distribution gives the maximum value of entropy for a given temperature. In a system composed of particles that can be in any number of states, at a given temperature the probabilities as given by the Boltzmann distribution give the maximum value of entropy. In short, Nature want to distribute energy in the most disordered—random—way possible.

9-3 NEGATIVE TEMPERATURES

Equation (1) tells us how energy is distributed as a function of temperature. But we can imagine a number of distribution that apparently cannot be realized. In particular, why can't we put all of the particles of our two-state system into state **B**? In fact, there is a temperature that would give rise to exactly this distribution. It is -0 K. Let's check. We begin by inverting Equation 1,

$$\left(\frac{p_B}{p_A}\right)^{-1} = \left(e^{-\frac{(\epsilon_B - \epsilon_A)}{kT}}\right)^{-1} = e^{\frac{(\epsilon_B - \epsilon_A)}{kT}} = \frac{p_A}{p_B}$$

At $T = -0$

$$\frac{p_A}{p_B} = e^{\frac{-(\epsilon_B - \epsilon_A)}{k \cdot 0}} = 0$$

which is satisfied only if $p_A = 0$ and $p_B = 1$. The entropy for this state is zero. Meaning it is fully ordered, as it must be because all particles must be in state **B**. As the temperature becomes increasingly negative, the probability of being in state **B** decreases and hence the probability of being in state **A** increases. At very large negative temperatures the probabilities of being in state **A** and state **B** are nearly equal and the entropy approaches its maximum value.

A system at negative temperatures contains more available energy than a system at positive temperatures, and at -0 K the system contains the greatest amount of energy possible. Though this may seem contrary from our typical picture of temperature, it makes perfect sense from the order-disorder perspective. The temperature of a system is positive, if the entropy increase with addition of energy. It is negative if the entropy decreases with the addition of energy. So, there must be some relationship between the change in entropy of a system, the heat added, and the resultant temperature. We postulate that that relation takes the following form,

$$T = \frac{q}{\Delta S}$$

which is consistent with what we have discovered about negative temperatures predicted by the Boltzmann equation. If the entropy decreases as heat is added to a system, i.e. ΔS is negative, then temperature is negative.

We have discovered something amazing: Temperature is not a measure of the average kinetic energy of a system, but in fact the change in entropy associated with addition of heat energy to the system. It just so happens that because second law requires that entropy of the universe always increases, we only observe positive temperatures.

However, we can force systems to negative temperatures though they are not stable. Given a chance they will increase their entropy while releasing energy. Lasers are example of systems where electrons have been encouraged to be ordered in a high-energy state. As the electrons increase their entropy, they release energy in the form of laser light. We will talk a little more about this in a couple of weeks.

9-4 FREE ENERGY

Up to this point we have considered only isolated systems, and in particular the universe. The second law tells us that any spontaneous process (anything that can happen) will lead to an increase in the entropy of the universe. Unfortunately, we cannot make measurements on the entirety of the universe, even with a great many graduate students working around the clock. Instead we typically consider a finite piece of the universe and ask if a process in that piece of the universe is spontaneous. In other words, we are looking for a statement of the second law that can be applied to these pieces of the universe.

We start by defining our terms precisely. The universe is thought of as divided in two pieces, one of these is our system of interest, which we call the *system* and the remainder of the universe—everything not included in the system—we call the *surroundings*. There is a real or imagined boundary separating the system from the surroundings. Unlike an isolated system, in an open system mass-energy can cross this boundary. Because there can be an exchange of energy with the surroundings, the system and surroundings will be in thermal equilibrium, i.e., will be at the same temperature T . Additionally because energy can move across the boundary, the entropy change associated with any process occurring in the system may appear both in the surroundings and in the

system. We may describe this fact mathematically as:

$$\Delta S_{univ} = \Delta S_{sur} + \Delta S_{sys} \quad (2)$$

where the subscripts denote universe, surroundings, and system respectively.

Now, ΔS_{sur} is the result of heat crossing the boundary into the surrounding, or perhaps coming from the surroundings into the system. Nonetheless, the heat appearing in the surroundings must be equal in magnitude but opposite in sign to the heat leaving the system,

$$q_{sur} = -q_{sys}. \quad (3)$$

We argued above that,

$$\Delta S = \frac{q}{T} \quad (4)$$

With equations 3 and 4, we may rewrite equation 2 as,

$$\Delta S_{univ} = \frac{-q_{sys}}{T} + \Delta S_{sys} \quad (5)$$

Equation 5 is remarkable. The entropy change of the universe is expressed in terms of purely system variables. Therefore for a system process to be spontaneous, the right hand side of equation 5 must be greater than zero! Let's manipulate this equation just a bit by multiplying through by $-T$. Then,

$$-T \Delta S_{univ} = q_{sys} - T \Delta S_{sys} \quad (6)$$

This quantity is called *free energy*. For a spontaneous process the change in free energy must be less than zero (Why?).

We can make a further simplification to this expression by noting that q_{sys} depends on the nature of the boundary around our system. If the boundary is rigid, then we say that the process is occurring at constant volume and $q_{sys} = \Delta E$. If the boundary can move, then we say that the process is occurring at constant pressure and $q_{sys} = \Delta H$, where H is a quantity called *enthalpy*. (Why is q_{sys} different if the process is carried out at constant pressure or constant volume?)

We now define two kinds of free energy change, Gibbs free energy,

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

and Helmholtz free energy,

$$\Delta A \equiv \Delta H - T\Delta S$$

We have dropped the *sys* suffix because all of our variables are now system variable. **A process occurring at constant pressure will be spontaneous if $\Delta G < 0$.** And **a process occurring at constant volume will be spontaneous if $\Delta A < 0$.**

By and large, the processes we will consider occur at constant pressure, often in open containers at atmospheric pressure. Hence, we will most often refer to Gibbs free energy.