

Introduction to Physical Chemistry – Lecture 6

I. LECTURE OVERVIEW

In this lecture, we will discuss the concept of *entropy*, which is perhaps the most difficult and yet most important concept in thermodynamics. In introductory physical chemistry courses, it is traditional to begin the discussion of entropy from the perspective of heat engines, in particular the *Carnot cycle*. This approach is more consistent with the actual history of thermodynamics, since entropy was first discovered from the study of heat engines. While we will discuss the Carnot cycle later in this course, I will take a shot at approaching entropy from the perspective of statistical mechanics. While this approach is somewhat more subtle and initially more difficult, I think it ultimately provides a physically clearer picture. The statistical mechanical approach to entropy provides the fundamental connection between temperature, energy, and entropy, and therefore leads to better understanding of the laws of thermodynamics.

This lecture is HARD. This is probably the most difficult lecture in the whole course. In terms of what you actually need to know for solving the homework problems and test questions, there is not that much material in this lecture. The one equation you will need to remember is $dS = (\delta Q/T)_{rev}$ (which will be explained later). Despite this, I have decided to give a fairly thorough theoretical treatment of entropy, because I think it is better to get exposed to the reasoning behind various scientific concepts as soon as they are introduced, even if one doesn't fully grasp them at first. For those of you who will continue in the physical sciences, you will probably find that it will take several more exposures to the concept of entropy, and in various contexts (thermodynamics, statistical mechanics, probability theory, etc.) before fully grasping it. Even at that point, subtle points may still arise, either in a course or in the context of your own research, that will force you to stop and think for a while.

II. A MISSING THERMODYNAMIC PRINCIPLE?

We begin our discussion with a box separated into two compartments by a wall (see Figure 1). One side of the box is filled with a gas (say an ideal gas such as air), and the second side is empty. There are n moles of gas inside the box, which has a volume V , and the gas is at a temperature T and P .

If we now remove the wall, then the gas will expand and eventually fill the whole compartment. Because no work was done on the system, and because no heat was added or removed, the First Law reads $\Delta U = 0$ for this process. If the gas is ideal, then this means the final

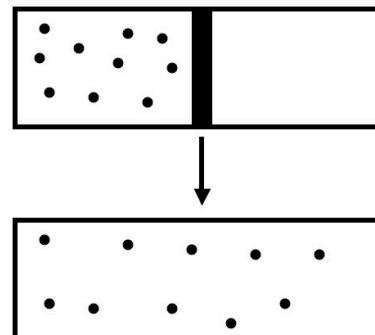


FIG. 1: An ideal gas confined to one side of a box disperses throughout the whole box when the barrier is removed.

temperature of the gas (after dispersing throughout the box) is the same as its starting temperature. The gas has expanded to twice its volume of course, and so its pressure has dropped to half its original value.

This process is clearly irreversible, since we will never see the gas spontaneously move into one half of the box (or at least, it will take much longer than the age of the universe for this to happen). And yet, the First Law of Thermodynamics gives us no information as to the directionality of this process. All it says is that the internal energy of the gas is not affected by its dispersion throughout the box.

Clearly, something is missing. There must be a principle that should be able to tell us whether or not the gas will disperse throughout the box. To find this principle, we look to the laws of probability.

III. THE PRINCIPLE OF MOST PROBABLE STATES

Assume that we have a box containing N balls. Each ball has an equal probability of being in the left or right side of the box. The question we wish to answer is, how many different ways are there of placing n balls on the left side, and $N - n$ balls on the right side?

The answer is a standard one from combinatorics, but we will provide the derivation here: First of all, let us label the balls 1 through N . We wish to place exactly n balls on the left side, which automatically means that $N - n$ balls are placed on the right side. So, we pick the first ball to be placed on the left side. Since there are N balls, there are N possibilities for this first pick. Let i_1 denote the first ball placed on the left side. For the second ball, there are $N - 1$ possibilities. Let i_2 denote the second ball placed on the left side. Continuing

in this way, we obtain that for the n^{th} ball, there are $N - n + 1$ possibilities. Therefore, we have that there are $N \times N - 1 \times \dots \times N - n + 1 = N!/(N - n)!$ possibilities in placing n balls on the left side. But we are not quite done, for notice that our algorithm has generated a sequence i_1, \dots, i_n of balls placed on the left side. Note, however, that we are interested in the number of distinct ways of placing n balls on the left side. We are not interested in the order in which those balls were placed. For example, if we placed balls 1, 2, 3 on the left side, we don't care if the balls were placed in the order 1, 2, 3, or 3, 1, 2 or 2, 3, 1. The end result is the same. Therefore, for a given configuration i_1, \dots, i_n of n balls, any permutation of the indices $1, \dots, n$ will still give the same final configuration of balls on the left side. Since there are $n!$ permutations of the indices $1, \dots, n$, a given set $\{i_1, \dots, i_n\}$ of balls on the left side is generated in $n!$ different ways by our algorithm. Therefore, the number $N!/(N - n)!$ must be divided by $n!$ to obtain the number of distinct ways of placing n balls on the left side of the box.

Putting everything together, we get that the number of different ways of placing n balls on the left side of the box and $N - n$ balls on the right side of the box is,

$$\binom{N}{n} = \frac{N!}{n!(N - n)!} \quad (1)$$

In English, the expression $\binom{N}{n}$ is read “N choose n.” It is an expression that appears time and again in combinatorics and probability. For example, the *binomial expansion* of $(a + b)^N$ is given by,

$$(a + b)^N = \sum_{n=0}^N \binom{N}{n} a^n b^{N-n} \quad (2)$$

It should be noted that since $0! = 1$, $\binom{N}{0} = 1$.

Now, if we plot $\binom{N}{n}$ versus n for various values of n , we will notice that $\binom{N}{n}$ reaches its maximum value at $n = N/2$. We will also notice that as N increases, the peak at $n = N/2$ becomes sharper and sharper.

What does this mean, physically? It means that the number of ways of putting half of the balls in one side of the box and half of the balls in the other side completely dominates all other configurations, as the number of balls goes to ∞ . Therefore, as the number of balls becomes very large, by far the most probable configuration is the one where half of the balls are on one side and half the balls are on the other (you can think of this in terms of flipping a coin, where “heads” corresponds to putting a ball in the left side of the box, and “tails” corresponds to putting a ball on the right side. By definition of probability, as the number of coin flips goes to ∞ , the fraction of “heads” goes to $1/2$, so that exactly half the balls will be placed in the left side of the box, and half will be placed in the right side of the box).

Going back to the example of the ideal gas dispersing throughout the box, we postulate that this happens because the ideal gas is simply going into its most probable

state. That is, it is far more likely for the gas to be evenly distributed throughout the box than it is for it to remain on one side. As the number of particles in the gas becomes infinite, the probability of the gas staying in only one side of the box goes to 0.

If we extend this to be a general principle, we can formulate the following

Hypothesis: *A system comes to thermodynamic equilibrium when it is in its most probable state, or equivalently, when it is in a configuration for which the number of ways of achieving that configuration is maximized.*

For a given configuration, the number of ways of achieving the configuration is denoted by Ω . Ω is referred to as the *degeneracy* of the system for the given configuration.

Returning to the example of the balls in the box, we have $N + 1$ distinct configurations, where n represents the configuration where n balls are on the left side of the box, and $N - n$ balls are on the right side of the box. The degeneracy for this configuration, denoted $\Omega(n)$, is given by,

$$\Omega(n) = \binom{N}{n} \quad (3)$$

Because $\Omega(n)$ is maximized when $n = N/2$, our system comes to thermodynamic equilibrium when $n = N/2$.

IV. ENTROPY: A NEW STATE FUNCTION

A. Definition of entropy

Given a system, we let Ω_{equil} denote the degeneracy of the system when it is in thermodynamic equilibrium (that is, Ω_{equil} is the degeneracy of the most probable configuration of the system). We would like to use Ω_{equil} to construct a state function for the system. In anticipation of what is to follow, we will call this state function the *entropy*, and denote it by S . We don't know yet what the functional relationship between S and Ω_{equil} will be, so for now we write $S = f(\Omega_{equil})$. Note that, by definition, S does indeed only depend on the state of the system, and not how the system got there, hence S is a state function.

To begin, we would like the entropy to be an *extensive* variable. This means that, if we have two systems in their respective equilibrium states, and if S_1 is the entropy of system 1, and S_2 is the entropy of system 2, then we would like the total entropy to be $S_1 + S_2$. Let Ω_1 denote the degeneracy of system 1 in its equilibrium state, and let Ω_2 denote the degeneracy of system 2 in its equilibrium state. Then the total degeneracy of the combined system is $\Omega_{12} = \Omega_1 \Omega_2$. Since we would like $S_{12} = S_1 + S_2$, then we have $f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$. We will show later that this implies that $f(\Omega) = C \ln \Omega$, where C is some constant.

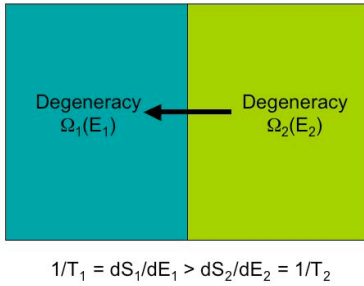


FIG. 2: Two systems in thermal contact will exchange thermal energy in such a way as to maximize the total degeneracy of states $\Omega_1\Omega_2$.

Therefore, the entropy S of a system in thermodynamic equilibrium is given by $S = C \ln \Omega$, where C is a constant which we will determine later.

B. The connection between entropy and temperature

Figure 2 illustrates two systems at fixed volume, both in their equilibrium states with internal energies E_1 and E_2 , respectively, which are placed in thermal contact with each other. The definition of thermal contact means

that the two systems can exchange energy with each other. If these two systems are isolated from the rest of the environment, then no matter what exchange of energy occurs, the total energy in the system must remain $E \equiv E_1 + E_2$ at all times. Therefore, if E'_1 and E'_2 denote the energies of systems 1 and 2 respectively at any given time, then we have $E'_1 + E'_2 = E$, so that $E'_2 = E - E'_1$.

Now, we know that energy will flow from the hotter system to the colder system. As explained in earlier lectures, this follows directly from the definition of temperature. However, we also know that the combined system will evolve in time to achieve a configuration with the maximal degeneracy. This of course dictates a direction of energy flow, since energy flow between the two systems will occur in such a way as to maximize the degeneracy of the combined system. Clearly, then, there must be a connection between entropy and temperature. We will determine this connection now:

Let $\Omega_1(E'_1)$ denote the degeneracy of system 1 when it is in its equilibrium state at total energy E'_1 . Let $\Omega_2(E'_2)$ denote the degeneracy of system 2 when it is in its equilibrium state at total energy E'_2 . The degeneracy of the combined systems, with system 1 at energy E'_1 , and system 2 at energy E'_2 , is $\Omega_1(E'_1)\Omega_2(E'_2)$. Now, if the two systems are in thermal contact, so that energy can flow between them, we know that energy will flow between them in such a way that $\Omega_1(E'_1)\Omega_2(E'_2)$ is maximized, subject to the constraint $E'_1 + E'_2 = E$. Redenoting E'_1 by E' , we then have that we wish to maximize $\Omega_1(E')\Omega_2(E - E')$.

Differentiating $\Omega_1(E')\Omega_2(E - E')$ with respect to E' gives,

$$\begin{aligned}
 \frac{d}{dE'}[\Omega_1(E')\Omega_2(E - E')] &= \Omega'_1(E')\Omega_2(E - E') - \Omega_1(E')\Omega'_2(E - E') \\
 &= \Omega_1(E')\Omega_2(E - E')\left(\frac{\Omega'_1(E')}{\Omega_1(E')} - \frac{\Omega'_2(E - E')}{\Omega_2(E - E')}\right) \\
 &= \Omega_1(E')\Omega_2(E - E')\left[\left(\frac{d \ln \Omega_1}{dE'_1}\right)_{E'_1=E'} - \left(\frac{d \ln \Omega_2}{dE'_2}\right)_{E'_2=E-E'}\right] \\
 &= \Omega_1(E')\Omega_2(E - E')\frac{1}{C}\left[\left(\frac{dS_1}{dE'_1}\right)_{E'_1=E'} - \left(\frac{dS_2}{dE'_2}\right)_{E'_2=E-E'}\right] \tag{4}
 \end{aligned}$$

Note then that when $(d/dE')[\Omega_1(E')\Omega_2(E - E')]$ is positive, it implies that to maximize the degeneracy of the combined systems, E' must increase, so that energy must flow from system 2 into system 1. However, the statement that $(d/dE')[\Omega_1(E')\Omega_2(E - E')]$ is positive is equivalent to the statement that $(dS_1/dE'_1)_{E'_1=E'} - (dS_2/dE'_2)_{E'_2=E-E'}$ is positive. Therefore, energy flows from system 2 into system 1 when $(dS_1/dE'_1)_{E'_1=E'} - (dS_2/dE'_2)_{E'_2=E-E'} > 0$.

Following a similar line of reasoning, we get that

energy flows from system 1 into system 2 when $(dS_1/dE'_1)_{E'_1=E'} - (dS_2/dE'_2)_{E'_2=E-E'} < 0$. Finally, the combined system has achieved thermodynamic equilibrium (that is, $(d/dE')[\Omega_1(E')\Omega_2(E - E')] = 0$) when $(dS_1/dE'_1)_{E'_1=E'} - (dS_2/dE'_2)_{E'_2=E-E'} = 0$. So let's summarize the results of this analysis, and compare with what we know about temperature, to see if we can guess the desired relationship.

1. Energy flows from system 2 into system 1 when $(dS_1/dE'_1)_{E'_1=E'} > (dS_2/dE'_2)_{E'_2=E-E'}$. This

statement must be equivalent to the statement that $T_1 < T_2$.

2. Energy flows from system 1 into system 2 when $(dS_1/dE'_1)_{E'_1=E'} < (dS_2/dE'_2)_{E'_2=E-E'}$. This statement must be equivalent to the statement that $T_1 > T_2$.
3. Thermal equilibrium is achieved when $(dS_1/dE'_1)_{E'_1=E'} = (dS_2/dE'_2)_{E'_2=E-E'}$. This statement must be equivalent to the statement that $T_1 = T_2$.

Note that a relationship between temperature and entropy that guarantees the equivalence of all three statements is to define the temperature T via,

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (5)$$

This is the fundamental connection between entropy and temperature that we have been looking for. It also reveals that although it is a more difficult concept to grasp, entropy is more fundamental than temperature.

The principle of most probable states allows us to unambiguously define a direction of energy flow between two systems in thermal contact. Because the direction of energy flow is what allows us to define a temperature scale, we see that temperature must be directly connected to entropy.

V. THE SECOND LAW OF THERMODYNAMICS

A. Entropy change of a process

If we consider a system at constant volume, as with the previous section, then we obtain for an infinitesimal change in the system state that $dS = dE/T$. Since E is the total energy of the system, we have that $E = U$, so that $dS = dU/T$. Furthermore, since for a system at constant volume we have $dU = \delta Q$, we obtain that $dS = \delta Q/T$.

This expression, while correct, leaves out a crucial point: When computing entropy changes infinitesimally, the path taken must be a reversible one. That is, $dS = (\delta Q/T)_{rev}$, meaning that heat transfer occurs in such a way that the system is in a thermodynamic equilibrium state at all times.

This is a subtle point, and therefore worth explaining: In the previous section, we defined entropy to be a state function that depends on the energy of the system. Volume was not explicitly included, since we were dealing with a constant volume process. Nevertheless, we can introduce a volume dependence as well, and write $S = S(E, V)$. However, we also have that $S = C \ln \Omega$, where Ω is the degeneracy of the system at energy E and volume V . For S to be well-defined, that is, for it to have one unambiguous value, it follows that Ω must

itself be a function of E and V . As we saw with the example of the gas dispersing throughout the box, for a given energy there are many different configurations with different degeneracies that are consistent with the given energy and volume. Therefore, to make S a state function that depends only on E and V , we have to select one configuration out of all possible configurations. The configuration we select is the one with the maximum degeneracy.

However, this means that entropy is only a relevant concept for a system in thermodynamic equilibrium. Therefore, if we wish to compute the entropy change of a system as it moves from one equilibrium state to another by computing an integral of the form $\int_{\text{State 1}}^{\text{State 2}} dS$, then we are implicitly considering infinitesimal changes to the system that lead to infinitesimal changes to the degeneracy of its most probable state. Since each most probable state defines an equilibrium state of the system, we are effectively moving along a path that takes us through a continuum of equilibrium states. And so, we have $dS = (\delta Q/T)_{rev}$.

Going back to the example with the gas in the box, when the wall is in place, the entropy of the system is given by $S = S(E, V)$. When the wall is removed, the entropy becomes $S = S(E, 2V)$. Note that the entropy is simply determined by the most probable state of the gas when it is allowed to disperse throughout the whole box. That the gas is not in that state when the wall is first removed is not a problem with the definition of entropy, rather, it simply takes time for the gas to disperse throughout the box and achieve a new equilibrium state. From the point of view of the formula $dS = (\delta Q/T)_{rev}$, however, this means that removing the wall does not define a valid path for computing the entropy change associated with isothermally doubling the volume of an ideal gas. The reason for this is that the most probable state of the system does not change smoothly, but rather jumps suddenly, making S discontinuous for this path. So, we have to find another path if we wish to compute the change in S by integration.

B. The first and second laws of thermodynamics

For a process that occurs at constant volume, we have $dU = TdS$, if the process is reversible. Allowing for PV -work gives,

$$dU = TdS - PdV \quad (6)$$

which is the first law of thermodynamics for reversible processes. The expression,

$$dS = (\delta Q/T)_{rev} \quad (7)$$

is known as the *Second Law of Thermodynamics*.

C. Determination of C

To determine the constant C in the formula for entropy, let us return to the example of the ideal gas expanding to fill out the whole box. Based on the formula for S , we have $\Delta S = C \ln \Omega_2 - C \ln \Omega_1 = C \ln(\Omega_2/\Omega_1)$, where Ω_1 denotes the degeneracy of the gas when confined to one half of the box, and Ω_2 denotes the degeneracy when the gas is allowed to disperse throughout the box. Now, for the purposes of this problem, there is only one way of putting all the gas molecules on the left side of the box (we simply put all of them on the left side!). However, for the most probable configuration when the gas is dispersed throughout the container, there are $N!/(N/2)!^2$ ways of putting half the gas molecules on the left side of the box, and half on the right side. This gives $\Omega_2/\Omega_1 = N!/(N/2)!^2$, and so,

$$\Delta S = C(\ln N! - 2 \ln(\frac{N}{2})!) \quad (8)$$

To evaluate this expression, we use an approximation known as *Stirling's formula*, which says that for large N , $\ln N! \approx N \ln N - N$. The precise formulation, which we will prove in the appendices, is that $\lim_{N \rightarrow \infty} (N \ln N - N)/\ln N! = 1$.

Using Stirling's formula, we get that, for large N ,

$$\begin{aligned} \ln N! - 2 \ln(\frac{N}{2})! &= N \ln N - N - N \ln \frac{N}{2} + N \\ &= N \ln \frac{N}{N/2} = N \ln 2 \end{aligned} \quad (9)$$

and so,

$$\Delta S = NC \ln 2 \quad (10)$$

We now compute the same entropy change using the infinitesimal expression for entropy change: First we allow the gas to undergo an adiabatic, reversible expansion from its initial volume to its final volume. Since the gas cools in this process, we then heat it back up to its original temperature.

During the adiabatic expansion phase, $\delta Q = 0$, and hence $dS = 0 \Rightarrow \Delta S = 0$. However, from the relation $T_2/T_1 = (\bar{V}_1/\bar{V}_2)^{R/\bar{C}_V}$, we have that after the adiabatic expansion the gas has cooled to a temperature $T_2 = T_1(1/2)^{R/\bar{C}_V}$, where T_1 is its starting temperature.

Therefore, in the second phase, the gas must be heated reversibly from $T_1(1/2)^{R/\bar{C}_V}$ to T_1 . In this phase, we have $dU = \delta Q = TdS \Rightarrow dS = n\bar{C}_V dT/T$, and so integrating we obtain,

$$\begin{aligned} \Delta S &= n\bar{C}_V \ln \frac{T_1}{T_2} \\ &= n\bar{C}_V \ln 2^{R/\bar{C}_V} \\ &= nR \ln 2 \end{aligned} \quad (11)$$

Since we have $\Delta S = NC \ln 2 = nN_A C \ln 2$ by using the degeneracy formula, we obtain $C = R/N_A = k$, giving,

finally, the famous Boltzmann formula for entropy,

$$S = k \ln \Omega \quad (12)$$

It should be noted that this formula is written as the epitaph on Boltzmann's grave.

What might seem a bit strange by this computation of C is the connection between two very different ways of determining ΔS . This apparent difference is only an illusion, however. The reason for this is that the ideal gas law itself is derivable from the principle of most probable states, assuming we have a set of non-interacting point particles. Therefore, all formulas (adiabatic expansion/compression, heating, etc.) associated with computing ΔS for an ideal gas are equivalent to formulas making explicit use of degeneracy of configurations. By formulating our expressions in terms of temperature, energy, etc., this equivalency is well-masked. Statistical mechanics is the tool that allows us to "remove the mask," so to speak, and to explicitly reveal the connection between the underlying molecular dynamics of a large number of particles and the thermodynamic properties of the resulting system.

As a result of the statistical mechanical approach to entropy taken in this lecture, you have already had an initial taste of this important field. If time permits, I will provide further exposure at the end of the semester and explicitly derive the ideal gas law.

D. Ensembles, statistical mechanics, and various formulas for entropy

Our development of the concept of entropy involved a constant volume, isolated system. When energy flow was allowed, it was with another such system, so that the composite system was itself isolated. Therefore, total energy remained a constant in the system, and we defined entropy as a function of the degeneracy of the most probable state at the given energy.

In statistical mechanics, this construct is known as a *microcanonical ensemble*. There are a number of other useful ensembles in statistical mechanics. Two such ensembles are the *canonical ensemble* and the *grand canonical ensemble*.

In the canonical ensemble, the system is placed in a thermal bath, and heat transfer is allowed between system and surroundings. Therefore, the system is closed, but not isolated. Because heat transfer is allowed, the total energy inside the system will in general fluctuate. The goal of the canonical ensemble is to determine the probability that the system will have a given energy.

In the grand canonical ensemble, the system is also placed in a thermal bath, and heat transfer is allowed. In addition, the system is open, so that particles can move in and out of the system. Therefore, both the energy and the total particle number inside the system will fluctuate. The goal of the grand canonical ensemble is to determine

the probability that the system will have a given energy and particle number.

We will not discuss these ensembles in this course, because to do so would take us far beyond the scope of this course. Even our discussion of the microcanonical ensemble was for the specific purpose of defining the concept of entropy. We will point out, however, that these various ensembles may ultimately be shown to be equivalent to one another. Depending on the particular problem at hand, one ensemble may simply be easier to work with than another. We will also point out that the canonical ensemble gives a different looking formula for entropy than the microcanonical ensemble: If p_i denotes the probability of the system being in state i , then the entropy is given by,

$$S = -k \sum_i p_i \ln p_i \quad (13)$$

This formula is known as the *Gibbs' entropy formula*.

In the context of the microcanonical ensemble, the Gibbs' entropy formula is identical to the Boltzmann formula. For, given a system in thermodynamic equilibrium with degeneracy Ω , each of the system states consistent with the equilibrium configuration are equally probable, hence have a probability of $1/\Omega$. Therefore, $p_i = 1/\Omega$, where i runs from 1 to Ω . So, by the Gibbs' formula,

$$S = -k\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega \quad (14)$$

which is exactly the Boltzmann expression.

In 1948, Claude Shannon developed Information Theory, used to analyze data transmission error-prone communication channels. Shannon made use of a quantity now called the *Shannon entropy*. The Shannon entropy is also called *uncertainty*, and is denoted by H instead of S (this should not be confused with enthalpy. These are two different sets of notations in two distinct but related fields). The Shannon entropy is defined as,

$$H = - \sum_i p_i \log_2 p_i \quad (15)$$

Note that we make use of the base-2 logarithm instead of the natural logarithm. Because $\log_2 x = \ln x / \ln 2$, the Shannon entropy differs from the Gibbs formula by a multiplicative constant (specifically $k \ln 2$). In contrast to Gibbs' entropy, which has units of [Energy]/[Temperature] (e.g. J/K), Shannon entropy is measured in *bits*.

We can make a much stronger statement about Shannon's Information Theory than the above paragraph suggests: Although it was a theory originally motivated by the study of communication channels, it is in fact the mathematical generalization of thermodynamics that has made thermodynamics applicable to nearly every branch of science and engineering. Shannon's approach has become so powerful that thermodynamics is now regarded as a subfield of Information Theory. Information Theory

itself has now emerged as one of the key scientific developments of the 20th century, on a par with Einstein's Theory of Relativity and Quantum Mechanics.

E. When is the concept of entropy useful?

Hopefully, this lecture has made it clear that the Second Law of Thermodynamics is not so much a law as it is a reasonable assumption about what the equilibrium state of a system should look like. So, the question that arises, is when would entropy be expected to be a useful concept?

Returning to the example of the box, if we have relatively few particles, say two, then there are as many ways of putting the balls on one side of the box as there are of having half the balls on one side and half on the other. Therefore, we are as likely to have both balls on the same side of the box as on different sides. Certainly, we could argue that the concept of entropy is not useful for predicting the configuration of the balls in the box.

As the number of balls grows larger and larger, the probability of having half the balls on one side of the box and half the balls on the other side goes to 1. Therefore, the principle of most probable states, and therefore of entropy, becomes a useful concept as the number of particles in the system goes to ∞ .

In fact (and this is a major point of confusion), strictly speaking, the principle of most probable states is only correct in the limit of infinite particles. In this case, the probability of observing the system in any state other than its most probable one goes to 0 (the ideal gas in the box example is again useful here). However, for a finite system, there is a positive, if small, probability that the system will be observed in one of its less probable states. So, returning to the example of the gas in the box, because there are a finite number of particles in the box, there is a finite probability that all the gas particles will be found on the left side of the box. Applying the observation that "something that can happen eventually will," we will find that at some point a gas evenly dispersed throughout a box will spontaneously segregate itself to one side (and then redisperse again, of course).

Boltzmann, in the course of developing a theory of dilute gases, derived a quantity analogous to the entropy, which he called H . In his famous *H-theorem*, Boltzmann showed that H never decreases (corresponding to a system going to its most probable state). One of the criticisms of Boltzmann's work was that an evenly dispersed gas will, given sufficient time, segregate itself into one corner of a room. At the time, Boltzmann had no definitive response to this criticism, except to point out that on average, one would have to wait for longer than the age of the universe to observe such a segregation. However, this response was not sufficient to counter criticism of Boltzmann's work, which went largely unaccepted during his lifetime. Boltzmann eventually committed suicide as a result. The apparent contradictions in Boltzmann's

theory were eventually resolved, and his theory of dilute gases is now accepted as largely correct. Boltzmann is now regarded as having made some of the most fundamental breakthroughs in thermodynamics and statistical mechanics.

We can resolve the criticism of Boltzmann's theory, and of the concept of entropy in general, if we understand that the principle of most probable states is something that is only correct for systems with an infinite number of particles. Going back to the example of the gas in the box, it is true that the gas will eventually segregate to one side. However, as the number of particles in the gas increases to ∞ , the time we would have to wait to observe this increases to ∞ as well. An even stronger statement is that as the number of particles in the gas goes to ∞ , the *fraction* of time that the gas spends not being evenly distributed between the left and right sides goes to 0.

Summarizing, then, the Second Law of Thermodynamics is only strictly correct for systems that are infinitely large. In practice, the Second Law may be safely applied to systems that have large numbers of particles, since the time scale on which we would observe significant violations of the principle of most probable states is itself very large.

F. Other statements of the second law

One phrasing of the second law of thermodynamics that you may have heard is that "Entropy is always increasing," or that "systems tend to maximum disorder." If we decide to assign entropy to measure the amount of "disorder" in a system, then the principle of most probable states tells us why this is true.

But there is a bit of a problem here, because entropy is defined in terms of the most probable state of a given system. That is, entropy is defined with respect to an equilibrium state of a system, so if a system's entropy is increasing, then it is clearly not in equilibrium. In this case, the concept of entropy makes no sense, which means that the statement "entropy is increasing" makes no sense either.

To resolve this apparent difficulty, let us go back to Figure 2, and consider two systems in thermal contact. As long as there is irreversible energy flow between the two systems, the composite system is *not* at equilibrium, and hence the concept of entropy for the composite system makes no sense. However, the concept of entropy may make sense for the systems separately. That is, if at some time during the energy transfer, system 1 has energy E_1 , it is possible that system 1 is in its most probable state at energy E_1 . Therefore, system 1 may be in an internal thermal equilibrium at energy E_1 , with a temperature T_1 defined by $1/T_1 = \partial S_1 / \partial E_1$. Similarly, system 2, at some energy E_2 , may be in its most probable state at energy E_2 .

What we are illustrating here is that a system that is not in its equilibrium state may therefore be divided into

subsystems which are themselves in thermal equilibrium at their respective energies. The different subsystems must have different temperatures (otherwise there would be no energy flow, and so we would be at global equilibrium). By making this assumption of *local equilibrium*, we can define an entropy for each subsystem, and define the *total entropy* to be the sum of the entropies of the individual subsystems.

Returning to our two system example, we can show that the total entropy $S_{12} = S_1 + S_2$ is always increasing. If system 1 is at temperature T_1 , and system 2 is at a temperature T_2 , then $dU_1 = T_1 dS_1$, and $dU_2 = T_2 dS_2$. By conservation of energy, $dU_1 = -dU_2$, so $T_1 dS_1 = -T_2 dS_2 \Rightarrow dS_2 = -(T_1/T_2) dS_1$. Therefore, $dS_1 + dS_2 = (1 - T_1/T_2) dS_1 = (1/T_1 - 1/T_2) dU_1 = (1/T_2 - 1/T_1) dU_2$. Now, if $dU_1 > 0$, then $T_1 < T_2$, so $(1/T_1 - 1/T_2) dU_1 > 0$. If $dU_1 < 0$, then $T_1 > T_2$, so $(1/T_1 - 1/T_2) dU_1 > 0$.

Therefore, in any case, the total entropy $S_1 + S_2$ is increasing, until it reaches a maximum. Hence, for an isolated system (the composite system of systems 1 and 2), the entropy is never decreasing.

APPENDIX A: DERIVATION OF S FROM Ω

In this section we will show that, given a function f satisfying $f(xy) = f(x) + f(y)$, it follows that $f(x) = C \ln x$, where C is some constant.

To show this, let us fix y , and differentiate both sides with respect to x . We obtain,

$$y f'(xy) = f'(x) \quad (\text{A1})$$

Setting $x = 1$ gives,

$$y f'(y) = f'(1) \Rightarrow \frac{df}{dy} = \frac{f'(1)}{y} \quad (\text{A2})$$

Setting $C = f'(1)$, we may integrate to obtain,

$$f(y) = C \ln y \quad (\text{A3})$$

Since y is just a "dummy" variable, this proves the claim.

APPENDIX B: THE ZEROETH LAW OF THERMODYNAMICS

The Zeroth Law of Thermodynamics states that if system A is in thermal equilibrium with system B , and if system B is in thermal equilibrium with system C , then system A is in thermal equilibrium with system C . Without this law, it would be impossible to construct a thermometer. The reason is simple: If we let system A be our thermometer, and if system A is in thermal equilibrium with system B , then this means that the reading on system A gives us the temperature of system B . If system B is in thermal equilibrium with system C , then these

two systems must be at the same temperature, hence the thermometer should give the same temperature for system C as it did for system B . Therefore, system A and system C must be in thermal equilibrium.

To prove the Zeroth Law, consider three systems A , B , C , with energies E_A , E_B , and E_C , respectively, and assume that A and B are in thermal equilibrium, and B and C are in thermal equilibrium. Then from the derivation earlier in this lecture, we have that, $(dS_A/dE'_A)_{E'_A=E_A} = (dS_B/dE'_B)_{E'_B=E_B} = (dS_C/dE'_C)_{E'_C=E_C}$, so that systems A and C are in thermal equilibrium. This establishes the Zeroth Law.

APPENDIX C: PROOF OF STIRLING'S FORMULA

In this section we prove that $\lim_{N \rightarrow \infty} [N \ln N - N]/\ln N! = 1$. To do this, we first prove the following:

$$\begin{aligned} \frac{b_1 + \dots + b_m + (1 - \epsilon)(a_{m+1} + \dots + a_N)}{a_1 + \dots + a_m + a_{m+1} + \dots + a_N} &< \frac{b_1 + \dots + b_m + b_{m+1} + \dots + b_N}{a_1 + \dots + a_m + a_{m+1} + \dots + a_N} < \frac{b_1 + \dots + b_m + (1 + \epsilon)(a_{m+1} + \dots + a_N)}{a_1 + \dots + a_m + a_{m+1} + \dots + a_N} \\ \Rightarrow \frac{\frac{b_1 + \dots + b_m}{a_{m+1} + \dots + a_N} + 1 - \epsilon}{\frac{a_1 + \dots + a_m}{a_{m+1} + \dots + a_N} + 1} &< \frac{b_1 + \dots + b_N}{a_1 + \dots + a_N} < \frac{\frac{b_1 + \dots + b_m}{a_{m+1} + \dots + a_N} + 1 + \epsilon}{\frac{a_1 + \dots + a_m}{a_{m+1} + \dots + a_N} + 1} \end{aligned} \quad (C2)$$

Since $\lim_{N \rightarrow \infty} a_N = \infty$, we get,

$$\lim_{N \rightarrow \infty} \frac{b_1 + \dots + b_m}{a_{m+1} + \dots + a_N} = \lim_{N \rightarrow \infty} \frac{a_1 + \dots + a_m}{a_{m+1} + \dots + a_N} = 0 \quad (C3)$$

so that,

$$1 - \epsilon \leq \lim_{N \rightarrow \infty} \frac{b_1 + \dots + b_N}{a_1 + \dots + a_N} \leq 1 + \epsilon \quad (C4)$$

Since this is true for any $\epsilon > 0$, it follows that $\lim_{N \rightarrow \infty} (b_1 + \dots + b_N)/(a_1 + \dots + a_N) = 1$, as we wished to show.

To use this to prove Stirling's formula, note that $\ln N! = \ln(1 \times 2 \times 3 \times \dots \times N) = \ln 1 + \ln 2 + \dots + \ln N$, so we can define $a_n = \ln n$, so that $\ln N! = a_1 + \dots + a_N$. Also, defining $b_n = [n \ln n - n] - [(n-1) \ln(n-1) - (n-1)]$, note that $N \ln N - N = b_1 + \dots + b_N$ (since $\lim_{x \rightarrow 0} x \ln x = \lim_{x \rightarrow \infty} (1/x) \ln(1/x) = \lim_{x \rightarrow \infty} -\ln x/x = 0$, it follows that $0 \ln 0 - 0 = 0$).

Therefore, since $\lim_{n \rightarrow \infty} \ln n = \infty$, we need only show that $\lim_{n \rightarrow \infty} ([n \ln n - n] - [(n-1) \ln(n-1) - (n-1)])/\ln n = 1$ to prove Stirling's formula. So, to prove this limit, note that,

Claim: Let $a_1, a_2, \dots, a_n, \dots$, and $b_1, b_2, \dots, b_n, \dots$ be two sequences of positive numbers with the following two properties: (1) $\lim_{n \rightarrow \infty} a_n = \infty$. (2) $\lim_{n \rightarrow \infty} (b_n/a_n) = 1$. Then,

$$\lim_{N \rightarrow \infty} \frac{\sum_{n=1}^N b_n}{\sum_{n=1}^N a_n} = 1 \quad (C1)$$

Proof: Since $\lim_{n \rightarrow \infty} (b_n/a_n) = 1$, then, given $\epsilon > 0$, there exists $m > 0$ such that $1 - \epsilon < b_n/a_n < 1 + \epsilon$ for all $n > m$. Then, for all $N > m$, we have,

1) $)]/\ln n = 1$ to prove Stirling's formula. So, to prove this limit, note that,

$$\begin{aligned} &[n \ln n - n] - [(n-1) \ln(n-1) - (n-1)] \\ &= \ln n + (n-1)[\ln n - \ln(n-1)] - 1 \\ &= \ln n + (n-1) \ln\left(1 + \frac{1}{n-1}\right) - 1 \\ &= \ln n + \ln\left(1 + \frac{1}{n-1}\right)^{n-1} - 1 \end{aligned} \quad (C5)$$

so that,

$$\begin{aligned} &\lim_{n \rightarrow \infty} \frac{[n \ln n - n] - [(n-1) \ln(n-1) - (n-1)]}{\ln n} \\ &= 1 + \lim_{n \rightarrow \infty} \frac{1}{\ln n} [\ln\left(1 + \frac{1}{n-1}\right)^{n-1} - 1] \\ &= 1 + 0 * (\ln e - 1) = 1 \end{aligned} \quad (C6)$$

where we have used the fact that $\lim_{n \rightarrow \infty} (1 + 1/n)^n = e$. With this, Stirling's formula is established.